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The application of the high-pressure thermochemical process for recycling of organic waste

Zastosowanie wysokociśnieniowego procesu termochemicznego do recyklingu odpadów organicznych

Doctoral dissertation conducted at the Department of Applied Bioeconomy
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ABSTRACT

Increased waste production has made it necessary to look for a new context and optimize previously known processes in waste management strategy. The research goal of the thesis is to propose an effective thermal conversion and biological treatment of food waste (FW) for phosphorus (P), volatile fatty acids (VAFs), yeast biomass, and energy sources product management focusing on recovery from FW via high-pressure thermochemical processes (HPTP) in particular hydrothermal carbonization (HTC) and characterize its end products which comprise hydrochar (HC) and hydrothermal carbonization aqueous phase (HTC-AP).

The state-of-the-art in the field of the thermal conversion process was reviewed, as well as research was designed and performed, including optimization of related parameters, and laboratory scale analyses, enabling the preparation of the concept of the suitable thermal conversion treatment of FW along with recommendations taking into account ensuring a better quality of the end products to guide our exploration and analysis, shedding light on the transformative potential of HTC treatment in addressing the global FW challenge while fostering sustainable and circular solutions.

This work presented the critical HTC parameters, including temperature, residence time, reactant concentration, and product quality. The results of a lab-scale experiment demonstrate: a) HTC converted FW into HTC-AP which exhibits the highest saturated fatty acids (SFA) percentages, reaching up to 58.5 wt%, and the P in HC with the highest recovery ($5.64\ g \cdot 100\ g^{-1}$), while the highest value of P in HTC-AP was $0.83\ g \cdot 100\ g^{-1}$, b) HTC-AP produced better at high operating parameters (340 ^{o}C) over lower operating parameters (220 °C), yielding approximately 95% at optimized conditions, c) the design of the experimental approach offered the optimization of HC and HTC-AP. Furthermore, a lab-scale experiment showed the maximum achievable yields of HC and HTC-AP were projected at 19.19% and 89.5%, respectively. An optimization run was conducted to validate these predictions with temperature and time set at 220°C and 270 min. Consequently, HC and HTC-AP were obtained as 18.9 ± 1.2% and 78.2 ± 2.2%, respectively. It was proved that the yield and quality of HTC products are affected by operating parameters. The HTC converted FW into HC with carbon (>55%), ash content (<2%), and higher heating value (19.2-32.5 MJ/kg). A lab-scale experiment also demonstrates the relationship between HTC-AP composition, yeast growth kinetics, and lipid production. The result showed: a) HTC-AP used by *Y lipolytica*, *Y. parophonii*, and *Y. keelungensis* yields 4.5 g/L dry biomass (10 -14% lipid), b) *Y. yakushimensis* showed the highest growth rate (indicated by kinetic constant) among all the media, c) HTC-AP produced at 260˚C serves as the best lipid source of nutrients. Finally, a lab-scale experiment of combined HTC and anaerobic digestion (AD) contributed to a better understanding of FW valorization through HTC and offered insights into sustainable biogas production from FW. HTC conditions were optimized to produce different HTC-AP variants, and the impact of titanium oxide/biochar addition to the HTC system for HTC-AP biomethane potential was examined. The obtained results suggest that using titanium oxide/biochar catalyst during HTC is crucial for using HTC-AP for methane fermentation and biomethane production.

ABSTRACT IN POLISH

Zwiększona produkcja odpadów spowodowała konieczność poszukiwania nowego kontekstu i optymalizacji wcześniej znanych procesów w strategii zarządzania odpadami. Celem badawczym rozprawy jest zaproponowanie skutecznej konwersji termicznej i biologicznego przetwarzania odpadów żywnościowych (FW) w celu zarządzania fosforem, lotnymi kwasami tłuszczowymi (VAF), biomasą drożdży i źródłami energii, koncentrując się na odzyskiwaniu z FW poprzez wysokociśnieniowe procesy termochemiczne (HPTP), w szczególności hydrotermalną karbonizację (HTC) i scharakteryzowanie jej produktów końcowych, które obejmują hydrochar (HC) i fazę wodną hydrotermalnej karbonizacji (HTC-AP).

Dokonano przeglądu najnowszego stanu wiedzy w dziedzinie procesu konwersji termicznej, a także zaprojektowano i przeprowadzono badania, w tym optymalizację powiązanych parametrów i analizy w skali laboratoryjnej, umożliwiając przygotowanie koncepcji odpowiedniej obróbki termicznej FW wraz z zaleceniami uwzględniającymi zapewnienie lepszej jakości produktów końcowych, aby pokierować poszukiwaniami i analizami, rzucając światło na transformacyjny potencjał obróbki HTC w rozwiązywaniu globalnych wyzwań związanych z FW przy jednoczesnym wspieraniu zrównoważonych i cyrkulacyjnych rozwiązań.

W niniejszej pracy przedstawiono krytyczne parametry HTC, w tym temperaturę, czas przebywania, stężenie reagentów i jakość produktu. Wyniki eksperymentu w skali laboratoryjnej wykazały: a) HTC przekształcił FW w HTC-AP, który wykazuje najwyższy procent nasyconych kwasów tłuszczowych (SFA), osiągając do 58,5% wag, i P w HC

wykazuje najwyższy odzysk (5,64 g-100 g-1), podczas gdy najwyższa wartość P w HTC-AP wynosiła 0,83 g-100 g-1, b) HTC-AP produkowała z większą wydajnością przy wysokich parametrach operacyjnych (340 ^{o}C) niż przy niższych (220 ^{o}C), uzyskując około 95% w zoptymalizowanych warunkach, c) projekt podejścia eksperymentalnego umożliwił optymalizację HC i HTC-AP. Co więcej, eksperyment w skali laboratoryjnej wykazał, że maksymalna osiągalna wydajność HC i HTC-AP wynosi odpowiednio 19,19% i 89,5%. Aby zweryfikować te przewidywania, przeprowadzono optymalizację z temperaturą i czasem ustawionymi na 220°C i 270 minut. W rezultacie uzyskano HC i HTC-AP odpowiednio na poziomie 18,9 ± 1,2% i 78,2 ± 2,2%. Wykazano, że wydajność i jakość produktów HTC zależy od parametrów operacyjnych. HTC przekształciła FW w HC z zawartością węgla (>55%), popiołu (<2%) i wyższą wartością opałową (19,2-32,5 MJ/kg). Dodatkowo, eksperyment w skali laboratoryjnej wykazał związek między składem HTC-AP, kinetyką wzrostu drożdży i produkcją lipidów. Wyniki wykazały: a) HTC-AP stosowany przez *Y lipolytica*, *Y. parophonii* i *Y. keelungensis* daje 4,5 g/l suchej biomasy (10-14% tłuszczy), b) *Y. yakushimensis* wykazała najwyższą szybkość wzrostu (wskazaną przez stałą kinetyczną) spośród wszystkich mediów, c) HTC-AP produkowany w temperaturze 260˚C służy jako najlepsze źródło tłuszczowych składników odżywczych. Wreszcie, eksperyment na skalę laboratoryjną połączonej HTC i fermentacji beztlenowej (AD) przyczynił się do lepszego zrozumienia waloryzacji FW poprzez HTC i zapewnił wgląd w zrównoważoną produkcję biogazu z FW. Zoptymalizowano warunki HTC w celu wytworzenia różnych wariantów HTC-AP i zbadano wpływ dodatku tlenku tytanu/biocharu do systemu HTC dla HTC-AP potencjał produkcji biometnau. Uzyskane wyniki sugerują, że zastosowanie katalizatora tlenku tytanu/biocharu podczas HTC ma kluczowe znaczenie dla wykorzystania HTC-AP do fermentacji metanowej i produkcji biometanu.

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LIST OF ABBREVIATIONS

AD - anaerobic digestion

BMP – biomethane potential

CCD - central composite design

DOE – design of experiment

FW - food waste

HPTP - high-pressure thermochemical processes

HTC - hydrothermal carbonization

HTC-AP – hydrothermal carbonization aqueous phase

HC - hydrochar

P - phosphorus

RSM - response surface methodology

SFA - saturated fatty acid

VFAs - volatile fatty acids

1. INTRODUCTION

Sustainable development is a wide, modern concept of organizing human needs to be met while preserving the integrity and stability of the natural systems. Increased waste production has made it necessary to seek optimization of existing waste management processes/strategies. The disposal of food waste (FW) constitutes a significant global environmental challenge, arising primarily from the organic fraction of municipal solid/industrial streams [1]. The global population in 2013 was estimated at 7.2 billion and is poised to increase by a billion in 2025, which makes the energy demand required for agricultural, industrial, and transportation development very crucial [2]. In this context, the circular economy emerges as a systematic methodology for environmental protection and economic growth, emphasizing the recovery of valuable materials, products, and energy from waste. One of the most promising strategies that are inextricably linked to the circular economy and sustainable development is the recovery of valuable materials, products, and energy from wastes [3].

The amount of generated FW, which is the main organic fraction of municipal solid waste and industrial waste from food production, shows an annual exponential growth, becoming one of the main global environmental problems [1]. In Europe alone, about 88 million tons of food is wasted annually, of which Poland is covered more than 10% [4]. Although, it was presented that 19% of food is wasted in China [5] and ~1.15 billion tons per year [6]. More so, it was demonstrated by Bilska et al. that the causes of the risk of FW by consumers determined the frequency of their occurrence. The most common causes of FW risk include food failure to arrange food in cabinets according to the expiry date, missing the expiry date, and spoiling [7]. The growing tendency to generate FW is highly required to find a solution to the problem connected with the management of this organic fraction. Therefore, FW with high lipid content (e.g., salad dressing, pumpkin, cheese, nuts, belly pork & bacon), high protein content (e.g., beef, pork & chicken), and high carbohydrate content (e.g., corn, rice, potatoes, hamburger bun, vegetable & fruit peels) can be repurposed to produce lipids and energy. This approach supports the circular economy by closing the loop on the FW stream [8,9]. One of the ways to perform this task is hydrothermal carbonization (HTC) due to its suitable operating and hydrothermal carbonization aqueous phase (HTC-AP) rich in volatile fatty acids (VFAs) and phosphorus (P), which may be converted to lipids using biotreatment from those mentioned feedstock to allow not only food waste management but also bioenergy and nutrients recovery at the same time [10–12]. This negatively impacts environmental well-being by causing nutrient runoff into water sources and increasing greenhouse gas emissions. This adversely affects environmental well-being because of causing nutrient-into-water contaminations and greenhouse gas emissions. The thesis aims and objectives have proposed that organic waste with high water content (>65%) can be converted into biofuels and biochemicals effectively via hydrothermal processing [13,14]. The selected feedstock(s) for the current work has been based on their individual properties, which makes them suitable for energy/lipids production from solid (which refers to hydrochar) and (liquid which refers to aqueous phase: HTC-AP) products.

In the current work, therefore, it was necessary to seek an effective thermal conversion and biological treatment of FW for P, VAFs, and energy sources product management focusing on recovery from FW, regarding renewability and sustainability from hydrothermal treatment end products (hydrochar and hydrothermal liquid). However, nutrient recovery from organic FW is a complex challenge and not a single-step process [15]. Specifically, the current work aimed to provide additional fundamental knowledge in the field of the thermal conversion process, which involved following objectives: (a) the determination of different HPTPs for organic waste conversion; (b) the determination of selected HPTPs for achieving higher quality and characterization of the HPTP products (HC and HTC-AP) for the production of by-products; (c) to optimize the HPTP operating conditions using DOE techniques to develop a model for yield and quality products including HC and HTC-AP, and their valuable nutrient recovery; and (d) to evaluate the feasibility of HPTP with biological treatment of HTC-AP to by-products such as VFAs, biomethane, and yeast growth.

One of the key components of this research is the use of catalysts to enhance biomethane production. The addition of catalysts during FW HTC can significantly improve the yield and quality of biomethane during the biological treatment of HTC-AP. Catalysts facilitate the breakdown of complex organic molecules into simpler compounds, which are more readily converted into biomethane by microbial activity. For the current work, a TiO_2/biochar catalyst was utilized to enhance biomethane production. TiO_2 nanoparticles are well-known for their photocatalytic properties, which accelerate the degradation of organic compounds and enhance biochemical reactions [16]. Biochar, on the other hand, enhances the adsorption of organic molecules, thereby increasing their accessibility to microbial enzymes. This process results in a higher concentration of fermentable substrates available for microbial metabolism, ultimately boosting biomethane production [17]. Furthermore, catalysts can mitigate the inhibitory effects of certain compounds present in food waste, such as phenolic compounds and heavy metals, which can impede microbial activity and methanogenic pathways [18]. TiO_2 nanoparticles have been demonstrated to adsorb and degrade various organic pollutants, thereby reducing their concentrations in the HTC liquid and alleviating the inhibition of methanogenic bacteria.

The schematic diagram of the performed research is given in **Figure 1**. The research started with the review of HPTPs for achieving higher quality and characterization of the HPTP products. Afterward, the optimization was carried out using the DOE to investigate the intricate relationships among independent parameters: HTC temperature, residence time, added water (liquid), and catalyst dosage, assessing their collective impact on dependent variables, including HC and HTC-AP yields, followed by preparation/analysis of the FW mixture. Next, at different HTC process parameters (temperature, stirring rate, and process time), HC combined with HTC-AP was produced. After the HTC process, emergent products were separated using vacuum filtration, followed by the liquid fraction subjected to biological treatment to produce biomethane/*yarrowia* growth. Finally, all data were analyzed for the best HTC conditions of which the products were characterized.

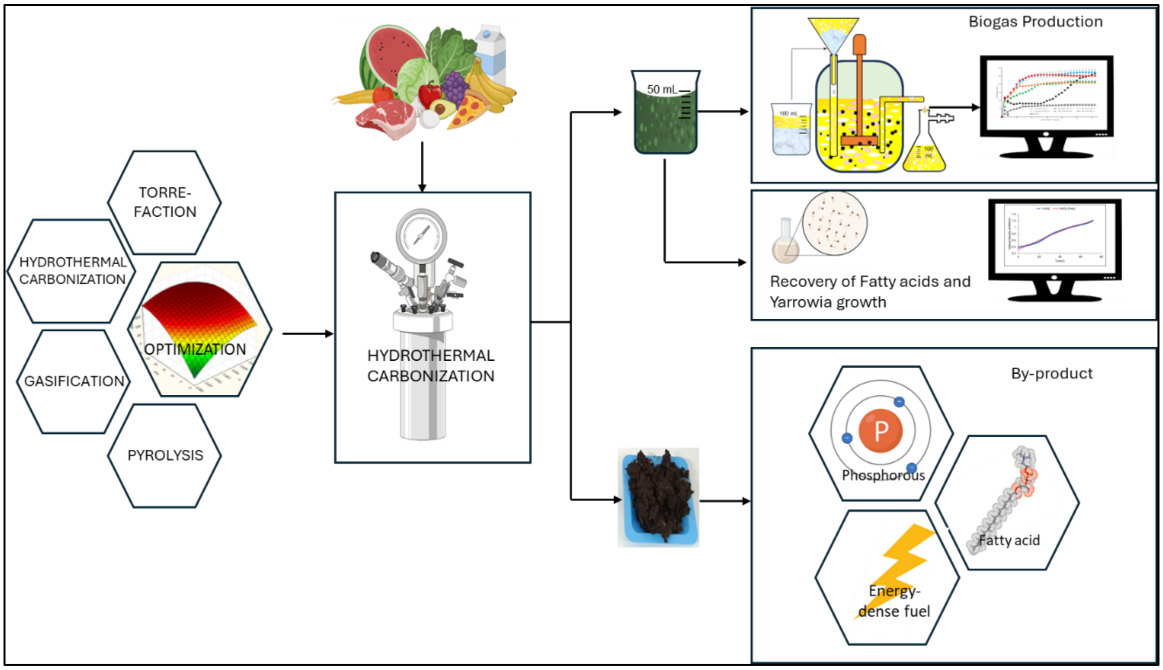

Figure 1. Schematic diagram representing the current experimental work

2. HIGH-PRESSURE THERMOCHEMICAL PROCESS

High-pressure thermochemical processes (HPTP) such as pyrolysis, gasification, torrefaction, and hydrothermal carbonization are employed worldwide to process various types of wastes with simultaneous energy recovery. These technologies are gaining momentum in recent times given the setbacks associated with the well-known biochemical processes such as anaerobic digestion (AD) to treat difficult wastes, such as lignin-rich materials. In addition, HPTP methods have shorter processing times and do not rely on maintaining biological communities [19,20]. Growing energy demands and environmental concerns have heightened global interest in renewable energy pathways to replace oil, coal, and natural gas [21]. Since biomass, organic waste, and agriculture waste feedstock have been recognized worldwide as promising in their conversion to biofuel, and other energy sources energy continues to be generated by developing technologies. HPTP, which includes pyrolysis, gasification, torrefaction, and HTC, can convert waste materials into valuable energy, offering a sustainable and eco-friendly solution [22–24].

On this premise, the thermochemical conversion process using a suitable thermal conversion reactor has become attractive for converting waste, which has been seen as an alternative renewable energy source over the last decade [21]. The energy associated with waste feedstock would be harnessed via thermochemical processes, which the latter being considered eco-friendly, would involve solid waste conversion technologies that operate at high temperatures. Essentially, this process provides a suitable and sustainable approach to transform low-value biomass/organic waste residues into energy and upcycled products. The CO_2 emission from fossil fuels, such as coal, is a major contributor to global warming. Therefore, CO_2 recycling via biomass thermochemical technology has a high promise to reduce the negative impact of global warming [25]. Pyrolysis, except the incineration, is the most researched thermochemical technique in the decade among the few well-established methods for treating biomass and biogenic waste to produce high-quality and yield energy products such as biochar, bio-oil, and pyrolytic gas.

Besides that, the context of thermal conversion technology (i.e., determination of operating parameters of pyrolysis-based) and reactor types have been based on the desired characteristics of the product (bio-oil, biochar, and pyrolytic gas), as well as on the field of biomass pyrolysis and upgrading. Feedstock properties, product characteristics, reactor type, and upgrading options are among key areas demonstrated as synthesized literature with relevant information. It is worth mentioning that some conducted literature has looked at systematic approaches for mapping biomass resources to conversion pathways, forming the basis for biomass valuation and informing when biomass pre-processing is needed to ensure feedstocks are conversion-ready [22]. Furthermore, bio-oil derived from pyrolysis biowaste would serve as chemicals/fuel products. More so, the production and composition of pyrolysis oil are affected by the biomass composition and process operating parameters [25].

2.1. Thermochemical Process Classification

With the global increase in food waste (FW), effective management and recycling are crucial to minimize health and environmental risks. The current work reviewed the available technologies for FW management. As illustrated in **Figure 2**, the most basic thermochemical conversion technologies are hydrothermal carbonization (HTC), gasification, pyrolysis, and torrefaction [20]. The HTC is operated between 180 and 374 °C within the pressure range of 4–22 MPa for producing HC and HTC-AP. Unlike pyrolysis, HTC does not require pre-drying [20,26]. Torrefaction typically occurs at a temperature range of 200–300 °C and a resident time of 15–60 min, respectively [27]. Biochar, bio-oil, and syngas are the by-products of the pyrolysis processes, which are typically carried out between 300 and 700 °C [28]. The gasification process involves heating feedstock to temperatures above 700 °C to produce syngas, containing mostly hydrogen and carbon monoxide [20]. Therefore, HTC is more considerable in the current work for FW conversion into valuable products like HTC-AP, HC, and other substances that are high in energy among the thermochemical processes mentioned above.

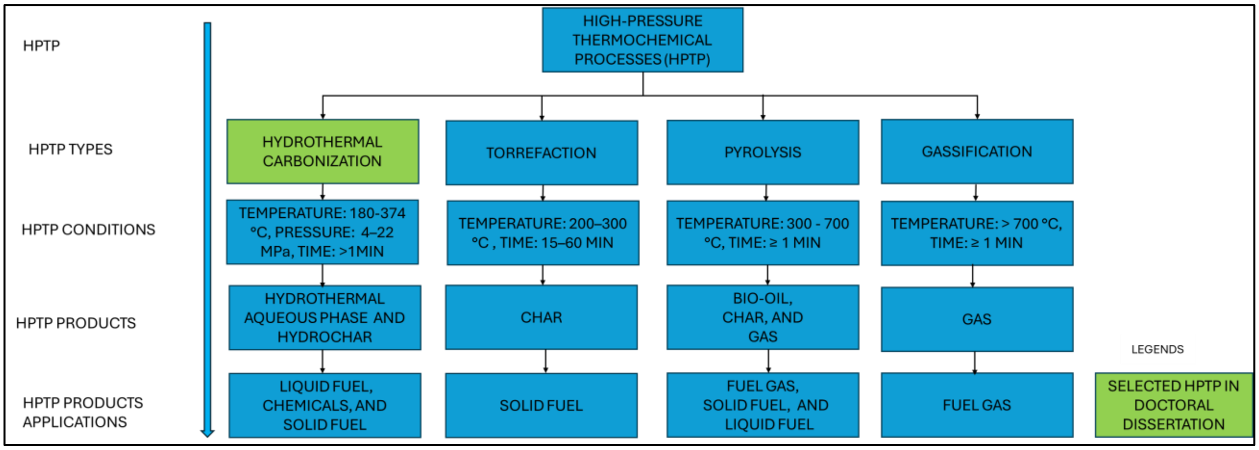

Figure 2. Thermochemical process classification and their operating conditions.

3. THE SELECTION OF THE THERMOCHEMICAL PROCESS

3.1. Hydrothermal carbonization and process conditions

Hydrothermal carbonization (HTC) is an efficient thermochemical conversion technique that transforms wet biomass into valuable energy and chemicals without pre-drying (the latter which would be considered optional). The solid product known as HC, has received attention because of its ability to prepare precursors of activated carbon in wastewater pollution remediation, soil remediation applications, solid fuels, and other carbonaceous materials, and the liquid fraction known as HTC-AP could be used for various applications. Given that the managing FW research focus is shifting toward eco-friendly methods. Consequently, FW disposal in landfills has already been controlled in many countries. Traditional FW management can include anaerobic digestion, combustion/composting, as well as direct land spreading [29–32]. Besides, HTC could find a suitable place in FW management, given its environment-friendly context of atmospheric emissions compared to other processes [33]. HTC could be a low-cost and feasible energy-efficient process to valorize waste, and synergistically maximize nutrient recovery [34]. The application of HTC can be considered advantageous over other treatment types, especially in the effective management of organic waste characterized by high moisture values [32,35,36].

This current work presented the critical hydrothermal parameters of HTC, including temperature, residence time, reactant concentration, and product quality. The chemical reaction mechanisms involved in the formation of HC and HTC-AP derived from single components and representative feedstock/FW were elucidated and summarized to understand the product formation process better. Specifically, HC physicochemical characteristics and VFAs profile of HTC-AP were investigated. The selected parameters in this work considered key aspects such as eco-friendly, waste management, and best operating process, aiming to obtain good quality end products. More so, FW comprises organic compounds and mineral salts, including a significant concentration of phosphorus, nitrogen, and potassium as essential nutrients [37,38]. However, the scarcity of these nutrients from natural sources makes it necessary to find new recovery pathways [38,39]. For the HTC process, using temperature ranges (200 – 340 °C) with pressure ranges from 0 to 200 bar, and a fixed residence time (60-260 min) in the entire experimental study in the current work. In addition, the selected HTC operating condition was based on post-processing, and given previous HTC experience, the target products to be produced should demonstrate both the operating condition(s) and feedstock type(s) would obtain high quality and yield of HC and HTC-AP by the application of high-pressure reactor Büchi Novoclave 600 ml, 400 bar, and 400 °C that available at Department of Applied Bioeconomy lab.

3.2. Optimization of Thermochemical Process

Despite the growing interest in HTC, there remains a research gap concerning the specific impact of process parameters, such as residence time and temperature, on the properties of HC and HTC-AP obtained from FW. To address this gap, we employed the response surface methodology (RSM) with a central composite design for optimizing HTC conditions for FW as demonstrated by [40]. RSM can help optimize HTC conditions for FW as influenced by several independent variables, via central composite design [40]. In particular, central composite design (CCD) in combination with RSM is considered a powerful tool to study, develop, and optimize several engineering processes [41]. Indeed, it appears as the better version of Box–Behnken design (BBD) that CCD constitutes fewer experimental numbers, reduces experimental errors, and equally helps in understanding the mechanism of the process. CCD is often considered more efficient for estimating model parameters compared to BBD. This is particularly true when a quadratic response surface is expected, as CCD includes additional points that improve the precision of parameter estimates. It includes both factorial points and axial points, allowing for the exploration of a broader region of the independent variable space. By optimizing the process parameters, RSM would predict outcomes via regression equation(s) engaging the interactive effects of temperature, resident time, HC energy densification ratio, and HTC-AP mass yield [42–44].

The current work involved a lab-scale pressure reactor, and optimization of HTC conditions: temperature (220-340 °C) and residence time (90-260 min) via CCD-RSM. Specifically, CCD-RSM was selected for optimization given its suitability for systematically exploring complex processes with multiple variables. Data-driven optimization is facilitated by RSM, while variable interactions are captured by CCD, making it ideal for the study's goal of optimizing HTC conditions for FW valorization. The study on the optimization of HTC to produce VFA and recovery of P has been given in the research article included in the current work **M3** [13], and additional work on VFA production due to HTC of FW has been presented in manuscript **M6** – submitted to Waste Management (under review). Notably, the combination of CCD and RSM proved to be a robust and effective tool for studying, developing, and optimizing various engineering processes [41].

3.3. Combined Thermochemical and Biological Treatment of Food Waste

One of the main biomasses produced in large quantities in urban areas is FW, which accounts for over one-third of greenhouse gas emissions worldwide. Effective management must be considered to minimize the negative impact of FW on the environment. Given that the combination of biological and HTC treatment of organic waste, especially FW, is currently considered a promising method in the waste management industry. Combined HTC and anaerobic digestion (AD) would produce significant energy and increase biomethane production from recurring waste such as FW [45,46]. The concept of combining HTC and the biological process AD has become a viable method for converting organic waste, including FW, into biogas, primarily composed of methane and carbon dioxide. It is the breakdown of organic matter by anaerobic microorganisms at 37 or 55 ◦C in an oxygen-free environment. Combustible biogas with a CO_2 to CH_4 ratio of roughly 1:1 and digestate residues that can be used as both solid fuel and fertilizer are the primary process products [47]. Biogas can be produced from almost any type of biological feedstock, including various organic waste streams from society and feedstocks from the major agricultural sectors [48]. Despite extensive research on enhancing methane production through processes like biochar addition, the potential benefits of incorporating HTC-AP into AD remain underexplored [49].

Using yeast species known for their abilities to utilize unconventional carbon courses, e.g. n-alkanes, provides significant improvement of processes proposed in the literature [24,42,50]. Consequently, I with collaborators reported that in the HTC conditions of organic biomass (especially at high operating conditions) HTC-AP with VFAs of over 80% w/w concentration can be obtained [51]. These *Yarrowia* species are known to use many alternative carbon sources, such as alkanes, fats, raw glycerol, or VFAs, and produce large quantities of intracellular lipids [12]. Current work exploring the utilization of HTC-AP derived from FW via the HTC process as a growth medium for yeast species, with a specific focus on lipid production. While previous studies have primarily concentrated on converting FW into biofuels and biochar using HTC, limited attention has been given to the potential of HTC-AP as a nutrient-rich substrate for microbial biotechnology applications. By investigating the kinetics of yeast growth and lipid biosynthesis in HTC-AP-based media, this study offers new insights into the feasibility of using HTC-AP as a sustainable alternative to traditional growth media in microbial bioprocessing. Moreover, the comparative analysis of different HTC-AP processing parameters and their impact on yeast metabolism provides valuable information for optimizing waste valorization strategies and enhancing the efficiency of bio-recovery processes. By elucidating the relationship between HTC-AP composition, yeast growth kinetics, and lipid production, this work contributes to advancing our understanding of waste-to-value technologies and offers practical implications for sustainable waste management and bioprocessing industries [14]. The microbiological treatment process of FW, after the production of the VFAs, entails such stages as microbial fermentation, isolation, and purification of intracellular lipids, which makes this process environmentally friendly and economically viable, as shown by previous studies [51–55]. The study on the synergistic combining of HTC with the *Yarrowia* yeast growth has been given in the research article **M4** of the current work [14], and additional work on linking the HTC enhanced by catalysts addition with anaerobic digestion has been presented in the manuscript **M7** – submitted to Renewable Energy (under review). The outcomes of the current work contribute to a better understanding of FW valorization through HTC and offer insights into sustainable biogas production and growth medium for yeast species from FW streams. As a result of this current work research, a feasible approach for boosting biomethane potential and promoting the dual utilization of FW is proposed, thereby contributing to sustainable waste management and renewable energy generation.

4. RESEARCH PROBLEM, CURRENT STUDY AIM, AND HYPOTHESES

4.1. Research problem

The growing population and changing diets are intensifying food production, leading to significant organic waste generation. In many countries including Poland more than 10 million tons annually [13], some of these wastes are being managed ineffectively; for example, with very high moisture content, hence they are usually deposited in landfills. This adversely affects environmental well-being because of causes nutrient-into-water contaminations and greenhouse gas emissions. The thesis aims to propose that food waste (FW) with high moisture content (>65% w/w) can be converted into biofuels and biochemicals effectively via hydrothermal processing [13].

Previously published reviews before the current work appear with less emphasis on high-pressure fast pyrolysis and its potential in biomass conversion. Besides, delving deeper into HPTP requires understanding not only heating methods/reactor types, the composition processing/prevailing condition, and stakeholder participation but also the merits/demerits (of HPTP) associated with its usage on various feedstocks. In this context, several questions are needed, from implementing a typical pyrolysis-based study, through adequate engagement in (pyrolysis–based research) processes and the various suitable reactors that would deliver valuable products.

Food waste (FW) remains a big problem around the globe and a great deal of research has been carried out seeking avenues to tackle as well as prevent it. HTC is poised as a promising candidate to help tackle FW. However, before this current work, there appears to be a paucity of research regarding HTC applied to FW with a specific focus on how it impacts the quality of emergent products. In addition to this, there seems to be little understanding of the recovery pathways of nutrients arising from FW. It may also be challenging to optimize such (HPTP) system, and this will require the use of robust statistical tools that are well-known in several engineering processes.

Besides serving as natural nutrient sources, converting FW into biofuels and biochar is also another challenge, which requires the potential HPTP to explore. To process FW, a sustainable form of microbial biotechnology application is required, which would extend to an effective (waste) valorization bio-recovery. Many researchers have explored the use of catalysts in HTC, it will be useful to understand the strengths (of catalysts) to generate fuels, including value-added chemicals from different feedstock. It is very important to understand the interplay between HTC parameters, catalyst addition, and biomethane production. There is also a challenge in understanding the efficiency of the HTC process, including the thermal transformation of FW, particularly how it affects the qualities of HTC-AP and HC.

4.2. Research study aim

The aim of the study designed and carried out as part of the doctoral dissertation was to gain new knowledge on food waste conversion into valuable products, using a high-pressure thermochemical process (HPTP) with biological treatment, with the following specific objectives:

a. The selection of a suitable high-pressure thermochemical process (HPTP) for food waste treatment; and
b. The optimization of the critical parameters of the high-pressure thermochemical process (HPTP) to enhance the yield and quality of it is an end product.

4.3. Research hypotheses

Hypotheses 1 (H1): It is possible to understand the HPTP and its principles including the process conditions (temperature, pressure, residence time) effect to achieve high quality and yields of emerging products.

Hypotheses 2 (H2): It is possible to identify specific HPTP and associated reactors and their role(s), in other to select a viable thermal conversion treatment (specific to HTC) and microbial fermenter capable of dealing with food waste challenges.

Hypotheses 3 (H3): It is possible to optimize the HTC operating conditions incorporating DOE techniques, and evaluate emergent product(s) (specific to HC and HTC-AP) quality, yield, and energy consumption required.

Hypotheses 4 (H4): It is possible to further optimize the HTC operating conditions incorporating DOE techniques, supplementing a catalyst (titanium oxide and biochar) to achieve HTC-AP for potential biomethane production.

5. CURRENT WORK STRUCTURE

This current work consists of 7 thematically coherent scientific articles published in the years 2021 – 2024 in peer-reviewed journals or being under review, listed chronologically in **Table 1**. In each of the presented manuscripts, the Ph.D. candidate is the first author. The total IF of the presented publications is 47.348 (published: 30.548), while their total Ministry of Science and Higher Education (MSHE, Poland) score is 1100 (published: 760). The topic undertaken in this current work has been discussed in publications on a total of 143 pages using 605 literature sources.

Table 1. Publications included in the doctoral dissertation with bibliometric data

No.	**Publication**	**Pages**	**No of Literature**	**IF**	**MSHE, points**
M1	**Waheed A. Rasaq**, Mateusz Golonka, Miklas Scholz, Andrzej Białowiec, 2021. "Opportunities and challenges of high-pressure fast pyrolysis of biomass: A review." *Energies* 14 (17), 1 – 20 doi: 10.3390/en14175426	20	91	3.252	140
M2	**Waheed A. Rasaq**, Charles Odilichukwu R. Okpala, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. "Navigating Pyrolysis Implementation—A Tutorial Review on Consideration Factors and Thermochemical Operating Methods for	44	151	3.748	140

	Biomass Conversion." *Materials* 17(3), 1 – 44 doi: 10.3390/ma17030725				
M3	**Waheed A. Rasaq**, Vaikunthavasan Thiruchenthooran, Paweł Telega, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. “Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste”. Journal of Environmental Management 357, 1 – 8 doi: 10.1016/j.jenvman.2024.120722	8	44	8.7	200
M4	**Waheed A. Rasaq**, Bartosz Matyjewicz, Kacper Świechowski, Zbigniew Lazar, Patryk Kupaj, Tomasz Janek, Marvin Valentin, Andrzej Białowiec, 2024. “Food waste recycling to *Yarrowia* biomass due to combined hydrothermal carbonization and biological treatment”. Journal of Cleaner Production 456, 1 - 10 doi:10.1016/j.jclepro.2024.142385	10	60	11.1	140
M5	**Waheed A. Rasaq**, Charles Odilichukwu R. Okpala, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. “Catalyst-Enhancing Hydrothermal Carbonization of Biomass for Hydrochar and Liquid Fuel Production—A Review”. *Materials* 17(11), 1 – 25 doi:10.3390/ma17112579	25	140	3.748	140
M6	**Waheed A. Rasaq**, Vaikunthavasan Thiruchenthooran, Katarzyna	36	86	8.1	200

	Wirkijowska, Marvin Valentin, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, "Hydrothermal carbonization of combined food waste: A critical evaluation of emergent products". Waste Management, is under review				
M7	**Waheed A. Rasaq**, Marvin Valentin, Kacper Świechowski, Chinenye Adaobi Igwegbe, Andrzej Białowiec. "Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization". Renewable Energy, is under review. Preprint: doi: 10.2139/ssrn.4827691	23	33	8.7	140

Due to two research objectives related to the high-pressure thermochemical process (HPTP) with combined biological for food waste treatment in this current work (refer to Chapter 4), the articles constituting it were divided into two groups and arranged in a logical order. In such manner, the data used to implement research objective I: *The selection of better high-pressure thermochemical process (HPTP) for food waste treatment* contained in the manuscripts numbered **M1**, **M2**, and **M4**, are presented first in the current work appendices. Thus, these articles are followed by data presenting research objective II: *The optimization of the critical parameters of the HPTP to enhance the yield and quality of it is an end product* (Manuscripts **M3**, **M5**, **M6**, and **M7**). The structure of the current work is also shown in **Figure 3**.

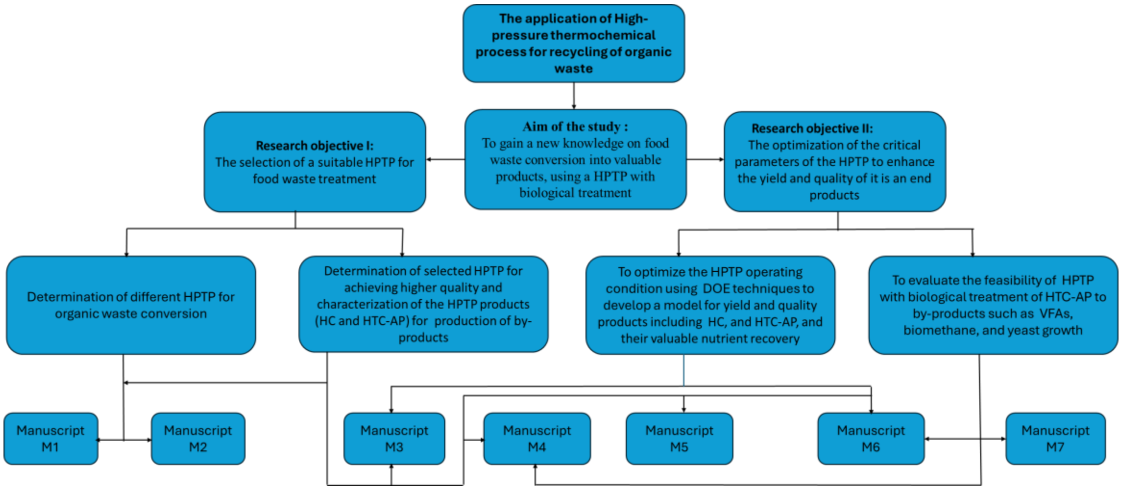

Figure 3. The structure of the current work.

A brief synopsis of each of the publications that make up this work is given. To fulfill the objectives of the current work, Chapter 6 provides the content of each of the manuscripts. The main scientific achievements of each article have been highlighted. Chapter 7 provides an overview of the materials and methods. Chapter 8 discusses the most significant outcomes of the research conducted and how they influence the environmental engineering, mining, and energy discipline. Subsequently, Chapter 9 presents the current work conclusions along with the research hypotheses that have been verified. Based on the summary of the conducted study, in Chapter 10, future perspectives of research in the field of the application of the HPTP for recycling the organic waste process are outlined.

6. DISCUSSION OF PUBLISHED PAPERS

6.1. Research objective I: The selection of a suitable high-pressure thermochemical process (HPTP) for food waste treatment

To understand the thermochemical process for food waste (FW) treatment, the literature on the subject was reviewed, and the various aspects were considered, including the process feasibility, and environmental aspects including natural ecosystems and waste treatment processes. The state-of-the-art in this field of the **determination of different HPTP for organic waste conversion** was accomplished in manuscripts M1, M2, and M4 (**Table 1**). The manuscript **M1** *Opportunities and challenges of high-pressure fast pyrolysis of biomass: A review* [22] is a review paper that provides more understanding of the thermal conversion process. It covers various aspects, including the classification of the process, types of feedstocks, and different reactor types, detailing how these factors influence the entire pyrolysis process. The literature sources analyze described different aspects of HPTP. It also reflected on the high-pressure fast pyrolysis as a novel solution to challenges related to heat transfer and, as well as product quantity and quality.

The next review paper builds on the insights from the previously discussed article. The **manuscript M2** *Navigating Pyrolysis Implementation—A Tutorial Review on Consideration Factors and Thermochemical Operating Methods for Biomass Conversion* [24] delves deeper into the topic by analyzing 151 literature sources. This comprehensive review focused on the critical factors and methodologies involved in the pre-to-main stages of pyrolysis, providing a thorough understanding of these processes and their expected outcomes. **M2** is a support to the existing information in **M1**, therefore, this review sought to seek how to navigate pyrolysis implementation, specifically considering factors and thermochemical operating methods for biomass conversion.

As a result of the above-discussed review papers, laboratory scale analyses were proposed. **To determine of selected HPTP for achieving higher quality and characterization of the HPTP products (HC and HTC-AP) for the production of by-products**, a lab-scale study was developed. The results are presented in one article: **M4**. The study presented in **the manuscript M4** *Food Waste Recycling to Yarrowia Biomass Due to Combined Hydrothermal Carbonization and Biological Treatment* [14]. The study aimed to (a) propose a novel approach to FW recycling and their conversion to lipids using HTC combined with biological treatment by *Yarrowia* sp., (b) the assessment on combining the HTC and fermentation of hydrothermal carbonization aqueous phase (HTC-AP) reach in volatile fatty acids with *Yarrowia* sp. for the production of the biomass as a method of the FW valorization and recycling, (c) evaluate the best *Yarrowia* sp. clade species for biomass yield, and compare it as a nutrient, rich in lipid including essential fatty acids obtained from HTC-AP. The article **M4** explored the HTC-AP from FW composition of model household FW found in Europe. The FW mixture consisted of 8.67% banana, 3.67% orange, 1.33% lemon, 7.33% apple, 24.33% potatoes, 4.67% onion, 3.33% cabbage, 3.33% salad, 2.33% tomatoes, 6% pasta, 6% rice, 3% bread, 12% fish meat, 3% meat, and 11% cheese by fresh mass. Then, subjected to HTC (temperatures 200, 220, 240, and 260 ˚C) with a uniform resident time of 60 min as media for microbial growth of 14 different *Yarrowia* species. Nine different media types (labeled as media 1 to media 9) were used in this study to determine and identify suitable conditions for the selected *Yarrowia* species' growth. These media were named based on the HTC operating conditions at 4 different temperatures and uniform residence time of 60 min shown **M4**. For the *Yarrowia* species growth optimization, the C/N ratio was adjusted to the value of 60 by the addition of ammonium chloride (Rakicka et al., 2015). Before, the ammonium ions concentration in different medium types was analyzed using the standard ninhydrin method.

6.2. Research objective II: To investigate and optimize the critical parameters of the HPTP process

The manuscript **M3** *Optimizing Hydrothermal Treatment for Sustainable Valorization and Fatty Acid Recovery from Food Waste* [13] employed response surface methodology and a central composite design (CCD) to optimize HTC conditions for the valorization of FW. The design of the experiment (DOE) was carried out to understand the influence of independent parameters (temperature and resident time) on dependent parameters [HC and HTC-AP yield and fatty acids content]. **To optimize the HPTP operating conditions using DOE techniques to develop a model for yield and quality products including HC and HTC-AP, and their valuable nutrient recovery.**

Lab-scale pressure reactor-based HTC processes are investigated to detect the effects of temperature. Firstly, the HTC process was conducted on potatoes, pork belly (PB), and pumpkin at 220g under different temperatures at 200, 240, and 280 ◦C with a uniform resident time of 60 min. Among different FW, the highest amount of lipid recovered was at 280 ◦C except for pumpkin. At this temperature, the highest quantity of lipid recovered was 3.4 ±0.2% from the PB samples. In addition to them, among all samples, the highest quantity of oleic acid was present in PB. Considering the possible recovery of several fatty acids, PB samples were further assessed for optimum yield of HC, HTC-AP, and free fatty acids. Whereas the center point temperature was maintained at 280 ◦C of the optimization using the design of experiments (DOE) approach in the next step.

Later HTC processes were carried out at five different temperatures of 220, 240, 280, 320, and 340 °C. After reaching a temperature of 5 °C lower than the set value, the process continued for 90, 120, 180, 240, and 260 min, respectively. Central to the study is the identification of temperature as the primary factor influencing FW conversion during the HTC process, showcasing its impact on HTC product yields. The results of this article demonstrate that the HTC-AP is rich in saturated fatty acids (SFA). Furthermore, a temperature-dependent trend is observed, with higher temperatures favoring increased SFA recovery.

To expand the findings, a second research article on a Lab-scale **M6** *Hydrothermal carbonization of combined food waste: A critical evaluation of emergent products* – submitted to Waste Management (under review), was developed following a similar approach to the model developed in research article **M3**. However, characterization of HC and additional analyses were able to be achieved in **M6.** Successfully and for the first time to our best knowledge, a combination of FW which comprised orange (3%), banana (10%), apple (5%), lemon (2%), potatoes (24%), onion (3%), lettuce (3%), cabbage (3%), tomatoes (2%), rice (10%), pasta (10%), bread (5%), meat (5%), fish (5%), and cheese (10%) subjected to HTC and emergent products were critically evaluated. HC produced with carbon (>55%), the heating value ranged from 19.2 to 32.5 MJ/kg. Temperature primarily influenced FW conversion, affecting carbonaceous properties. SFAs were found to be predominant in the HTC-AP under all tested operating conditions (77.3, 48.4, and 37.1 wt% for HTC at 340, 280, and 220 ℃ in 180 min, respectively). Total phosphorus recovery in HC and HTC-AP respectively peaked at 340°C and 220°C in 180 min. The study concludes that HTC holds promise for energy-dense biofuel production, nutrient recovery, and fostering a circular economy.

Furthermore, a review article was developed to investigate the impact of HTC condition and the addition of catalyst effect on HC and HTC-AP manuscript **M5** *Catalyst-Enhancing Hydrothermal Carbonization of Biomass for Hydrochar and Liquid Fuel Production—A Review* [56]. The analysis of 140 literature sources over the ongoing debate regarding the impact of catalysts on the HTC process underscores the importance of understanding how catalysts optimize biomass conversion into fuels and chemicals. Manuscript **M5** highlighted the significant role of catalysts in progressing carbonization degree, surface modification, and the alteration of key heteroatoms, thereby enhancing the performance of activated carbon. As catalytic HTC technology advances, the production of carbon materials for thermochemical activities becomes more cost-effective, meeting the growing demands for high-performance thermochemical technologies.

Subsequently, as a result of the above-discussed review paper **M5** and the research study of **M4** [14,56], there was a need **to evaluate the feasibility of HPTP with biological treatment of HTC-AP to by-products such as VFAs, biomethane, and yeast growth**. A laboratory scale analysis was proposed in **M7** *Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization* – submitted to Renewable Energy (under review). This investigation not only enriches our understanding of FW valorization through HTC but also offers novel insights into sustainable biomethane production from organic waste streams. Six different samples based on various HTC operating conditions using a systematic approach guided by RSM were investigated. The outcomes of the research contribute to a better understanding of FW valorization through HTC and offer insights into sustainable biogas production from organic waste streams.

7. MATERIAL AND METHODS

Three of the articles included in the current work are review papers (**M1**, **M2**, and **M5**), while the remaining four are research manuscripts presenting the outcomes obtained as a result of combining hydrothermal and biological treatment (manuscript **M4** and **M7**), and optimization of HTC parameters and laboratory-scale analyzes (manuscript **M3** and **M6**). **Table 2** summarizes the materials used in the research and the implemented methodology for each of the manuscripts **M1** to **M7**.

The research presented in the current work focused on analyzing food waste (FW) from a local grocery store. The decision to exclude actual FW aimed to tackle challenges related to variability in composition, ensuring reproducibility and generalizability. Actual FW often contains contaminants, making isolation difficult due to its diverse composition within collection points. To overcome these challenges, we opted for a controlled laboratory environment. Fifteen mixtures of different FW on a laboratory technical scale (manuscripts **M4** and **M7**) were subjected to HTC to utilize the obtained hydrothermal carbonization aqueous phase (HTC-AP) for microbial growth of *Yarrowia* species and potential biomethane production. Furthermore, (manuscripts **M6**) study: **a**) Characterization of raw FW/feedstock and fuel properties of HC from HTC; **b**) Optimization and efficiency of the HTC parameters (temperature and residence time); **c**) Examination of fatty acid content in both FW and the resulting HC and HTC-AP, alongside an investigation into phosphorus recovery in the HC and HTC-AP generated through HTC. Subsequently, investigate and optimize the critical parameters of the HTC process and effects on the HTC performance based on the optimization of three different FW including pork belly, potatoes, and pumpkins to enhance the yield of products and valuable compounds, with a specific emphasis on fatty acids, and validation of energy balance determination (manuscripts **M3**).

Table 2. Summary of materials and methods presented in the manuscripts **M1** to **M7**

Manuscript	**Type of the research**	**Materials**	**Methods**
M1	Review	Analysis of 91 literature sources	Google Scholar database used to identify research papers related to pyrolysis-based treatment classification and feedstock composition, reactor types used in HPTP, common heat transfer methods in HPTP treatment, the HPTP parameters' influence the end products' properties/yields, the catalyst types and their application HPTP.
M2	Review	Analysis of 151 literature sources	Web of Science Core Collection bibliometric analysis for keyword combinations: a) "Thermal conversion process" + "operating parameters", (b) "Thermal conversion process" + "feedstock", (c) "Feedstocks" + "treatment methods", and (d) "Thermochemical conversion" + "reactors"
M3	Laboratory scale analyzes	Food waste from a local grocery store including (pork belly, potatoes, and pumpkins)	➢ 10 kg of fresh ground pork belly (PB), 5 kg of potatoes, and 5 kg of pumpkins were procured from a local grocery store. ➢ Potatoes and pumpkins were ground using an electric grinder (Royal Catering, RCMZ-800, Wuppertal, Germany). ➢ The PB, potatoes, and pumpkins were separately homogenized using a drill (Bosch, model Professional GSB 16 RE, Gerlingen, Germany) with a mortar stirrer to ensure uniformity.

			➢ Feedstock preparation for the hydrothermal carbonization (HTC) treatment: homogenized feedstocks were then divided into samples weighing 230 g each and stored in a freezer (Electrolux, model EC5231A0W, Stockholm, Sweden) at a temperature of −27 ◦C until further experiments. ➢ Design of Experiment Setup for HTC process: The design of the experiment (DOE) was carried out to understand the influence of independent parameters (temperature and resident time) on dependent parameters [hydrochar (HC) and hydrothermal carbonization aqueous phase (HTC-AP) yield and fatty acids]. ➢ HTC process: A sample of 220g of PB, potatoes, and pumpkins, once thawed, was placed in the feedstock vessel of the high-temperature high-pressure reactor (HPHT) (Büchi AG, Uster, Switzerland), which was then placed in the heating jacket, closed, and sealed. The speed of the stirrer was set to 120 rpm and the desired temperature inside the vessel was set. The HTC processes were carried out at five different temperatures of 220, 240, 280, 320, and 340 ◦C. After reaching a temperature of 5 ◦C lower than the set value, the process continued for 90, 120, 180, 240, and 260. ➢ Optimization of the parameters for hydrothermal treatment of PB. ➢ Determination of fatty acid recovery from PB during the HTC process. ➢ Determination of HTC's performance and efficiency.

M4	Laboratory scale analyzes	Fresh FW were procured from a local grocery store including (fifteen different FW)	➢ The collection and the composition of the FW used in this study were performed as previously explained elsewhere [57] ➢ Feedstock for HTC process: It ensures morphological similarity and percentage of individual food components to ensure reproducibility. The FW mixture consists of 8.67% banana, 3.67% orange, 1.33% lemon, 7.33% apple, 24.33% potatoes, 4.67% onion, 3.33% of cabbage, 3.33% salad, 2.33% tomatoes, 6% pasta, 6% rice, 3% bread, 12% fish meat, 3% meat, and 11% cheese by fresh mass. ➢ Feedstock characterization: Drying and grinding of FW: The drying process took place at 105°C for 24 h with the application of a laboratory dryer (WAMED, KBC-65W, Warsaw, Poland). The pre-mixed FW components were ground with the help of a laboratory mill (Testchem knife mill LMN100), to create a homogeneous material. The prepared (kitchen waste) mix was sieved using a sieve mesh of 5 mm diameter. The raw and processed samples were tested in three replicates to ensure reproducibility. The MC was determined following. Samples were also tested for the content of volatile solids (VS), according to the PNEN 15935:2022-01 standard. ➢ HTC process: An HTC reactor (RBMT-2020-1.0) was used as previously explained elsewhere [47]. Using a prototype batch laboratory reactor (WUELS, RBMT2020-1.1, Wrocław, Poland). The prepared wet FW mixtures were divided into 5 portions and placed into

			aluminium trays that were placed on the grill (approximately 250 g of wet FW). Then the reactor was closed and filled with CO_2 inert gas. The reactor was operated at 4 different temperatures (200, 220, 240, and 260 ^{o}C) with a constant duration (60 min) to obtain four different HTC-AP products while the pressure was generated autogenously. ➢ *Yarrowia* clade species used for growth test on HTC–AP: fourteen different yeast strains belonging to the *Yarrowia* clade were used during this study to determine and identify the suitable conditions for the selected *Yarrowia* species' growth. ➢ Modelling of yeast growth kinetics: the *Yarrowia* species cumulative growth in all prepared HTC-AP was fitted into the Gompertz equation for individual growth of yeast in each tested media. ➢ Lipid production using *Yarrowia* species determination using the previous method elsewhere [58] ➢ Biomass and lipid production by *Yarrowia* clade species: determination of the total amount of biomass and lipids in the cells in individual tested strains in each media.
M5	Review	Analysis of 140 literature sources	Web of Science Core Collection bibliometric analysis for keyword combinations: a) "hydrothermal carbonization process" + "operating parameters", b) "hydrothermal carbonization process" + "catalyst types", c) "Catalyst effect" + "hydrothermal carbonization products",

M6	Laboratory scale analyzes	Fresh FW were purchased from a local grocery store including (fifteen different FW)	➢ Feedstock preparation for HTC process: It ensures morphological similarity and percentage of individual food components to ensure reproducibility. The FW mixture consists of 10% banana, 3% orange, 2% lemons, 5% apple, 24% potatoes, 3% onion, 3% cabbage, 3% lettuce, 2% tomatoes, 10% pasta, 10% rice, 5% bread, 5% fish, 5% meat, and 10% cheese by fresh mass. ➢ Feedstock and HC characterization: followed the same method as M4. ➢ Optimization of the HTC parameters: To obtain desired quantity of HC and HTC-AP, at their maximal quantity, the DOE approach was carried out. The influence of temperature and residence time was evaluated on HC and HTC-AP mass yield (%). In the design, 10 experiments (4 factorial points, 4 axial points, and 2 center points) were repeated randomly in 2 blocks to improve the significance and the obtained results. ➢ HTC process: The HTC process was performed using a high-temperature high-pressure reactor (HPHT) (Büchi AG, Uster, Switzerland) available at the Waste and Biomass Valorization Group Laboratory. A sample of 285.71 g was placed in the feedstock vessel, which consist of 100 g of dry FW and 185.71 g of water added in order to obtain 65% MC. The HTC processes were carried out at five different temperatures of 220, 240, 280, 320, and 340 °C. After reaching the

			temperature of 5 °C lower than the set value, the process continued for 90, 120, 180, 240, and 260 min. ➢ HC and raw feedstock/FW properties analyses: All substrates used in the study were analyzed for VS, TS, and AC, CHNS/O. The VS and TS were determined using a laboratory dryer (WAMED, model KBC-65W, Warsaw, Poland) according to previous research [59]. Additionally, the FW mixture and HC were subjected to thermogravimetric analysis (TGA) under isothermal conditions (950 ºC) and 7 min. The process was performed with the use of the TGA equipment as previously described [60]. ➢ Lipids analyses: The measurement of fatty acid composition was achieved by using GC-MS. Total lipid was extracted following the procedures as described previously [61] ➢ Phosphorous (P) and fatty acids content analyses**:** The quantification of P was determined using an equation listed in M6 for fatty acids and P content in HTC-AP and HC in compared to the raw FW ➢ HTC performance and efficiency: The impact of HTC operating conditions on products properties and energy consumption of individual experiment.
M7	Laboratory scale analyzes	Fresh FW were purchased from a local	➢ Feedstock preparation: it is the same process with M4 and M6

		grocery store including (fifteen different FW)	➢ Catalyst preparation: TiO_2 nanoparticles (<100 nm particle size, 99.5%), acetic acid (≥99.7%), and ethanol (96%) were obtained from Sigma Aldrich, Germany. Biochar derived from wheat straw was used. ➢ For preparation of the composite catalyst, the TiO_2 nanoparticles were initially subjected to a cleaning process by washing with ethanol, aiming to eliminate impurities and surface contaminants. A solution of 10% acetic acid was then prepared by dissolving acetic acid in deionized water, with subsequent mixing of 10 mL of acetic acid with 90 mL of deionized water to achieve a total volume of 100 mL. ➢ In the next step of the composite catalyst preparation, the functionalized TiO_2 nanoparticles were mixed with biochar in a specified proportion of 1:10 by mass. ➢ Inoculum preparation: Digestate from the 1 MWel commercial agricultural biogas plant (Bio-Wat Sp. z o.o., Świdnica, Poland) was used as an inoculum for biomethane potential tests. The biogas plant is running in mesophilic (37 °C) and wet conditions (dry mass less than 10%). After being collected into plastic canisters, the digestate was brought to the lab and left to stand at room temperature for roughly 24 hours. The digestate was filtered through gauze the next day to remove solid particles, such as plastics and unprocessed substrate, from the liquid portion. After that, the liquid digestate was kept in a climate

			chamber (Pollab, model 140/40, Wilkowice, Poland) at 4 °C until the biomethane potential test was conducted. ➢ Experimental design for HTC process for biomethane production: a thorough DOE was carefully conducted to investigate the intricate relationships among independent parameters: temperature, residence time, added water (liquid), and catalyst dosage, assessing their collective impact on dependent variables, including HC and HTC-AP yields, as well as biomethane production ➢ HTC process: The HTC processes were carried out at five different temperatures and residence times of 120, 180, 240, 300, and 360 °C; and 30, 90, 150, 210, and 270 min respectively, while the pressure was generated autogenously in accordance with M6 ➢ Tested experimental conditions were labelled by HTC operating conditions of selected HTC-AP samples as variant 1 (T120-RT150-W200-C1); variant 2 (T300-RT90-W150-C1.5); variant 3 (T240-RT150-W200-C2); variant 4 (T180-RT210-W250-C0.5); variant 5 (T240-RT150-W200-C0); and variant 6 (T360-RT150-W200-C1), respectively for the biomethane test ➢ Biomethane production test experimental setup: The experimental setup adhered to the protocol that had been previously described in the lab by [47]

			➢ The (BPC Instruments AB, AMPTS® II, Lund, Sweden) automated methane potential test system was used. The AD experiment was carried out at a mesophilic temperature of 37 °C in 500 mL glass reactors with agitation [49] ➢ The experiment was conducted in a single batch. The working volume of the reactor was set to (123.9 – 236.0 mL. To ensure homogeneity throughout the AD process, the automatic mixer was operated every hour for three minutes on the AMPTS's default mixing setting ➢ The produced biomethane was automatically measured and recorded by the AMPTS equipment. The biomethane production test took 30 days. ➢ Investigated the influence of HTC conditions and TiO_2/biochar catalyst addition on the BMP from HTC-AP during the AD. Employing central composite design-response surface methodology, HTC conditions were optimized to produce different HTC-AP variants, and the impact of TiO_2/biochar addition to the HTC system for BMP was examined.

8. RESEARCH EFFECTS

8.1. Determination of different HPTP for organic waste conversion

According to the literature, a high-pressure thermochemical process (HPTP) of biowaste has been reported. Thermochemical treatment routes such as pyrolysis, gasification, torrefaction, and hydrothermal carbonization (HTC) are employed worldwide to process various types of wastes with simultaneous energy recovery. The current work increases the understanding regarding HPTP. An attempt has been made to demonstrate how high-pressure fast pyrolysis can bring about high-quality biomass conversion into new products: **a**) It has been shown that fluidized bed (bubbling and circulating) reactors are most suitable and profitable in terms of product yield, **b**) evident that the increase of process pressure and biomass particle size decrease should be considered as variables for optimization **M1** [22].

8.2. Determination of selected HPTP for achieving higher quality and characterization of the HPTP products (HC and HTC-AP) for production of by-products.

Manuscript **M4** was developed to implement the practical approach related to suitable HPTP to obtain better end products. HTC is considered a suitable approach to food waste (FW) management in this current work because, it is more environmentally friendly [33], cost-effective, and able to maximize the recovery of water and nutrients while retaining carbon [14]. **The most important scientific achievement of manuscript M4 was the determination of biomass and lipids by *Yarrowia* species**. Result of lipid biosynthesis, *Y. lipolytica*, *Y. parophonii*, and *Y. keelungensis* produced approximately 4.5 g/L of dry biomass containing 10–14% lipids. Lipid recovery by HTC-AP-based media that combined HTC and biological treatment of FW appears a feasible process. Notably, HTC-AP obtained at 240 ◦C for 60 min would effectively support the growth and lipid biosynthesis of *Y. lipolytica*, *Y. parophonii*, and *Y. keelungensis* [14].

8.3. To optimize the HPTP operating conditions using DOE techniques to develop a model for yield and quality products including HC and HTC-AP, and their valuable nutrient recovery

A lab-scale pressure reactor was employed to subject FW to HTC, and the optimization of HTC conditions: temperature (220-340 °C), and residence time (90-260 min) was accomplished by applying a central composite design type of response surface methodology (CCD-RSM) of a research article (**M3**) in the current work (refer to **Figure 4**). In continuation of the previous research article of the current work (**M3**) [13], additional research carried out on a laboratory scale as part of the current work contributed to the production of volatile fatty acids (VFAs) from HTC of three different FW including potatoes, pumpkin, and pork belly (PB) by employing the DOE approach stated in (**M3**). This allows us to determine the best FW to achieve high content quality for VFAs.

In order to optimize the process parameters, RSM predicted outcomes via regression equation(s) engaging the interactive effects of, residence time, temperature, and product yield. A model was developed before the HTC of FW for a better understanding of the process mechanisms. The two-way interaction (X_{AB}) of temperature and resident time was not significant on either HC or HTC-AP yields. Considering their level of significance, HC yield mass was modeled in a quadratic polynomial equation with high coefficient of determination (R^2 value = 0.94; R^2 adjusted value = 0.91) corresponding to obtained correlation values (Eq. 1). The model representation was further examined for HTC-AP yield mass, representing where quadratic interaction of time (X_B^2) and linear effect of temperature (X_A) and time (X_B) had significant impact on HTC-AP yield mass and the equation (R^2 value = 0.91; R^2 adjusted value = 0.89) is presented based on them (Eq. 2).

$$HC\ (\%) = 2.4958 + 0.0070\ (X_A) + 0.0578\ (X_B) - 0.0001\ (X_B)^2 \tag{1}$$

$$HTC - AP\ (\%) = 97.5042 - 0.0070\ (X_A) - 0.0578\ (X_B) + 0.0001\ (X_B)^2 \tag{2}$$

The optimal yields for HC and HTC-AP were projected at 6.15% and 93.85%, respectively at 320 °C for 200 min. To validate these predictions, optimization was conducted in triplicate at above said temperature and resident time. Consequently, HC and HTC-AP were obtained at 6 ± 1% and 94 ± 1%, respectively. Most interestingly, to complete the HTC process, the PB was submitted to 340 °C temperature at 260 min resident time to digest HC and maximize HTC-AP yield.

The most important scientific achievement of the manuscript M3 was the determination of HTC parameters influence on FW valorization: **a**) The FW valorization is a potential source of quality HTC-AP, **b**) HTC converted FW into HTC-AP which exhibits the highest SFA percentages, reaching up to 58.5 wt%, **c**) HTC-AP produced better at high operating parameters (340 °C) over lower operating parameters (220 °C), yielding approximately 95% at optimized conditions, and **d**) the design of the experimental approach offered the optimization of HC and HTC-AP.

To expand the findings, a second research article on a Lab-scale **M6** – submitted to Waste Management (under review), was developed following a similar approach to the model developed in research article **M3.** By optimizing the process parameters, RSM predicted outcomes via regression equation(s) engaging the interactive effects of, residence time, temperature, liquid/mass yield, and HC fuel properties. A model was developed before the HTC of FW for a better understanding of the process mechanisms. The two-way interaction (X_{AB}) of temperature (A) and resident time (B) was not significant on HC yield. Considering their level of significance, HC yield mass was modelled in a quadratic polynomial equation (R^2 value = 0.94; R^2 adjusted value = 0.91) corresponding to obtained correlation values (Eq. 3). The model representation was further examined for HTC-AP yield mass, where quadratic interaction (X_{A2} and X_{B2}) and linear effect (XB) of time had no significant impact on its yield mass and the equation (R^2 value = 0.91; R^2 adjusted value = 0.89) is presented based on them (Eq. 4) (**M6**).

$$HC\ (\%) = 61.78 - 0.307(X_A) - 0.0209(X_B) + 0.0005(X_A)^2 + 0.0001(X_B)^2 \tag{3}$$

$$HTC - AP\ (\%) = 49346 - 0.1435\ (X_A) + \ 0.0012\ (X_{AB}) \tag{4}$$

The maximum achievable yields for HC and HTC-AP were projected at 19.19% and 89.5%, respectively. To validate these predictions, an optimization run was conducted with temperature and time set at 220°C and 270 minutes. Consequently, HC and HTC-AP were obtained as 18.9 ± 1.2% and 78.2 ± 2.2%, respectively.

The most important scientific achievement of manuscript M6 was the determination of the HTC parameter's influence on FW valorization. The result concluded the following: **a**) HTC converted food waste into HC with C (>55%), AC (<2%), and HHV (19.2-32.5 MJ/kg), **b**) HC produced better at high operating parameters (320 and 340 ^{o}C) over lower operating parameters (220 ^{o}C), **c**) The highest total phosphorus (TP) recovery in hydrochar produced at 340°C and 180 min, while the HTC-AP showed low TP, peaking at 220°C.

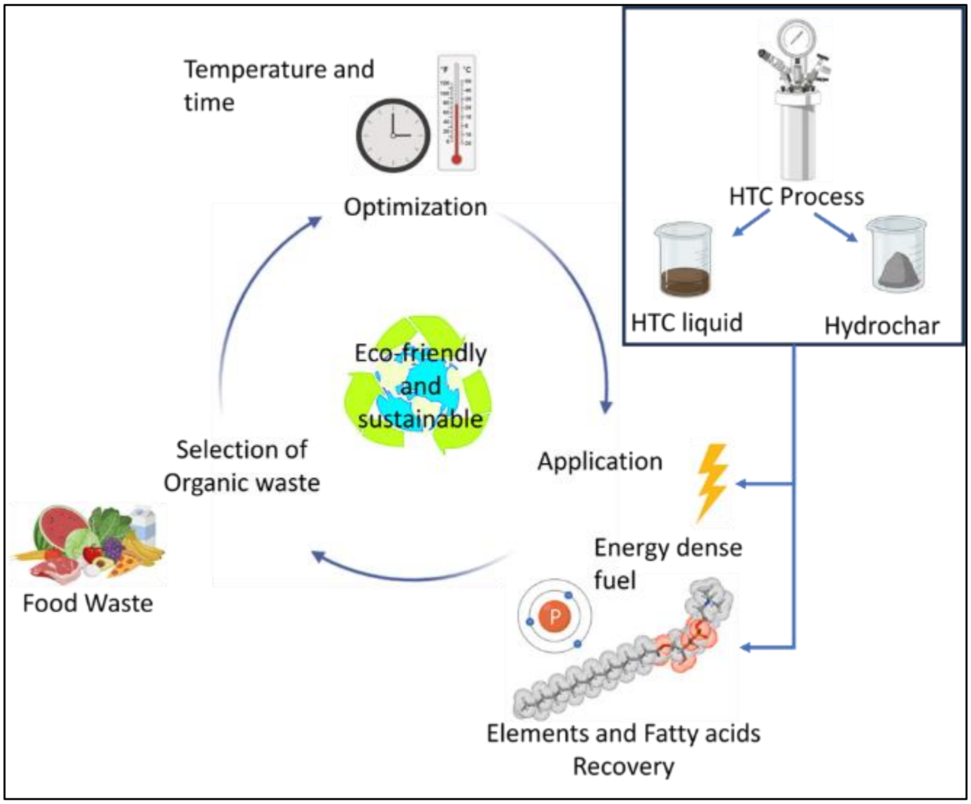

Figure 4. HTC treatment optimization to valuable end products.

8.4. To evaluate the feasibility of HPTP with biological treatment of HTC-AP to by-products such as VFAs, biomethane, and yeast growth.

The exploration of the utilization of HTC-AP derived from FW through the HTC process as a growth medium for yeast species, with a specific focus on lipid and biomass production **M4** [14], this study researched 14 different yeast from *Yarrowia* species using HTC-AP as a nutrient-rich substrate for microbial biotechnology applications, while previous research has primarily concentrated on converting FW into biofuels and biochar via HTC, limited attention has been given to the potential of HTC-AP. By investigating the kinetics of yeast growth and lipids with biomass biosynthesis in HTC-AP-based media, this current work offers new insights into the feasibility of using HTC-AP as a sustainable alternative to traditional growth media in microbial bioprocessing. Moreover, the comparative analysis of different HTC-AP processing parameters and their impact on yeast metabolism provides valuable information for optimizing waste valorization strategies and enhancing the efficiency of bio-recovery processes. **The most important scientific achievement of manuscript M4 was the determination of biomass and lipids by *Yarrowia* species** presented in (section **8.2)** of the current work.

In addition to the research article **M4**. Subsequently, research was carried out on a laboratory scale as part of the current work. Following the HTC experiments, the HTC-AP component was utilized for biomethane production (**M7**) **(Figure 5)** – submitted to Renewable Energy (under review) in the current work. Employing central composite design-response surface methodology, HTC conditions were optimized to produce different HTC-AP variants, and the impact of TiO_2/biochar addition to the HTC system for HTC-AP biomethane production (BMP) was examined. This research aimed to optimize the HTC process conditions with the addition of catalyst effect on HTC-AP for potential biomethane production. Leveraging a laboratory-scale pressure reactor and the DOE methodology, the study underscores the significance of optimizing process parameters to enhance BMP from FW HTC-AP during anaerobic digestion (AD). Six different samples based on various HTC operating conditions using a systematic approach guided by RSM were investigated. **The most important scientific achievement of manuscript M7 was the determination of the HTC parameter's influence on FW valorization**, which indicated the following conclusions: **a**) TiO_2/biochar catalyst enhances biomethane production from HTC-AP of FW, **b**) HTC variant 3, with the highest catalyst addition (HTC at temperature 240 ˚C in 150 min, added water 200 g, and added catalyst 2 g) demonstrated the highest BMP (274.03 mL/gVS), **c**) variant 5, without catalyst, shows inhibition of the anaerobic digestion process, **d**) a feasible approach proposed for boosting BMP from FW. By elucidating the combination of HTC and biological treatment contributed to advancing understanding of waste-to-value technologies and offers practical implications for sustainable waste management and bioprocessing industries.

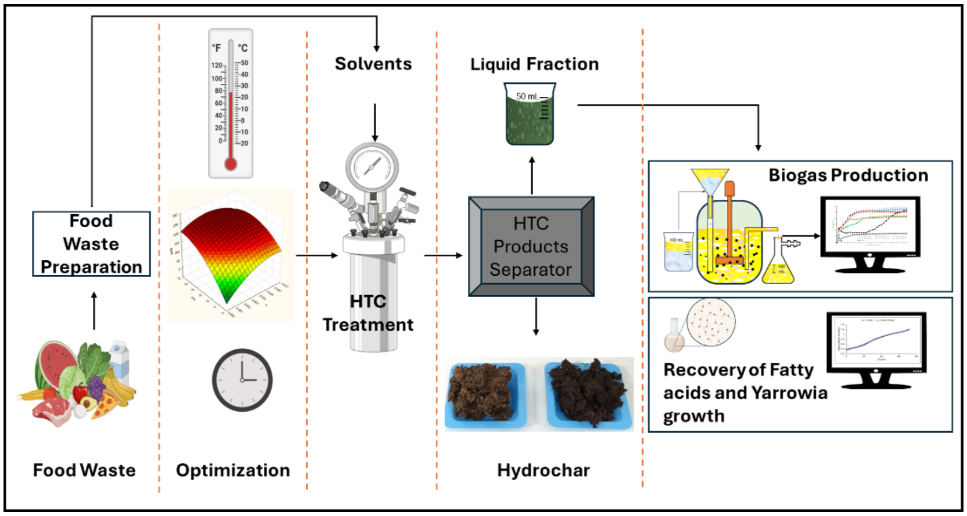

Figure 5. Feasibility of HPTP with biological treatment of HTC-AP to by-products.

9. CONCLUSIONS AND HYPOTHESES VERIFICATION

The research problem of the current work concerned the knowledge of better high-pressure thermochemical process (HPTP) for food waste (FW) treatment, **H1**: including pyrolysis, torrefaction, gasification, and hydrothermal carbonization, while the optimal critical parameters and mechanism of the HPTP especially hydrothermal carbonization (HTC) process of FW to investigate the validity of the theoretical concept of using the HPTP for the recycling/conversion of FW into valuable products including hydrochar (HC) and hydrothermal aqueous phase (HTC-AP), (refer to manuscripts **M1** and **M2**). For this purpose, studies were designed and conducted to enable the determination of suitable HPTP and optimize the critical parameters of the HTC process, including **a**) the determination of the operating conditions (temperature, resident time, feedstock moisture content, and additive of solvents) effects on the HTC performance based on optimization, to enhance the yield of valuable compounds, with a specific emphasis on fatty acids, biogas potential, *Yarrowia* growth, and characterization of raw FW/feedstock and HC fuel properties from HTC, and **b**) validation of energy balance determination of HTC process.

According to the research results indicated in chapter **8.2** and manuscripts **M4**, despite the advancement of above mentioned HPTP, the idea of combining thermochemical with biological treatment is more likely to be achieved using HTC. For that reason, **H2**: HTC is considered a suitable approach to FW management in this current work because it is cost-effective and able to maximize the recovery of HC and HTC-AP and nutrients while retaining carbon. According to the results presented in chapter **8.2** and manuscript **M4**, a technical lab scale experiment demonstrates the relationship between HTC-AP composition, yeast growth kinetics, and lipid production, this study contributed to advancing understanding of waste-to-value technologies and offers practical implications for sustainable waste management and bioprocessing industries. **H3**: the result of the research article (**M4**) indicated the following conclusions: **a**) HTC-AP used by *Y lipolytica*, *Y. parophonii*, and *Y. keelungensis* yields 4.5 g/L dry biomass (10 -14% lipids), **b**) *Y. yakushimensis* showed the highest growth rate (indicated by kinetic constant) among all the media, **c**) HTC-A produced at 260˚C serves as the best lipid source of nutrients.

Per the results presented in chapter **8.3** and manuscript **M3**, a technical lab scale experiment demonstrates, **H3**: **a**) HTC converted FW into HTC-AP which exhibits the highest saturated fatty acids percentages, reaching up to 58.5 wt%, **b**) HTC-AP produced better at high operating parameters (340 ^{o}C) over lower operating parameters (220 ^{o}C), yielding approximately 95% at optimized conditions, **c**) the design of the Experimental approach offered the optimization of HC and HTC-AP. According to the results presented in chapter **8.3** and manuscript **M6**, a technical lab scale experiment demonstrates the maximum achievable yields of HC and HTC-AP were projected at 19.19% and 89.5%, respectively. To validate these predictions, an optimization run was conducted with temperature and time set at 220°C and 270 minutes. Consequently, HC and HTC-AP were obtained as 18.9 ± 1.2% and 78.2 ± 2.2%, respectively. It was proved that the yield and quality of HTC products are affected by operating parameters, **H3**: **a**) HTC converted FW into HC with C (>55%), AC (<2%), and HHV (19.2-32.5 MJ/kg), **b**) HC produced better at high operating parameters (320 and 340 ^{o}C) over lower operating parameters (220 ^{o}C), **c**) The highest total phosphorus (TP) recovery in HC produced at 340°C and 180 min, while the HTC-AP showed low TP, peaking at 220°C. The results presented in chapter **8.4** and manuscript **M7**, from a technical lab scale experiment contributed to a better understanding of FW valorization through HTC and offered insights into sustainable biomethane production from organic waste streams. The key findings include. **H4:** **a**) TiO_2/biochar catalyst enhances biomethane production from HTC-AP of FW, **b**) HTC variant 3, with higher catalyst addition exhibited the highest biomethane production yield, **c**) variant 5 (HTC at temperature 240 ^{o}C in 150 min, and added water 200 g) without catalyst addition showed the lowest biomethane production (40.09 mL) shows inhibition of the anaerobic digestion process, **d**) a feasible approach proposed for boosting biomethane potential from FW.

10. FUTURE RESEARCH DIRECTIONS

The results presented in the current work contribute to a better understanding of food waste (FW) valorization through the high-pressure thermochemical process (HPTP) specifically hydrothermal carbonization (HTC) and offer insights into sustainable valuable nutrients, which serves as biomethane production from organic waste streams and are used as microbial growth. However, it is still required to delve into some parts of the treatment strategy to overcome some challenges. The directions of future research involving the application of HPTP treatment can be seen which involve considerations like **a)** environmental, economy, analytical method, feedstock/catalyst selection, as well as HTC operating conditions, **b)** future research on a larger scale is recommended to delve deeper into energy consumption reduction and maximize the efficiency of FW utilization in the HTC process, providing further insights that would contribute to a more sustainable and efficient circular economy [13].

The results presented in the current work also indicated an important direction for future research on the HPTP of FW. The direction of future work should look at the challenges associated with low-cost catalysts as well as those of best product quality being employed in thermochemical conversion technologies. More so, the prior-treatment process is essential to hydrothermal carbonization aqueous phase (HTC-AP) and hydrochar (HC) for nutrient substances, such as phosphorus and nitrogen recovery. For emphasis, the distribution, transformation mechanism, recovery, and future initiatives should also seriously consider the relevant analysis and treatment [62,63]. From an environmental perspective, HTC products offer numerous benefits for their applications. However, the economic aspects need to be estimated based on the investments in the conversion technology and production cost [64]. This could be achieved by the addition of a suitable catalyst to a specific feedstock regarding the target product application. In addition to performance, the following environmental and recycling perspectives could be considered: **a**) environmental impact and cost, which might necessitate testing of novel activating agents and HTC catalysts with less environmental impact; **b**) recycling of the activation agent and HTC-AP where possible [64,65]. The HTC-AP processing temperature on bio-recovery, yeast growth, biomass yield, and lipid production from FW suggests a strong potential for cleaner and more sustainable production practices. Quantitative assessments, such as comparing energy consumption, and life cycle assessment (LCA) between traditional methods and the proposed process, or estimating emission reductions, could further support these potential improvements measurably. HTC conversion of FW into HC and HTC-AP which can be considered as easily stored energy-rich resources.

11. REFERENCES

1. Uçkun Kiran, E.; Trzcinski, A.P.; Ng, W.J.; Liu, Y. Bioconversion of Food Waste to Energy: A Review. *Fuel* **2014**, *134*, 389–399, doi:10.1016/j.fuel.2014.05.074.

2. Tripathi, M.; Sahu, J.N.; Ganesan, P. Effect of Process Parameters on Production of Biochar from Biomass Waste through Pyrolysis: A Review. *Renew. Sustain. Energy Rev.* **2016**, *55*, 467–481, doi:10.1016/j.rser.2015.10.122.

3. Hahladakis, J.N.; Iacovidou, E.; Gerassimidou, S. *Plastic Waste in a Circular Economy*; Elsevier Inc., 2020; ISBN 9780128178805.

4. Borowski, M. *Raport Federacji Polskich Banków Żywności - Nie Marnuję Jedzenia 2018*; Poland, 2018;

5. Liu, J.; Lundqvist, J.; Weinberg, J.; Gustafsson, J. Food Losses and Waste in China and Their Implication for Water and Land. *Environ. Sci. Technol.* **2013**, *47*, 10137–10144, doi:10.1021/es401426b.

6. Sheng, Y.; Song, L. Agricultural Production and Food Consumption in China: A Long-Term Projection. *China Econ. Rev.* **2019**, *53*, 15–29, doi:10.1016/j.chieco.2018.08.006.

7. Bilska, B.; Tomaszewska, M. Analysis of the Behaviors of Polish Consumers in Relation to Food Waste. *Sustainability* **2020**, *12*, 1–16, doi:10.3390/su12010304.

8. Osman, A.I.; O'Connor, E.; McSpadden, G.; Abu-Dahrieh, J.K.; Farrell, C.; Al-Muhtaseb, A.H.; Harrison, J.; Rooney, D.W. Upcycling Brewer's Spent Grain Waste into Activated Carbon and Carbon Nanotubes for Energy and Other Applications via Two-Stage Activation. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 183–195, doi:10.1002/jctb.6220.

9. Malảák, J.; Dlabaja, T. Hydrothermal Carbonization of Stabilized Sludge and Meat and Bone Meal. *Res. Agric. Eng.* **2015**, *61*, 21–28, doi:10.17221/59/2013-RAE.

10. Theppitak, S.; Hungwe, D.; Ding, L.; Xin, D.; Yu, G.; Yoshikawa, K. Comparison on Solid Biofuel Production from Wet and Dry Carbonization Processes of Food

Wastes. *Appl. Energy* **2020**, *272*, 115264, doi:10.1016/j.apenergy.2020.115264.

11. Chen, X.; Ma, X.; Peng, X.; Lin, Y.; Yao, Z. Conversion of Sweet Potato Waste to Solid Fuel via Hydrothermal Carbonization. *Bioresour. Technol.* **2018**, *249*, 900–907, doi:10.1016/j.biortech.2017.10.096.

12. Quarterman, J.; Slininger, P.J.; Kurtzman, C.P.; Thompson, S.R.; Dien, B.S. A Survey of Yeast from the Yarrowia Clade for Lipid Production in Dilute Acid Pretreated Lignocellulosic Biomass Hydrolysate. *Appl. Microbiol. Biotechnol.* **2017**, *101*, 3319–3334, doi:10.1007/s00253-016-8062-y.

13. Rasaq, W.A.; Thiruchenthooran, V.; Telega, P.; Bobak, Ł.; Igwegbe, C.A.; Białowiec, A. Optimizing Hydrothermal Treatment for Sustainable Valorization and Fatty Acid Recovery from Food Waste. *J. Environ. Manage.* **2024**, *357*, 3–10, doi:10.1016/j.jenvman.2024.120722.

14. Rasaq, W.A.; Matyjewicz, B.; Lazar, Z.; Kupaj, P.; Janek, T.; Valentin, M.; Białowiec, A. Food Waste Recycling to Yarrowia Biomass Due to Combined Hydrothermal Carbonization and Biological Treatment. **2024**, *456*, doi:10.1016/j.jclepro.2024.142385.

15. Jama-Rodzeńska, A.; Białowiec, A.; Koziel, J.A.; Sowiński, J. Waste to Phosphorus: A Transdisciplinary Solution to P Recovery from Wastewater Based on the TRIZ Approach. *J. Environ. Manage.* **2021**, *287*, doi:10.1016/j.jenvman.2021.112235.

16. Chen, D.; Cheng, Y.; Zhou, N.; Chen, P.; Wang, Y.; Li, K.; Huo, S.; Cheng, P.; Peng, P.; Zhang, R.; et al. Photocatalytic Degradation of Organic Pollutants Using TiO2-Based Photocatalysts: A Review. *J. Clean. Prod.* **2020**, *268*, 121725, doi:10.1016/j.jclepro.2020.121725.

17. Igwegbe, C.A.; Kozłowski Kozłowski; Wasowicz, J.; Edyta, P.; Białowiec, A. Nitrogen Removal from Landfill Leachate Using Biochar Derived from Wheat Straw. *Materials (Basel).* **2024**, *928*, 20, doi:/doi.org/10.3390/ma17040928.

18. Montecchio, D.; Astals, S.; Di Castro, V.; Gallipoli, A.; Gianico, A.; Pagliaccia, P.;

Piemonte, V.; Rossetti, S.; Tonanzi, B.; Braguglia, C.M. Anaerobic Co-Digestion of Food Waste and Waste Activated Sludge: ADM1 Modelling and Microbial Analysis to Gain Insights into the Two Substrates' Synergistic Effects. *Waste Manag.* **2019**, *97*, 27–37, doi:10.1016/j.wasman.2019.07.036.

19. Sikarwar, V.S.; Pohořelý, M.; Meers, E.; Skoblia, S.; Moško, J.; Jeremiáš, M. Potential of Coupling Anaerobic Digestion with Thermochemical Technologies for Waste Valorization. *Fuel* **2021**, *294*, doi:10.1016/j.fuel.2021.120533.

20. Ong, H.C.; Chen, W.H.; Farooq, A.; Gan, Y.Y.; Lee, K.T.; Ashokkumar, V. Catalytic Thermochemical Conversion of Biomass for Biofuel Production: A Comprehensive Review. *Renew. Sustain. Energy Rev.* **2019**, *113*, 109266, doi:10.1016/j.rser.2019.109266.

21. Basile, L.; Tugnoli, A.; Cozzani, V. The Role of Pressure in the Heat of Pyrolysis of a Lignocellulosic Biomass. **2015**, *43*, 451–456, doi:10.3303/CET1543076.

22. Rasaq, W.A.; Golonka, M.; Scholz, M.; Białowiec, A. Opportunities and Challenges of High-pressure Fast Pyrolysis of Biomass: A Review. *Energies* **2021**, *14*, 1–20, doi:10.3390/en14175426.

23. Lee, S.Y.; Sankaran, R.; Chew, K.W.; Tan, C.H.; Krishnamoorthy, R. Waste to Bioenergy : A Review on the Recent Conversion Technologies. **2019**, 1–22.

24. Rasaq, W.A.; Okpala, C.O.R.; Igwegbe, C.A.; Białowiec, A. Navigating Pyrolysis Implementation—A Tutorial Review on Consideration Factors and Thermochemical Operating Methods for Biomass Conversion. *Materials (Basel).* **2024**, *17*, doi:10.3390/ma17030725.

25. Auersvald, M.; Macek, T.; Schulzke, T.; Staš, M.; Šimáček, P. Influence of Biomass Type on the Composition of Bio-Oils from Ablative Fast Pyrolysis. *J. Anal. Appl. Pyrolysis* **2020**, *150*, 104838, doi:10.1016/j.jaap.2020.104838.

26. Ischia, G.; Fiori, L. Hydrothermal Carbonization of Organic Waste and Biomass: A Review on Process, Reactor, and Plant Modeling. *Waste and Biomass Valorization* **2021**, *12*, 2797–2824, doi:10.1007/s12649-020-01255-3.

27. da Silva, C.M.S.; Carneiro, A. de C.O.; Vital, B.R.; Figueiró, C.G.; Fialho, L. de F.; de Magalhães, M.A.; Carvalho, A.G.; Cândido, W.L. Biomass Torrefaction for Energy Purposes – Definitions and an Overview of Challenges and Opportunities in Brazil. *Renew. Sustain. Energy Rev.* **2018**, *82*, 2426–2432, doi:10.1016/j.rser.2017.08.095.

28. Faba, L.; Díaz, E.; Ordóñez, S. Recent Developments on the Catalytic Technologies for the Transformation of Biomass into Biofuels: A Patent Survey. *Renew. Sustain. Energy Rev.* **2015**, *51*, 273–287, doi:10.1016/j.rser.2015.06.020.

29. Hejna, M.; Świechowski, K.; Rasaq, W.A.; Białowiec, A. Study on the Effect of Hydrothermal Carbonization Parameters on Fuel Properties of Chicken Manure Hydrochar. *Materials (Basel).* **2022**, *15*, 2022–2023, doi:10.3390/ma15165564.

30. Połomka, J.; Jedrczak, A. Potential Ofmineral Fraction in Compost-like-Output, Methods of Its Obtaining and the Possibility of Using It in the Context of Circular Economy. *Materials (Basel).* **2020**, *13*, doi:10.3390/ma13133023.

31. Avagyan, A.B. Environmental Building Policy by the Use of Microalgae and Decreasing of Risks for Canadian Oil Sand Sector Development. *Environ. Sci. Pollut. Res.* **2017**, *24*, 20241–20253, doi:10.1007/s11356-017-9864-x.

32. Avagyan, A. *Algae to Energy and Sustainable Development. Technologies, Resources, Economics and System Analyses. New Design of Global Environmental Policy and Live Conserve Industry*; Amazon, 2018; ISBN 978-1718722552.

33. Zabaniotou, A.; Rovas, D.; Delivand, M.K.; Francavilla, M.; Libutti, A.; Cammerino, A.R.; Monteleone, M. Conceptual Vision of Bioenergy Sector Development in Mediterranean Regions Based on Decentralized Thermochemical Systems. *Sustain. Energy Technol. Assessments* **2017**, *23*, 33–47, doi:10.1016/j.seta.2017.09.006.

34. Taylor, P.; Demirbas, A. Production of Gasoline and Diesel Fuels from Bio-Materials. **2007**, 753–760, doi:10.1080/00908310500281288.

35. Hoekman, S.K.; Broch, A.; Robbins, C. Hydrothermal Carbonization (HTC) of

Lignocellulosic Biomass. *Energy and Fuels* **2011**, *25*, 1802–1810, doi:10.1021/ef101745n.

36. Lachos-Perez, D.; César Torres-Mayanga, P.; Abaide, E.R.; Zabot, G.L.; De Castilhos, F. Hydrothermal Carbonization and Liquefaction: Differences, Progress, Challenges, and Opportunities. *Bioresour. Technol.* **2022**, *343*, 126084, doi:10.1016/j.biortech.2021.126084.

37. Sarrion, A.; Diaz, E.; Rubia, M.A. De; Mohedano, A.F. Bioresource Technology Fate of Nutrients during Hydrothermal Treatment of Food Waste. *Bioresour. Technol.* **2021**, *342*, 125954, doi:10.1016/j.biortech.2021.125954.

38. Zhao, X.; Becker, G.C.; Faweya, N.; Correa, C.R.; Yang, S.; Xie, X. Fertilizer and Activated Carbon Production by Hydrothermal Carbonization of Digestate. **2018**, 423–436.

39. Smol, M. The Importance of Sustainable Phosphorus Management in the Circular Economy (CE) Model : The Polish Case Study. *J. Mater. Cycles Waste Manag.* **2019**, *21*, 227–238, doi:10.1007/s10163-018-0794-6.

40. Chelladurai, S.J.S.; Murugan, K.; Ray, A.P.; Upadhyaya, M.; Narasimharaj, V.; Gnanasekaran, S. Optimization of Process Parameters Using Response Surface Methodology: A Review. *Mater. Today Proc.* **2020**, *37*, 1301–1304, doi:10.1016/j.matpr.2020.06.466.

41. Anfar, Z.; Ait Ahsaine, H.; Zbair, M.; Amedlous, A.; Ait El Fakir, A.; Jada, A.; El Alem, N. Recent Trends on Numerical Investigations of Response Surface Methodology for Pollutants Adsorption onto Activated Carbon Materials: A Review. *Crit. Rev. Environ. Sci. Technol.* **2020**, *50*, 1043–1084, doi:10.1080/10643389.2019.1642835.

42. Marzbali, M.H.; Kundu, S.; Halder, P.; Patel, S.; Hakeem, I.G.; Paz-Ferreiro, J.; Madapusi, S.; Surapaneni, A.; Shah, K. Wet Organic Waste Treatment via Hydrothermal Processing: A Critical Review. *Chemosphere* **2021**, *279*, 130557, doi:10.1016/j.chemosphere.2021.130557.

43. Toptas Tag, A.; Duman, G.; Yanik, J. Influences of Feedstock Type and Process Variables on Hydrochar Properties. *Bioresour. Technol.* **2018**, *250*, 337–344, doi:10.1016/j.biortech.2017.11.058.

44. Udaya Prakash, J.; Sivaprakasam, P.; Jebarose Juliyana, S.; Ananth, S.; Sarala Rubi, C.; Divya Sadhana, A. Multi-Objective Optimization Using Grey Relational Analysis for Wire EDM of Aluminium Matrix Composites. *Mater. Today Proc.* **2022**, doi:10.1016/j.matpr.2022.09.415.

45. Periyavaram, S.R.; Bella, K.; Uppala, L.; Reddy, P.H.P. Hydrothermal Carbonization of Food Waste : Process Parameters Optimization and Biomethane Potential Evaluation of Process Water. **2023**, *347*, 1–7.

46. Zhao, K.; Li, Y.; Zhou, Y.; Guo, W.; Jiang, H.; Xu, Q. Characterization of Hydrothermal Carbonization Products (Hydrochars and Spent Liquor) and Their Biomethane Production Performance. *Bioresour. Technol.* **2018**, *267*, 9–16, doi:10.1016/j.biortech.2018.07.006.

47. Świechowski, K.; Matyjewicz, B.; Telega, P.; Białowiec, A. The Influence of Low-Temperature Food Waste Biochars on Anaerobic Digestion of Food Waste. *Materials (Basel).* **2022**, *15*, doi:10.3390/ma15030945.

48. Holm-Nielsen, J.B.; Al Seadi, T.; Oleskowicz-Popiel, P. The Future of Anaerobic Digestion and Biogas Utilization. *Bioresour. Technol.* **2009**, *100*, 5478–5484, doi:10.1016/j.biortech.2008.12.046.

49. Valentin, M.T.; Świechowski, K.; Białowiec, A. Influence of Pre-Incubation of Inoculum with Biochar on Anaerobic Digestion Performance. *Materials (Basel).* **2023**, *16*, 1–13, doi:10.3390/ma16206655.

50. Fukuda, R. Utilization of N-Alkane and Roles of Lipid Transfer Proteins in Yarrowia Lipolytica. *World J. Microbiol. Biotechnol.* **2023**, *39*, 1–11, doi:10.1007/s11274-023-03541-3.

51. Ma, X.; Gao, Z.; Gao, M.; Ma, Y.; Ma, H.; Zhang, M.; Liu, Y.; Wang, Q. Microbial Lipid Production from Food Waste Saccharified Liquid and the Effects of

Compositions. *Energy Convers. Manag.* **2018**, *172*, 306–315, doi:10.1016/j.enconman.2018.07.005.

52. Gao, Z.; Ma, Y.; Liu, Y.; Wang, Q. Waste Cooking Oil Used as Carbon Source for Microbial Lipid Production: Promoter or Inhibitor. *Environ. Res.* **2022**, *203*, 111881, doi:10.1016/j.envres.2021.111881.

53. Lu, Y.; Levine, R.B.; Savage, P.E. Fatty Acids for Nutraceuticals and Biofuels from Hydrothermal Carbonization of Microalgae. *Ind. Eng. Chem. Res.* **2015**, *54*, 4066–4071, doi:10.1021/ie503448u.

54. Lu, X.; Ma, X.; Chen, X. Co-Hydrothermal Carbonization of Sewage Sludge and Lignocellulosic Biomass: Fuel Properties and Heavy Metal Transformation Behaviour of Hydrochars. *Energy* **2021**, *221*, 119896, doi:10.1016/j.energy.2021.119896.

55. Vajpeyi, S.; Chandran, K. Microbial Conversion of Synthetic and Food Waste-Derived Volatile Fatty Acids to Lipids. *Bioresour. Technol.* **2015**, *188*, 49–55, doi:10.1016/j.biortech.2015.01.099.

56. Rasaq, W.A.; Okpala, C.O.R.; Igwegbe, C.A.; Białowiec, A. Catalyst-Enhancing Hydrothermal Carbonization of Biomass for Hydrochar and Liquid Fuel Production — A Review. **2024**, *17*, 1–25, doi:10.3390/ma17112579.

57. Valta, K.; Sotiropoulos, A.; Malamis, D.; Kosanovic, T.; Antonopoulou, G.; Alexandropoulou, M.; Jonuzay, S.; Lyberatos, G.; Loizidou, M. Assessment of the Effect of Drying Temperature and Composition on the Biochemical Methane Potential of In-House Dried Household Food Waste. *Waste Manag. Res.* **2019**, *37*, 461–468.

58. Browse, J.; McCourt, P.J.; Somerville, C.R. Fatty Acid Composition of Leaf Lipids Determined after Combined Digestion and Fatty Acid Methyl Ester Formation from Fresh Tissue. *Anal. Biochem.* **1986**, *152*, 141–145, doi:10.1016/0003-2697(86)90132-6.

59. Stępień, P.; Świechowski, K.; Hnat, M.; Kugler, S.; Stegenta-Dąbrowska, S.;

Koziel, J.A.; Manczarski, P.; Białowiec, A. Waste to Carbon: Biocoal from Elephant Dung as New Cooking Fuel. *Energies* **2019**, *12*, doi:10.3390/en12224344.

60. Świechowski, K.; Liszewski, M.; Babelewski, P.; Koziel, J.A.; Białowiec, A. Fuel Properties of Torrefied Biomass from Pruning of Oxytree. *Data* **2019**, *4*, 2–11, doi:10.3390/data4020055.

61. Fărcaş, A.C.; Socaci, S.A.; Dulf, F. V.; Tofană, M.; Mudura, E.; Diaconeasa, Z. Volatile Profile, Fatty Acids Composition and Total Phenolics Content of Brewers' Spent Grain by-Product with Potential Use in the Development of New Functional Foods. *J. Cereal Sci.* **2015**, *64*, 34–42, doi:10.1016/j.jcs.2015.04.003.

62. Wang, T.; Zhai, Y.; Zhu, Y.; Li, C.; Zeng, G. A Review of the Hydrothermal Carbonization of Biomass Waste for Hydrochar Formation: Process Conditions, Fundamentals, and Physicochemical Properties. *Renew. Sustain. Energy Rev.* **2018**, *90*, 223–247, doi:10.1016/j.rser.2018.03.071.

63. Long, J.; Li, Y.; Zhang, X.; Tang, L.; Song, C.; Wang, F. Comparative Investigation on Hydrothermal and Alkali Catalytic Liquefaction of Bagasse: Process Efficiency and Product Properties. *Fuel* **2016**, *186*, 685–693, doi:10.1016/j.fuel.2016.09.016.

64. Thúy, N.; Chi, L.; Anto, S.; Shan, T.; Kumar, S.S.; Shanmugam, S.; Samuel, M.S.; Mathimani, T.; Brindhadevi, K.; Pugazhendhi, A. A Review on Biochar Production Techniques and Biochar Based Catalyst for Biofuel Production from Algae. *Fuel* **2021**, *287*, 119411, doi:10.1016/j.fuel.2020.119411.

65. MacDermid-Watts, K.; Pradhan, R.; Dutta, A. Catalytic Hydrothermal Carbonization Treatment of Biomass for Enhanced Activated Carbon: A Review. *Waste and Biomass Valorization* **2021**, *12*, 2171–2186, doi:10.1007/s12649-020-01134-x.

12. LIST OF ANNEXES

[1]. **Waheed A. Rasaq**, Mateusz Golonka, Miklas Scholz, Andrzej Białowiec, 2021. "Opportunities and challenges of high-pressure fast pyrolysis of biomass: A review." Energies 14 (17), 1 – 20 doi: 10.3390/en14175426,

[2]. **Waheed A. Rasaq**, Charles Odilichukwu R. Okpala, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. "Navigating Pyrolysis Implementation—A Tutorial Review on Consideration Factors and Thermochemical Operating Methods for Biomass Conversion." Materials 17(3), 1 – 44 doi: 10.3390/ma17030725,

[3]. **Waheed A. Rasaq**, Vaikunthavasan Thiruchenthooran, Paweł Telega, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. "Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste". Journal of Environmental Management 357, 1 – 8 doi: 10.1016/j.jenvman.2024.120722,

[4]. **Waheed A. Rasaq**, Bartosz Matyjewicz, Kacper Świechowski, Zbigniew Lazar, Patryk Kupaj, Tomasz Janek, Marvin Valentin, Andrzej Białowiec, 2024. "Food waste recycling to Yarrowia biomass due to combined hydrothermal carbonization and biological treatment". Journal of Cleaner Production 456, 1 - 10 doi:10.1016/j.jclepro.2024.142385,

[5]. **Waheed A. Rasaq**, Charles Odilichukwu R. Okpala, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. "Catalyst-Enhancing Hydrothermal Carbonization of Biomass for Hydrochar and Liquid Fuel Production—A Review". Materials 17(11), 1 – 25 doi:10.3390/ma17112579,

[6]. **Waheed A. Rasaq**, Vaikunthavasan Thiruchenthooran, Katarzyna Wirkijowska, Marvin Valentin, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, "Hydrothermal carbonization of combined food waste: A critical evaluation of emergent products". Waste Management, is under review,

[7]. **Waheed A. Rasaq**, Marvin Valentin, Kacper Świechowski, Chinenye Adaobi Igwegbe, Andrzej Białowiec. "Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization". Renewable Energy, is under review. Preprint: doi: 10.2139/ssrn.4827691.

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Review

Opportunities and Challenges of High-Pressure Fast Pyrolysis of Biomass: A Review

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Abstract: Most pyrolysis reactors require small sizes of biomass particles to achieve high-quality products. Moreover, understanding the usefulness of high-pressure systems in pyrolysis is important, given the operational challenges they exhibit specific to various biomass materials. To actualize these aspects, the authors first checked previous reviews involving pyrolysis on different biomass and different conditions/situations with their respective objectives and subsections. From these already existing reviews, the team found that there has not been much emphasis on high-pressure fast pyrolysis and its potential in biomass conversion, showing that it is a novel direction in the pyrolysis technology development. Therefore, this review aims to shed more light on high-pressure fast pyrolysis, drawing from (a) classification of pyrolysis; (b) reactors used in fast pyrolysis; (c) heat transfer in pyrolysis feedstock; (d) fast pyrolysis parameters; (e) properties/yields of fast pyrolysis products; (f) high pressure on pyrolysis process; (g) catalyst types and their application; and (h) problems to overcome in the pyrolysis process. This review increases the understanding regarding high-pressure fast pyrolysis. An attempt has been made to demonstrate how high-pressure fast pyrolysis can bring about high-quality biomass conversion into new products. It has been shown that fluidized bed (bubbling and circulating) reactors are most suitable and profitable in terms of product yield. The high-pressure, especially combined with the fast-heating rate, may be more efficient and beneficial than working under ambient pressure. However, the challenges of pyrolysis on a technical scale appear to be associated with obtaining high product quality and yield. The direction of future work should focus on the design of high-pressure process reactors and material types that might have greater biomass promise, as well understanding the impact of pyrolysis technology on the various output products, especially those with lower energy demands. We propose that the increase of process pressure and biomass particle size decrease should be considered as variables for optimization.

Keywords: feedstock; temperature; pressure; pyrolysis process; reactors; liquid fraction; heat transfer; biochar; catalysts; biorefineries

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1. Introduction

Energy demand concerns and environmental problems have increased the global attention on renewable energy pathways to replace coal, oil, and natural gas [1]. Since biomass feedstock has been recognized worldwide as promising in its conversion to biofuel and other energy sources, energy continues to be generated by developing technologies known to be capable of converting waste materials (in particular biomass), all of which soon require environmental consideration [1–3]. As the first step in gasification, pyrolysis is key in exploiting biomass energy, even in other thermochemical conversion processes [1]. On this premise, the pyrolysis conversion process using a suitable (pyrolytic) reactor has become attractive for converting waste, which has been seen as an alternative renewable energy source over the last decade [4]. Essentially, this process provides a suitable and sustainable approach to transform low-value biomass residues into energy and upcycled products. Additionally, biomass is believed to bring about insignificant greenhouse gas emissions, for example, methane and carbon dioxide [5]. The CO_2 emission from fossil fuels, such as coal, is a major contributor to global warming. Therefore, CO_2 recycling via biomass gasification and pyrolysis technology has a high promise to reduce the negative impact of global warming [6]. Imperatively, there is a need for pragmatic efforts by governments and organizations responsible for environmental protection to ensure that legislations/regulations are robust to reduce the CO_2 emission from fossil fuels (coal, etc.) [7]. Over the recent decade, there has been increased pressure on environmental protection, which has particularly revamped many companies to become eager to embrace new technologies that favor green production [8].

From a technical standpoint, among the challenges of pyrolysis that remain of great concern is how to obtain high product quality and yield [9,10]. Another challenge of pyrolysis, which is of greater concern, is how to completely pyrolyze biomass particles, given the nature of rapid heat transfer specifically from the heating medium. Most pyrolysis reactors require small sizes of biomass particles to achieve high-quality products [8,10,11]. The data generated by, for example, high-pressure gasification and pyrolysis processes in terms of the product yields are underscored by biomass conversion, and its corresponding thermal effects [1]. Over the years, the applications associated with the reactor's structure have significantly increased, specifically in terms of design and testing. To actualize better product yield, for instance, such applications have aimed to maximize energy transfer and mass concerns. This is largely because many of the reactors, like those involved in a high degree of heat exchange given by exothermic reactions, have to avoid catalyst deactivation to obtain strong performance [12]. Nonetheless, high-pressure pyrolytic reactors for biomass transformation to biochar, bio-oil, and pyrolytic gas production have several benefits, such as product quality, lower operating costs, higher product yields, increased reaction rate, and reduced required heat of reaction [1]. Therefore, it is important to understand the usefulness of high-pressure systems in pyrolysis, given the operational challenges they exhibit specific to various biomasses.

Previous reviews involving pyrolysis on different biomasses and different conditions/situations with their respective objectives and subsections captured are shown in Table 1. Besides the acquisition of the knowledge regarding how catalysts function in the biorefinery industry [13], the context of pyrolysis technology (i.e., determination of operating parameters of pyrolysis) and reactor types has been based on the desired characteristics of the product (biochar, bio-oil, and pyrolytic gas) [14], as well as on the field of biomass pyrolysis and upgrading [10]. Feedstock properties, the reactor type, product characteristics and upgrading options [15], biochar catalysts for fuel production [16], and the properties of the bio-oil [5] are among key areas demonstrated as synthesized literature with relevant information. It is important to note that some conducted reviews have looked at systematic approaches for mapping biomass resources to conversion pathways, forming the basis for biomass valuation and informing when biomass pre-processing is needed to ensure feedstocks are conversion-ready [17]. These reviews have also considered the fundamental process mechanisms of slow pyrolysis and hydrothermal carbonization processes by identifying research needs and summarizing the characteristics of products as a useful potential for industrial applications [18]. It is clear from these reviews that not much emphasis has been on the high-pressure fast pyrolysis and its potential in biomass conversion. Therefore, the objective of this review is to throw more light on high-pressure fast pyrolysis, drawing from (a) classification of pyrolysis; (b) reactors used in fast pyrolysis;

(c) heat transfer in pyrolysis feedstock; (d) fast pyrolysis parameters; (e) properties/yields of fast pyrolysis products; (f) high pressure on pyrolysis process; (g) catalyst types and their application; and (h) problems to overcome in the pyrolysis process.

Table 1. Previously conducted reviews involving pyrolysis on different biomasses and different conditions/situations, with their respective objectives and subsections captured.

Objective	Subsections Captured	Years	References
To harness deep insights into how catalysts perform in the production of carbohydrates from biomass.	Depolymerization; Chemo-catalytic reaction pathways in the conversions of carbohydrates; Epimerization; Retro-aldol reactions; Oxidation/Reduction Catalytic; Dehydration/hydration; Cascade catalysis of cellulose; Isomerization	2019	[13]
To identify how the pyrolysis technology pathways/routes perform, i.e., how operating parameters of pyrolysis are selected, and reactor types based on the desired product characteristics (biochar, bio-oil, or pyrolytic gas).	Pyrolysis principles; Pyrolysis classification; Slow pyrolysis; Fast pyrolysis; Flash pyrolysis; Biomass feedstock; Biomass composition; Physical, chemical biomass characteristics; Pyrolysis reactor types like fixed bed, fluidized bed, bubbling fluidized bed, circulating fluidized bed, and ablative; Pyrolysis process include feed preparation and biomass heating; Pyrolysis products	2012	[14]
To create a systematic approach for mapping biomass resources to conversion pathways, forming the basis for biomass valuation, and informing when biomass pre-processing is needed to ensure feedstocks are conversion ready.	A biomass grading system for biofuels; Management approach; Technical accomplishments; and Relevance	2017	[17]
Review update of the slow pyrolysis basics and process mechanisms, hydrothermal carbonization processes, spot out research gaps, and briefs about the characteristics of biochars for potential industrial use.	Biochar and hydrochar production; chemical process mechanisms underscoring biochar and hydrochar production; Biochar and hydrochar characterization; potential applications/benefits associated with biochar and hydrochar industrial use	2019	[18]
Field of biomass pyrolysis and upgrading	Conceptual design; Catalysis; Bio-oil characterization; Mechanisms and thermal kinetics; Modeling; Economic viability; Environmental performance; Supply chain	2019	[10]
Characterization of the biomass; type of reactors dedicated for fast/slow pyrolysis, the composition of products/upgrading.	Feedstock characterization; Reactor types; Products formation; Biomass upgrading	2012	[15]
Highlighting the reason why biochar catalysts are key elements for production of fuel and their merits	Biochar production techniques; Biochar composition; Catalysts produced from biochar; Biochar-based catalyst utilized to produce fuel	2021	[16]
Review of the characteristics of pyrolysis oil derived from different types of biomasses under different technological conditions used so far.	Review the pyrolysis oil characteristics, such as acidity and pH, alkali elements, ash content, density, heating value, oxygen content, solids, viscosity, and content of water.	2015	[5]

2. Pyrolysis and Its Technological Challenges

Pyrolysis refers to the irreversible chemical change brought about by heat without the involvement of oxygen [1,2]. It is considered one of the technologies of waste recycling, resulting in the production of pyrolysis of bio-oil, biochar, pyrolytic gas, and tar as the main products. One of the technological solutions is the application of fast pyrolysis for bio-oil production with high mass yield [19–22]. One of the identified technological problems is the effective transport of heat, both in the reactor and the substrate itself so that the feedstock reaches the set temperature in the shortest possible time [7,14]. In traditional externally heated reactors, heat transport occurs through conduction [22]. The introduction of mixing and the flow of hot gases inside the reactor allows the acceleration of feedstock heating through convection [1,5,6,23–25]. Additional fragmentation of the feedstock to a very small size results in shortening the time required to reach the process temperature within the volume of the entire feedstock [25]. However, when striving to further reduce the feedstock's heating time and at the same time increase the efficiency energy of the pyrolysis, the proposal would be to run the process under high-pressure conditions.

The application of the high-pressure fast pyrolysis may reduce the energy demand, which has the potential to shift the process from endo- to exothermic. Notably, the energy demand depicts the energy necessary to increase the temperature of pyrolysis to the target level, which is influenced by biomass moisture and process temperature. There is a general agreement that there is a linear increase in the heat capacity of biomass with the increase of temperature. Hence, an increase from 5 to 423 K would depend on the intended purpose of the pyrolysis study [26]. Additionally, the processes of biomass decomposition and volatilization may give some thermal effects [27] Basile et al. [1] performed an experiment using four different types of biomass samples, such as corn stalks and poplar, as well as switchgrass types, "Alamo" or "Trailblazer". By analyzing the influence of high pressure in each biomass type, these workers understood that pressure increases would decrease the energy demand for the pyrolysis in the case of studied materials. For instance, Trailblazer changed noticeably to affect a shift from endo- to exothermic. Pressure increases between 0.1 and 4 MPa can shift the total energy that the pyrolysis requires between −50 and −272 J/g for corn stalks, 29 and −283 J/g for poplar, 37 and −199 J/g for Alamo, and 92 and −210 J/g for Trailblazer, wherein the values with a negative sign (−) express exothermic processes [1].

3. Classification of Pyrolysis

Pyrolysis usually begins with temperature ranges of between 250 and 300 °C, as the volatiles in the absence of oxygen are rapidly released atbetween 750 °C and 800 °C [28–39]. Largely, this occurrence anchors on the pyrolysis types and the purpose of any given (pyrolysis-based) project [40–70]. The characteristics of the identified types of pyrolysis have been summarized in the Table 2 [15,49,71–75] Generally, pyrolysis comprises four (diverse) process types, namely: conventional (also called 'slow'), flash, fast, and slow [28]. These types could also be classified based on operational conditions. In addition, processing the pyrolysis heat at a very high rate, such as 10,000 K/s, and short duration, such as 20–500 ms, helps to classify the pyrolysis as ultra-rapid [28].

Table 2. The technological parameters and product yield typically linked to pyrolysis [15,49,71–75].

Pyrolysis Type	Rate of Heating, K/s	Size of Particle, mm	Process Duration, s	Temperature, °C	* Product Yields, %		
					Bio-Oil	Biochar	Gas
Flash	>1000	<0.2	<0.5	550–1000	75	12	13
Fast	10–200	<1	0.5–10	400–550	50	20	30
Slow	0.1–1	5–50	450–550	300–400	30	35	35

* Approximate and/or expected product yield.

3.1. Slow Pyrolysis

Slow pyrolysis takes place at low temperatures at a range of 300–400 °C, with a heating rate from 0.1 to 1 K/s and duration between 5–30 min. These conditions yield good quality charcoal of around 35% biomass quantity normally obtained in this process, while the bio-oil is rather slightly lower. A longer duration of the process can bring about reduced yield of bio-oil production due to further cracking. However, the process has some technical limitations compared to other processes, such as extra energy input demand due to a lengthened duration and a reduced transfer of heat rate within the process [13,15,72].

3.2. Fast Pyrolysis

In the progress of the fast pyrolysis process, the biomass usually reaches the temperature of around 500 to 600 °C, using a higher heating rate of 10–200 K/s, with a short duration of 0.5–10 s. The fast pyrolysis would produce up to 50% of the bio-oil, 20% of biochar, and 30% pyrolytic gas, respectively. The process usually occurs under a small vapor retention time, and high bio-oil yield is always achieved for the turbine, engine, boiler, and power supply for industrial applications due to its technical advantages [73–75].

3.3. Flash Pyrolysis

The biomass flash pyrolysis can produce biochar, pyrolytic, bio-oil, and gases with respective share(s) of 12%, 13%, and 75% of initial biomass weight. Particles are usually heated for a very short time of about <0.5 s and with a very high rate of heating, greater than 1000 K/s, with a high-temperature level in this process between 550 and 1000 °C. However, the process is not thermally stable. Despite the catalytic activity of the biochar, which affects the oil making, it can become viscous to contain some solid particles [2,31]. This process still provides a high potential of good quality bio-oil at minimum water content [36].

4. Reactors for Fast Pyrolysis

4.1. Classification of Reactors

The reactor is one of the most significant design parameters that influence the fast pyrolysis product yield. The pyrolysis reaction occurs in the reactor. The production quality of the target products depends on the heat transfer method [37]. There are various fast pyrolysis reactor types designed to pyrolyze a variety of biomass into three main products, for instance, bio-oil, biochar, and pyrolytic gas. The pyrolysis reactor properties is shown in Table 3 [62–66]. Besides, the production yield depends on the reactor design and operation processes. The classes of the reactor are as follows: rotating cone reactor (RCR), fluidized bed reactor (FBR), entrained flow reactor (EFR), circulating fluidized bed reactor (CFBR), ablative reactor (AbR), and auger reactor (AuR) [55–57].

Table 3. The pyrolysis reactor properties [62–66].

Reactor Type	Capacity, kg/h	Temperature, °C	Pressure, Bar	Method of Heat Transfer	Residence Time, s	Particle Size, mm	Products Yield, %		
							Oil	Gas	Char
Rotating cone	10	500	0.8	Conduction	0.3–0,5	<0.5	49	15–20	10–15
Fluidized bed	500	450–560	0.01	90% Conduction	0.5–2	2–3	50–80	10	10–15
Entrained flow	50	400–550	5–20	Convection	0.5–1	0.5	60	30	10
Circulating fluid bed	30	500	1	Conduction	0.5–1	1–2	39–70	25	10–15
Ablative	2.5	450–600	1	Conduction	0.5	5	70	10–20	10–15
Auger	1–6	450–550	1	Conduction	2	<5	30–50	20–35	20–30

4.2. Description of the Reactors

4.2.1. Rotating Cone Reactors (RCR)

These types of reactors are comparable to CFBR reactors. Typically, hot sand with a biomass particles mixture is utilized in this reactor as the reaction medium. The way in whcih the particles move removes the rationale for a carrier gas, which must be achieved by centrifugal force within RCR. During the pyrolysis process, both biomass and sand must be introduced into this reactor type (that is, RCR), particularly from the bottom of the cone. When the biomass particles move up to the lip of the cone to become subject to pyrolysis reactions, the sand and char are, at that point, transferred to the combustor, condensing the vapors, thereby separating the bio-oil. According to Mahdi et al., the bio-oil yield product of this reactor is up to 70% (Table 3) [10].

4.2.2. Fluidized Bed Reactor (FBR)

Advances in the bubbling FBR have been attributed to the Dynamotive Energy System, a reactor type that is globally widespread given its simple process operation. Frequently made of sand, the bed media being supported on a perforated plate has the inert gas typically fluidized, such that, from the reactor bottom, it flows upward. By developing a model of this reactor type, Felice et al. determined the physical and chemical properties of output products under-thigh temperature of about 425 °C, where the product yield of the gaseous component is higher than that of liquid [40]. Generally, the bio-oil yield associated with this reactor type ranged between 70% and 75% (Table 3), which is very high in comparison to the other reactors. Additionally, this reactor is of the feedstock input type and continuously produces bio-oil [15,25].

4.2.3. Circulating Fluidized Bed Reactor (CFBR)

The CFBR resembles bubbling FBR, especially where the gas transports the hot sand (that is, with a sand/feed proportion from 20% to 25%). Biochar, together with the sand, then gets separated from other products by the cyclone. The burning of unreacted particles empowers heat supply relevant to the endothermic pyrolysis process, which in turn, facilitates the drawbacks associated with the scale up of circulating FBR. A short residence time is required for char and sand in this type of reactor (0.5–1 s) (Table 3) compared to the bubbling FBR, for which small particle sizes are required because of the high residence time at a range of 2–3 s [25,59].

4.2.4. Entrained Flow Reactor (EFR)

EFR is motivated by the technologies associated with the gasification process. A preheated inert gas stream can entrain the biomass particles in this reactor. Typically, the reactor temperature can exit at 500 °C. If the production of bio-oil yield is about 50%, the char yield could be between 20% and 30% (Table 3) [10]. Such a reactor type has demerits, such as the lack of heat transfer between the biomass particles and gas, which usually is of high process temperature and results in increased gas flow rate and challenges associated with scaling-up [42].

4.2.5. Ablative Reactor (AbR)

In the heat transfer linked with AbR, the biomass during the pyrolysis reactions is driven against a hot plate (reactor wall). The process resembles the standard method of melting butter in the frying pan. This reactor accepts a bigger feedstock particle size (20 mm) relative to other reactor types. However, the main disadvantages are linked to heat supply and the low reaction rate.

An experiment was performed in an AbR that involved the National Renewable Energy Laboratory (NREL) facility, which aimed to scale up a reactor from a small private firm that designed a reactor capacity of 35 tons per day. The feedstock particles, transported with superheated steam with a velocity of 200 m/s, were tangentially fed at 625 °C to the reactor. Via the heat transfer rate at the level of 1000 W/cm^2 high, up to 70% (Table 3) of bio-oil yield was achieved [6,61].

4.2.6. Auger Reactor (AuR)

Another reactor design type utilized for biomass feedstock is the auger. This AuR allows the biomass feedstock to be moved via a heated cylinder. Further, the process is such that the tube creates a passage through which the feedstock is raised to achieve a desirable pyrolysis temperature range between 400 and 800 °C (Table 3). Additionally, it is this temperature range that allows which feedstock to devolatilize and gasify. The output product includes char and associated gases, which can be condensed as bio-oil. There could also be other non-condensable vapor, which can be collected as syngas (also synthesis gas). Notably, the AuR's design would allow for process duration to be modified, which could take place by applying changes within the heated zone. Through this approach, the vapor can pass through the system before entry into the condenser train [14]. The basic properties of the above-mentioned pyrolysis reactors are demonstrated in Table 3.

5. Heat Transfer Pyrolysis

The heat transfer methods are divided into two parts according to the type of reactor. The heat can be transferred by the method of conduction using an external device to the reactor or convection method, which means that heat can be generated within the reactor. By assessing the high heat transfer rate to the biomass particles, Sharifzadeh et al. [10] found that the initial products are being removed quickly. Hence, the biomass feed composition is a very key parameter within the fast pyrolysis, able to produce reduced char with increased bio-oil product yield [10]. Two major components to consider before heat transfer in fast pyrolysis reactors include heat transfer to the reactor wall and heat transfer from the reactor wall to the biomass particles. Lødeng et al. [48] believed that the fast pyrolysis warrants an increased heat transfer rate that rapidly makes the biomass particles but sufficiently arrives at a target temperature level for the reaction to be optimal. There are these two different ways to heat the biomass particles under the fast pyrolysis process: solid-solid or gas-solid, depending on the type of operating reactor. Generally, heating rates are between 1 and 1000 C/s; however, the high (local) heating rates may reach 10,000 C/s [48]. The heat transfer methods within the pyrolysis process vary with reactor operating conditions, which are presented in Table 4 [14]

Table 4. The common methods of heating applicable to different types of reactors [14].

Reactor Type	Heating Method
AuR	Fire tube
AbR	Wall heating
CFBR	Sand and wall heating
EFR	Heating (Electric) elements
FBR	Solar radiation
RCR	Gasification of biochar on heat sand

6. Pyrolysis Feedstock

Feedstock can be categorized into different types in the pyrolysis process, including lignocellulosic biomass, municipal solid waste, and refuse-derived fuel. Promising as a bio-renewable resource, the lignocellulosic biomass as a focus [49] has often replaced fossil fuel resources, particularly in the biorefinery industries [12,13]. The biomass comprises three main components: cellulose, hemicellulose, and lignin. The percentage covered by the individual biomass components is presented in Table 5 [14–18].

Table 5. Cellulose, hemicellulose, and lignin content of some selected biomasses [14–18].

Biomass Type	Lignin, %	Cellulose, %	Hemicellulose, %
Wheat straw	15–20	33–40	20–25
Rice straw	18	32.1	24
Tobacco stalk	27	42.4	28.2
Softwood stem	25–35	45–50	25–35
Corn stover	16–21	28	35
Switch grass	5–20	30–50	10–40
Olive husk	48.4	24	23.6
Hazelnut shell	42.9	28.8	30.4
Tea waste	40	30.20	19.9
Hardwood stem	18–25	40–55	24–40
Walnut shell	52.3	25.6	22.7
Sunflower shell	17	48.4	34.6
Nutshell	30–40	25–30	25–30
Cottonseed hairs	0	80–95	5–20
Oat straw	16–19	31–37	24–29
Bamboo	21–31	26–43	15–26
Banana waste	14	13.2	14.8
Sugarcane bagasse	23–32	19–24	32–48

Biomass Properties Affecting the Pyrolysis Process

The properties of biomass affecting the process of pyrolysis are the thermal degradability of biomass components, calorific value, elemental composition, and specific heat capacity. The structure of biomass comprises three main bio-macromolecules, such as hemicellulose, cellulose, and lignin, along with some minerals such as ash [19,20]. The above-mentioned layers of lignocellulosic biomass are pyrolyzed at different temperature levels during the pyrolysis reaction, where bio-oil, biochar, pyrolytic-gas, and tar are produced as the main target products. The hydrophobicity of cellulose is normally considered moderate, and it has a high heating value between 17 and 18 $\mathrm{MJkg^{-1}}$ [55]. Hemicellulose is thermally stable in comparison to other structural biomass components due to its amorphous shape. Hydrolysis of hemicellulose takes place at approximately 200–300 °C. The hydrophobicity is short lived, and the calorific value is between 17 and 18 $\mathrm{MJkg^{-1}}$ [55]. Biomass degradation of lignin takes place at around 600 °C. The hydrophobicity (23.3–26.6 $\mathrm{MJkg^{-1}}$) is high compared to other biomass structures [55]. The decomposition rates of three biomass components with pyrolysis temperatures are shown in Figure 1 [14]. The water mass loss rate pyrolysis temperature below 100 °C appears to be minimal. Besides water, the mass loss rates of hemicellulose and cellulose noticeably differ at respective pyrolysis temperatures of 325 and 375 °C. Additionally, there appears to be no distinct mass loss rate difference in the case of lignin from pyrolysis temperatures between 250 and 500 °C.

Understanding the decomposition behavior of the main biomass requires useful knowledge about its properties and structure, particularly in the context of moisture status and the specific temperature points in obtaining different pyrolysis products. To throw more light on this, the rate of thermal decomposition involving cellulose, hemicellulose, and lignin with moisture/water operating within pyrolysis temperature is shown in Figure 2 [31]. The temperature ranges within the pyrolysis process reflect different layers of biomass structure. Given that these three main layers are understood to pyrolyze at different temperature ranges, the emergent products would be achieved at specific temperature levels. Previous studies involving approximate and ultimate analyses have shown the fundamental fuel trademark to be among effective ways that relate to general properties of biomass composition, particularly with regards to ash, carbon, hydrogen, oxygen, nitrogen, sulfur, moisture, and volatile matter [56]. Volatiles and ash presence might affect the pyrolysis reaction, and, therefore, it would result in a considerable effect on the quality and bio-oil yield [16,22]. When the volatile content is higher, it is subjected to high volatility, and this could change the characteristics desired of bio-oil production [56]. However, the ash content lowers the calorific value of the feedstock and subsequently impacts the production of bio-oil. A higher water content results in an increase of the aqueous phase under the pyrolysis process, which will cause a reduction of calorific values of the biomass-derived bio-oil. Furthermore, the carbon burn rate is considerably lower during the process [22,24].

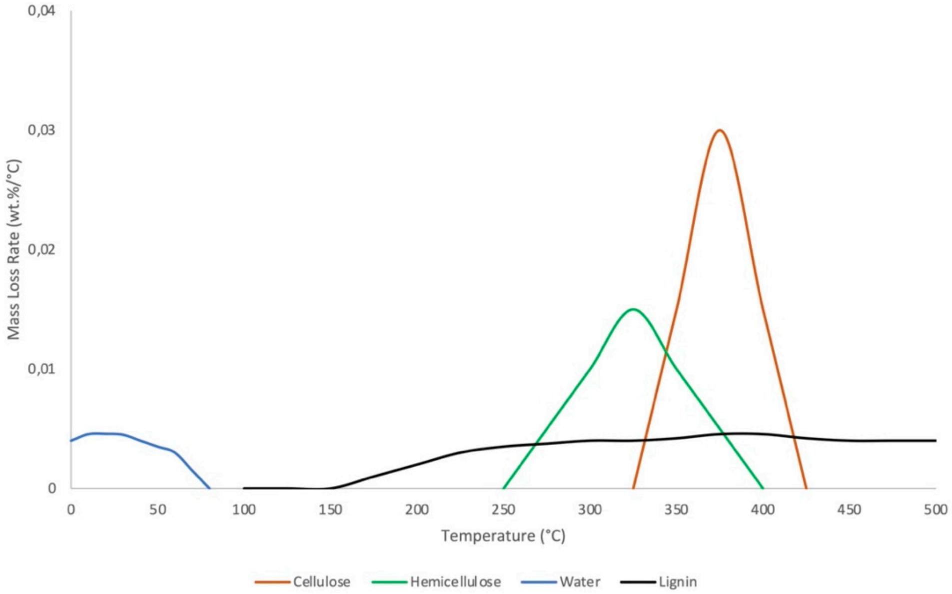

Figure 1. The rate of thermal decomposition of cellulose, hemicellulose, and lignin with moisture/water operating within pyrolysis temperature. Adapted with slight modifications from [14].

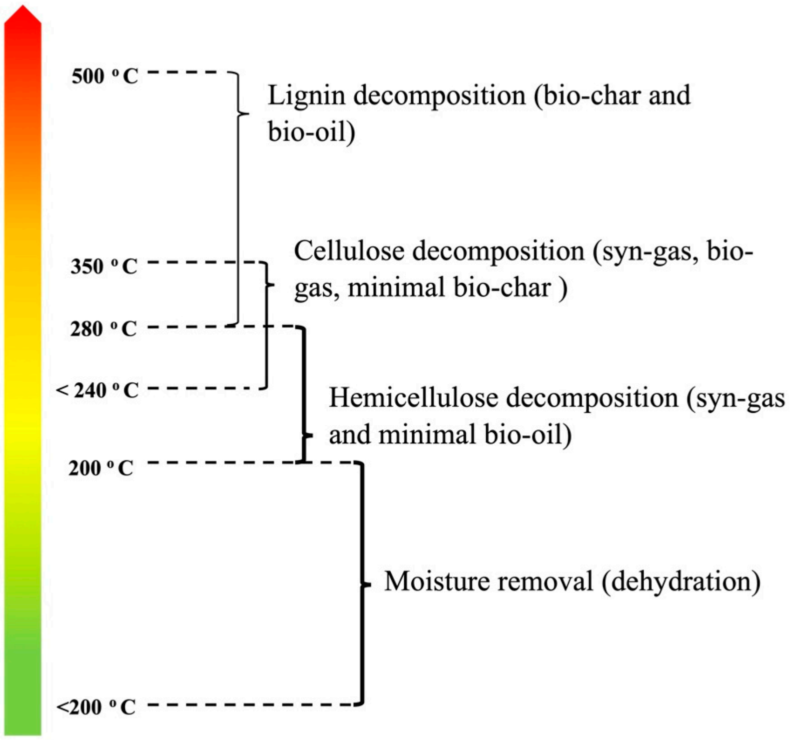

Figure 2. The decomposition processes and products of biomass components under different temperatures of pyrolysis. Modified from [31].

7. Fast Pyrolysis Parameters

7.1. Temperature Effects

Numerous parameters influence fast pyrolysis product yields and properties. Key parameters are commonly temperature, pressure, reactor type, residence time, particle size, and energy demand effect. Variable product yield from fast pyrolysis with ranging temperatures is shown in Figure 3 [29]. To measure a specific temperature demand for pyrolysis, the biomass particles (specific to the fast pyrolysis process) are very sensitive. This is because it can be measured by either the reaction or reactor temperatures [42,53–55]. Given the heat loss during the heat transfer from the reactor side wall to biomass particles, the temperature of the reactor usually appears higher than the reaction temperature, which can result in a paucity of completely pyrolyzed biomass particles. Therefore, any changes in reactor temperature would affect the reaction temperature. For instance, the temperature of the reactor would correspondingly rise with the temperature of the process. Hence, authors of such scientific experiments should specify where the temperature was measured [42,53–55]. Typically, increases in temperature within the pyrolysis process occur with gas production yield and with a corresponding lowering of the biochar production. However, the maximum pyrolytic oil production can be achieved at the desired temperature range (480 to 550 °C). Additionally, the water content would be decreasing at 550 °C operating temperature (Figure 3) [42,53–55].

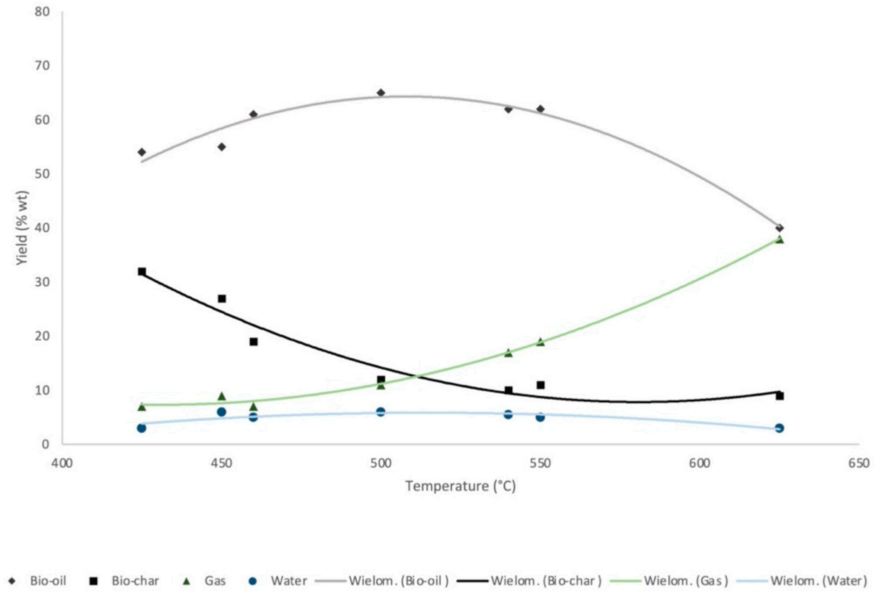

Figure 3. Variable product yield from fast pyrolysis at different temperatures; adapted from the International Energy Agency [29].

The way in which temperature impacts bio-oil production appears to be more complex. This is because the bio-oil yield suggests the gross of organics/water yields. Hence, the best way to achieve that is to look at the yields of water and organic liquids independently. Mostly when the pyrolysis process is operating at a range between 400 and 600 °C temperature level, the yield of the organic liquids tends to achieve a peak value under specific temperature, but it depends on the feedstock type. In the case of wood feedstock, usually, the maximum temperature is 500 °C. The influence of temperature on bio-oil qualitative characteristics was investigated by Elliot [62], who characterized a fast pyrolysis process with a short residence time. In that study, the chemical composition showed a direct association with the process temperature [62]. Despite this, the temperature increase would feasibly decrease the released oxygen content [55]. Additionally, the pyrolytic gas increases with temperature but decreases in bio-oil, biochar, and water [29].

7.2. Pressure Effects

Pressure is a significant factor in the fast pyrolysis of biomass, given its influence on product yield. Generally, critical parameters involved in fast pyrolysis include a high rate of heat exchange to the biomass and a speedy removal of initial biomass feed composition/products, which results in an increase in liquids yields and a reduction of biochar yield. Many studies have shown that increasing pyrolysis pressure would result in proportionally more oil with decreased gas yield. Higher pressure would lower the obtained gas product yield [63]. By using three different pressure values, 5, 10, and 20 bar, to generate char samples without change in temperature condition, the pyrolysis pressure would have a demonstrated impact on the shape and size of particles, through the proportional rise in the void and reduction in thickness of a cell wall. Most swelling occurs at pressures with low values, whereas an increase of the pressure of pyrolysis would lead to bubbles forming with the increased size of biochar particles [64]. Another study that used four types of biomasses, namely poplar, switchgrass Alamo, switchgrass Trailblazer, and corn stalks, evaluated the relationship between heat and high-pressure values of pyrolysis by proximate analysis equation, and the resultant outputs are shown in Figure 4 [1]. The process pressure would noticeably affect the biochar yield. This is governed by pressure rising from 1 bar to 5 bars, which resulted in increased biochar yields from 23.8% to 28.3%, from 17.3% to 30.7%, from 15.2% to 27.3%, and from 19.1% to 28.5%, for corn stalk, poplar, Alamo, and Trailblazer, respectively. An increase in pressure in all biomass samples would shift the process from an endothermic to an exothermic reaction [1].

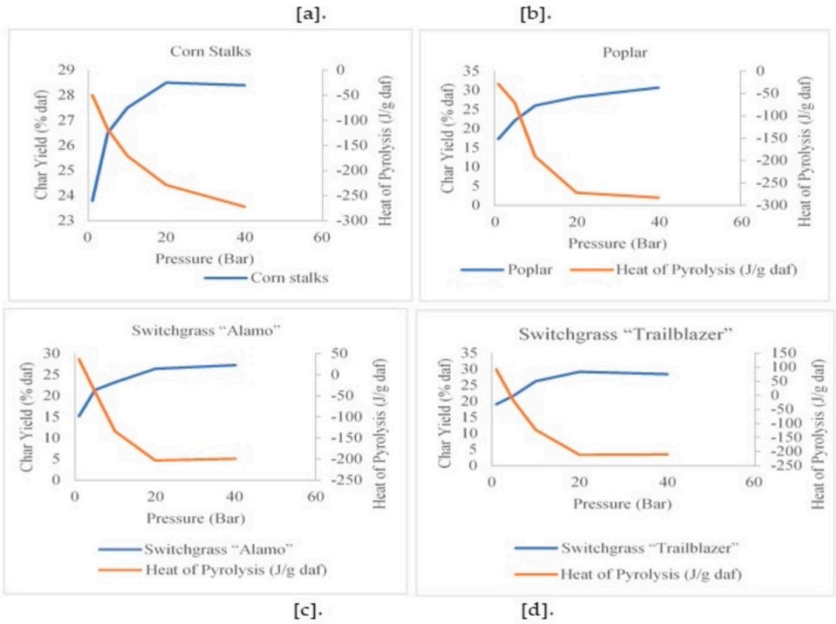

Figure 4. The influence of pressure on heat of pyrolysis for (**a**) corn stalks (with biomass weight of volatiles = 77.7%, fixed carbon =16.0%, and ash = 6.3%); (**b**) poplar (with biomass weight of volatiles = 81.8%, fixed carbon = 14.8%, and ash = 8.4%); (**c**) switchgrass Alamo (with biomass weight of volatiles = 79.3%, fixed carbon = 12.1% and ash = 2.1%); and (**d**) switchgrass Trailblazer (with biomass weight of volatiles = 64.1%, fixed carbon = 8.6%, and ash = 27.3%) [1].

7.3. Reactor Type Effects

The reactor is among the parameters that influence the fast pyrolysis yield products. Nonetheless, different reactor types vary with operating processes, which would eventually impact the energy demand/transfer, gas emission, particle size, product quality, and reactor capacity. Indeed, the reactor is at the heart of the pyrolysis process, influencing product quality, even when compared to various pyrolytic reactor types, corresponding operating procedures, and product yield. The fluidized beds (bubbling and circulating) are suitable, more profitable among others in terms of product yield because those mentioned types could produce bio-oil of about 75% [7,58,59].

7.4. The Process Duration Effects

The process duration (residence time of the feedstock under desired conditions) refers to the total time it takes to pyrolysis within the hot environment to achieve the point of condensation, and fast pyrolysis needs a short residence time. Generally, the fast pyrolysis vapor residence time is usually <2 s [25], typically to decrease the secondary reaction, such as recondensation, thermal cracking, repolymerization, and formation of biochar, which results in a decrease of liquids yields, while the yield of permanent gas and biochar increases.

7.5. Particle Size Effects

The feedstock particle size is a key parameter that impacts the production yield and overall energy requirement in fast pyrolysis. The size of the biomass particle is related to reactor type. The biomass particle size impacts biomass composition. The increment in particle dimensions leads to a decreased content of ash, with an increase in the content of fixed carbon and volatile solids. However, the ash content usually increases when the biomass particle size is too small (typically <0.1 mm). However, biomass ash is influenced by increasing the reactivity of the pyrolyzing biomass, which results in the generation of non-condensable gasses, such as CO, CO_2, and H_2 [11,67]. According to Vinu et al. [8], an experiment was performed to observe trends of biomass particle size in yields of the biochar from fast and slow pyrolysis, and the findings of this specific study appeared to be consistent with previous literature. Onay et al. [68] investigated the influence of the heating rate and particle size on rapeseed pyrolysis products yields [68]. They revealed that under the fast pyrolysis conditions at 400 °C, 300 °C min^{-1}, with 0.425–1.25 mm dimensions, a higher biochar yield was obtained, reaching ~30 mass%, relative to that under slow pyrolysis (30 °C min^{-1}), not exceeding 25 mass%. However, at an increased temperature from 500 to 550 °C, the biochar yield was lower: ~10–15 mass% in the case of fast pyrolysis and ~17–20 mass% in the case of slow pyrolysis. This points to the fact that results might differ from the literature as the fast mode of this process appeared to be on the lower side. Additionally, a comparison of the final biochar yield obtained under 750 and 800 °C in the case of slow pyrolysis with fast pyrolysis (500 °C) indicates significant variations in biochar yields [11,67].

7.6. Energy Demand Effects

The energy demand in fast pyrolysis processes is among the essential parameters impacting pyrolysis product yields. This depends on biomass properties and the operating reactor [11,67]. Understanding how the kinetics of pyrolysis function is essential, particularly for energy demand evaluations. This is because, for instance, the kinetics of pyrolysis are underpinned by parameters such as heating rate, as well as the size of feedstock particles. These two parameters are believed to influence the overall energy requirement for the process. On the other hand, the size of the particles can also influence biomass composition [11,67]. It is also believed that decreases in ash content would increase volatile matter, fixed carbon, and biomass particle size. Notwithstanding that a very small particle size makes the ash content more evident (typically <100 µm), the critical size would equally depend on the biomass type, for instance, in the situations of agro residues functioning against woody biomass [11,67].

8. Quantitative and Qualitative Characteristics of Products from Fast Pyrolysis

8.1. Bio-Oil

Fast pyrolysis of biomass has attracted high interest worldwide given its product advantages. Fast pyrolysis involves a biomass-to-energy conversion process, which results in the three primary products, char, pyrolytic gas, and liquid, known as bio-oil or biofuel, but also with some by-products, such as tar, whose gasses usually condense at low temperature. Generally, bio-oil is the liquid oil obtained via the pyrolysis of biomass. Heavily colored (often dark red, brown, or black) and viscous, the bio-oil comprises a mixture of many compounds, which vary both in their content, proportion, and physical properties depending on feedstock type, production method, and age of the sample [21,25]. Bio-oil maximum yield production usually occurs at temperatures between 450 and 500 °C [26,28]. Michailof et al. [72] considered bio-oil properties determination among the greater challenges that hinders achieving consistent production. Additionally, mixing or upgrading of bio-oils may be difficult [72]. A proper analysis of bio-oil property behavior is essential given that the quality of the product would anchor on both chemical and physical properties. This helps to identify a suitable potential application of the bio-oil, as shown in Table 6 [5,24,25,29,31].

Table 6. Properties and common measurement methods of bio-oil [24,25,29,31].

Property	Unit	Analytical Method	Range of Values
Heating value	MJ/kg	Calorimetry (ASTM D 4809)	16.5–19
Moisture	Wt.%	ASTM E871	-
Water	Wt.%	Karl-Fisher (ASTM D 1744)	15–35
Volatile matter	Wt.%	EN15148-2009	-
Ash	Wt.%	DIN EN 7	0.01–0.2
Carbon	Wt.%	ASTM E 777	50–64
Hydrogen	Wt.%	ASTM E 777	5–7
Nitrogen	Wt.%	ASTM D 5291	0.05–0.4
Oxygen	Wt.%	EN 15296:2011	35–40
Sulfur	Wt.%	XRF (ASTM D 4294)	0–0.05
Density	kg/dm^3	Densimeter (ASTM D 4052)	1.10–1.30 (at 15 °C)
Copper corrosion test	-	ASTM D 130	1A–1B
Acidity	pH	E70	2–3

The physicochemical properties of bio-oils are influenced by the conditions associated with feedstock, production, and reactor type. Major challenges can include the increase of acidity, oxygen, and water, which affects the supplementary scale up of bio-oil usage, given that the miscibility with fossil fuels is to be obstructed, with decreased calorific value, etc. Additionally, the instability of bio-oil, attributed to polymerization, characterizes the bio-oils, and this phenomenon has been associated with either the phenols undergoing oxidative coupling or when some components failed to saturate [72]. The potential applications of bio-oil, as demonstrated by relevant literature, could be seen as an alternative candidate to fossil fuel [12,19,25,34,51,52]. The applications involving the areas of fuel, chemistry, power, and heat are summarized in Figure 5 [55].

8.2. Biochar

Biochar is a solid pyrolysis product that is commonly produced under low temperature, typically consisting of 0.5–5% ash, 50–90% fixed carbon, 1–15% moisture, and 0–40% volatiles solids. However, the mentioned proportions depend on the feedstock type and technological parameters of the process [74]. Typically, biochar pyrolysis is at a temperature between 200 and 900 °C [75]. Biochar can serve, for example, as energy fuel or soil amendment. The quantity and quality of biochar derived from the fast pyrolysis process depend on the reactor type, feedstock, and temperature of pyrolysis, which have a considerable effect on product composition/yield [76–80]. The release of gases, while it changes with different temperatures, would decrease in biochar yield with temperature increase. Temperature decrease would bring about a higher amount of biochar. However, the char heating rate would increase with temperature increase [32,34–36,81–84]. Normally, the separation of char is achieved by a cyclone, removing it from the vapor stream. The main component of biochar is carbon, but it contains a small amount of hydrogen and oxygen as well. Furthermore, it may contain high proportions of inorganics [32,34–36,81–84].

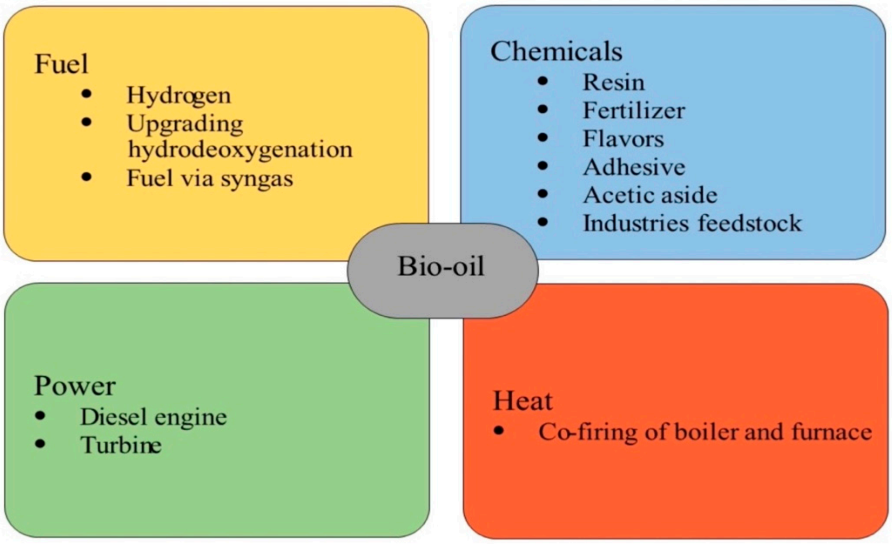

Figure 5. The potential applications of pyrolysis-based bio-oils adapted from [55] with modifications.

The biochar characteristics at different temperatures and selected feedstock types are presented in Table 7 [37–42]. The feedstock type, pyrolysis temperature, and production conditions have a role to play towards these (physicochemical) properties.

Table 7. Biochar characteristics at different temperatures and feedstock types [37–42].

Feedstock	Temperature, °C	Product Yield, %	Specific Surface Area, M^2/G	Ash Content, %	pH (-)	Volatile Solids, %	Carbon, %
Rice straw	300	50.1	-	25.4	9.3	48.4	72.5
Corn stover	300	66.2	3.2	5.7	7.7	54	45.5
Cottonseed hull	350	36.8	4.7	5.7	7.0	34.9	77.0
Oakwood	450	-	1.9	64.5	-	15.6	71.3
Corn cobs	500	18.9	0	13.3	7.8	-	77.6
Soybean stover	700	29.6	420.3	17.2	11.3	14.7	82.0
Vine pruning	350	64.6	8.1	8.3	10.3	30.2	64.7
Orange pomace	350	71.9	1.2	11.3	9.9	32.3	56.8
Fescue straw	100	99.9	1.8	6.9		69.6	48.6
Sugarcane bagasse	750	26.9	-	2.2	9.7	7.7	90.5

The potential application of the pyrolytic biochar may involve the following:

- Soil amendment and carbon sequestration;
- The use of biochar to generate heat energy because it contains a high heat value of about 23 MJ/kg;
- The use of biochar in hydrogen or syngas production, which could be useful due to thermal cracking or steam reforming;
- Application of biochar as a solid fuel [31,42,43].

8.3. Pyrolytic Gas

When fast pyrolysis involves biomass, the non-condensable gases mainly constitute CO_2, CO, C_2H_6, C2H4, H_2, CH_4, C_3H_8, and C_3H_6 [25]. Furthermore, the liquid collection unit must be highly effective to avoid the presence of some light volatiles in the gaseous stream, for example, acetaldehyde, benzene, pentane, toluene, and xylenes. The pyrolysis temperature impacts the composition and product yield of pyrolytic gas, and the relative gas changes with different temperatures. An increase in temperature correlates with a higher pyrolytic gas yield [10]. The pyrolysis gas could serve as a fuel because it has reasonable quantities of CO, alongside CH_4 and several other flammable gases. The most suitable application for pyrolytic gas is its use as a carrier gas or fluidized gas. It may be utilized within plants providing cycle heat [83]. The operating temperature increases with the gas production yield, whereas bio-oil and biochar decrease [84].

8.4. Tar

Biomass is a significant essential fuel source and an environmentally-friendly power source. Pyrolysis delivers biochar, liquid fraction, and valuable fuel gases, but some by-products, such as fly ash, NO_x, SO_2, and tar, are associated with it. Generally, tar condenses at low temperatures and causes obstruction or blockage in fuel lines, piping, filters, engines, and other devices. Additionally, if tar is present in the pyrolytic gas, it may cause a reduction in biomass usage efficiency. Hence, the removal of tar from pyrolytic gases is crucial for its use as a fuel. The tar removal methods have been assessed in literature [85]. They can be categorized into five different groups based on their characteristics: catalyst cracking, mechanism methods, plasma methods, self-modification, and thermal cracking. Tar separation is of more concern in pyrolysis product quality assessments. The methods and effective reduction efficiencies of tar in pyrolysis processes are presented in Table 8 [85].

Table 8. Methods of tar reduction [85].

Methods	Tar Removal Efficiency, %
Fabric filters	0–50
Fixed bed adsorbers	50
Rotational particle separators	30–70
Sand bed filters	50–97
Venturi scrubbers	50–90

9. Impact of High Pressure on Emergent Products

The pressure level is crucial in fast pyrolysis, which influences production yield. Pressure influences the reduction of volatile yield at a range of 10–14 bars and affects the fluidity of the metaplast, swelling, and char morphology. The swelling problem rises with pressure up to 5–10 bar, and as such, the reduction occurs as the pressure increases [86]. The pressure increase can significantly impact some gas yields under the fast pyrolysis process. This reaction increases the products of CO_2 and methane, while propene and H_2 decrease, but have fewer impacts on the CO yield because it is constant [87].

An experiment carried out at a range between 0 and 5 bars indicated that pressure had a significant impact on the quality and characteristics of the product. Pressure improves both dehydrogenation and deoxygenation reactions of bio-oil, resulting in increases of CH_4, H_2, and CO_2 in the gas. Despite the unrestored combustible features of biochar, high pressure increases the biochar surface compactness and structure [88].

10. Catalyst Types and Their Application

The catalyst's low cost with high effectiveness under the fast pyrolysis process needs to be seen as an economically sustainable strategy, able to effectively compete within the existing energy market. Areas of interest in this subject area include foundation catalysts, such as MgO. Another that is considered attractive and emerging is calcium-based materials, which some consider to be relatively economical catalysts, able to deliver catalytic pyrolysis. The fast catalytic pyrolysis could also involve the commercial lignocellulosic biomass, which, at a specific scale, would be performed by the CFBR facility. The latter is understood to involve both MgO catalysts and commercial zeolites. Ketonization and aldol condensation reactions would, therefore, be promoted by the foundation sites of MgO, which would bring about sufficient hydrogen bio-oil [89].

10.1. Classification of Deoxygenation Catalysts

Catalytic cracking is another way of upgrading the bio-oil production, aiming for low oxygen content by solid acid catalysts, for instance, zeolites at an ambient pressure where hydrogen is not required. Although the process would bring forth low-grade products, which include benzene and toluene, as well as small chain alkanes, it is very important to undergo further refining. Generally, the catalytic cracking process usually produces a low carbon yield due to its high formation of coke that leads to a reduced short lifetime of the catalyst [90,91].

The application of hydro-treating is very effective in the fast pyrolysis, in which the production of bio-oil would be the main target intending to achieve good product quality. It is a hydrogenation process to eliminate contaminating molecules from the product in the range of 90%, such as nitrogen, sulfur, oxygen, and metals from bio-oil products to improve the qualities. This process is very widely used as the quality of the product is of very high grade [85,86,91].

10.2. Catalysts' Influence on the Products of Pyrolysis

Catalyst processing is a high potential upgrading processes used in the fast pyrolysis reaction of biomass to increase the product quality/yield [89]. However, to scale up the catalytic process, careful development of the catalyst is needed. Good knowledge of process design must be employed if a premature deactivation of the catalyst is to be avoided. In the context of the fast pyrolysis reaction of biomass, the catalyst upgrading process considers two different routes when bio-oil is among the main target products during bio-oil pyrolysis vapor upgrading [25].

11. Concluding Remarks and Prospects

Over the last decade, advances in fast pyrolysis (particularly of bio-oil and biochar) and pyrolytic gas production have gained increased research attention. This is largely because fast pyrolysis processes have been providing appropriate pathways to transform low-value biomass residues into value-added energy-based products. However, the challenges of pyrolysis on a technical scale include the requirement to obtain high product quality and yield, such as rapid heat transport from the source onto the particles of biomass to completely pyrolyze. Most of the pyrolysis reactors require very small sizes of biomass particles to achieve good quality products, which could be considered as another challenge.

This review has reflected on the high-pressure fast pyrolysis as a novel solution to challenges related to heat transfer, as well as product quantity and quality. The authors have attempted to demonstrate that high-pressure fast pyrolysis can bring about high-quality biomass conversion into new products. It has been shown that fluidized beds (bubbling and circulating) are more suitable and profitable among others in terms of product yield because those mentioned types could produce improved bio-oil quality and quantity. In recent years, the pyrolysis technologies of biomass conversion to energy production have gained more attention and are increasingly attaining advances, given their production environment considerations specific to emission and waste management. Therefore, and from an economic point of view, there is a need for future research to focus more on optimization processes. Moreover, it is important to mention that high-pressure pyrolytic reactors for biomass conversion into bio-oil and biochar, together with pyrolytic gas, presents several benefits, such as better product quality, lower operating costs, higher liquid product yield, increased reaction rates, and decreases in the required heat of reaction. High pressure, especially combined with a fast-heating rate, is more efficient and beneficial than working under ambient pressure.

The challenges of pyrolysis on a technical scale have been associated with obtaining high product quality and yield. Of greater concern is the rapid heat transport from the heating source to the feedstock to pyrolyze completely. A scale up of the pyrolytic reactors specific to high-pressure processes to achieve good quality products continues to be a great concern. The increase of process pressure and biomass particle size decrease should be considered as variables to be optimized. This suggests that there is a need for future studies to investigate the designs of high-pressure process reactors and material types that might have greater biomass promise such that there could be a way to achieve an improved quality product. Future studies should also seek to understand the impact of pyrolysis technology on the various output products, which are bio-oil, biochar, and syngas, having lower energy demands.

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Abbreviations

Rotating cone reactor (RCR), fluidized bed reactor (FBR), entrained flow reactor (EFR), circulating fluid-bed reactor (CFBR), ablative reactor (AbR), and auger reactor (AuR)

References

1. Basile, L.; Tugnoli, A.; Cozzani, V. The Role of Pressure in the Heat of Pyrolysis of a Lignocellulosic Biomass. *Chem. Eng. Trans.* **2015**, *43*, 451–456. [CrossRef]
2. Balat, M. Mechanisms of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis mechanisms of thermochemical biomass conversion processes. *Energy Sources A Recovery Util. Environ. Eff.* **2008**, *7036*, 620–635. [CrossRef]
3. Lee, S.Y.; Sankaran, R.; Chew, K.W.; Tan, C.H.; Krishnamoorthy, R. Waste to bioenergy: A review on the recent conversion technologies. *BMC Energy* **2019**, *1*, 4. [CrossRef]
4. Mao, C.; Feng, Y.; Wang, X.; Ren, G. Review on research achievements of biogas from anaerobic digestion. *Renew. Sustain. Energy Rev.* **2015**, *45*, 540–555. [CrossRef]
5. Bardalai, M.; Mahanta, D.K. A Review of physical properties of biomass pyrolysis oil. *Int. J. Renew. Energy Res.* **2015**, *5*, 278–286.
6. Abdalazeez, A.; Li, T.; Wang, W.; Abuelgasim, S. A Brief Review of CO_2 utilization for alkali carbonate gasification and biomass/Coal co-gasification: Reactivity, products and process. *J. CO_2 Util.* **2021**, *43*, 101370. [CrossRef]
7. Zhang, Y.; Fang, Y.; Jin, B.; Zhang, Y.; Zhou, C.; Sher, F. Effect of slot wall jet on combustion process in a 660 MW Opposed wall fired pulverized coal boiler. *Int. J. Chem. React. Eng.* **2019**, *17*, 4. [CrossRef]
8. Yin, C.; Qiu, S.; Zhang, S.; Sher, F.; Zhang, H.; Xu, J.; Wen, L. Strength Degradation mechanism of iron coke prepared by mixed coal and Fe_2O_3. *J. Anal. Appl. Pyrolysis* **2020**, *150*, 104897. [CrossRef]
9. Meier, D.; Faix, O. State of the art of applied fast pyrolysis of lignocellulosic materials—A review. *Bioresour. Technol.* **1999**, *68*, 71–77. [CrossRef]
10. Sharifzadeh, M.; Sadeqzadeh, M.; Guo, M.; Borhani, T.N.; Murthy Konda, N.V.S.N.; Cortada, M.; Wang, L.; Hallett, J.; Shah, N. The multi-scale challenges of biomass fast pyrolysis and bio-oil upgrading: Review of the state of art and future research directions. *Prog. Energy Combust. Sci.* **2019**, *71*, 1–80. [CrossRef]
11. Vinu, R.; Surriaparao, D.V. Effects of Biomass Particle Size on Slow Pyrolysis Kinetics and Fast Pyrolysis Product Distribution. *Waste Biomass Valorization* **2017**, *9*, 465–467. [CrossRef]
12. Pérez, S.; Del Molino, E.; Barrio, V.L. Modeling and testing of a milli-structured reactor for carbon dioxide methanation. *Int. J. Chem. React. Eng.* **2019**, *17*, 11. [CrossRef]
13. Bayu, A.; Abudula, A.; Guan, G. Reaction Pathways and Selectivity in Chemo-Catalytic Conversion of Biomass- Derived Carbohydrates to High-Value Chemicals: A Review. *Fuel Process. Technol.* **2019**, *196*, 106162. [CrossRef]
14. Jahirul, M.I.; Rasul, M.G.; Chowdhury, A.A.; Ashwath, N. Biofuels production through biomass pyrolysis—A Technological review. *Energies* **2012**, *5*, 4952–5001. [CrossRef]

15. Nor, W.; Wan, R.; Hisham, M.W.M.; Ambar, M.; Hin, T.Y. A Review on bio-oil production from biomass by using pyrolysis method. *Renew. Sustain. Energy Rev.* **2012**, *16*, 5910–5923. [CrossRef]
16. Thúy, N.; Chi, L.; Anto, S.; Shan, T.; Kumar, S.S.; Shanmugam, S.; Samuel, M.S.; Mathimani, T.; Brindhadevi, K.; Pugazhendhi, A. A review on biochar production techniques and biochar based catalyst for biofuel production from algae. *Fuel* **2021**, *287*, 119411. [CrossRef]
17. Magdalena Ramirez, A.H. *Bioenergy Technologies Office (BETO) 2017 Project Peer Review Technology Area: Conversion Platform*; Energy Efficiency & Renewable Energy; Idaho National Laboratory INL: Idaho Falls, ID, USA, 2017; pp. 1–25.
18. Kambo, H.S.; Dutta, A. A Comparative Review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renew. Sustain. Energy Rev.* **2015**, *45*, 359–378. [CrossRef]
19. Sugathapala, A.G.T. *Technologies for Converting Waste Agricultural Biomass to Energy*; UNEP: Osaka, Japan, 2013; pp. 1–214.
20. Bridgwater, A.V.; Peacocke, G.V.C. Fast pyrolysis processes for biomass. *Renew. Sustain. Energy Rev.* **2000**, *4*, 1–73. [CrossRef]
21. Bridgwater, T. Challenges and opportunities in fast pyrolysis of biomass: Part I. *Johns. Matthey Technol. Rev.* **2018**, *62*, 118–130. [CrossRef]
22. Gong, K.; Cao, Y.; Feng, Y. Influence of secondary reactions on heat transfer process during pyrolysis of hydrocarbon fuel under supercritical conditions. *Appl. Therm. Eng.* **2019**, *159*, 113912. [CrossRef]
23. Barbooti, M.M.; Mohamed, T.J.; Hussain, A.A.; Abas, F.O. Optimization of pyrolysis conditions of scrap tires under inert gas atmosphere. *J. Anal. Appl. Pyrolysis* **2004**, *72*, 165–170. [CrossRef]
24. Diebold, J.P.; Scahit, J.W.L. Improvements in the vortex reactor design. In *Developments in Thermochemical Biomass Conversion*; Springer: Dodrecht, The Netherlands, 1997; pp. 242–252.
25. Pattiya, A. *Fast Pyrolysis*; Elsevier: Amsterdam, The Netherlands, 2018.
26. Dupont, C.; Chiriac, R.; Gauthier, G.; Toche, F. Heat capacity measurements of various biomass types and pyrolysis residues. *Fuel* **2014**, *115*, 644–651. [CrossRef]
27. Syguła, E.; Swiechowski, K.; Stępień, P.; Koziel, J.A.; Białowiec, A. The Prediction of Calorific Value of Carbonized Solid Fuel Produced from Refuse-Derived Fuel in the Low-Temperature Pyrolysis in CO_2. *Materials* **2021**, *14*, 49. [CrossRef] [PubMed]
28. Zabaniotou, A.; Rovas, D.; Delivand, M.K.; Francavilla, M.; Libutti, A.; Cammerino, A.R.; Monteleone, M. Conceptual vision of bioenergy sector development in mediterranean regions based on decentralized thermochemical systems. *Sustain. Energy Technol. Assess.* **2017**, *23*, 33–47. [CrossRef]
29. International Energy Agency. *IEA Bioenergy Pyrolysis of Biomass*; Annual Report 2006; International Energy Agency: Paris, France, 2006.
30. Taylor, P.; Demirbas, A. Production of gasoline and diesel fuels from bio-materials. *Energy Sources A Recovery Util. Environ. Eff.* **2007**, *29*, 753–760. [CrossRef]
31. Chowdhury, Z.Z.; Pal, K.; Yehye, W.; Suresh, S. *Pyrolysis: A Sustainable Way to Generate Energy from Waste*; IntechOpen: Rijeka, Croatia, 2017; Volume 1. Available online: https://www.intechopen.com/chapters/56034 (accessed on 20 April 2021). [CrossRef]
32. Demirbaş, A.H. Yields and heating values of liquids and chars from spruce trunkbark pyrolysis. *Energy Sources* **2005**, *8312*, 1367–1373. [CrossRef]
33. Venderbosch, R.H.; Prins, W. Fast pyrolysis technology development. *Biofuels Bioprod. Biorefining* **2010**, *4*, 178–208. [CrossRef]
34. Chiaramonti, D.; Oasmaa, A. Power Generation using fast pyrolysis liquids from biomass. *Renew. Sustain. Energy Rev.* **2007**, *11*, 1056–1086. [CrossRef]
35. Gust, S.; Oy, N. *Combustion Properties of Biomass Flash Pyrolysis Oils: Final Project Report*; US Department of Energy: Washington, DC, USA, 1999.
36. Cornelissen, T.; Yperman, J.; Reggers, G.; Schreurs, S.; Carleer, R. Flash co-pyrolysis of biomass with polylactic acid. Part 1: Influence on Bio-oil yield and heating value. *Fuel* **2008**, *87*, 1031–1041. [CrossRef]
37. Fan, L.; Zhang, Y.; Liu, S.; Zhou, N.; Chen, P.; Cheng, Y.; Addy, M.; Lu, Q.; Mubashar, M.; Liu, Y.; et al. Bioresource technology bio-oil from fast pyrolysis of lignin: Effects of process and upgrading parameters. *Bioresour. Technol.* **2017**, *241*, 1118–1126. [CrossRef]
38. Seok, H.; Meier, D. Fast pyrolysis of Kraft lignin—Vapor cracking over various fixed-bed catalysts. *J. Anal. Appl. Pyrolysis* **2013**, *100*, 207–212. [CrossRef]
39. De Wild, P.; Huijgen, W.J.J.; Heeres, H.J. Pyrolysis of wheat straw-derived organosolv lignin. *J. Anal. Appl. Pyrolysis* **2012**, *93*, 95–103. [CrossRef]
40. Difelice, R.; Coppola, G.; Rapagna, S.; Jand, N. Modeling of biomass devolatilization in a fluidized bed reactor. *Can. J. Chem. Eng.* **1999**, *77*, 325–332. [CrossRef]
41. Li, X.T.; Grace, J.R.; Lim, C.J.; Watkinson, A.P.; Chen, H.P.; Kim, J.R. Biomass gasification in a circulating fluidized bed. *Biomass Bioenergy* **2004**, *26*, 171–193. [CrossRef]
42. Mielke, K.; Kolb, T.; Müller, M. Chemical Fractionation of inorganic constituents in entrained flow gasification of slurry from straw pyrolysis. *Biomass Bioenergy* **2020**, *141*, 105732. [CrossRef]
43. Diebold, J.; Scahill, J. Production of primary pyrolysis oils in a vortex reactor. In *Pyrolysis Oils from Biomass*; American Chemical Society: Washington, DC, USA, 1988; pp. 31–40.

44. Junsheng, L. Study on the Maize straw process of fast pyrolysis in the rotating cone reactor and process. In Proceedings of the International Conference on Challenges in Environmental Science and Computer Engineering Study, Wuhan, China, 6–7 March 2010; pp. 538–542. [CrossRef]
45. Hussain, R.; Ghosh, K.K.; Ravi, K. Impact of biochar produced from hardwood of mesquite on the hydraulic and physical properties of compacted soils for potential application in engineered structures. *Geoderma* **2021**, *385*, 114836. [CrossRef]
46. Peacocke, G.V.C.; Dick, C.M.; Hague, R.A.; Cooke, L.A.; Bridgwater, A.V. Comparison of ablative and fluid bed fast pyrolysis products: Yields and analyses. In *Biomass for Energy and the Environment*; Elsevier: Birmingham, UK, 1996. [CrossRef]
47. Campuzano, F.; Brown, R.C.; Martínez, J.D. Auger reactors for pyrolysis of biomass and wastes. *Renew. Sustain. Energy Rev.* **2019**, *102*, 372–409. [CrossRef]
48. Lodeng, R.; Hannevold, L.; Bergem, H.; Stocker, M. Chapter 11—Catalytic hydrotreatment of bio-oils for high-quality fuel production. In *The Role of Catalysis for the Sustainable Production of Bio-Fuels and Bio-Chemicals*; Elsevier: Trondheim, Norway, 2013; pp. 351–396. [CrossRef]
49. Huang, X.; Kudo, S.; Asano, S.; Hayashi, J.-I. Improvement of levoglucosenone selectivity in liquid phase conversion of cellulose-derived anhydrosugar over solid acid catalysts. *Fuel Process. Technol.* **2021**, *212*, 106625. [CrossRef]
50. Abbasi, T.; Abbasi, S.A. Biomass energy and the environmental impacts associated with its production and utilization. *Renew. Sustain. Energy Rev.* **2010**, *14*, 919–937. [CrossRef]
51. Yang, H. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* **2007**, *86*, 1781–1788. [CrossRef]
52. Demirba, A. Calculation of higher heating values of biomass fuels. *Fuel* **1997**, *76*, 431–434. [CrossRef]
53. Butler, E.; Devlin, G.; Meier, D.; Mcdonnell, K. A Review of Recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renew. Sustain. Energy Rev.* **2011**, *15*, 4171–4186. [CrossRef]
54. Lynam, J.G. Pretreatment of Lignocellulosic Biomass with Acetic Acid, Salts and Ionic Liquids. Master's Thesis, University of Nevada, Reno, NV, USA, 2011; pp. 1–132.
55. Safanaa, A.; Idowu, I.I.; Saadu, I.; Adamu, B.I.; Murtala, I. Potential application of pyrolysis bio-oil as a substitute for diesel and petroleum fuel. *J. Pet. Eng. Technol.* **2017**, *7*, 19–29.
56. Hao, J.; Qi, B.; Li, D.; Zeng, F. Catalytic Co-pyrolysis of rice straw and ulva prolifera macroalgae: Effects of Process parameter on bio-oil up-gradation. *Renew. Energy* **2021**, *164*, 460–471. [CrossRef]
57. Cavalaglio, G.; Cotana, F.; Nicolini, A.; Coccia, V.; Petrozzi, A.; Formica, A.; Bertini, A. Characterization of various biomass feedstock suitable for small-scale energy plants as preliminary activity of biocheaper project. *Sustainability* **2020**, *12*, 6678. [CrossRef]
58. Demirbas, A. Relationships between heating value and lignin, moisture, ash and extractive contents of biomass fuels. *Energy Explor. Exploit.* **2002**, *20*, 105–111. [CrossRef]
59. Demirbas, A. Effect of temperature on pyrolysis products from biomass effect of temperature on pyrolysis products from biomass. *Energy Sources* **2010**, *7036*, 329–336. [CrossRef]
60. Yan, Q. Effects of pyrolysis conditions on yield of bio-chars from pine chips. *For. Prod. J.* **2011**, *61*, 367–371. [CrossRef]
61. Sinha, R.; Kumar, S.; Singh, R.K. Production of biofuel and biochar by thermal pyrolysis of linseed seed. *Biomass Convers. Biorefin.* **2013**, *3*, 327–335. [CrossRef]
62. Elliott, D.C. Relation of reaction time and temperature to chemical composition of pyrolysis oils. In *Pyrolysis Oils from Biomass*; American Chemical Society: Washington, DC, USA, 1988; pp. 55–65.
63. Mahinpey, N.; Murugan, P.; Mani, T.; Raina, R. Analysis of Bio-oil, biogas and biochar from pressurized pyrolysis of wheat straw using a tubular reactor. *Energy Fuels* **2009**, *23*, 2736–2742. [CrossRef]
64. Cetin, E.; Moghtaderi, B.; Gupta, R.; Wall, T.F. Influence of Pyrolysis conditions on the structure and gasification reactivity of biomass chars. *Fuel* **2004**, *83*, 2139–2150. [CrossRef]
65. Uddin, M.N.; Techato, K.; Taweekun, J.; Rahman, M. An Overview of Recent Developments in Biomass Pyrolysis Technologies. *Energies* **2018**, *11*, 3115. [CrossRef]
66. Qureshi, M.S.; Oasmaa, A.; Pihkola, H.; Deviatkin, I.; Tenhunen, A.; Mannila, J.; Minkkinen, H.; Pohjakallio, M.; Laine-Ylijoki, J. Pyrolysis of Plastic waste: Opportunities and challenges. *J. Anal. Appl. Pyrolysis* **2020**, *152*. [CrossRef]
67. Wang, W.; Lu, Y.; Xu, K.; Wu, K.; Zhang, Z.; Duan, J. Experimental and simulated study of fluidization characteristics of particle shrinkage in multi-chamber fluidized bed for biomass fast pyrolysis. *Fuel Process. Technol.* **2021**, *216*, 1–12. [CrossRef]
68. Onay, O.; Kockar, M. Pyrolysis of rapeseed in a free fall reactor for production of bio-oil. *Fuel* **2006**, *85*, 1921–1928. [CrossRef]
69. Demirbas, A. Current technologies for the thermo-conversion of biomass into fuels and chemicals. *Energy Sources* **2010**, *26*, 715–730. [CrossRef]
70. Nyakuma, B.B.; Johari, A.; Ahmad, A.; Tuan, T.A. Comparative analysis of the calorific fuel properties of empty fruit bunch fiber and briquette. *Energy Procedia* **2014**, *52*, 466–473. [CrossRef]
71. Naik, D.K.; Monika, K.; Prabhakar, S.; Parthasarathy, R.; Satyavathi, B. Pyrolysis of sorghum bagasse biomass into bio-char and bio-oil products: A Thorough physicochemical characterization. *J. Therm. Anal. Calorim.* **2017**, *127*, 1277–1289. [CrossRef]
72. Michailof, C.M.; Kalogiannis, K.G.; Sfetsas, T.; Patiaka, D.T.; Lappas, A.A. Advanced Analytical techniques for bio-oil characterization. *Wiley Interdiscip. Rev. Energy Environ.* **2016**, *5*, 614–639. [CrossRef]
73. Pattiya, A. Bio-Oil Production via fast pyrolysis of biomass residues from cassava plants in a fluidised-bed reactor. *Bioresour. Technol.* **2011**, *102*, 1959–1967. [CrossRef]

74. Guizani, C.; Jeguirim, M.; Valin, S.; Limousy, L. Biomass Chars: The effects of pyrolysis conditions on their morphology, structure, chemical properties and reactivity. *Energies* **2017**, *10*, 796. [CrossRef]
75. Fu, P.; Hu, S.; Sun, L.; Xiang, J.; Yang, T.; Zhang, A.; Zhang, J. Structural evolution of maize stalk/char particles during pyrolysis. *Bioresour. Technol.* **2009**, *100*, 4877–4883. [CrossRef]
76. Kabir, M.J.; Chowdhury, A.A.; Rasul, M.G. Pyrolysis of municipal green waste: A Modelling, simulation and experimental analysis. *Energies* **2015**, *8*, 7522–7541. [CrossRef]
77. Tomczyk, A. Biochar physicochemical properties: Pyrolysis temperature and feedstock kind effects. *Rev. Environ. Sci. Bio/Technol.* **2020**, *19*, 191–215. [CrossRef]
78. Wu, W.; Yang, M.; Feng, Q.; Mcgrouther, K.; Wang, H.; Lu, H.; Chen, Y. Chemical characterization of rice straw-derived biochar for soil amendment. *Biomass Bioenergy* **2012**, *47*, 268–276. [CrossRef]
79. Rafiq, M.K.; Bachmann, R.T.; Rafiq, M.T.; Shang, Z.; Joseph, S.; Long, R. Influence of Pyrolysis temperature on physico-chemical properties of corn stover (*Zea mays* L.) Biochar and feasibility for carbon capture and energy balance. *PLoS ONE* **2016**, *11*, e0156894. [CrossRef]
80. Mohan, D.; Rajput, S.; Singh, V.K.; Steele, P.H.; Pittman, C.U. Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. *J. Hazard. Mater.* **2011**, *188*, 319–333. [CrossRef]
81. Zama, E.F.; Zhu, Y.; Reid, B.J.; Sun, G. The role of biochar properties in influencing the sorption and desorption of Pb(II), Cd(II) and As(III) in aqueous solution. *J. Clean. Prod.* **2017**, *148*, 127–136. [CrossRef]
82. Kumar, A.; Abhijeet, S.; Priyanka, A. Production, activation and applications of biochar in recent times. *Biochar* **2020**, *2*, 1–33. [CrossRef]
83. Bridgwater, A.V. A Catalysis in thermal biomass conversion. *Appl. Catal. A Gen.* **1994**, *116*, 5–47. [CrossRef]
84. Thangalazhy-Gopakumar, S.; Adhikari, S.; Ravindran, H.; Gupta, R.B.; Fasina, O.; Tu, M.; Fernando, S.D. Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor. *Bioresour. Technol.* **2010**, *101*, 8389–8395. [CrossRef]
85. Han, J.; Kim, H. The reduction and control technology of Tar during biomass gasification/pyrolysis: An overview. *Renew. Sustain. Energy Rev.* **2008**, *12*, 397–416. [CrossRef]
86. Senneca, O.; Cortese, L. Thermal Annealing of coal at high temperature and high pressure. Effects on fragmentation and on rate of combustion, gasification and oxy-combustion. *Fuel* **2014**, *116*, 221–228. [CrossRef]
87. Basu, P. *Biomass Gasification, Pyrolysis and Torrefaction*, 3rd ed.; Practical Design and Theory, Pyrolysis; Academic Press: Cambridge, MA, USA, 2018; pp. 1–582.
88. Xu, B.; Li, A. Effect of high-pressure on pine sawdust pyrolysis: Products distribution and characteristics. *AIP Conf. Proc.* **2017**, *1864*, 020116. [CrossRef]
89. Sanahuja-Parejo, O.; Veses, A.; Manuel, L. Ca-Based Catalysts for the production of high-quality bio-oils from the catalytic co-pyrolysis of grape seeds and waste tyres. *Catalysts* **2019**, *9*, 992. [CrossRef]
90. Liu, C.; Wang, H.; Karim, A.M.; Sun, J.; Wang, Y. Catalytic fast pyrolysis of lignocellulosic biomass. *Chem. Soc. Rev.* **2014**, *43*, 7594–7623. [CrossRef]
91. Saleh, A.; Al-Hammadi, S.A.; Munkaila, I.; Mustaqeem, M. Synthesis of Molybdenum Cobalt Nanocatalysts Supported on Carbon for Hydrodesulfurization of Liquid Fuels. *J. Mol. Liq.* **2018**, *272*, 715–721. [CrossRef]

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STATEMENT

I hereby declare that in the publication:

Waheed A Rasaq, Mateusz Golonka, Miklas Scholz, and Andrzej Białowiec, 2021. "Opportunities and challenges of high-pressure fast pyrolysis of biomass: A review." Energies 14 (17), 1 – 20, doi: 10.3390/en14175426

My contribution included:
Developing the concept and design of the study. I prepared the entire text of the article as well as Figures. During the review process, I made corrections to the text of the manuscript and prepared responses to the reviewers. I obtained funding for the publication of the manuscript.

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My contribution included:
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My contribution included:
Developing the concept and design of the study. I participated in the revision and supervision of the manuscript. I participated in the review process and the related modifications to the manuscript. I was also the corresponding author.

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Review

Navigating Pyrolysis Implementation—A Tutorial Review on Consideration Factors and Thermochemical Operating Methods for Biomass Conversion

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Abstract: Pyrolysis and related thermal conversion processes have shown increased research momentum in recent decades. Understanding the underlying thermal conversion process principles alongside the associated/exhibited operational challenges that are specific to biomass types is crucial for beginners in this research area. From an extensive literature search, the authors are convinced that a tutorial review that guides beginners particularly towards pyrolysis implementation, from different biomasses to the thermal conversion process and conditions, is scarce. An effective understanding of pre-to-main pyrolysis stages, alongside corresponding standard methodologies, would help beginners discuss anticipated results. To support the existing information, therefore, this review sought to seek how to navigate pyrolysis implementation, specifically considering factors and thermochemical operating methods for biomass conversion, drawing the ideas from: (a) the evolving nature of the thermal conversion process; (b) the potential inter-relatedness between individual components affecting pyrolysis-based research; (c) pre- to post-pyrolysis' engagement strategies; (d) potential feedstock employed in the thermal conversion processes; (e) the major pre-treatment strategies applied to feedstocks; (f) system performance considerations between pyrolysis reactors; and (g) differentiating between the reactor and operation parameters involved in the thermal conversion processes. Moreover, pre-pyrolysis activity tackles biomass selection/analytical measurements, whereas the main pyrolysis activity tackles treatment methods, reactor types, operating processes, and the eventual product output. Other areas that need beginners' attention include high-pressure process reactor design strategies and material types that have a greater potential for biomass.

Keywords: thermal conversion process; feedstock; temperature; pressure; process reactors; learners

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1. Introduction

The environment today is confronted by an unending cascade of global anthropogenic and ecosystem-based challenges. Biomass is considered to have the potential to be utilized as an alternative energy source. The conversion of the high carbon content of biomass through thermochemical treatment resulted in better fuel properties of biochar production. Pyrolysis is the most researched thermochemical technique in the past decade among the few well-established methods for treating biomass and biogenic waste in order to produce high-quality and yield energy products such as biochar, bio-oil, and pyrolytic gas. The obvious aftermath of the industrial revolution brought about a steady geometric increase in population growth, which noticeably altered the balance of global carbon. The global population in 2013 was estimated at 7.2 billion and is estimated to increase by a billion in 2025; this makes the energy demand that is required for agricultural, industrial, and transportation development very crucial [1]. Global waste management, on the one hand, is among the United Nations' Millennium Development Goals (MDGs) from 2000, and particularly key here is its 7th Goal: To Ensure Environmental Sustainability, which subsequently progressed in the 2008 Waste Framework Directive [2], which aims to improve (waste) management strategies in accordance with the Sustainable Development Goals (SDG) [3]. On the other hand, waste disposal methods like, for example, composting should be effective in helping to reduce greenhouse gas emissions [4]. Moreover, the generated bio-waste materials would noticeably vary, especially in composition, largely due to some factors like the type of community and its consumers, industrialization, institutions, and commercial entities [2]. A great portion of bio-waste material, and how it transforms into biofuel, as well as other energy sources remains a major research focus, especially from the environmental standpoint [5]. Biomass, however, is increasingly considered to be the potential alternative renewable energy source. Pyrolysis, among the initial stage(s) in gasification, would help utilize biomass energy, alongside other thermochemical conversion procedures. In addition to the prevailing environmental issues, there are other pressing biomass-related challenges that involve many pyrolysis-based studies. Besides that, the context of thermal conversion technology (i.e., determination of operating parameters of pyrolysis-based) and reactor types have been based on the desired characteristics of the product (bio-oil, biochar, and pyrolytic gas), as well as on the field of biomass pyrolysis and upgrading. Feedstock properties, product characteristics, reactor type, and upgrading options are among the key areas demonstrated in the synthesized literature, providing relevant information. It is worth mentioning that some conducted reviews have looked at the systematic approaches for mapping biomass resources to conversion pathways, forming the basis for biomass valuation and informing when biomass pre-processing is needed in order to ensure feedstocks are ready for conversion [5]. Furthermore, bio-oil derived from pyrolysis biowaste would serve as chemicals/fuel products. The production and composition of pyrolysis oil are affected by the biomass composition and process operating parameters [6].

In recent decades, the research momentum about pyrolysis and related thermal conversion processes is on the rise, involving a wide range of biomass/feedstock targets. For emphasis, pyrolysis simply depicts the use of heat treatment to bring about an irreversible chemical change in the absence of oxygen, specifically [5,7,8]. Moreover, pyrolysis remains one of the most efficient techniques for thermochemical conversion without the involvement of oxygen. This process yields carbon-enriched hydrocarbons (bio-oils), biochar, and volatile gases containing molecules that are rich in oxygen and hydrogen [9]. Generally, the major pyrolysis products include biochar, bio-oil, pyrolytic gas, and tar, among others, which largely depends on the process type, whether it is slow, fast, or flash, considering their tightly linked technological/product yield components [10–16]. The harnessing of the associated biomass energy via thermochemical processes should be eco-friendly and should be completed with solid waste conversion technologies at high temperatures [17]. If the target product(s) is to be achieved, a thorough prior knowledge and understanding of different biomasses, as well as the conditions/situations of their pyrolysis is warranted [5]. For the temperature of pyrolysis to achieve a target level, the specific energy demand largely depends on biomass moisture and the process temperature and duration [18]. To reiterate, the pyrolysis type would directly connect with the reactor types [19–23]. To learn the pyrolysis operating process, the description of reactors alongside their peculiarities that make them well suited for one or more biomass feedstocks is also warranted, as this has a direct influence on the type of the anticipated product output.

In addition to the heating methods and their reactor types, biomass properties can affect the pyrolysis process [24–26], especially when considering the wide range of decomposition processes and realized products (of biomass) [27]. In addition to the different biomasses and their prevailing conditions, understanding the intentions of specialists/stakeholders to engage in pyrolysis/thermal conversion activities emanates from the quest to achieve a desirable end-product (of a given biomass/feedstock). Some major advantages of pyrolysis can include the following: (a) a high degree of efficiency and profitability, as well as the suitability to convert a wide range of solid waste into storage energy; (b) the minimal nature of greenhouse gases like HCl, NO_x, and SO_x; (c) the absence of corrupt organic matter in the pyrolyzed residue to prevent the extraction of metal substances via solvent; (d) pyrolysis is capable of processing garbage waste that is not suitable for landfill and incineration; and (e) the fixing of harmful components like heavy metals and sulfur that are present in the (raw material) waste. Some disadvantages, however, can include: (a) the waste processing, if not properly developed, could still pose environmental problems, and (b) to implement the process in a large-scale pyrolysis project will require a permit by the government, given the differences in the prevailing policies [28–30]. Despite the abovementioned advantages and disadvantages associated with thermal conversion, there still remains some research concerns. For examples, what are the primary essentials that a thermal conversion enthusiast, especially a beginner, needs to grasp/understand regarding the implementation of a typical pyrolysis-based study? If this question were to be answered, another fundamental question could be guided by the following: (a) Why is it important to shed more light on implementing a typical pyrolysis-based study? (b) Could it be to strengthen the subject area? (c) Could it be to attract more enthusiasts into becoming more engaged in pyrolysis-based studies? (d) Additionally, if the implementation process were to be better understood, what would be the benefit(s)? (e) Could it enable/help new investigators increase their proactivity, as well as emerge better engaged in any given pyrolysis-based study? (f) Could it enable/help in enhancing their creativity, as well as their initiative of research ideas/questions for the implementation activity of pyrolysis-based studies? These above-mentioned questions underscore the justification/rationale of why the authors herein have deemed it needful to conduct a captivating review synthesis in order to support the existing information and to seek how to navigate pyrolysis implementation, specifically when considering the factors and thermochemical operating methods for biomass conversion, drawing the ideas from: (a) the evolving nature of the thermal conversion process; (b) the potential inter-relatedness between individual components affecting pyrolysis-based research; (c) pre- to post-pyrolysis' engagement strategies; (d) the potential feedstock employed in the thermal conversion processes; (e) the major pre-treatment strategies applied to feedstocks; (f) the system performance considerations between pyrolysis reactors; and (g) differentiating between reactor and operation parameters involved in the thermal conversion processes. In addition to pre-to-main pyrolysis stages and their respective analyses, either developed or adopted from other fields, this tutorial review has provided some understanding about the operational standpoints, including (a) that pre-pyrolysis activity involves biomass selection and analytical measurements, and (b) that the main pyrolysis activity involves treatment methods, reactor-types, operating processes, and eventual product outputs, as shown in Figure 1.

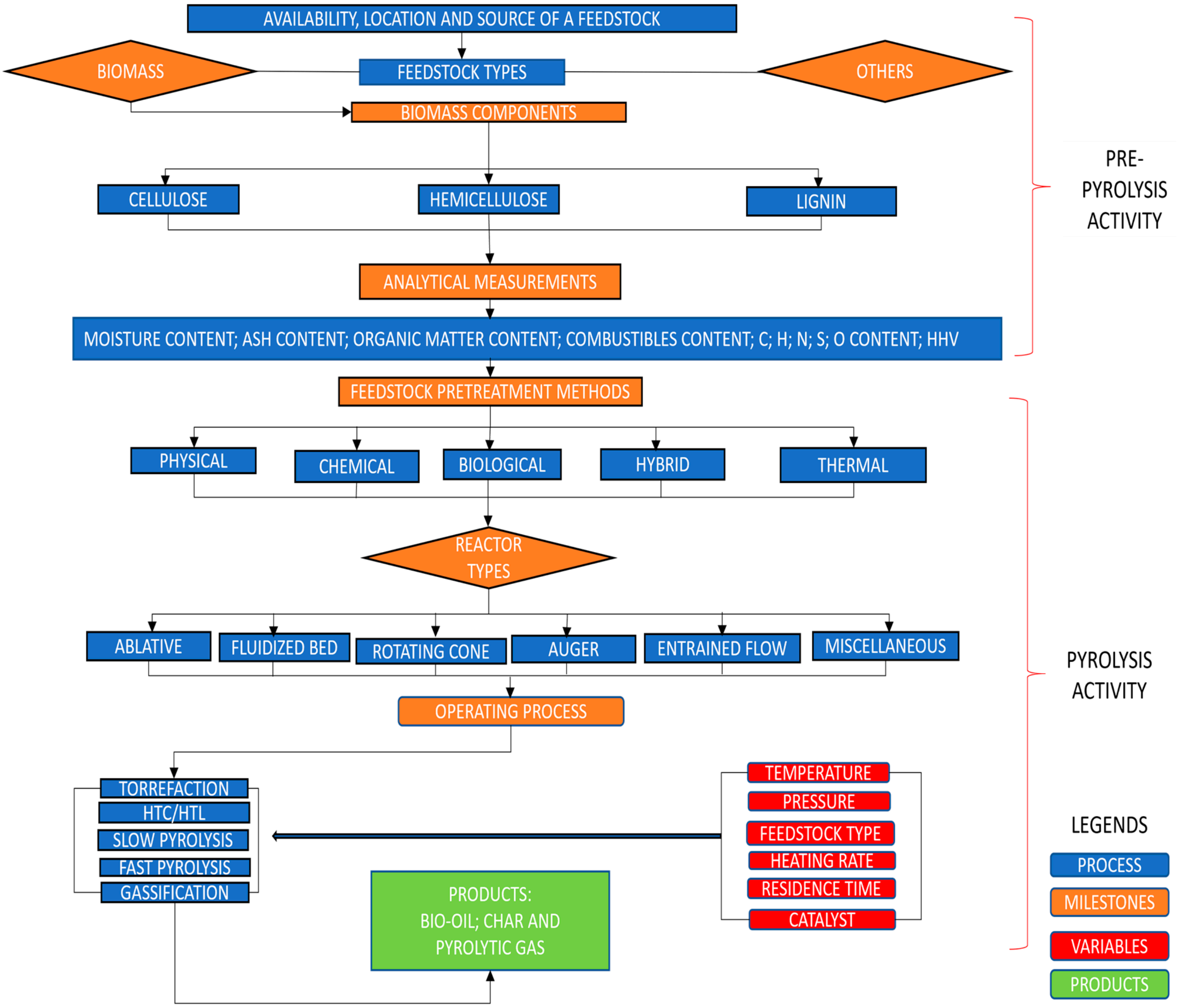

Figure 1. Key pre-to-main pyrolysis stages, from biomass selection, analytical measurements, treatment methods, to operating reactor-type processes output.

2. The Evolving Nature of Thermal Conversion Process

Previous findings involving the implementation of thermal conversion based-studies on conditions/situations and different biomasses, along with how these experimental aim(s)/objective(s) of the various studies were developed and the respective subsections captured are all present in Table 1. Additionally, the pyrolysis-based studies shown engaged with varying aims/objectives. More so, to carry out the experimental procedures developed on the basis of pyrolysis, strong considerations need to be given to the parameters involved, such as the materials, the characteristics of biomass samples, the sample preparation and pyrolysis, the economic analysis, as well as validation via the experimental procedures. Additionally, there could be various thermo-kinetics of the feedstock, which would associate with the thermal operating conditions, if high quality pyrolytic products like biochar, bio-oil, and pyrolytic gas were to be achieved. Tian and colleagues' experiments that were conducted on rice husks were carried out using two pyrolysis-coupled real-time volatile monitoring techniques (TGA–FTIR and Py-GC/TOF-MS). The findings demonstrated that in the temperature range of 200 to 330 °C, 330 to 390 °C, and 390 to 600 °C, respectively, rice husks showed three mass loss and gaseous product evolution stages. It was shown that 2,3-dihydro-benzofuran was the main hemicellulose product after speculating on the formation pathways of the 24 main volatile species. On the other hand, 2-methoxy-4-(1-propenyl)-phenol was a potentially key active intermediate and was highly unstable during the pyrolysis of the lignin constituent in RHs [31]. Besides the acquisition of knowledge regarding primary volatile compositions, the behavior of mass loss in a given feedstock, as well as the reaction kinetics properties [31,32] are important. For instance, seven partners participated in an international round-robin study, conducting TGA pyrolysis experiments on pure cellulose and beechwood at various heating rates. The activation energies of cellulose, hemicellulose, and conversions of up to 0.9 with beechwood showed deviations of about 20–30 kJ/mol in all experiments [33], feedstock preparation via the adoption of the biochar catalyst method upgrading options, hybrid pretreatment methods, and the comparisons of untreated and hydrochloric acid treatment of various biomass feedstock [34–36]; these are all examples of studies where feedstock was directly associated with the thermal operating conditions. In Téllez and colleagues' study, using lab-scale fast pyrolysis in a vacuum, rice husks (RHs) were converted into pyrolytic oils, enriched with levoglucosan (LG). They investigated how the pretreatment of the biomass and the pyrolysis temperature (300–700 °C) affected the yields of pyrolysis products and the selectivity for the LG formation. RHs pretreated with hydrochloric acid at 400 °C produced a maximum oil yield of 47 wt.%, which was 1.4 times more than the amount of oil produced at the same temperature from untreated RHs [36]. Also, activated carbon would help purify the bio-oil organic compounds, which could lead to environmental pollution [37]. Besides the thermal conversion operating parameters, like temperature [38] alongside the catalyst sorbent addition, there is the application of the Coats–Redfern method that could impact the end products' properties. Thus, understanding the influence of temperature on the evolution of the structures and the organic content of biochar [39–43] is key. The co-pyrolysis of rice straw (RS) and *Ulva prolifera* macroalgae (UPM) was investigated by Hoa et al., using a range of activated biochar catalysts supported by nickel-iron layered double oxides (NiFe-LDO). The bio-oil yield from co-pyrolysis was higher than that from individual pyrolysis. At 500 °C, the biomass mixture of RS/A-UPM produced the highest bio-oil yield (46.68 wt.%). However, the combination of RS and UPM without acid-treated UPM demonstrated a reduced bio-oil yield. Because of the coke formation during the catalytic pyrolysis up-gradation, the bio-oil was reduced. However, using the 5% Ga/NiFe-LDO/AC catalyst improved the bio-oil quality [39]. The correlations of pyrolysis characteristics with biomass types should be considered alongside the associated mechanisms [44]. A bio-fuel could be upgraded by various thermal conversion methods from the feedstock [45,46]. Furthermore, conventional thermogravimetric analysis could be applied to investigate the mechanism interaction of the co-pyrolysis process [47], which might offer fresh perspectives for eco-innovative circular economy solutions [48].

Table 1. A summary of various experimental procedures of pyrolysis specific to their aims/objectives and analytical methods.

Aims/Objective	Methods	Ref.
Nine holocelluloses (two forestry and seven agricultural wastes) were selected as the feedstock to investigate the impact on the compositions of bio-oils and to screen the best feedstock suitable for the production of long-chain ethers precursor, for the ensuing improvement of yield and selectivity	Preparation of native holocellulose, evaluation of the sample, experimental apparatus, and procedures	[49]
To offer details on the yields and features of char produced from ten types of wood that are common in Southern Europe, undergoing biomass carbonization technologies condition	Biomass feedstocks, experimental facility, experimental procedure, charcoal characterization, and overview of the experiments	[50]

Table 1. *Cont.*

Aims/Objective	Methods	Ref.
To perform intricate experimental analysis as well as the numerical modeling of oat straw's slow pyrolysis. The pyrolysis products are described using advanced methods of analysis, with tests focusing on the properties and yield of the solid, liquid, and gaseous species	Feedstock sample, ultimate and proximate analyses and employing semi-batch vertical reactor where simultaneous thermal, infrared spectroscopy, qualitative of tars were analyzed, and pyrolysis gas analyzation, and numerical computations	[51]
The wet torrefaction of corn stalk was studied, and the biomass pyrolysis polygeneration performance of the wet torrefied sample was examined. More so, the solid material, energy, carbon, and hydrogen yields, as well as the effectiveness of removing ash and oxygen were also compared between WT and dry torrefied (DT) of corn stalks	Materials, torrefaction technique, characterization of torrefied samples, and pyrolysis technique	[52]
The determination of the thermal degradation characteristics of heating residues of eucalyptus (EU) and corncob (CC) for gasification using TGA rates of 10 °C/min in a nitrogen environment. The study covers the impact of biomass composition and kinetic parameters on heating rate	Preparation of biomass samples and experimental procedures	[32]
This experimental study set out to characterize the bioenergy potential of DS pyrolysis, measure gas emissions and byproducts, estimate kinetic and thermodynamic parameters, and detect the joint optimization of multiple responses in response to changing biofeedstock, heating rate, and temperature, as well as significant interactions between operational conditions	Sample preparation, physical and chemical analysis, TG experiments beforehand, activation energy, pyrolytic characteristic parameters, Friedman and Starink methods, Py-GC/MS experiments, TGA–FTIR experiments, and joint optimizations	[53]
To provide a thorough understanding of primary volatile compositions, mass loss behavior, reaction kinetics, and formation pathway during fast RH pyrolysis	Materials, pyrolysis process and kinetic methods	[31]
The impact of feedstock particle size on the distribution of fast pyrolysis products and the kinetics of slow pyrolysis	Characterization of MWSD, thermogravimetric analysis, evaluation of apparent activation energy, the pyrolysis of MWSD and product characterization, different profiles of mass loss and the impact of particle size on mass loss	[54]
To look into the reproducibility of TGA biomass pyrolysis experiments and potential deviations when mass loss kinetics are calculated from the same sample using various TGA technologies	TGA experiments and kinetic analysis	[33]
To fill the knowledge gap in orange and potatoes peel pyrolysis kinetics that was discovered during the literature review	Materials, TGA, and kinetics	[55]
To accurately evaluate the HHV using lumped-parameter pyrolysis kinetic models, and to demonstrate a straightforward correlation that can be used to assess HHV without relying on three different biomass species	Experimental samples, experimental procedures, and experimental results	[56]
Examine the combustion kinetics and study the combustion properties of five different types of biomass fuel pellets that can be used as biomass fuel	Analysis of the thermal weight loss and the components of five different biomass fuel pellet types	[44]
To investigate how the content of the biomass influences the kinetics, temporal evolution of the pyrolysis vapors, and production of the main bio-oil components during biomass pyrolysis	Materials, Py-FTIR analysis, isothermal mass loss of biomass, and using Py-GC/MS for the product analysis	[57]

Table 1. *Cont.*

Aims/Objective	Methods	Ref.
To investigate the thermal decomposition of stalk and sour cherry flesh using thermogravimetric analysis, and to evaluate the activation energies using three kind of isoconversional approaches—Flynn–Wall–Ozawa, Friedman, or Kissinger–Akahira–Sunose. The findings reveal the pyrolysis kinetics and characteristics, as well as the ideal conditions for designing, optimizing, and simulating the pyrolysis process	Materials, physicochemical characterization, thermogravimetric analysis, and kinetic modeling	[58]
TGA/DTG investigation in an inert environment was performed to examine the thermal degrading and pyrolysis kinetics of biowastes.	Collection and preparation of biomass, proximate and ultimate investigation of samples as well as the calorific value, thermogravimetric/FTIR analysis	[59]
To carry out an extensive study that includes biochemical and physicochemical characterization, and the kinetic thermodynamic study of pyrolysis and thermal breakdown behavior of biomass from banana leaves	Sample preparation, banana leaves biomass pyrolysis reaction model determination using kinetic modeling, thermodynamic analysis, and thermogravimetric experiments	[60]
To clarify the pyrolytic behavior in terms of thermodynamic and kinetic characteristics, as well as the bioenergy potential of biological wastes resulting from the manufacturing of bio-products	The processing of bacterial biomass produced in a pilot-scale operation, sample characterization, FTIR spectroscopy, data processing using PCA, a TGA experiment, the characteristics of pyrolysis, thermo-kinetic studies pyrolysis, Py-GC/MS analysis, and the development of a model based on SVR	[61]
Pyrolyze three samples using thermogravimetric analysis and characterize them by determining how well various Phragmites Hirsuta components pyrolyze, thus this study offers theoretical direction for the formulation of the Phragmites preparation process, bioenergy is converted into Hirsuta by a thermochemical process	Material, characterization, Thermogravimetric analysis, kinetic modeling, reaction model determination, and thermodynamic analysis	[62]
To outline a straightforward method for analyzing the kinetic parameters (frequency factor, activation energy, and reaction model) of biomass with complicated thermal behavior. A multi-step mechanism for the biomass pyrolysis processes was employed to get the kinetic parameters using a deconvolution algorithm process coupled with isoconversional approaches.	Sample selection, preparation, and characterization, performed kinetics, and thermogravimetric analysis	[63]
In-depth research was conducted on the mechanisms causing the variations and the correlations between the pyrolysis characteristics and the various types of biomass. By improving our knowledge of the pyrolysis process in various biomass types, this work also serves as a reference for their thermal conversion methods	Materials, physicochemical of biomass, thermogravimetric, and kinetic analysis using the Coats–Redfern method TG and multi-peak fitting in the derivative thermogravimetric analysis.	[64]
Using a laboratory-scale (5 kg/h) AFP unit to accurately assess the impact of feedstock type on the characteristics of bio-oils produced from straw, miscanthus, and beech and poplar wood	Biomass that has been pyrolyzed, the pyrolysis process, the physicochemical characteristics of bio-oils, and a quantitative analysis of the chemical makeup of bio-oils	[6]
On the physical and chemical characteristics of biochar, particularly their effects on nitrogen (N) content and composition, the impact of feedstock type and temperature of pyrolysis were examined	Materials, preparation of biochar and sample preparation, and analytical methods	[65]
Studies involving feedstock, pyrolysis, and biochar, including policies on emission	Reviewing different concepts	[66]

Table 1. *Cont.*

Aims/Objective	Methods	Ref.
The investigation of the effects of CaO addition sorbent and the temperature of pyrolysis on the chemical and the physical characteristics of obtained biochar and syngas	Material characteristics, experimental procedure, and methods	[38]
To look into how the structure of the resulting bio-char changed as the gaseous and liquid products evolved in relation to the pyrolysis temperature, and understanding how temperature affects the development of organics and the composition of biochar	Feedstock and chemicals, pyrolysis experiments, characterization of the products, and kinetic analysis	[43]
To ascertain how the duration time and pyrolysis temperature affect the properties of hydrochars in comparison to biochars produced through direct slow pyrolysis. In order to do this, hydrochar produced by HTC of waste biomass was pyrolyzed at two different temperatures (350 and 500 °C) and three different times (1, 3 and 5 h), and the testing was conducted to establish a number of properties relevant to the use of chars as soil amendment, inexpensive adsorbent, or fuel, and growing media, including pH, electrical conductivity, electrochemical potential, porosity, phytotoxicity, and elemental composition	Selection of hydrochar, pyrolysis of hydrochar made from waste biomass, pyrolysis of waste biomass, and char characterization	[67]
To investigate the impact of the pyrolysis temperature using fluidized bed pyrolysis system, three reactions were carried out to convert solid waste into renewable aviation fuel in attempt to show the distributions of the liquid and gas products at different temperatures	Feedstock, equipment, experimental procedures, and product analysis	[26]
The reaction mechanism of the co-pyrolysis of biomass and coal in the TGA analyzer was investigated using both conventional TGA and a novel congruent-mass TGA analyses. Studies that compare how these two approaches differ in how they assess the likelihood of a coal–biomass interaction	Materials and TGA	[47]
To research the kinetics of the co-pyrolysis of the coal and pretreated watermelon rind (WMR) blends	Selection of the biomass, pretreatment, compositional analysis, determination of the (WMR) higher heating value, calculation of its exergy, preparation of sample blends, thermogravimetric analysis of the coal and pretreated (WMR), kinetic analysis, and estimation of the thermodynamic parameters	[68]
The following research goals were achieved: (a) performing a thorough thermogravimetric analysis (TGA) of the nut shells; (b) identifying the characteristic points in the nut shells' thermal decomposition process; (c) determining the temperature range at which hemicellulose, cellulose, and lignin decomposed in the examined nut shells; (d) estimating the fundamental kinetic parameters of the nut shells thermal decomposition; and (e) the physiochemical properties of the nut shells conversion rates as a function of the process temperature	Characteristics of the feedstock used in the research, thermogravimetric analysis, kinetic modelling, and model-fitting method: Coats–Redfern Method	[42]
TGA–FTIR (thermogravimetric analysis with FTIR analysis of evolved gases) pyrolysis experiment combined with advanced data analysis and modeling methods to assess the viability of developing an advanced methodology for the evaluation of biomass materials	Selection of the sample and testing on a suite of biomass materials	[41]
To assess the pyrolysis behavior of corks with various properties that might be used in scaling up the pyrolysis of cork-rich materials, in the strengthening of their value as well as their integration in thermochemical platforms	Materials, thermogravimetric analysis, kinetic analysis, estimation of chemical composition, wet chemical characterization, and FTIR analysis	[69]

Table 1. *Cont.*

Aims/Objective	Methods	Ref.
The characteristics of green corn husks were described and analyzed in order to determine the thermokinetics conversion parameters through pyrolysis reactions that were kinetically studied using TGA and DTG, where the Flynn–Wall–Ozawa was used to compare the energetic efficiency from corn husk	Materials, biomass composition analysis, higher calorific value, non-isothermal thermogravimetric analyses, thermokinetics studies, master plots method, kinetic model proposed by Kissinger, kinetic model of Friedman, thermogravimetric analysis, and the mathematical simulation of the thermal decomposition kinetic of green corn husk biomass	[70]
To look into the technical and financial effects of different lignocellulosic elements on biomass pyrolysis, this work specifically investigates the basic mechanisms of cellulose, hemicellulose, and lignin transformation during pyrolysis	Characterization of biomass samples, sample preparation, pyrolysis, economic analysis, and validation via experimental values	[71]
To make available a theoretic framework for advancing the pyrolysis process and the efficient use of corn straw resources	Experimental materials, Instruments, and methods, analytical methods, and kinetics theory	[72]
Utilizing the pyrolysis poly-generation method to provide renewable energy and materials while overcoming the drawbacks of using rice husks	Materials, the preparation of an activated bio-char catalyst, a catalytic fast pyrolysis process, derived of amorphous SiO2 and porous carbon from bio-char, experiments on the adsorption of organic compounds, and physicochemical analysis	[34]
To research, ascertain, and comprehend these solids' digestibility, as well as how the various hybrid method process parameters affected it	Feedstock and inoculum, pretreatment of wood chips, anaerobic digestion of pretreated solids and other analytical methods	[35]
In light of the fantastic outcomes produced in the chemical activation of rice husks (RHs), an assessment of bio-char made from RH pyrolysis was conducted to see if it could be used as a solid-phase extraction (SPE) to filter out harmful organic compounds from the biooil aqueous phase	Pyrolysis, chemical activation, characterization of activated carbon, SPE procedures, HPLC-DAD analysis, and method validation	[37]
Researchers have looked into the non-catalytic and catalytic co-pyrolysis of Ulva prolifera macroalgae (UPM) and straw (RS). To establish their ideal values, it has been investigated how temperature and mixing ratio affect the product's distribution	Feedstock characterization, experimental setup and procedures, catalysts preparation, catalyst characterization methods, and liquid products analysis methods	[39]
Studies of techno-economic performance of involving biorefinery concepts and steam pretreatment techniques	Feedstock composition/economic analysis	[73]
Based on the composition of the ash, the investigation's goal was to pinpoint the pertinent fractionation processes; the findings will later be applied to create a model for predicting slag composition and viscosity based on process parameters and fuel ash composition	Materials, feedstock preparation, and gasification process, and product char and gas analysis	[74]
To create the biofuel using a variety of techniques and examine the fuel's characteristics	Pyrolysis, extraction of pyrolysis oil, gasification, and procedure for producer gas generation, the analysis of the coconut shell using TGA, ultimate analysis, producer gas composition, and proximate analysis	[45]
A comparative investigation on the two-step pyrolysis (TSP) of lignocellulosic biomass was carried out on samples of walnut shell (WS), cotton stalk (CS), corncob (CC), and their acid-washed counterparts using TGA–FTIR and Py-GC/MS	Materials and preparation, samples characterizations, and TGA–FTIR and Py-GC/MS analysis	[40]
To assess how relations between lignin and cellulose, which occur during the co-pyrolysis of lignin and cellulose at temperatures between 100 and 350 °C, affect char structure changes	Sample preparation, fast pyrolysis experiments, and sample characterization	[75]

Table 1. *Cont.*

Aims/Objective	Methods	Ref.
To examine the viability of spent coffee grounds (SCG) upcycling via pyrolysis for the production of biochar and energy, while also proposing a circular economy scenario for the effective use of SGC produced in the city of Larisa, Greece	Materials characteristics, pyrolysis and process protocol	[48]
To determine the levoglucosan percentage in the bio-oils prepared from fast pyrolysis of hydrochloric acid-treated and untreated rice husks (RHs) under vacuum conditions	Materials, characterization of RHs, pretreatment of RHs, Fast pyrolysis procedure, bio-oil characterization, and quantification of levoglucosan in bio-oils	[36]
To research the impact of total pressure, pyrolysis temperature, and CO2 concentration on biomass char gasification at various temperatures	Biomass samples, char preparation, and char reaction models	[76]
To research (a) the influence of biochar made from mesquite on the combined physical and hydraulic properties of various compacted soils, and (b) the interdependence of hydraulic properties of biochar-amended soil on the physical properties for possible use in bioengineered structures	Biochar, soils, physical properties, hydraulic properties, FTIR, FESEM, XRD, BET, and statistical analysis	[77]
To investigate levoglucosenone (LGO) production used levoglucosan (LGA) as feedstock. LGA dehydration has a lower activation energy and is chemically simpler than cellulose pyrolysis, enabling the reaction to occur at low temperatures	Materials, reaction, and product analysis	[11]
To look into how pressure affects the pyrolysis of biomass's thermal effects. Corn stalks, popular, switchgrass Trail-blazer, and switchgrass Alamo were the four energy crops chosen for experimental characterization	Materials, experimental techniques, and procedures	[78]
To assess the physicochemical potential of palm waste for pyrolysis processes that result in the production of biofuels	Preparation of biomass samples, and determination of physicochemical properties	[79]
To clarify differences and similarities among the combustion of the original raw biowaste and the combustion of bio-oil and biochar in order to better understand how fly ash forms during these processes	Biomass, biochar and bio-oil, fuel preparation prior to combustion experiments, combustion experiments, particle sampling system, operational procedure, and experimental plan, chemical analysis of the particulate matter, and multivariate data analysis are all covered in this study	[80]
To look into the possibility of preventing agglomeration and enhancing sugar formation during the pyrolysis of herbaceous biomass by combining ferrous, magnesium, and ammonium cations with sulfate anions	Methods for pretreatment, controlled pyrolysis duration-quench, continuous pyrolysis reactor system, assessment of sustainable throughput, quantification of sugar, ICP digestion, scanning, and electron microscopy analysis	[81]
To research the energy potential of hydrochar made from straw, Virginia mallow, and wood (pine) biomass. The hydrochars' pyrolysis process was therefore investigated in order to determine how the gaseous byproducts changed with pyrolysis temperature	Materials, hydrothermal carbonization process, and pyrolysis	[82]
As an alternative technique for using waste biomass in the Polish context, a thorough study of slow solar pyrolysis of various waste biomass feedstock is presented. Although slow solar pyrolysis is the least expensive technology available due to the low heat input, it has the potential to produce highly porous solid fuels and provide a long-term solution for difficult waste disposal	Feedstock characterization includes determining the amount of lignocellulose in the feedstock as well as its ultimate and proximate analyses.sample preparation, sample analysis for C, H, and N, and BET surface area measurement of porosity	[83]
In order to comprehend pyrolysis behavior and potential interactions, investigations into the thermal decomposition of lignin and lignocellulosic biomass (watermelon rind) WMR were carried out at 325–625 °C to pyrolyze various lignin components in order to improve the pyrolytic products	Materials, experimental set-up and procedures, and product analysis	[84]

3. Potential Inter-Relatedness between Individual Components Affecting Pyrolysis-Based Research

The application of the thermal conversion process requires considering numerous factors, including the specific reactors, the corresponding biomass/feedstock, the choice of research/objective, the target products, the feedstock type, the funding for research, the time/period for study, and the geographical location. The potential inter-relatedness of the individual components affecting pyrolysis-based research, presented in Figure 2, requires some considerations prior to the design of an experiment/methodology. Several aspects that require focus include the research objective, process cost based on the plant size, the types of reactors, the extents of supply and feedstocks, and the experiment location. Other pyrolysis-related components that directly relate to the pyrolysis process operational costs would depend on the size, quality, reactor types, and the laboratory/enterprise, wherein the experiment is performed. However, technology is just one aspect of innovation for more waste-based sustainable thermal systems, which should provide systematic yet innovative solutions towards a more resource-efficient economy with waste management [48].

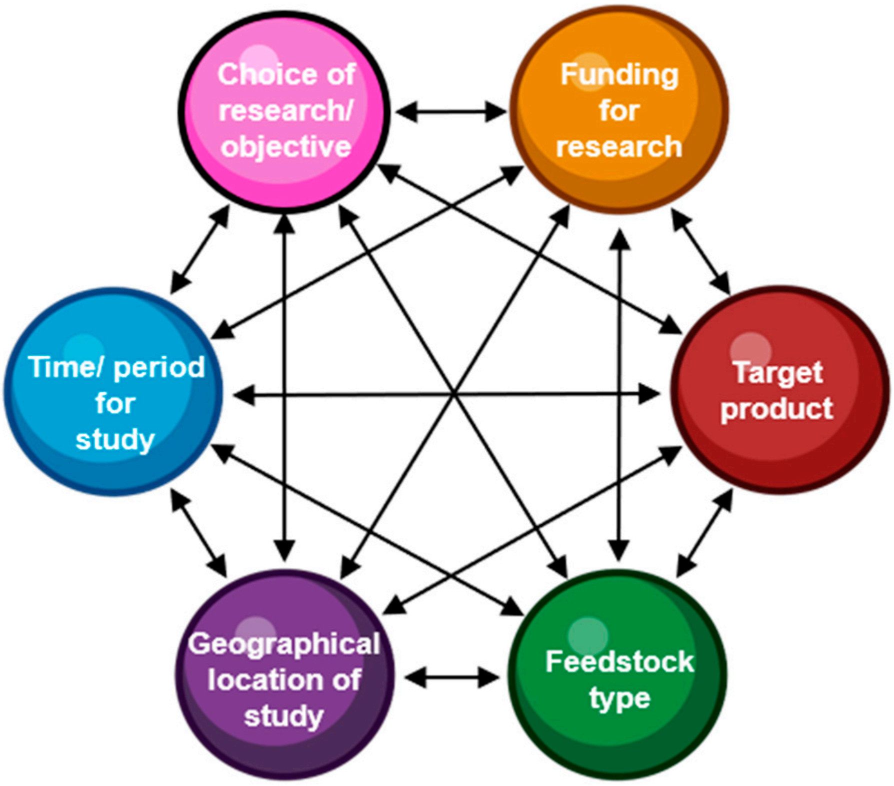

Figure 2. Potential inter-relatedness between individual components affecting pyrolysis-based research.

A number of pyrolysis-based investigations have had to consider the cost and time required for the pyrolysis process, according to Ringer et al. [85], which provided a broad perspective of pyrolysis technology in converting biomass material to bio-oil, and other valuable products. It was presented through a thorough technical and financial analysis of a plant that could produce 16 tons of bio-oil per day [85]. The Circulating Fluidizing Bed (CFB) reactor type is able to provide a high-quality product yield, and a solid foundation for scaling up and for a high-quality product yield was identified, which estimated the investment and operating costs for 550 tons per day of moisture ash free (MAF) biomass, with a 48.3 MM capital investment and an estimated total installation cost of 28.4 MM USD [85]. Suntivarakorn et al. used a Circulating Fluidized Bed Reactor (CFB) with sand as the bed material in order to study the production costs of pyrolysis oil production from Napier Grass. The maximum oil production from pyrolysis was 36.93 wt. percent, demonstrated at bed temperatures of 480 °C, superficial velocities of 7 m/s, and feed rates of 60 kg/h. Based on pyrolysis oil production properties, water content, density, heating value, viscosity, and pH, the results were 48.15 wt.%, 1274 kg/m 19.79 MJ/kg, 2.32 cSt, 2.3, respectively. Additionally, the values of total energy conversion and cold efficiency to pyrolysis oil were 19.77% and 24.88%, respectively. The energy used in the heating process was the source of the bulk of energy consumption, with an estimated pyrolysis oil production cost of 0.481 $/L at 75 kg/h of feed rate [86].

Furthermore, the pyrolysis-based study as a choice of (research) objective would be crucial, which potentially connects the individual components affecting the (pyrolysis-based) research and the other related factors associated with the procedure, reactor type, feedstock types, the time required, target products, and the application method of the experiment. If the experiment undergoes fast pyrolysis, in which less time is required when compared to the low-temperature thermal process type, selecting the process type would depend on the desired products, especially where all the three possible common products (bio-oil, biochar, and pyrolytic gas) are targeted. For instance, Wu et al. performed an experiment with three different feedstocks, namely rice, maize, and wheat straw, with the same pyrolysis reactor (rotating bed) operating at five different temperatures from 300–700 °C, where the rice, maize, and wheat straw product yield were observed at 500 °C, accordingly: (a) liquid: 37.02, 38.91, and 35.89%; (b) char: 38.25, 34.04, and 35.25%, and (c) gas: 26.73, 27.94, and 28.86, respectively [87]. Generally, the thermal conversion process requires more time in each step before pyrolysis products can be achieved.

4. Pre- to Post-Pyrolysis' Engagement Strategies

The knowledge and understanding needed for pyrolysis connects largely with reduced gas emissions and its implementation cost together with its small-scale nature. Prior to biomass selection and its components, the availability and location should be considered. Before identifying which reactor type to use, the biomass feedstock materials, the required specificities associated with a reactor, and the visualization of the anticipated product, together with the (reactor) energy demand should all be considered. Prior to anticipating the target pyrolysis-based product, consideration should be given to the operating conditions, the intricacies associated with the thermal conversion process, and any (internal/external) influencing features (Refer to Figure 1).

Particularly in the context of pyrolysis implementation, the constituents of some selected recent experimental works revealing the pre-to-main pyrolysis stages, respectively, from biomass selection and analytical methods, to the biomass treatment methods, reactor types, operating process, and product outputs are shown in Table 2. Besides the differing specific objectives, differences would still emerge in the contents of both pre- and main pyrolysis stages. However, there could arise some situations where the feedstock and its pretreatment reflect each other. Furthermore, the individual study shows specific objectives, which in turn would either directly or indirectly determine the subsequent experimental method/design requirements. For example, corn stalks were among the biomass selected for use by two workers [88]; despite this, both studies clearly had different objectives, hence different study design approaches. On the one hand, the study of Zhu and colleagues determined the recovery efficiency of minimizing VFAs and sugars at different HTS and cornstalk structure characterizations, which employed a batch reactor and an HTC operating process, wherein the product output included sugars and volatile fatty acids (VFAs). According to their findings, 92.39% of aqueous products had the highest recovery of reducing sugars and VFAs, which is equivalent to 34.79%, based on dry biomass. In addition, significant changes in organic groups at different HTS were identified through FTIR and TGA, and, as HTS parameters increased, the cornstalk's structure gradually changed from stiff, highly ordered fibrils to a molten and grainy structure, via SEM [88]. On the other hand, the study of Wang et al. explored the corn stalk performance of the wet torrefied sample's performance in biomass pyrolysis polygeneration, wherein the fixed-bed reactor was employed, and which had biochar as the output product. Aside from the above-mentioned, all the studies shown in Table 2 appear to have resembling analytical methods, which largely involved moisture, organic matter, and ash content, with very few exceptions [15,25,52,54,60,65,83,88–103]. Palamanit and colleagues used an agitated bed pyrolysis reactor to examine the yields and characteristics of pyrolysis products obtained from oil palm fronds, trunks, and shells. The pyrolysis temperatures of 400, 450, and 500 °C were applied to these feedstocks. The findings demonstrated that the pyrolysis temperatures and varieties of oil palm biomass had an impact on the yields and characteristics of the final product. The maximum liquid yield was obtained from oil palm fronds pyrolyzed at 500 °C. The HHV of the liquid and biochar product was 18.95–22.52 MJ/kg and 25.14–28.45 MJ/kg, respectively. Furthermore, the SEM result demonstrated that the produced biochar had a porous structure surface with a surface area of 1.15–4.43 m^2/g [103]. Moreover, the biomass treatment method involved chemical [25,102,104], hybrid [35], and physical and thermal [15,52,88,97–101] types. For instance, TGA–FTIR and PY-GC/MS were used to investigate the reaction mechanism for the pyrolysis of cellulose, hemicellulose, and lignin in the presence of CaO. The results showed that CaO would react with acids and phenols from hemicellulose pyrolysis, sugars from cellulose pyrolysis, and phenols from lignin pyrolysis at low temperatures (400–600 °C). However, at higher temperatures (600–800 °C), the CaO catalytic effect was more noticeable. Specifically, CaO facilitated the catalytic decarbonylation of ketones to form CO during hemicellulose pyrolysis, while also increasing the formation of hydrocarbons. Additionally, CaO addition promoted radical reactions during lignin pyrolysis, increasing the CH4 yield [25]. Duman and Janik attempted to enhance the production of hydrogen from the steam pyrolysis of olive pomace in a two-stage fixed-bed reactor system, where various char-based catalysts were evaluated. The catalysts included biomass char, nickel-loaded biomass char, nickel or iron-loaded coal chars, and coal char used as catalysts. Thus, BET, XRD, XRF, and TGA were used to characterize catalysts. Their results showed that the steam obtained without a catalyst had no influence on hydrogen production, and the production of hydrogen was improved when the temperature increased from 500 °C to 700 °C, when both Ni-impregnated and non-impregnated biomass char were present [100]. Additionally, the differences in the study objectives of the various researches produced various output products, like biochar, bio-oil, pyrolytic gas [15,54,101,102], sugars and volatile fatty acids (VFAs) [88], hydrogen [100], char, phenols, and anhydro sugars [94], glucose [104], and furan [96]. The reactor selection and operating conditions appear to connect with the feedstock and its resultant product output, as well as the preparatory materials required before or during the engagement of pyrolysis/thermal conversion-based study.

Table 2. Constituents of some selected recent experimental works revealing pre-to-main pyrolysis stages, respectively, from biomass selection, and analytical methods, to biomass treatment method, reactor types, operating process, and product output.

Experimental Objectives	Pre-Pyrolysis			Main-Pyrolysis				Ref.
	Biomass Selection		Analytical Method	Biomass Treatment Method	Reactor Types	Operating Process	Product Output	
	One or More	Biomass Type	Moisture, Organic Matter, Ash Content, and others					
To look into the yield and characteristics of the pyrolysis reaction products made from palm oil (trunk, frond, and shell) in an agitated reactor	Palm (trunk, frond and shell)	Palm tree	Moisture, ash content, and others	Physical and thermal	Agitated pyrolysis reactor, TGA, and DTA	Pyrolysis	Gas, bio-oil, and char	[103]
To investigate the influence of pyrolysis temperature (500–800 °C) on product yields in a conical spouted bed reactor with steam as a fluidizing source	Pine wood sawdust	Wood	Moisture, ash content, and others	Physical and thermal	Conical spouted bed	Pyrolysis	Gas, bio-oil, and char	[99]
Using steam pyrolysis of olive pomace, it was investigated how well various char-based catalysts (including biochar and coal char) produced hydrogen	Olive pomace	Olive	Moisture, ash content, and others	Physical and thermal	Fixed bed, TGA and others	Pyrolysis	Gas, bio-oil, char, and hydrogen	[100]
It was investigated how well the wet torrefied sample performed in the biomass pyrolysis polygeneration process as well as the WT of corn stalk	Corn stalk	Corn	Moisture, ash content, and others	Physical and thermal	Fixed bed	Pyrolysis	Biochar	[52]
Based on the characteristics of the pyrolysis process and its effectiveness in catalytic upgrading, the catalytic and non-catalytic pyrolysis of demineralized biowaste was examined and compared to raw biomass	Sawdust	Softwood	Moisture, ash content, and others	Chemical, physical and thermal	Fixed bed, Py-GC/MS,	Pyrolysis	Gas, bio-oil, and char	[102]
Examining the energetic, physical, and chemical characteristics of various biomass feedstocks in order to characterize their performances	Grapevine, olive trees, and others	Lignocellulosic residues	Moisture, ash content, and others	Physical and thermal	TGA	Pyrolysis	Bio-char and bio-fuel	[89]
To successfully scale up the pyrolysis process, it is crucial to thoroughly understand the effects of key variables on the devolatilization kinetics and bio-oil composition, such as biomass particle size, shape, content, heating rate, and residence period.	Saw dust	Wood	Moisture, ash content, and others	Physical and thermal	Pyroprobe® 5200	Pyrolysis	Biochar and bio-oil	[54]

Table 2. *Cont.*

Experimental Objectives	Pre-Pyrolysis			Main-Pyrolysis				Ref.
	Biomass Selection		Analytical Method	Biomass Treatment Method	Reactor Types	Operating Process	Product Output	
	One or More	Biomass Type	Moisture, Organic Matter, Ash Content, and others					
To ascertain the thermodynamic parameters and the kinetic triplet (activation energy, pre-exponential variable, and reaction model)	Banana leaves	Banana						[60]
Devoted to researching the online characterization, kinetic and thermodynamic analysis, thermal decomposition, and physicochemical characterization of hot vapors released during pyrolysis	Switchgrass	Crop	Moisture, ash content, and others	Physical and thermal	TGA-FTIR, Py-GC–MS examination	Pyrolysis	Gas, bio-oil, and char	[98]
This study looks at the effects of CaO on the evolution properties of cellulose, hemicellulose, and lignin pyrolysis products using TGA–FTIR and Py-GC/MS, and it also discusses the reaction mechanism of CaO-assisted pyrolysis of biowaste components	Cellulose and beechwood	Mixed	Moisture, ash content, and others	Chemical, physical and thermal	TGA–FTIR and PY-GC/MS	Pyrolysis	Bio-oil from	[25]
Using slow pyrolysis in a thermogravimetric analyzer, investigate the decomposition mechanism of the lab-scale grown microalga	Algal biomass	Algal	Moisture, ash content, and others	Physical and thermal	TGA	Pyrolysis	Biochar	[92]
(a) To methodically examine the recovery effectiveness of reducing sugars and VFAs at various HTS (4.17–8.28, 190–320 °C), and (b) to characterize the structure of the cornstalk following hydrothermal treatment at various HTS	Cornstalk	Corn	Moisture, ash content, and others	Physical	Batch	HTC	Volatile fatty acids (VFAs) and sugars	[88]
Determine the entrained flow reactor (EFR) used for the beech wood pyrolysis experiments, which were conducted at various gas residence times with temperature between 500 and 1400 °C. These experimental conditions were broad enough to produce chars with a range of characteristics	Beech	Wood	Moisture, ash content, and others	Physical and thermal	Entrained flow	Pyrolysis	Biochar	[15]
To investigate the characteristics of MD2 pineapple waste and its potential to become a feedstock for alternative solid biofuel	Pineapple	Pineapple	Moisture, fixed carbon content, and others	Physical and thermal	TGA	Pyrolysis	Biochar	[101]

Table 2. *Cont.*

	Pre-Pyrolysis			Main-Pyrolysis				
	Biomass Selection		Analytical Method					
Experimental Objectives	**One or More**	**Biomass Type**	**Moisture, Organic Matter, Ash Content, and others**	**Biomass Treatment Method**	**Reactor Types**	**Operating Process**	**Product Output**	**Ref.**
To illustrate how canola residue may be a suitable biofuel feedstock for low-temperature (<450 °C) slow pyrolysis with energetically favorable conversions of up to 70 wt.% of volatile matter	Canola residue	Canola	Moisture, ash content, and others	Physical and thermal	TGA–FTIR	Slow pyrolysis	Bio-fuel	[105]
(1) To determine the transformation behavior of HMs during co-HTC, and (2) to investigate the fuel properties of the hydrochar from co-HTC. The results could provide support for SS utilization, particularly for fuel production with the targeted regulation of HMs	Sludge and biomass	Sludge and lignocellulosic	Moisture, ash content, and others	Physical	Autoclave reactor	HTC	Liquid and hydrochar	[90]
HTL thermal transformation of tobacco industry biowaste to oil in a multiple batch reactor	Tobacco	Tobacco	-	Physical	Batch reactor	HTL	Biocrude	[91]
Having in mind the literature presented on solar pyrolysis so far, a thorough study on slow solar pyrolysis of various waste biomass feedstocks is presented as an alternative method for using waste biomass in the Polish scenario, with a primary focus on fast and flash pyrolysis	Wood, stray sewage sludge	Mixed	Moisture, ash content, and others	Physical and thermal	Fixed-bed, TGA, and others	Pyrolysis	Gas, bio-oil, and char	[83]
To thoroughly investigate the catalytic potential of NZ (commonly found in Pakistan) in comparison to that of commercial ZSM-5 for raw and pretreated rice straw	Rice straw	Rice	Moisture, ash content, and others	Physical, chemical, and thermal	Fixed-bed	Pyrolysis	Gas and bio-oil	[93]
By combining acid impregnation and two-staged pyrolysis, the study aims to achieve staged and directional valorization of holocellulose and lignin in biomass waste	Eucalyptus waste	Wood	Moisture, ash content, and others	Physical, chemical, and thermal		Torrefaction and fast pyrolysis	Char, anhydro-sugars, and phenols	[94]
In order to maximize utilization, it is important to compare specifically how well two common agricultural and forestry biomasses are suited for bioenergy production	Rice husk and poplar bark	Rice and wood	Moisture, ash content, and others	Physical and thermal	TG/DTG	Pyrolysis	Biochar	[95]

Table 2. *Cont.*

Experimental Objectives	Pre-Pyrolysis			Main-Pyrolysis				Ref.
	Biomass Selection		Analytical Method	Biomass Treatment Method	Reactor Types	Operating Process	Product Output	
	One or More	Biomass Type	Moisture, Organic Matter, Ash Content, and others					
In particular, the effects on nitrogen (N) content and composition were examined, along with the impact of biomass type and pyrolysis temperature on the physical and chemical properties of biochar	Soybean straw and chlorella	Crop type	Moisture, ash content, and others	Physical and thermal	Stainless steel cylinder and electric muffle furnace	HTC/pyrolysis	Hydrochar and biochar	[65]
Study to lower energy consumption and increase glucose concentrations in enzymatic hydrolysis reactors	Wheat straw	Wheat	-	Chemical	Hydrolysis reactor	Hydrolysis and fermentation	Glucose	[104]
In the work, the catalytic activity of supported Al-containing bimetals was studied, and the synergy between the bimetals was discussed. In addition, the reaction pathways on the formation of furans were proposed	Corncob, wood, and others	Mixed	Moisture, ash content, and others	Physical and thermal	Py-GC × GC/MS	Pyrolysis	Furan	[96]
To research the microwave heating properties of coal gasification fine slag and its pyrolysis of biomass catalytic properties	Pine sawdust	Wood	Moisture, ash content, and others	Physical and thermal	Quartz tube, microwave-induced	Pyrolysis and gasification	Gas, bio-oil, and char	[97]

5. Potential Feedstock Employed in Thermal Conversion Processes

5.1. Feedstock Composition by Various Thermo-Chemical Reactors

A summary of different biomasses/feedstocks as classified by various thermo-chemical reactors (considerations/factors of research objective) is presented in Table 3. The various biomass/feedstock types and their commercial importance within the energy sector aspects of sustainability/sustainable development goals are vital. In the thermal process, this can be divided into a number of different types, such as lignocellulosic biomass, municipal solid waste, and fuel derived from refuse, and how its properties affect the pyrolysis process parameters. Due to its potential to serve as a bio-renewable source of fine/commodity chemicals and fuels, we focused on all potential feedstocks for thermal conversion activities [11] with both a single and a combination of reactors. Feedstock pretreatment is also important and is required in many cases to achieve the high quality and quantity of pyrolytic target product, and the treatment could be performed through different methods, such as chemical pretreatment, physical pretreatment, thermal pretreatment, biological pretreatment, and hybrid pretreatment with suitable reactors to achieve the best quality end product in any thermal conversion study (Refer to Table 2). But, in order to have a clear understanding of how the main biomass decomposes, it is important to be aware of its features and structure, especially in relation to the moisture content and the precise temperatures needed to produce various pyrolytic products. Furthermore, the pyrolysis process' temperature variations reflect various layers, including the hemicellulose, cellulose, and lignin of biomass structure [27]. Given that it is known that these three main layers pyrolyze at various temperatures range (200–300; 300–350; and 350–500 °C), respectively, the emergent products, such as chemicals, fuels, and materials through different biochemical and thermo-chemical processes, would be achieved at specific temperature points [27,106]. Previous biomass samples were investigated by Bahcivanji et al. [67] and the pyrolysis yield of hydrochar at 350 °C for 5 h was comparable to the pyrolysis yield of waste biomass using the same experimental conditions, when compared to the direct pyrolysis of waste biomass via the HTC process. Only when the pyrolysis temperature was raised to 550 °C for 5 h did the pyrolysis yield of the feedstock fall below that of hydrochar. The higher the temperature of pyrolysis (from 350 to 550 °C) and the duration time (from 1 to 5 h), the more microporosity was produced, while the phytotoxicity was decreased [67]. In addition, similar results were obtained by numerous studies, where the hydrochar showed a lower pH than the original feedstock [80,107].

5.2. Importance of Feedstock Composition in the Thermal Conversion Process

The use of biomass wastes as a fuel source has drawn significant attention in the green society and in environmental management. Therefore, the typical composition of the feedstock group in the thermal conversion process is shown in Figure 3; the groups of feedstocks subjected to the thermal conversion process and the possibility of the combination/mixture of them to obtain a high-quality yield of the target products is described in Figure 3. From the available feedstock, 10 clusters were identified, with woody biomass being the dominant, although we were more focused on biomass materials in this study. However, it clearly shows in the map that the group of woody feedstock is more likely to appear with a high percentage of oak, followed by other feedstock types, including shell-nut, corn stalk, rice straw, coffee husk, banana leaves, poultry manure, garden material, and fruit. More so, several related studies investigated such feedstock(s) for different end products targets, and this is necessary to shed more light on this. It is very possible to perform any kind of thermal conversion process in combination with different feedstocks while considering the thermal and kinetic characterization for the target end product; this can be performed by knowing the physical and chemical properties of the material, thus allowing for the right selection, based on the characteristic properties of the individual types.

Table 3. Summary of different biomass/feedstock as classified by various thermo-chemical reactors/analytical tools (considerations/factors of research objective).

Reactor/Analytical Tools		**Biomass/Feedstock**		**Ref.**
Mode	**Types**	**Group Name**	**Group Examples**	
Single	TGA	Woody	Eucalyptus	[32]
		Woody	Pellet	[44]
		Corn	Straw	[72]
		Walnut	Nut shell	[42]
		Hazelnut	Nut shell	[42]
		Pistachio	Nut shell	[42]
		Cork species	Cork	[69]
		Sugarcane	Bagasse	[63]
		Corn	Husk	[70]
		Wheat	Straw	[47]
		Woody	Bamboo	[47]
		Rice	Husk	[31]
		Woody	beech	[33]
		Peanut	Straw	[64]
		Sesame	Stalk	[64]
		Rape	Pod	[64]
		Tobacco	Stem	[64]
		Pecan	Shell	[64]
		Bada wood	Shell	[64]
		Woody	Camphor Tree	[64]
		Woody	Sapele	[64]
		Peanut	Straw	[64]
		Sesame	Stalk	[64]
		Woody	Poplar	[64]
		Woody	Willow	[64]
		Sour cherry	Stalk	[41]
		Sour cherry	Flesh	[41]
		Phragmites hirsuta	Root	[62]
		Phragmites hirsuta	Stem	[62]
		Phragmites hirsuta	Leaves	[62]
	Fixed bed	Rice	Husk	[34]
		Corn	Stalk	[34]
		Oak	Cork	[50]
		Oak	Holm	[50]
		Wood	Waste wood	[83]
		Herbaceous	Waste straw	[83]
		Sewage sludge	Sludge	[83]
		Woody	Anhydro sugar	[11]
		Model compounds	Cellulose	[43]
		Woody	Kraft	[75]
			Alkali	[75]
			Avicel	[75]
	Ablative	Woody	Poplar	[6]
			Straw	[6]
			Miscanthus	[6]
	Fluidized bed	Herbaceous	Corn stover	[81]
			Rice husk	[26]
	Entrained flow	Straw	Straw	[74]
	Furnace	Rice	Straw	[39]
		Vival prolifera macroalgae	*Vival prolifera* macroalgae	[39]
		Wood	Shavings	[66]
	Tubular quartz	Rice	Husk	[36]

Table 3. *Cont.*

Reactor/Analytical Tools		Biomass/Feedstock		Ref.
Mode	**Types**	**Group Name**	**Group Examples**	
Single	Adiabatic oxygen bomb calorimeter	Watermelon	Ring	[68]
	HTC	Parks Gardens	Park Garden	[67] [67]
	Wire mesh	Sigma-Aldrich	Sigma-Aldrich	[71]
	Semi-batch vertical	Oat wood	Straw	[51]
	DTG	Woody Woody Rice	Japanese cedar Castanopsis Straw	[56] [56] [56]
	Rotary-klin prototype	Plant	Coffee plant	[48]
	Furnace	Woody Woody	Stem Bark	[80] [80]
Combined	TGA and DSC	Corn Switchgrass alamo Woody	Stalk Grass Poplar	[78] [78] [78]
	TGA and STA	Banana	Leaves	[60]
	Pyro-Probe and CDS	Energy crop Woody Grass	Virginia mallow Pine Straw	[82] [82] [82]
	Gasifier and cylindrical reactor	Coconut	Shell	[45]
	TGA-FTIR and Py-Gc/MS	Corn Cotton Walnut	Cob Stalk Shell	[40] [40] [40]
	TGA and DTG	Orange Potato Coffee Coffee	Peels Peels Husk Residue	[55] [55] [59] [59]
		Palm oil tree	Fronds Shells Roots Trunk	[79] [79] [79] [79]
	Fixed bed and quartz	Rice	Husk	[37]
	TGA, DTG and fixed bed	Leaves Wood	Birch Spruce	[73] [73]
	TGA and CDS	Wood	Sawdust	[54]
		Herbaceous	Corncob Wheat straw Rice husk	[49] [49] [49]
	Py-FTIR and Pyro-probe	Rice Woody Fruit	Husk Pine Bunch	[57] [57] [57]
	TGA and Py-GC/MS	Durian	Shells	[53]
	TGA-FTIR	Woody	Populus deltoides Pinus radiata Willow chips Roasted cashew nut	[41] [41] [41] [41]
		Shells	Almond Hazelnut Brazil-nut Roasted cashew nut	[41] [41] [41] [41]

Table 3. *Cont.*

Reactor/Analytical Tools		Biomass/Feedstock		Ref.
Mode	**Types**	**Group Name**	**Group Examples**	
Combined	TGA–FTIR	Herbaceous	Reed canary grass	[41]
			Miscanthus giganteus	[41]
			Spinach	[41]
		Animal Product	Chicken manure	[41]
		Model compounds	cellulose (avicel)	[41]
			ALC lignin	[41]
			Xylan	[41]
			Dglucose	[41]
			Pectin	[41]
			Chlorogenic acid	[41]
	TGA and furnace	Herbaceous	Pine	[76]

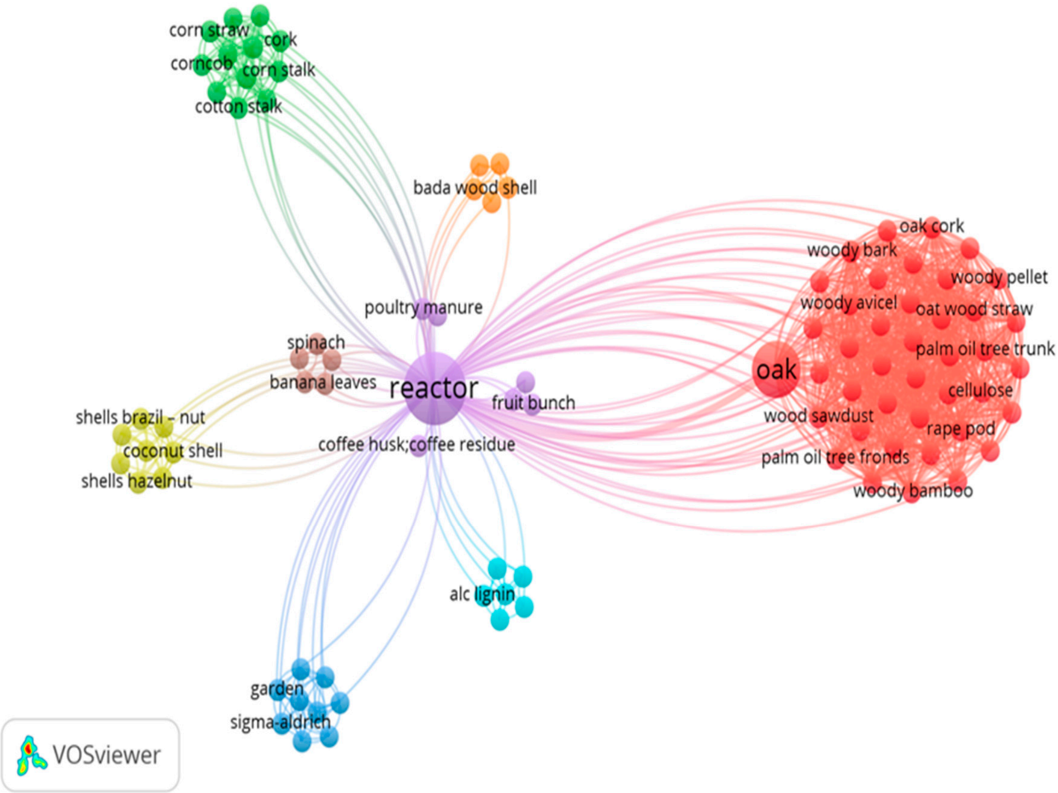

Figure 3. Occurrence mapping of different feedstock types (n = 97), which resulted in 10 groups.

Furthermore, Braz and Ribeiro [108] investigated a mixture of sewage sludge with pruning residues in a proportion of (50 mass%); they compared the results with the sewage sludge without a mixture to determine the thermal and kinetic characterization of the samples. The result shows that the average activation energy value of the sewage sludge sample and of the mixture, respectively, was 219 and 161 kJ mol^{-1}, supporting the incorporation of pruning residues in the sewage sludge. In the degradation process, a remarkable increase in activation energy was observed, which ranged from 20–70% via conversion in the sewage sludge sample, despite the almost linear behavior noticed within the mixture decomposition reaction [108]. For some time, the process of combining biomass with other wastes for a power generation purpose has been studied as a way of reducing the waste material disposed into landfills, which involve the mixture of biomasses, such as pine, eucalyptus, sawdust, chestnut, pulp waste, grape, and coffee husks, all of which have aimed to choose the best raw materials for making pellets that were available in the study area. Furthermore, blends of pine sawdust with 10–30 percent chestnut sawdust were considered best for pellet production [109]. Elsewhere, Lajili and colleagues, to measure the moisture, ash content, bulk density, and heating values, made agropellets from olive waste, a by-product of an olive mill, which was mixed in various ratios with sawdust from pine trees. Olive waste's high moisture content decreased during the process, and each chosen sample's ash content was found to be in compliance with the recognized French agropellets standards [110].

Additionally, Boumanchar et al. conducted a study where parameters were evaluated for various abundant materials (including two types of biochar, different biomasses, synthetic rubber, cardboard as a potential municipal solid waste, and plastic). The objective was to contrast the calorific value of each substance when used separately with the combined experimental and theoretical HHVs of the two substances. Various mixtures in proportions of 25/75, 50/50, and 75/25 percent were prepared. The experiment's findings revealed that the heating values of lignocellulosic materials ranged from 12 to 20 MJ/kg: 13 MJ/kg for cardboard, 27 and 32 MJ/kg for the first and second batches of biochar, respectively, and 37 and 38 MJ/kg for plastic and synthetic rubber [111]. Furthermore, the biomass mixture of feedstock was studied using a reaction vessel for the HTC process. HTC was performed on rice hulls, Loblolly pine, Tahoe mix (Jeffrey pine and white fir), corn stover, and switch grass. The results showed that the energy densification of biomass increased up to 43%, and the reaction temperature significantly impacted the energy densification and mass yield. The production of hydrochar increased the fixed carbon and decreased volatiles at a process temperature of 260 °C [112].

6. Major Pre-Treatment Strategies Applied to Feedstocks

Feedstock pretreatment is very important during any form of thermal process to remove or change the biomass components and to improve the target product's quality. And this can be completed in different ways, such as physical, chemical, thermal, and hybrid treatment [113], and the description of each method is as follows:

(a) Physical pretreatment

The first step of biomass feedstock pretreatment as a preliminary to feeding into a pyrolysis reactor is grinding the particle according to the reactor requirement particle size for the perfect process. Since the biomass thermal conductivity is very low (about 0.1 W/(mK), then the biomass pyrolysis mechanism might be affected by the temperature gradient across the particles in the process. Therefore, quick heating to achieve the target pyrolysis temperature level is difficult, and the only way to accomplish the target is to reduce the particle size to much smaller sizes. Usually, biomass particle size depends on the reactor type in the pyrolysis process; for instance, a fluidized bed requires 2–5 mm in biomass particle size, and some reactors require much larger particle sizes. Importantly, if the biomass particle size is bigger than the reactor requirement, it could result in less bio-oil and a higher char production yield, respectively, because biomass might partially be pyrolyzed [113].

(b) Chemical pretreatment

This is one of the pretreatment processes of biomass involving the use of liquid solvents for washing or cleaning, such as an acid or water, for the purpose of eliminating minerals or inorganics materials in biomass. According to Blasi et al., straw's pyrolysis properties are affected by washing with water; this increases the bio-oil yield, while the char production decreases [114]. A similar experiment investigated by Carrier et al. [115] showed the application of an acid as a biomass washing, such as HNO_3 and HF, resulted in a reduction of the mineral content of biomass [115].

(c) Thermal pretreatment

The thermal pretreatment of biomass is achieved by drying, which can be completed by the application of an additional heat process or by natural sunlight. This process could lead to the reduction of the heat load for the evaporation of the water content from the reactor. For commercial purposes, the evaporated water obtained during the drying process of biomass can be sold as steam to support the pyrolysis plant financially [113]. Torrefaction is another thermal pretreatment technique that has been used for the preliminary treatment of biomass for a fast pyrolysis process; this can be classified as mild pyrolysis, because it is processed at a temperature point below 300 °C [116]. The removal of water content to enhance the grind ability, energy density, hydrophobicity, and bacteria resistance is the main purpose of torrefaction [113]. Some authors stated that the application of torrefaction for biomass treatment caused a reduction in bio-oil yield and has an effect on its properties [115–117]. Also, when using torrefaction as a pretreatment process so that the bio-oil quality improved, acidity levels are lowered, and energy density is increased [118].

(d) Biological pretreatment

The use of white-rot fungus as a biological pretreatment of biomass in the pyrolysis process enhanced the process performance in the context of pyrolysis temperature and the decomposition of the lignin element [119–121]. Also, it was discovered that the application of fungus as a pretreatment might lead to a reduced activation energy demand and an estimated pyrolysis temperature of around 36 °C for cellulose and hemicellulose [121].

(e) Hybrid pretreatment

The hybrid method of pretreatment for biomass is suitable to achieve good quality and environmentally friendly biofuel, pyrolytic gas, and biochar as the target products from lignocellulose biomass in the pyrolysis processes. An experiment performed by Matsakas et al. [35], which narrated a hybrid organosolv–steam explosion resulted in superior digestibility. The experiment was accomplished by the application of ethanol and H_2SO_4 into the softwood (spruce) and hardwood (birch) feedstock; the result demonstrated a significant influence of the method parameters on digestibility. Furthermore, the results show that the method favored the birch sample in the production of methane, when compared to the spruce biomass sample. This experiment concluded that the methane production under this method was higher than the conventional process [35].

Also, Charisteidis et al. [122] carried out a similar experiment using spruce and birch biomass samples, which were isolated by the hybrid organosolv–steam explosion technique. It was accomplished by the fast pyrolysis processes resulting in a high content of oxygen, hydrogen, and carbon, while the sulfur and nitrogen content is lower. However, the spruce and birch lignin isolated by the hybrid organoslov–steam explosion method has a minimum amount of ash (<0.1 wt.%), and also contains less carbohydrate impurities, in the sense that hemicellulose and cellulose were (<2 wt.%) and (<1 wt.%), respectively [122].

Generally, the benefit of organoslov-type lignin characteristics is the considerably low content of sulfur and inorganic ash with regard to their valorization, particularly when compared to the kraft lignin and lignosulphonates methods. For instance, in an experiment performed by [123], two different kraft lignin samples, A and B, were quickly pyrolyzed in a Curie-point pyrolyzer in both the absence and presence of HZSM-5. The result showed that sample A contained significantly more coke and less aromatic hydrocarbons than that of sample B and could also result in a negative effect on bio-oil qualities within the higher sulfur content [123].

7. System Performance Considerations between Pyrolysis Reactors

When the characteristics/properties of a given biomass are to be determined, particularly when in terms of temperature requirements and the product quality, there is a need for a detailed understanding of the operating system of pyrolysis reactors. For instance, by subjecting the biomass to pyrolysis, Bridgwater [124] reiterated that an understanding of practices/principles is required for the operating processes to happen, with considerations like the (thermal process) characteristics and technology requirements, product characteristics, and even their economics. Besides the key thermochemical approaches of biomass conversion, namely combustion, gasification, liquefaction, and pyrolysis, Bridgwater and

Bridge [125] added that anticipated products can be either primary and/or secondary, largely based on the pyrolysis implementation process, all of which create different (pyrolysis) opportunities, constraints, and requirements. In the course of implementing any given biomass gasification as a project, [126] understood that some background knowledge about the gasifier fuel requirements, gasification process, and installation can be useful in understanding its operating performance. Despite these, it is well established that the pyrolysis type is temperature dependent [127,128]. Cotton residue has slowly been pyrolyzed at 300, 350, 400, and 450 °C, and the yields have been measured (Refer to Table 1). Additionally, the production of bio-oil grew continuously as the temperature climbed from 300 to 400 °C. After a temperature rise to 450 °C, the bio-oil output declined to 36.40 wt.%. The gas production grew continuously, as the temperature climbed from 300 to 400 °C. However, secondary cracking was also noted, because the yields of bio-oil were declining as the gas yield increased [128]. As the pyrolysis temperature rises, the amount of char produced by the pyrolysis of shell samples decreases. Between 650 and 800 K, the peak of the liquid yields were recorded. As a result, it seems that pyrolysis temperature affects the char yield and chemical composition. A stronger correlation was found between pyrolysis temperatures and the char components and the higher heating values (HHVs) of shell fuels. Additionally, a highly significant linear correlation was discovered between the pyrolysis temperature of the fuel, HHV, and the fixed carbon content of the char [129].

Temperature has been shown by López and colleagues [130] to have a substantial effect on the characteristics of pyrolysis liquids and, to a lesser degree, both gases and solids. At the lowest measured temperature of 460 °C, a high percentage of highly viscous liquids with a high amount of long hydrocarbon chains are formed, whereas at the maximum evaluated temperature of 600 °C, a low percentage of liquids with a large concentration of aromatics are created [130]. These findings demonstrated that the yield and the quality of biochar are primarily influenced by the temperature applied, with pyrolysis at 600 °C producing biochar with higher fixed carbon (80.70%), carbon (73.75%), higher heating value (30.27 MJ/kg), and lower volatile matter content (9.80%) than the original feedstock, safflower seed press cake (SPC) [131]. PyGC-MS was used to examine how the pyrolysis products of two types of lignin—Asian and Alcell lignin—reacted with temperature. For each type of lignin, 50 or so compounds were discovered and measured over a 400–800 °C temperature range. At 600 °C, both lignins generated the largest production of phenolics, 17.2 wt.% for Alcell lignin and 15.5% for Asian lignin. A phenolic compound's average yield was less than 1%, while 5-hydroxyvanillin had the greatest output for Alcell lignin (4.29 wt.% on dry ash-free lignin), and 2-methoxy-4-vinylphenol had the best yield for Asian lignin (4.15 wt.% on dry ash-free lignin) [107]. The pyrolysis of poplar wood was thoroughly explored at various reaction temperatures (400, 450, 500, 550, and 600 °C) and heating rates (10–50 °C/min). At the working conditions of 600 °C and 30 °C/min, 600 °C and 50 °C/min, and 550 °C and 50 °C/min, respectively, the BET surface area of biochar, the HHV of non-condensable gas, and bio-oil all obtained maximum values of 411.06 m^2/g, 14.56 MJ/m^3, and 14.39 MJ/kg. At 500 °C and greater heating rates, it was possible to achieve a high energy and mass yield of bio-oil, but both lower process temperatures and heating rates lead to a higher mass output and energy output of biochar. Higher pyrolysis temperature and heating rate, on the other hand, lead to a greater non-condensable gas mass production and energy yield. In general, the pyrolysis temperature had a greater influence on the product qualities than the heating rate [132].

Zhang and colleagues studied the yield and physicochemical characteristics of biochar by producing biochar from four feedstocks (wheat straw, corn straw, rape straw, and rice straw) pyrolyzed at 300, 400, 500, and 600 °C for 1 h, respectively. The findings demonstrated that all biochar yields decreased steadily over 400 °C with increasing temperature during the pyrolysis [40]. Due to its higher ash content, biochar made from rice straw had a higher yield advantage. The properties of biochar are significantly impacted by the pyrolysis temperature; these effects can be seen in the negative relationships between H, O, H/C, O/C, (O N)/C, and the functional groups, and the positive relationships between

C, ash, pH, electrical conductivity, and surface roughness. Greater pyrolysis temperatures aided in the production of a more resistant constitution and crystal structure, allowing it to be used as a material [133]; this was based on the principle that reactors have been classified [107]. Biomass is composed of hemicellulose, cellulose, lignin, and trace quantities of other organic components, which all pyrolyze or decompose in various ways and at different rates. Lignin's apparent thermal resilience during pyrolysis is owing to the fact that it decomposes across a greater range of temperatures than cellulose and hemicellulose, which breakdown relatively quickly over smaller temperature ranges. The temperature, rate, and pressure of the reactor (used for pyrolysis) determine how quickly and how thoroughly each of these components decompose. The amount of the secondary reaction (and hence the product yields) of those products is determined by the time–temperature history that the gas/vapor products are subjected to before collection, which includes the impact of the reactor setup [124].

In a study conducted by Yufeng and colleagues, the technology used in China's landfills, incinerators, and other methods of disposing of municipal solid waste were all examined. In China, a new device has been created for waste disposal that is based on the traditional pyrolysis principle. In China, where waste is not sorted, it is particularly helpful. By adjusting the residence time and temperature, the experiment demonstrates that the concentration of dioxins satisfies the emission standard of 0.1 ng-TE/N m3. As little as 5–7 percent of the total weight of the waste is expulsive solid. The treatment process also produced a significant amount of fire gas [134]. In addition to the term "pyrolysis", which relates to the process of decomposing biomass using heat and no oxygen to produce charcoal, liquid, and gaseous products, the term "pyrolysis" also refers to three subclasses of the process: conventional pyrolysis, fast pyrolysis, and ash pyrolysis. Hemicelluloses decompose at temperatures between 470 and 530 K, cellulose follows at 510 to 620 K, and lignin is the last material to pyrolyze at 550 to 770 K. To increase the output of liquid products generated by biomass pyrolysis, a low temperature, high heating rate, and brief gas residence period process would be required [135]. There are other differences between the operational methods of pyrolysis reactors, namely snapshots of the single-operated pyrolysis method; snapshots of combined thermal conversion treatments and analytical methods; and other miscellaneous/pyrolysis-mimicking operations. Upon a thorough check of the relevant literature, we authors observed that there are an array of pyrolysis reactors that have been used across various studies. Additionally, being the heart of any pyrolysis process, authors like Jahirul et al. [24] understood reactors to be considerable for research interests and sustainable routes for diverse biomass innovation/development. To improve the pyrolysis process, operational aspects like heating/temperature rates and (product) residence times are among the essentials that have to be considered [24]. A schematic representation of the pyrolysis temperature reactor increases based on (1) single, (2) combined, and (3) miscellaneous operating systems, reflecting a distinct categorization of various reactors, is shown in Figure 4. The essence of creating the abovementioned operating systems is to evaluate such pyrolysis reactors, specific to which context the reactors were used, and also which condition had to be fulfilled for a specific reactor to perform. Subsequently, herein, we discuss the above-mentioned operating systems in greater detail, largely in the context of pyrolysis temperature reactor increases.

7.1. Snapshots of The Single-Operated Pyrolysis Method

The single-operated pyrolysis includes a fixed bed, thermogravimetric analysis (TGA), an automatic methane potential test system, vertical dual-bed tubular quartz, tubular quartz, extrained flow gasification, a cylindrical reactor, a furnace reactor, a drop-tube furnace, a rotary kiln, wire mesh, ablative, a fluidized bed, semi-batch vertical, and hydrothermal carbonization (HTC). Each of these is succinctly discussed below:

(a) Fluidized bed reactor

The quality of renewable jet fuel-like iso-alkanes, especially those in the products, has been considered necessary for improvement. This is what Chen and colleagues envisaged, when they used a fluidized bed reactor connected to a hydro-conversion system for the processing of rice husks. At a temperature between 320 and 400 °C, the hydro-cracking and isomerization processes were carried out. These authors described their operation process as fast pyrolysis [26]. There is a paucity of literature regarding catalysts that are able to promote lignin depolymerization. On this basis, a continuous fluidized bed reactor was utilized to investigate the ability of ferrous, ammonium, and magnesium cations in combination with sulfate anions, directly aimed to prevent the agglomeration, and at the same time, to promote the formation of sugar during the herbaceous biomass pyrolysis. The char cyclones are subjected to a high temperature of 500 °C in a heat tape, which signals a fast pyrolysis process [81].

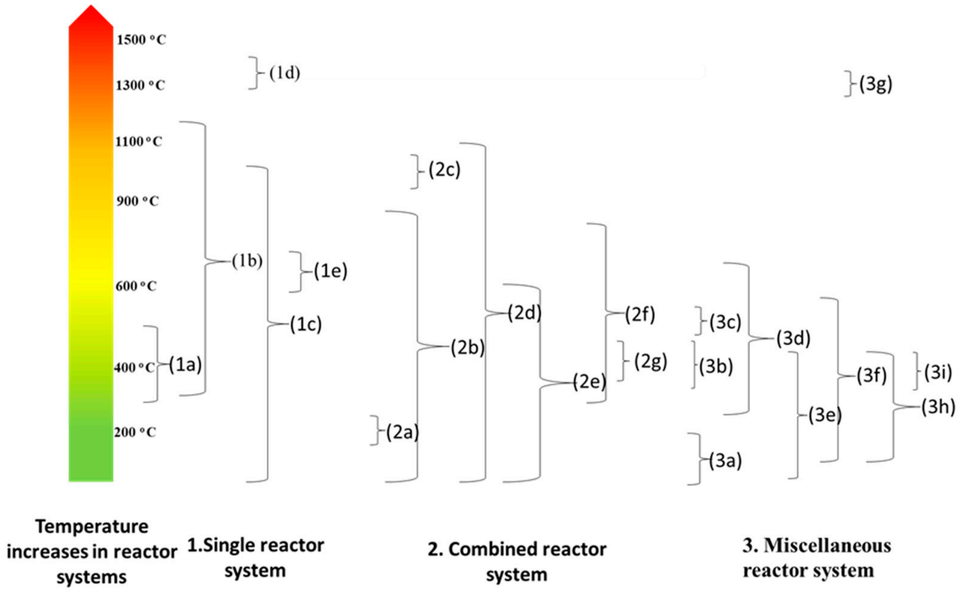

Figure 4. Schematic representation of pyrolysis temperature increases, reactors based on (1) single, (2) combined, and (3) miscellaneous operating systems. Here, the (1) single operating system includes: (1a) = fluidized bed reactor; (1b) = fixed-bed reactor; (1c) = TGA; (1d) = pressurized entrained flow gasification reactor; (1e) = ablative reactor. The (2) combined operating system includes: (2a) fixed bed with torrefaction; (2b) = TGA/FTIR; (2c) = TGA/DTG; (2d) = TGA/PyGCMS; (2e) = TGA/vertical dual bed tubular quartz; (2f) = analytical PyroProbe reactor; (2g) = TGA/DSC. (3) Miscellaneous reactors system include: | (3a) = hybrid organsolv steam; (3b) = Greenfield Eco. Pvt. Ltd. Pyrolyse instrument; (3c) = Cylindric furnace reactor; (3d) = HTC; (3e) = Muffle furnace; (3f) = Tubular quartz; (3g) = drop tube furnace; (3h) = semi-batch vertical; (3i) = continuous stirred tank reactor + plug flow reactor.

(b) Fixed bed

Sieradzka et al. [38] integrated the capturing of CO_2 with biomass thermochemical conversion pyrolysis and used a fixed bed in the process. In this instance, the effects of the pyrolysis temperature (500, 600, and 700 °C) and CaO sorbent addition were evaluated, considering both chemical and physical properties; this aimed to obtain the char and syngas [38]. Given the above temperature range, this study showed an example of fast pyrolysis conditions, where the increasing temperature in syngas brought about changes in solid products, with a decreased CO_2 concentration. Su and colleagues [34], in their attempt to overcome the rice husk defects, so as to provide renewable energy/materials via the pyrolysis poly-generation method, used a fixed-bed reactor for char and bio-oil as the target products. These authors deemed rice husks as a promising target product with less emissions. From the activation process that operated at 500 °C for 90 min under N_2 protection, the fast-pyrolysis method was obviously supported by catalytic means, which employed Na_2CO_3 for an enhanced product quality [34].

Given the limited knowledge of the characteristic features of chars produced from the co-pyrolysis of cellulose and lignin in Chua et al. [75], who utilized a drop-tube/fixed-bed quartz reactor with pulsed feeding at temperatures under 350 °C, it was specifically studied how cellulose, and lignin interacted during fast pyrolysis. These authors were able to better the understanding regarding the fundamental pyrolysis mechanisms of lignocellulosic biomass. The release of volatiles from cellulose and lignin was enhanced at temperatures below 300 °C, due to the decline of lignin functional groups and sugar structures within the char. The co-pyrolysis of cellulose and lignin, however, increased the char yield to about 300 °C [75].

Given the existing uncertainties regarding the fundamentals of the levoglucosan (LGA) conversion to the levoglucosenone (LGO) reaction system, the liquid phase transformation of anhydrosugars over solid acid catalysts was investigated. To achieve this, an updraft fixed-bed pyrolyzer was employed and operated at 500 °C, which had LGA with a yield of 38.4%-C and negligible LGO, after which there was a reaction and product analysis that involved high-performance liquid chromatography. As LGO is produced with a yield of up to 32.3%-C, a portion of heavier saccharides would contribute as a source of LGO without impeding the conversion of LGA [11]. Given the need to reduce the fuel load in the forests as is consistent with the national biomass valorization policies, the workers looked into the yield and properties of charcoal produced from ten common Southern Europe wood types, subject to operational conditions that were deemed relevant for biomass carbonization technologies. Particularly, a fixed-bed reactor was used, which allowed large fuel particles to be subjected to different heating rates of between 0.1 and 5 °C/min, with final temperatures of between 300 and 450 °C. Fast pyrolysis was the operation process that best fit this temperature range and the use of a fixed-bed reactor [50].

In order to comprehend the cellulose pyrolysis mechanisms and the development of its biochar structures, Zhang et al. [43] used a fixed-bed reactor at temperatures between of 200 and 800 °C when studying the product output at each increment of 50 °C, by characterizing the emergent gaseous products, liquid products, and bio-char. This temperature range of 200–800 °C, together with the fixed-bed reactor type, confirmed that the operation process had moved from slow to fast pyrolysis. To determine the worth of the apparent isoconversional activation energy profiles, *Sobek* and Werle [83] applied fixed-bed-based solar pyrolysis to three waste biomass types: waste straw (WS), sewage sludge (SS), and waste wood (WW). The aim primarily was to study the heating behavior, the products quality, and the yields. Specifically, the temperature range of 0–1200 °C showed the operation process had clearly moved from slow to fast pyrolysis. Considering the excellent results that the chemical activation of bio-char had generated from the rice husk pyrolysis, a horizontal oven with a quartz tube was used to chemically activate the rice husk biochar, using a K_2CO_3 activating agent, while also using solid-phase extraction (SPE) in order to remove any potentially harmful organic compounds, specifically from the bio-oil aqueous phase. The operation temperature of the tubular fixed-bed oven ranged between 430 and 620 °C, whereas that of the horizontal oven containing a quartz tube that did the activation ranged 800–900 °C and was maintained for 2 h, which clearly demonstrates fast pyrolysis [37].

(c) Thermogravimetric analysis (TGA)

For the better utilization of biomass fuel, Jia et al. [44] determined the main chemical components of pellet types (namely Chinese fir, Masson pine, Slash pine, and Poplar) using the thermogravimetric analysis method (and Coats–Redfern method), which involved a kinetic analysis. The experimental operation utilized raised temperatures of up to 845 and 900 °C, respectively, subjected to a nitrogen and oxygen atmosphere at 5 mL/min. These temperatures attests to the fact that this operation process was an example of fast pyrolysis [44]. To determine the variations in the pyrolysis properties of different biomass types, H. Chen et al. [64] used the thermogravimetric analysis method to determine the pyrolysis and to categorize the 20 types of biomass in three groups (stalk, wood, and shell type). The pyrolysis characteristics were explored based on how the biomass types and mechanisms were affected. With 60 mL/min of pure nitrogen purging, the sample heating rate is 15 °C/min from 30 °C to 900 °C; this operation process attests to the combination of slow and fast pyrolysis [64].

Some concerns were associated with the reliability of both the experimental and modeling aspects of previously conducted TGA-pyrolysis studies. This was understood by [33], when they performed TGA pyrolysis investigations on pure cellulose and beech wood, taken at several heating rates, incorporating holding times of 10–15 min, with temperatures of between 150 °C and 500 °C, and at the peak which allowed for char yield. The idea behind their study was to improve TGA for biomass pyrolysis specific to the consistency of kinetic analysis and data acquisition. Given these temperatures of between 150 °C and 500 °C, the operation process can be considered an example of slow to fast pyrolysis. To analytically assess the energy characteristics of torrefied biomass under specified pyrolysis conditions involving typical woody and herbaceous biomass, based on isothermal pyrolysis kinetics, TGA was used to investigate the assessment methods of the HHV and mass yield of torrefied biomass on three biomass species: (i) hardwood; castanopsis, (ii) herbaceous biomass; rice straw, and (iii) softwood; Japanese cedar. Overall, the temperature ranged from 105 °C to a predetermined torrefaction temperature (230–310 °C) at 20 °C/min, some of which involved a predetermined residence time (0.5–4 h). This temperature range of between 105–310 °C typified that of slow pyrolysis [56].

There is a paucity of information regarding the pyrolysis kinetics of orange and potato peels. TGA was applied to ascertain the kinetic parameters, which included (a) a pre-exponential factor, (b) activation energy, and (c) a reaction order, which involved either model-fitting or model-free methods, both differential and integral ones. Using the heating rates of between 2–15 °C/min and the TGA temperatures ranging from ambient to 650 °C, this operation process can be typified as moving from slow to fast pyrolysis [55]. To consider the potential secondary gas–fuel reactions, particularly when applying large-scale pyrolysis processes, in a study that used congruent–mass thermogravimetric analysis and conventional thermogravimetric analysis methods to pyrolyze individual coal (Datong bituminous coal) or biomass (bamboo and wheat straw) samples, using the same operating conditions, specifically heating temperatures from room to 900 °C. This temperature range typified the operation process that moved from slow to fast pyrolysis [47].

Given that different heating rates could change the reaction kinetics, many model-fitting techniques seem to be less effective for the pyrolysis of biomass. Fakayode et al. [68] used TGA to examine the energy and higher heating value (HHV) of ultrasound-assisted deep eutectic solvent pretreated watermelon rind biomass (WMR). The TGA heated at rates of 5, 10, and 20 °C/min from 35 to 1000 °C. In particular, the heating temperature was held at 1000 °C, until attaining steady conditions that detected no further mass loss [68]. Overall, these temperature ranges between 35 to 1000 °C typifies moving from slow to fast pyrolysis. Considering the difficulties associated with highly complex models for practical application purposes, particularly in evaluating char preparation, Fermoso et al. [76] utilized a pressurized thermogravimetric analyzer (PTGA), using CO_2 as a gasifying agent under isothermal conditions at different temperatures (750–900 °C) at 40 °C/min, and pyrolyzed the chars at temperatures between 1000 and 1400 °C, with residence times for the particles of approximately 7 s. Overall, these temperature ranges between 750 to 1000 °C typify gasification/fast pyrolysis.

Providing a theoretical basis to optimize a pyrolysis process that effectively utilizes corn straw resources is very important. This is what Chen et al. [72] understood when they used a thermogravimetric analyzer from room temperature to 700 °C, under five heating rates (10 °C/min, 20 °C/min, 30 °C/min, 40 °C/min, and 50 °C/min) on HCl-washed corn straw, and then determined the biomass and pyrolysis of the material. Overall, these temperatures from room temperature to 700 °C would typify a movement from slow to fast pyrolysis. Considering the dependency of the yield and quality of bio-oil that emerged from these pyrolysis processes on several factors, which can involve biomass property, operating conditions, pyrolysis types, and reactor types, is incredibly important. Shrivastava et al. used thermogravimetric analysis (TGA), largely involving a range of

200–450 °C, to produce bio-oil via pyrolysis processes, and subsequently determined the potentiality of oil palm biomass, as well as oil palm fronds (OPF), an oil palm decanter (DC), oil palm trunk (OPT), and oil palm root (OPR). The 200–450 °C temperature range of the operating process suggests slow pyrolysis [79].

To know the kinetic parameters and energy properties of a given biowaste at thermal decomposition, Noszczyk et al. [42] used a thermogravimetric analyzer—the Pyrolysis Biomass Gasifier—to study the energy and kinetic parameters of peanut, hazelnut, pistachio, and walnut shells. The TGA operated at heating rates of 5, 10, 20 °C/min, from 30 °C to 900 °C, which typifies slow to fast pyrolysis. Due to the lack of comparative pyrolysis investigations on different corks that would enable an understanding of its behavior and how it can be used in the reactor/process design for industrial biochar/bio-oil, [69] used the (TGA) analysis to evaluate the different characteristics of corks by pyrolysis behavior to target scaling up, both in the valorization strengthening of these materials, and the integration in thermochemical platforms. The TGA operated isothermally from 30 °C for 10 min, linearly heating up stepwise until 800 °C, with varying heating rates (10, 2,0 and 50 °C/min). This operating process typifies movement from slow to fast pyrolysis [42].

Given the paucity of the understanding of the thermal behavior of specific biomass processing, Gözke and Açıkalın used thermogravimetric analysis to determine the (pyrolysis) properties and kinetics of sour cherry flesh and stalk. The TGA temperatures were set from ambient to a maximum of 1000 °C at 5, 10, 20, 30, and 40 °C/min. This operating process typifies movement from slow to fast pyrolysis [58]. Moreover, there is a scarcity of data on the kinetics of exhausted coffee residue (ECR) and coffee husks (CHs). To supplement existing information, Mukherjee et al. used TGA analyses to study the pyrolysis kinetics and thermal degradation of ECR and CHs in an inert atmosphere. The operating temperature program ranged between 25 and 800 °C, with heating rates ranging from 5–20 °C/min, with an interval of 5 °C/min, which typified movement from slow to fast pyrolysis [59].

Singh et al. [60] used thermogravimetric analysis (TGA) to study the thermal degradation of banana leaves waste based on the kinetic triplet (pre-exponential variable, activation energy, and reaction model) at 10, 20, and 30 °C/min. The operating temperature ranged from ambient to 900 °C, which typified movement from slow to fast pyrolysis. Because of the little information regarding thermo-kinetic investigations involving the pyrolysis of bacterial biomass (BB), the bioenergy capability of a subset of biological waste from butanol, acetic acid, ethanol, and lactic acid producing facilities was tested using TGA analysis. Together with (three) heating rates of 10, 20, and 30 °C/min, the operating temperature ranged from room 25 °C to 700 °C, which typified movement from slow to fast pyrolysis [61].

As hydrochar-derived biomass via pyrolysis has strongly depended on its origin, Magdziarz et al. [82] used hydrothermal carbonization (HTC) and a pyrolyzer (Pyroprobe model 5200, CDS Analytical) with GC-MS and thermogravimetric analysis (TGA) to determine the energy potential of hydrochars derived from energy crop (Virginia mallow), agriculture biomass (straw), and wood biomass (pine). The HTC operation process involved 220 °C and 4 h temperature and residence time, respectively. The TGA, with a heating rate of 10 °C/min, had a temperature range from ambient to 700 °C. However, the Py-GC/MS had a temperature range from 40 to 600 °C. Overall, the operation process appears to be a combination of slow and rapid pyrolysis. The pyrolysis behavior of *Phragmites hirsuta* is seldom studied, especially with respect to the pyrolysis mechanism. Therefore, in Liu et al. [62], *Phragmites hirsuta* root, stem, and leaves were subjected to a thermogravimetric analysis in order to ascertain their pyrolysis behavior and kinetic properties as a potential source of bioenergy. The thermogravimetric analyzer was able to operate between 30 and 900 °C at different heating rates (10–50 °C/min). The operation process typifies a movement from slow to fast pyrolysis [62].

(d) Other peculiar pressure gas-based reactors

The pressurized entrained-flow gasification (PEFG) of straw biomass as a potentially sustainable and commercially viable process to produce fuels, and the understanding of the fractionation of inorganic constituents with respect to gasifier conditions and various straw compositions are two areas of interest. Mielke et al. used PEFG to identify the relevant fractionation processes that are dependent on ash composition, employing predicting slag composition and viscosity models based on the ash composition of the fuel and the process parameters. Pressurized entrained-flow gasification (PEFG) operated at 1400 °C, with varying retention times from 10 s to 50 s, which typified a fast pyrolysis process [74].

There was a paucity of detailed and complex analytical exposure to ablative fast pyrolyzed (AFP) bio-oils, especially with insight into prevailing differences. It was this gap that made [6] use a 5 kg/h unit ablative fast pyrolysis (AFP) lab-scale reactor to evaluate the biomass type, properties, and composition of bio-oils that have been produced from poplar wood and beech, miscanthus, and straw. The pyrolysis operated at a 550 °C constant temperature. This operation process signaled fast pyrolysis. Elsewhere, because eco-social business models that are more cascading and have circular-based environmental, social, and economic benefits within the food waste sector are needed, Matrapazi and Zabaniotou applied wire mesh captive sample type reactors on spent coffee grounds in a large-scale slow pyrolysis [48].

7.2. Snapshots of Combined Thermal Conversion Treatment and Analytical Methods

(a) Fixed bed with torrefaction

In studying the evolution of functional groups during the wet torrefaction process, Wang et al. [52] conducted a comparative analysis of torrefied corn stalk using a vertical fixed-bed, investigating how biomass pyrolysis polygeneration takes place under optimal conditions. It should be noted that the reactor heating was at a torrefaction temperature (200–290 °C), then the sample (5 g) was swiftly placed in the reactor center. These workers found biochar yield after wet torrefied less than dry torrefied, with the upgraded biochar quality given the high ash removal. This was followed by pyrolysis properties of torrefied samples in terms of bio-char, pyrolytic gas, bio-oil, and yield distribution. This exemplified a combination of slow (torrefaction) and fast (vertical fixed-bed reactor) pyrolysis operation.

(b) Thermogravimetric analysis–Fourier transform infrared (TGA–FTIR)

Considering the processing of mixed solid waste that can adopt a two-stage solid prototype, Serio and Wójtowicz used TGA–FTIR analysis with the FTIR analysis of the evolved gases system to determine how feasible it is that an advanced methodology can be developed to evaluate the biomass materials. To actualize the pyrolysis process, the TGA–FTIR operated from 150 (for 3–4 min) to 900 °C, which typifies the move from slow to fast pyrolysis [41].

Researchers have pursued more information due to a requirement for more knowledge on the kinetic characteristics of biomass with complicated thermal properties. Da Silva et al. [63] analyzed the kinetic parameters using a thermogravimetric analyzer (activation energy, frequency factor, and reaction model) to investigate the pyrolysis of biomass with complex thermal behavior, including cashew nut shell waste (CSW) and sugarcane bagasse waste (SBW). Five different heating rates were used during this operation, ranging from room temperature to 1073 K (about 800 °C), showing the progression from slow to fast pyrolysis. Furthermore, particularly from the agro-industry standpoint, the green corn husks as biomass, via pyrolysis, can be an alternative energy source [63]. It is on this premise that Reinehr and colleagues [70] used a thermogravimetric analyzer, through pyrolysis reaction kinetics, and were able to perform the analysis of green corn husk properties and characterizations, so as to find the thermokinetic conversion parameters. The TGA operated at 30 to 900 °C, with heating rates of 5, 10, 15, and 20 °C/min, which depicts movement from slow to fast pyrolysis.

(c) Thermogravimetric analysis (TGA) and differential thermo-gravimetry (DTG)

To identify the future biofuel potential use of corncob and eucalypts, Kumar and colleagues investigated the thermal degradation, kinetic parameters/properties, and the deconvolution of biomass/combustion characteristics, after having them subjected to differential thermo-gravimetry (DTG) and thermogravimetric analysis (TGA). The pyrolysis temperature was found to have attained up to 1000 °C, which demonstrates that this operation process was fast pyrolysis [32].

(d) TGA–FTIR and Py-GC/MS

In order to understand the volatile compositions and their formation pathways/kinetics during biomass pyrolysis that help in regulating the target products' quality, Tian et al. applied two pyrolysis stages that coupled real-time volatile monitoring techniques (Py-GC/TOF-MS and (TGA–FTIR) to rice husks that were subjected to three different heating rates (10, 20, and 30 $^{\circ}C\ min^{-1}$), starting from room to 800 °C. In particular, the temperatures from room to 800 °C demonstrated that this operation process moved from slow to fast pyrolysis [31].

Given that information on comparative studies on two-step pyrolysis (TSP) of different lignocellulosic biomass and the effects of components on TSP were scant, Zhang et al. [40] applied TGA–FTIR and Py-GC/MS in studying the effects of TSP on lignocellulosic biomass, by comparing corncob (CC), cotton stalk (CS), walnut shell (WS), and their acid-washed samples (ACC, ACS, and AWS). The TGA–FTIR, at a heating rate of 20 °C/min, operated from room temperature to 750 °C in order to realize the vapors, whereas Py-GC/MS operated a two-step process, first conducted at 400 °C for 20 s, and second, at 650 °C with a residence time of 20 s, to realize the volatiles. Given these 650–750 °C temperature ranges, the operation process can be considered as a fast pyrolysis.

(e) Thermogravimetric analysis (TGA) and Pyrolysis-GC/MS

To better understand the effects and importance of parameters (like biomass composition, particle size, shape, residence time, and heating rate) on the devolatilization and bio-oil composition kinetics for a successful process scale-up, Vinu [54] employed Py-GC/MS and TGA to pyrolyze mixed wood sawdust (MWSD) of eight different particle sizes (26.5–925 μm) at different heating rates of very slow (<3 °C/min), slow (5–20 °C/min), medium (50–100 °C/min), and fast (10,000 °C/s). Specifically, the TGA temperature ranged between 25 and 900 °C, whereas the filament temperature of Py-GC/MS was set at 600 °C and maintained for a period of 30 s. Considering the temperature ranges of 25 and 900 °C, the operation process can be considered to have moved from slow to fast pyrolysis.

Because of the fact that investigations into the correlation of aldehydes, furans, and ketones with carbonyl groups in bio-oil with holocellulose appear scantly, Y. Liu et al. [49] used a Pyroprobe 6200 pyrolizer (Py-GC/MS) and TGA to study the pyrolysis behaviors of nine biomass-derived holocelluloses (from seven agricultural and two forestry residues). The TGA operated from room temperature to 800 °C at 40 °C/min, whereas the pyrolysis-GC/MS had its platinum spiral coil's heating rate of 10,000 °C/s operating heated from 50 °C to 550 °C, maintained for 15 s. The process from slow to fast pyrolysis is typified by the entire temperature range between room temperature and 800 °C. In order to produce and use syngas, bio-oils, and value-added chemicals, while reducing waste stream and greenhouse gas emissions, it is possible to use TGA–FTIR and Py-GC/MS analyses. This was the foundation [53] used in their combination of TGA, FTIR, and Py-GC/MS analyses used to quantify the bioenergy and by-product outputs at different heating rates. The TGA operated from room temperature to 1000 °C at 5, 10, 20, and 40 K/min heating rates, which typifies movement from slow to fast pyrolysis.

(f) Other thermogravimetric analysis combinations

Besides conventional pyrolysis processes used to bring about thermally unstable oxygenated bio-oils, carbon-rich solids in biomass pyrolysis (i.e., biochar) remain the economical choice for catalytic applications. Hao et al. [39] used a thermogravimetric analysis for pyrolysis at temperatures of 20–750 °C and used a vertical dual-bed tubular quartz reactor at a temperature of 300 °C for 2 h in order to study how temperature and mixing ratio affect the straw (RS) and *Ulva prolifera* macroalgae (UPM) product distribution by catalytic and non-catalytic co-pyrolysis. Generally, the operation temperature range of 20–750 °C demonstrated slow to fast pyrolysis. Elsewhere, there is a paucity of relevant data regarding how operating pressure influences the thermal effects of the pyrolysis process, and that is why Basile and colleaguesused the thermogravimetric analyzer (TGA) at a heating rate of 10 °C/min and a final temperature of 950 °C, whereas the differential scanning calorimetry (DSC) for pressures at 0.1, 0.5, 1, 2, and 4 MPa, the constant heating rate was 10 °C/min, then arriving at the final temperature of 550 °C. The temperature of the operating process suggests fast pyrolysis [78].

(g) Analytical pyroprobe® reactor and Pyrolysis-GC/MS

Given the differences in the lower and faster heating rate conditions, which obtain kinetic parameter validation as the requirement for weight loss profile data to be reliable, Ojha et al. [57] used an analytical pyroprobe® reactor, first with FTIR, to study the isothermal mass loss of biomass, and then, combined with gas chromatograph/mass spectrometer (Py-GCMS) to look into the kinetics of fast pyrolysis of three lignocellulosic biomasses, i.e.,. empty fruit bunch (EFB), pinewood (PW), and rice straw (RS). These authors used a Pyroprobe® reactor with FTIR which operated at 400, 450, 500, 550, 600, 650, and 700 °C, using hold times of 2, 4, 6, 8, 10, 15, 20, 30, and 60 s, whereas the Py-GCMS used temperatures (400, 500, 650, and 800 °C) and held for 30 s. Overall, these temperature ranges between 400–800 °C typify fast pyrolysis [57].

7.3. Other Miscellaneous/Pyrolysis-Mimicking Operations

(a) Hybrid organosolv–steam explosion reactor

In order to combine the fractionation ability of the organosolv system to physically reduce the size of the biomass during the steam explosion, and at the same time, to pretreat and fractionate the birch and spruce biomass, Matsakas et al. [35] studied how the digestibility was influenced by the different process parameters of the hybrid method. To achieve this, these workers used both a hybrid organosolv–steam explosion reactor and Automatic Methane Potential Test System II, subjected to temperatures of 200 °C and 55 °C for up to 18 days, respectively. Even though a reactor was used, and despite the temperature of 200 °C, we opine it to be a biological process, given the nature of this study. A performance evaluation of the novel process steps for converting biomass should take into account the high fractionation efficiency of organosolv pretreatment. Mesfun et al. [106] utilized a hybrid organic solvent and steam explosion pretreatment technique to separate lignocellulosic biomass onto streams rich in cellulose, hemicellulose, and lignin in order to determine how well it would perform in a biorefinery setup. With a holding period of 15 min, the used hybrid organic solvent and steam explosion pretreatment reactor were ran at 200 °C, which typifies a slow type of pyrolysis.

(b) Greenfield Eco. Pvt. Ltd./Cylindrical furnace reactor

Consequently, the production of biochar from invasive weed mesquite biomass could benefit waste management, prevent CO_2 emissions, and soil amendment could also aid in carbon sequestration and soil improvement. Hussain et al. [77] used the Greenfield Eco. Pvt. Ltd. pyrolysis instrument to determine the impact of biochar on the soil's hydraulic characteristics, thereby assessing its suitability for farming. The temperature was set at 500 °C, which typifies slow pyrolysis, as stated by the authors. To contribute to the quest to discover various alternate fuels, like the depletion of fossil fuels and environmental impacts due to emissions of IC engines, Thamizhvel et al. [45] developed a bio-fuel using various techniques from feedstock, and subsequently conducted an analysis on its properties. This pyrolysis used a cylindrical reactor placed in a furnace, the temperature was set to 600 °C and connected to a gasifier, which the operation typifies as a fast pyrolysis/gasification condition, as stated by the authors.

(c) Hydrothermal carbonization (HTC)

Because different biomass components would bring about changes in the thermal conversion, which would then influence the physical/chemical properties of the char, Xu et al. [65] used hydrothermal carbonization (HTC) (temperature 220 °C for 4 h with 2.0–2.5 MPa pressure), combined with a stainless steel cylinder reactor (having a temperature between 300–800 °C at 10 °C/min), to pyrolyze biochar and compare with hydrochar, with the operation process being implemented from ambient to the desired temperature, which typifies slow pyrolysis. The nature of hydrochar is guaranteed with high carbon content and porosity. Additionally, both hydrothermal carbonization and pyrolysis can deliver more porous materials with a higher carbon content. Bahcivanji et al. [67] opined this when they applied hydrothermal carbonization (HTC) to waste biomass (WB) feedstock, eventually pyrolyzing the samples at temperature ranges between 350 and 550 °C, across 1, 3, and 5 h periods, which signals a slow system approach. Moreover, there are numerous thermal conversion reactors used to conduct any pyrolysis based-study to determine and investigate any given feedstock properties and the target products, namely muffle furnace-based pyrolysis, a tubular quartz reactor, a drop tube furnace (DTF), a semi-batch vertical reactor, a plug flow reactor (PFR), and a continuous stirred tank reactor (CSTR), via simulation.

(d) Other pyrolysis instruments

There are other pyrolysis instrument reported, namely muffle furnace-based pyrolysis; a tubular quartz reactor; a drop tube furnace (DTF); a semi-batch vertical reactor; a continuous stirred tank reactor (CSTR), and a plug flow reactor (PFR) via simulation.

In order to understand the temporal changes associated with particulate matter (PM) characteristic/properties and its emission during combustion, Itoh et al. [136] used a muffle furnace to evaluate the impacts of the operating temperature on dairy cattle manure and wood shavings. They pyrolyzed the samples at temperatures of 200, 300, 400, or 500 °C for 1 h. The operating process clearly demonstrates the combination of slow and fast pyrolysis. Because the quantification of anhydro-sugars appears challenging and its conventional analysis requires pretreatment, Téllez et al. [36] employed a tubular quartz reactor in order to evaluate the content of Levoglucosan (LG) in the bio-oils from pyrolyzed (hydrochloric acid-treated and untreated) rice husks. The temperature operation fell between 300 and 700 °C, which demonstrated both slow and fast pyrolysis.

There was the need to provide additional information and understanding regarding fly ash formation during bio-oil/biochar combustion, as well as to elucidate the differences and similarities when compared to another relative raw biomass. Based on this, Johansson et al. [80] utilized a drop tube furnace (DTF) with a maximum process temperature (of 1400 °C) to pyrolyze five different biomass powders (forest residue, stem wood, willow, bark, and reed canary grass), in order to ascertain the formation of fly ash during suspension combustion and the corresponding products. This maximum process temperature (1400 °C) signals the fast pyrolysis of the biochar and bio-oil of the powders. There is believed to be a high potential of biowaste application as the energy source in Poland; this is in-line with the growing world demand for the pyrolysis of waste materials. It was based on this that Mlonka-Mędrala et al. [51] used a semi-batch vertical reactor at 300–600 °C on oat straw in order to examine its potential as a technology for managing biomass waste. This temperature range, 300–600 °C, signals from a slow to a fast form of pyrolysis. SuperPro Designer (SPD) has been poised to perform modeling and simulation tasks that engage various biomass conversion processes. Pang et al. [71] simulated a pyrolysis process that employed a CSTR for the primary decomposition of biomass, and a PFR to model the remaining fragmentation of unreacted components that would form bio-char, gas, and oil. It was shown that both reactors were set to operate at 550 °C and 1 atm in order to simulate the actual biomass pyrolysis, which signals a fast process.

8. Differentiating between the Reactor and Operation Parameters Involved in Thermal Conversion Processes

It is important to understand the operation (parameters), especially where the pyrolysis reaction takes place, since the reactor is one of the most significant elements determining the yield of the fast pyrolysis product. This would make the target product(s) from feedstock associate with the heating rate of the system, as well as the heat transfer method. Notably, reactor types and operating methods play major role in pyrolytic products' quality, yield, and cost efficiency, as shown in Table 4. Many researchers show fluidized beds (bubbling and circulating) as advantageous and more lucrative, in terms of product output [127,137,138]. Examples of pyrolysis reactors include rotating cone reactors, fluidized beds, ablatives, circulating fluid beds, and auger reactors [5,138], as shown in Figure 5.

Table 4. Reactors with their properties.

Reactor Type	Technology Readiness	Advantages	Disadvantages	Ref.
Bubbling fluidized bed	Commercialized	Simplicity and ease to operation; efficient heat transfer; high bio-oil yield of 70–75%	Fine feedstock particles require	[127]
Circulating fluidized bed	Commercialized	suitable heat transfer, simpler scaling, and a useable particle size of 6 mm	More complex to operate and less liquid yield to achieve	[127,135]
Vacuum	Scaled up to about 3000 kg/h	No gas carrier is necessary, there are no complicated operating conditions, and it is possible to employ bigger biomass particles	Liquid yield (35–50%); large process equipment; slow heat transfer rate; greater coal content	[135]
Vortex	NREL	Particle sizes up to 20 mm, biomass particles were accelerated with high velocity, and yields of 65% liquids	High entering velocities of material into the reactor led to erosion at the transition from linear to angular momentum	[85]
Ablative	Laboratory scale	Larger particles may be used; there is no need for inert gas; heat transfer through hot reactor wall	Limitation on scale-up and heat supply issue	[138]
Auger	Pilot-scale, Understudy	Ceramic or still ball; sand as the heat carrier; mechanically driven	Bigger particles can be used; lesser liquid yield	[127]

One of the criteria influencing the quick pyrolysis yield of products is the reactor. There are several varieties that differ in their working process (Table 4), which influence the quality of the products, energy demand, reactor capacity, energy transfer, particle size, and gas emission. Fluidized beds (bubbling and circulating) have been found to be more profitable and suitable, in terms of product yield and quality in numerous studies that have looked into the matter [137]. According to Peacocke et al. [139] an experiment was performed, aiming to compare the fluid bed and ablative pyrolysis reactors under the same operating parameters, including the process temperature value. The results showed that, in both reactors, char yields increased above 515 °C. The ablative produced higher volatile content char than the fluid bed results, where the chars decreased rapidly. However, in the case of liquid yields, the results are similarly in the range of 11–16 wt.%, and gas yields were recorded lower in the content of the ablative reactor, indicating a less severe environment for the vapor [139]. The shift in the chemistry of the gaseous products in the fluidized bed with temperature indicates that secondary vapor phase cracking in the fluidized bed is more prevalent when compared to the ablative process [139].

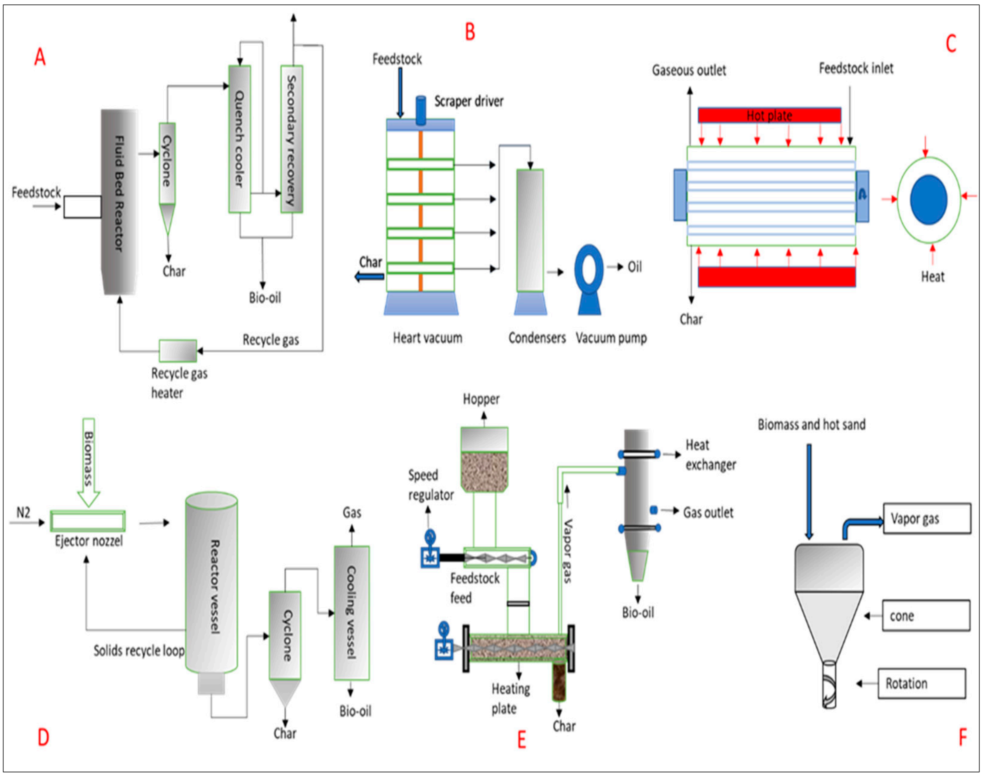

Figure 5. Thermochemical conversion technologies/reactors; schematic representation of thermochemical operating system based on reactor types. Where: (**A**) = Bubbling fluidized bed reactor; (**B**) = Vacuum reactor; (**C**) = Ablative reactor; (**D**) = Vortex reactor; (**E**) = Auger reactor; and (**F**) = Recirculating fluidized bed reactor. Adapted with modified from [5,127,137,138].

The thermal conversion-based process normally begins at temperatures between 200 and 300 °C, while volatiles are quickly liberated in the absence of oxygen at temperatures between 750 and 800 °C [140,141]. Generally, this process comprises five (diverse) process types, namely pyrolysis, hydrothermal carbonization, gasification, combustion, and torrefaction [1]. Each process gives a different range of products and employs different equipment configurations, operating in various modes. The main characteristics of these processes are described in Figure 6, including the product properties and yield [1,39,46,140,142].

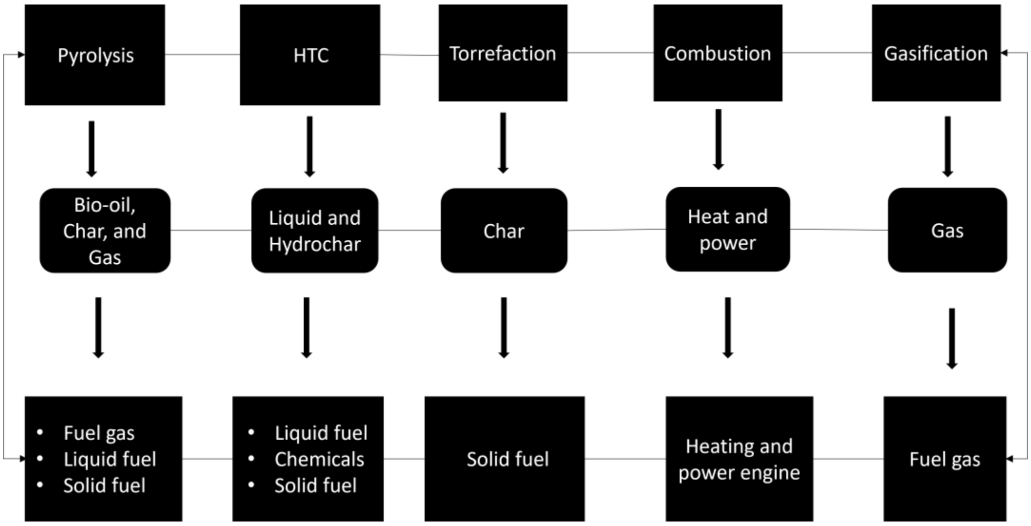

Figure 6. Thermochemical conversion technologies and expected products.

8.1. Snapshots of Single-Operated Pyrolysis Method

When temperature increases in the pyrolysis process, it would lead to increasing the gas production yield and decreasing the char yield. A maximum bio-oil yield tends to be achieved at a range of 400–600 °C pyrolysis process temperature levels, and at a water content decrease, as a result of a higher organic yield [143,144]. However, it depends on the feedstock. It was investigated in many studies that, in the case of wood feedstock, around 500 °C is usually the maximum temperature point [145]. Higher process temperatures leads to a decrease in the hydrogen-to-carbon ratio and the oxygen content. The heat flux and heating rate increase in direct proportion to the environment temperature [145].

Pressure is one of the pyrolysis parameters which impacts the pyrolytic products' yield and quality. Generally, pyrolysis pressure has a significant effect on the size and the shape of the particles through increasing the proportion of void space, resulting in decreasing the cell wall thickness. Biomass particle swelling occurs at low pressures, and higher pressure pyrolysis leads to larger char particle size and bubble formation, while an increased pyrolytic pressure leads to slight decreases in the total surface area, for instance, 1 bar compared with 20 bars [21,76]. In addition, it was investigated in numerous studies that a raise in the operating pressure led to the decline of the heat requirements of the pyrolysis process, and the high-pressure operating process may lead to a shift in the process heat from an endothermic to an exothermic process [78,144]. For example, Lucia Basile et al. [78] utilized a specially designed experimental configuration method, in which DSC was employed to determine the heat demand of the pyrolysis process at operating pressures ranging from 0.1 to 4 MPa. The results showed that, as the operating pressure was raised, the heat demand declined, and the final char yield improved. The obtained results suggest that there is a competing mechanism between the endothermic reaction of the primary decomposition process, which results in the synthesis of volatiles, and the exothermic vapor–solid contact, which results in the development of secondary char [78].

8.2. Considerations of Residence Time and Particle Size

In general, the residence period for rapid pyrolysis is less than 2 s, while for slow and moderate pyrolysis, it is higher [146]. Typically, this decreases the secondary reactions such as thermal cracking, bio-char development, recondensation, and repolymerization, leading to a decline in organic yields while the yield of char and permanent gas increases. Additionally, an experiment was carried out by Xu and Tomita [144] where the effects of residence time and the pyrolysis cracking temperature of volatiles on pyrolytic product yields were determined, ranging from 0.2 to 14 seconds and between 500 to 900°C, respectively. The results showed that as the residence time becomes longer at a given cracking temperature, the tar yield decreased while the yield of gas and light hydrocarbon liquid increased [144].

The majority of pyrolysis operating reactors required small particle sizes in a vertical riser, which allows for high heat transfer rates in the process ranging between 0.5 to 5 mm [146]. The ash content of biomass decreases as the fixed carbon and volatile matter content increase, and vice versa, as the biomass particle size increases, although the size depends on the operating reactor types. In addition, the limited heat transfer between particles as a result of the larger particle size led to relatively higher average activation energies. Therefore, small particle size is an advantage to achieving the pyrolysis process with low energy transfer [54,147].

8.3. Considerations of Energy Demand

The energy consumption in pyrolytic operations is one of the factors to consider due to its impact on the yield and quality of pyrolytic products. However, it is dependent on the feedstock qualities and the operating reactor. Heat transfer requirements are crucial for the efficient conversion of biomass and must be fulfilled. Reducing the size of biomass particles can increase heat transfer rates because biomass has poor thermal conductivity. The insulating char layer developed on the surface of biomass during pyrolysis progression also contributes to the heat transfer resistance. The incremental impact of char formation on heat transfer resistance can also be lessened by decreasing the size of the biomass particle [147]. However, size reduction adds to the cost of feedstock preparation because it is an energy-intensive process. Rapid heating rates promote the quick breakdown of biomass, resulting in more gases and less char in the process. Rapid heating also leads to a high production of bio-oil [148].

9. Knowledge Gaps and Future Prospects

Based on this review, several interesting gaps in knowledge were identified. Researchers in this field may use this as a foundation for further research. Although a number of technologies and approaches have been investigated for a decade, the attempt to lag/isolate the external part of most thermal technologies has not been explored. However, achieving high product quality and yield remains one of the technical challenges of thermal technology that is of great concern [149,150]. Due to the nature of fast heat transmission, especially from the heating media, another important difficulty of pyrolysis to address is how to completely pyrolyze biowaste particles [5]. To produce high-quality products, the majority of pyrolysis reactors require small biomass particle sizes [149]. Insulation plays a crucial role in thermal energy conservation and assists the system in reaching even higher process temperatures. A product of higher quality can be produced at higher temperatures. These techniques aim to lessen emissions, specifically CO_2 pollution. Nevertheless, there has not been a thorough investigation into the release of polluting gases. It will be advantageous to consider different chimney designs and configurations that could aid in the capturing of particulate carbon and lower environmental pollution in said technologies that needed improvement. The term "computational fluid dynamics" (CFD) refers to a class of computational methods for the studying of fluid and energy flows using numerical analyses [151]. The patterns of heat transfer in the reactor can be investigated using CFD. Understanding the main heat zones, the pattern of heat conduction and convection, and the potential for a synergistic heating effects on the carbonization chamber may be aided by this. Moreover, the biomass pyrolysis community also recognizes the issue of how to remove char fines from the liquid product as a concern [85]. There is still a need for consensus on how this can be performed easily at a low cost. In summary, design configuration, modeling, feedstock type, and the application of thermal conversion products have all been found to have knowledge gaps. It can be said that this method is an environmentally friendly technology for the thermal process-based products from biomass and that it may have significant effects on energy and environmental sustainability.

10. Concluding Remarks

Over the last decade, advances in the thermal conversion of potential feedstock, coupled with the application of suitable reactors for producing valuable products (particularly biochar, bio-oil, and pyrolytic gas), have garnered increased research interest. This is significant because thermochemical methods have provided viable pathways for converting low-value biowaste residues into important energy-based products, thus addressing globally significant energy. Biomass is increasingly seen as a potential source of alternative renewable energy. However, considering environmental concerns associated with their production, particularly regarding emission and waste control, recent years have witnessed advancements in thermochemical technologies for feedstock conversion to energy production. While several technologies and methods are still emerging, the attempt to lag/insulate the external body of the majority of the thermal technology needs further exploration. Technically speaking, thermal technology faces challenges related to the heat transfer from the source/particles of feedstock to fully pyrolyze, high product quality, and yield. Therefore, the high-pressure pyrolysis-based study is a novel solution to problems with insulation and product quantity/quality. The writers of this paper aimed to establish the fact that fluidized bed reactor types are more suitable and profitable among others, because those could enhance the product quality and quantity. Future research into high-pressure reactor designs and materials, along with promising feedstock varieties, is necessary to achieve further improvements in end product quality and quantity.

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Abbreviations

BET	Brunauer–Emmett–Teller analyzer
CSF	Carbonized solid fuel
CSTR	Continuous stirred tank reactor
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetric analysis
FESEM	Field emission scanning electron microscopy
H/C	Hydrogen to carbon ratio
HHV	High heating value
HPLC-DAD	High performance liquid chromatography with photodiode-array detection
HTC/L	Hydrothermal carbonization/liquefaction
HTS	Hydrothermal treatment severity
LHV	Low heating value
MBMS	Molecular-beam mass spectrometry
MWSD	Mixed wood sawdust
O/C	Oxygen/carbon ratio
PCA	Principal component analysis
PFR	Plug flow reactor
Py-GCMS	Pyrolysis–gas chromatography–mass spectrometry
SPC	Safflower seed press cake
SVR	Support vector regression
TG/FTIR	Thermogravimetric analysis combined with Fourier transform infrared spectroscopy
TGA	Thermogravimetric analyzer
VFAs	Volatile fatty acids
WMR	Watermelon rind
XRD	X-ray diffraction

References

1. Tripathi, M.; Sahu, J.N.; Ganesan, P. Effect of Process Parameters on Production of Biochar from Biomass Waste through Pyrolysis: A Review. *Renew. Sustain. Energy Rev.* **2016**, *55*, 467–481. [CrossRef]
2. Czajczyńska, D.; Anguilano, L.; Ghazal, H.; Krzyżyńska, R.; Reynolds, A.J.; Spencer, N.; Jouhara, H. Potential of Pyrolysis Processes in the Waste Management Sector. *Therm. Sci. Eng. Prog.* **2017**, *3*, 171–197. [CrossRef]

3. Putra, P.H.M.; Rozali, S.; Patah, M.F.A.; Idris, A. A Review of Microwave Pyrolysis as a Sustainable Plastic Waste Management Technique. *J. Environ. Manag.* **2022**, *303*, 114240. [CrossRef]
4. Kim, S.; Lee, Y.; Andrew Lin, K.Y.; Hong, E.; Kwon, E.E.; Lee, J. The Valorization of Food Waste via Pyrolysis. *J. Clean. Prod.* **2020**, *259*, 120816. [CrossRef]
5. Rasaq, W.A.; Golonka, M.; Scholz, M.; Białowiec, A. Opportunities and Challenges of High-pressure Fast Pyrolysis of Biomass: A Review. *Energies* **2021**, *14*, 5426. [CrossRef]
6. Auersvald, M.; Macek, T.; Schulzke, T.; Staš, M.; Šimáček, P. Influence of Biomass Type on the Composition of Bio-Oils from Ablative Fast Pyrolysis. *J. Anal. Appl. Pyrolysis* **2020**, *150*, 104838. [CrossRef]
7. Basile, L.; Tugnoli, A.; Cozzani, V. The Role of Pressure in the Heat of Pyrolysis of a Lignocellulosic Biomass. *Chem. Eng. Trans.* **2015**, *43*, 451–456. [CrossRef]
8. Kambo, H.S.; Dutta, A. A Comparative Review of Biochar and Hydrochar in Terms of Production, Physico-Chemical Properties and Applications. *Renew. Sustain. Energy Rev.* **2015**, *45*, 359–378. [CrossRef]
9. Rangabhashiyam, S.; do Lins, P.V.S.; Oliveira, L.M.T.d.M.; Sepulveda, P.; Ighalo, J.O.; Rajapaksha, A.U.; Meili, L. Sewage Sludge-Derived Biochar for the Adsorptive Removal of Wastewater Pollutants: A Critical Review. *Environ. Pollut.* **2022**, *293*, 118581. [CrossRef]
10. Nor, W.; Wan, R.; Hisham, M.W.M.; Ambar, M.; Hin, T.Y. A Review on Bio-Oil Production from Biomass by Using Pyrolysis Method. *Renew. Sustain. Energy Rev.* **2012**, *16*, 5910–5923. [CrossRef]
11. Huang, X.; Kudo, S.; Shusaku Asano, J.H. Improvement of Levoglucosenone Selectivity in Liquid Phase Conversion of Cellulose-Derived Anhydrosugar over Solid Acid Catalysts. *Fuel Process. Technol.* **2021**, *212*, 106625. [CrossRef]
12. Naik, D.K.; Monika, K.; Prabhakar, S.; Parthasarathy, R.; Satyavathi, B. Pyrolysis of Sorghum Bagasse Biomass into Bio-Char and Bio-Oil Products: A Thorough Physicochemical Characterization Pyrolysis of Sorghum Bagasse Biomass into Bio-Char and Bio-Oil Products A Thorough Physicochemical Characterization. *J. Therm. Anal. Calorim.* **2017**, *127*, 1277–1289. [CrossRef]
13. Michailof, C.M.; Kalogiannis, K.G.; Sfetsas, T.; Patiaka, D.T.; Lappas, A.A. Advanced Analytical Techniques for Bio-Oil Characterization. *WIREs Energy Environ.* **2016**, *6*, 614–639. [CrossRef]
14. Pattiya, A. Bio-Oil Production via Fast Pyrolysis of Biomass Residues from Cassava Plants in a Fluidised-Bed Reactor. *Bioresour. Technol.* **2011**, *102*, 1959–1967. [CrossRef] [PubMed]
15. Guizani, C.; Jeguirim, M.; Valin, S.; Limousy, L. Biomass Chars: The Effects of Pyrolysis Conditions on Their Morphology, Structure, Chemical Properties and Reactivity. *Energies* **2017**, *10*, 796. [CrossRef]
16. Fu, P.; Hu, S.; Sun, L.; Xiang, J.; Yang, T.; Zhang, A.; Zhang, J. Structural Evolution of Maize Stalk/Char Particles during Pyrolysis. *Bioresour. Technol.* **2009**, *100*, 4877–4883. [CrossRef]
17. Ighalo, J.O.; Eletta, O.A.A.; Adeniyi, A.G. Biomass Carbonisation in Retort Kilns: Process Techniques, Product Quality and Future Perspectives. *Bioresour. Technol. Rep.* **2022**, *17*, 100934. [CrossRef]
18. Dupont, C.; Chiriac, R.; Gauthier, G.; Toche, F. Heat Capacity Measurements of Various Biomass Types and Pyrolysis Residues. *Fuel* **2014**, *115*, 644–651. [CrossRef]
19. Elliott, D.C. *Relation of Reaction Time and Temperature to Chemical Composition of Pyrolysis Oils*; ACS Publications: Washington, DC, USA, 1988.
20. Mahinpey, N.; Murugan, P.; Mani, T.; Raina, R. Analysis of Bio-Oil, Biogas, and Biochar from Pressurized Pyrolysis of Wheat Straw Using a Tubular Reactor. *Energy Fuels* **2009**, *23*, 2736–2742. [CrossRef]
21. Cetin, E.; Moghtaderi, B.; Gupta, R.; Wall, T.F. Influence of Pyrolysis Conditions on the Structure and Gasification Reactivity of Biomass Chars. *Fuel* **2004**, *83*, 2139–2150. [CrossRef]
22. Uddin, M.N.; Techato, K.; Taweekun, J.; Rahman, M. An Overview of Recent Developments in Biomass Pyrolysis Technologies. *Energies* **2018**, *11*, 3115. [CrossRef]
23. Qureshi, M.S.; Oasmaa, A.; Pihkola, H.; Deviatkin, I.; Tenhunen, A.; Mannila, J.; Minkkinen, H.; Pohjakallio, M.; Laine-ylijoki, J. Pyrolysis of Plastic Waste: Opportunities and Challenges. *J. Anal. Appl. Pyrolysis* **2020**, *152*, 104804. [CrossRef]
24. Jahirul, M.I.; Rasul, M.G.; Chowdhury, A.A.; Ashwath, N. Biofuels Production through Biomass Pyrolysis—A Technological Review. *Energies* **2012**, *5*, 4959. [CrossRef]
25. Chen, X.; Li, S.; Liu, Z.; Chen, Y.; Yang, H.; Wang, X.; Che, Q.; Chen, W.; Chen, H. Pyrolysis Characteristics of Lignocellulosic Biomass Components in the Presence of CaO. *Bioresour. Technol.* **2019**, *287*, 121493. [CrossRef] [PubMed]
26. Chen, Y.K.; Lin, C.H.; Wang, W.C. The Conversion of Biomass into Renewable Jet Fuel. *Energy* **2020**, *201*, 117655. [CrossRef]
27. Chowdhury, Z.Z.; Pal, K.; Yehye, W.; Suresh, S.; Detection, H. *Pyrolysis: A Sustainable Way to Generate Energy from Waste*; IntechOpen: London, UK, 2017; Volume 69036, pp. 1–36. [CrossRef]
28. Dong, J.; Tang, Y.; Nzihou, A.; Chi, Y. Key Factors Influencing the Environmental Performance of Pyrolysis, Gasification and Incineration Waste-to-Energy Technologies. *Energy Convers. Manag.* **2019**, *196*, 497–512. [CrossRef]
29. Lue, S. Principles and Advantages of Pyrolysis Moregreen. 2019, pp. 1–10. Available online: https://tomoregreen.com/principles-and-advantages-of-pyrolysis/ (accessed on 4 January 2024).
30. Henan Doing Environmental Protection Technology Co., Ltd. *What Is the Advantage and Disadvantage of Using Pyrolysis Technology to Convert Plastic to Oil?* Henan Doing Environmental Protection Technology Co., Ltd.: Zhengzhou, China, 2019; pp. 1–4.
31. Tian, B.; Xu, L.; Jing, M.; Liu, N.; Tian, Y. A Comprehensive Evaluation on Pyrolysis Behavior, Kinetics, and Primary Volatile Formation Pathways of Rice Husk for Application to Catalytic Valorization. *Fuel Process. Technol.* **2021**, *214*, 106715. [CrossRef]

32. Kumar, P.; Subbarao, P.M.V.; Vijay, V.K. Assessment of Pyrolysis-Kinetics of Corncob and Eucalyptus Biomass Residue Using Thermo Gravimetric Analysis. *Int. J. Sustain. Energy* **2021**, *40*, 910–922. [CrossRef]
33. Anca-Couce, A.; Tsekos, C.; Retschitzegger, S.; Zimbardi, F.; Funke, A.; Banks, S.; Kraia, T.; Marques, P.; Scharler, R.; de Jong, W.; et al. Biomass Pyrolysis TGA Assessment with an International Round Robin. *Fuel* **2020**, *276*, 118002. [CrossRef]
34. Su, Y.; Liu, L.; Zhang, S.; Xu, D.; Du, H.; Cheng, Y.; Wang, Z.; Xiong, Y. A Green Route for Pyrolysis Poly-Generation of Typical High Ash Biomass, Rice Husk: Effects on Simultaneous Production of Carbonic Oxide-Rich Syngas, Phenol-Abundant Bio-Oil, High-Adsorption Porous Carbon and Amorphous Silicon Dioxide. *Bioresour. Technol.* **2020**, *295*, 122243. [CrossRef]
35. Matsakas, L.; Sarkar, O.; Jansson, S.; Rova, U.; Christakopoulos, P. A Novel Hybrid Organosolv-Steam Explosion Pretreatment and Fractionation Method Delivers Solids with Superior Thermophilic Digestibility to Methane. *Bioresour. Technol.* **2020**, *316*, 123973. [CrossRef]
36. Téllez, J.F.; Silva, M.P.; Simister, R.; Gomez, L.D.; Fuertes, V.C.; De Paoli, J.M.; Moyano, E.L. Fast Pyrolysis of Rice Husk under Vacuum Conditions to Produce Levoglucosan. *J. Anal. Appl. Pyrolysis* **2021**, *156*, 105105. [CrossRef]
37. Scapin, E.; Lazzari, E.; Benvenutti, E.V.; Falcade, T. Activated Carbon from Rice Husk Biochar with High Surface Area. *Biointerface Res. Appl. Chem.* **2021**, *11*, 10265–10277.
38. Sieradzka, M.; Gao, N.; Quan, C.; Mlonka-Mędrala, A.; Magdziarz, A. Biomass Thermochemical Conversion via Pyrolysis with Integrated CO_2 Capture. *Energies* **2020**, *13*, 1050. [CrossRef]
39. Hao, J.; Qi, B.; Li, D.; Zeng, F. Catalytic Co-Pyrolysis of Rice Straw and Ulva Prolifera Macroalgae: Effects of Process Parameter on Bio-Oil up-Gradation. *Renew. Energy* **2021**, *164*, 460–471. [CrossRef]
40. Zhang, L.; Yang, Z.; Li, S.; Wang, X.; Lin, R. Comparative Study on the Two-Step Pyrolysis of Different Lignocellulosic Biomass: Effects of Components. *J. Anal. Appl. Pyrolysis* **2020**, *152*, 104966. [CrossRef]
41. Serio, M.A.; Wójtowicz, M.A. *Methodology for Identification and Classification of Biomass Pyrolysis Behavior*; SAE Technical Paper; Advanced Fuel Research, Inc.: East Hartford, CT, USA, 2009. [CrossRef]
42. Noszczyk, T.; Dyjakon, A.; Koziel, J.A. Kinetic Parameters of Nut Shells Pyrolysis. *Energies* **2021**, *14*, 682. [CrossRef]
43. Zhang, C.; Chao, L.; Zhang, Z.; Zhang, L.; Li, Q.; Fan, H.; Zhang, S.; Liu, Q.; Qiao, Y.; Tian, Y.; et al. Pyrolysis of Cellulose: Evolution of Functionalities and Structure of Bio-Char versus Temperature. *Renew. Sustain. Energy Rev.* **2021**, *135*, 110416. [CrossRef]
44. Jia, G. Combustion Characteristics and Kinetic Analysis of Biomass Pellet Fuel Using Thermogravimetric Analysis. *Processes* **2021**, *9*, 868. [CrossRef]
45. Thamizhvel, R.; Suryavarman, K.; Velmurugan, V.; Sethuraman, N. Comparative Study of Gasification and Pyrolysis Derived from Coconut Shell on the Performance and Emission of CI Engine. *Mater. Today Proc.* **2021**, *47*, 978–983. [CrossRef]
46. Swiechowski, K.; Koziel, J.A. The prediction of calorific value of carbonized solid fuel produced from refuse-derived fuel in the low-temperature pyrolysis in CO_2. *Materials* **2020**, *14*, 49.
47. Mu, L.; Wang, R.; Zhai, Z.; Zhang, B.; Shang, Y.; Yin, H. Evaluation of Thermokinetics Methodology, Parameters, and Coke Characterization of Co-Pyrolysis of Bituminous Coal with Herbaceous and Agricultural Biomass. *Biomass Convers. Biorefinery* **2021**, *13*, 5957–5972. [CrossRef]
48. Matrapazi, V.K.; Zabaniotou, A. Experimental and Feasibility Study of Spent Coffee Grounds Upscaling via Pyrolysis towards Proposing an Eco-Social Innovation Circular Economy Solution. *Sci. Total Environ.* **2020**, *718*, 137316. [CrossRef] [PubMed]
49. Liu, Y.; Wu, S.; Zhang, H.; Xiao, R. Fast Pyrolysis of Holocellulose for the Preparation of Long-Chain Ether Fuel Precursors: Effect of Holocellulose Types. *Bioresour. Technol.* **2021**, *338*, 125519. [CrossRef] [PubMed]
50. Charvet, F.; Silva, F.; Ruivo, L.; Tarelho, L.; Matos, A.; da Silva, J.F.; Neves, D. Pyrolysis Characteristics of Undervalued Wood Varieties in the Portuguese Charcoal Sector. *Energies* **2021**, *14*, 2537. [CrossRef]
51. Mlonka-Mędrala, A.; Evangelopoulos, P.; Sieradzka, M.; Zajemska, M.; Magdziarz, A. Pyrolysis of Agricultural Waste Biomass towards Production of Gas Fuel and High-Quality Char: Experimental and Numerical Investigations. *Fuel* **2021**, *296*, 120611. [CrossRef]
52. Wang, X.; Wu, J.; Chen, Y.; Pattiya, A.; Yang, H.; Chen, H. Comparative Study of Wet and Dry Torrefaction of Corn Stalk and the e Ff Ect on Biomass Pyrolysis Polygeneration. *Bioresour. Technol.* **2018**, *258*, 88–97. [CrossRef] [PubMed]
53. Liu, H.; Liu, J.; Huang, H.; Evrendilek, F.; Wen, S.; Li, W. Optimizing Bioenergy and By-Product Outputs from Durian Shell Pyrolysis. *Renew. Energy* **2021**, *164*, 407–418. [CrossRef]
54. Vinu, D.V.S.R. Effects of Biomass Particle Size on Slow Pyrolysis Kinetics and Fast Pyrolysis Product Distribution. *Waste Biomass Valorization* **2018**, *9*, 465–477. [CrossRef]
55. Açıkalın, K. Evaluation of Orange and Potato Peels as an Energy Source: A Comprehensive Study on Their Pyrolysis Characteristics and Kinetics. *Biomass Convers. Biorefinery* **2021**, *12*, 501–514. [CrossRef]
56. Moriyama, F.; Mizuno, S.; Tagami-Kanada, N.; Sawai, T. Evaluation of Energy Properties of Torrefied Biomass for a given Pyrolysis Condition by Isothermal Pyrolysis Kinetics. *Mech. Eng. J.* **2021**, *8*, 21-00069. [CrossRef]
57. Ojha, D.K.; Viju, D.; Vinu, R. Fast Pyrolysis Kinetics of Lignocellulosic Biomass of Varying Compositions. *Energy Convers. Manag. X* **2021**, *10*, 100071. [CrossRef]
58. Gözke, G.; Açıkalın, K. Pyrolysis Characteristics and Kinetics of Sour Cherry Stalk and Flesh via Thermogravimetric Analysis Using Isoconversional Methods. *J. Therm. Anal. Calorim.* **2020**, *146*, 893–910. [CrossRef]

59. Mukherjee, A.; Okolie, J.A.; Tyagi, R.; Dalai, A.K.; Niu, C. Pyrolysis Kinetics and Activation Thermodynamic Parameters of Exhausted Coffee Residue and Coffee Husk Using Thermogravimetric Analysis. *Can. J. Chem. Eng.* **2021**, *99*, 1683–1695. [CrossRef]
60. Singh, R.K.; Pandey, D.; Patil, T.; Sawarkar, A.N. Pyrolysis of Banana Leaves Biomass: Physico-Chemical Characterization, Thermal Decomposition Behavior, Kinetic and Thermodynamic Analyses. *Bioresour. Technol.* **2020**, *310*, 123464. [CrossRef] [PubMed]
61. Shahbeig, H.; Nosrati, M. Pyrolysis of Biological Wastes for Bioenergy Production: Thermo-Kinetic Studies with Machine-Learning Method and Py-GC/MS Analysis. *Fuel* **2020**, *269*, 117238. [CrossRef]
62. Liu, L.; Zhang, X.; Zhao, R.; Song, G.; Tian, L. Pyrolysis of Phragmites Hirsuta Study on Pyrolysis Characteristics, Kinetic and Thermodynamic Analyses. *Int. J. Energy Res.* **2021**, *45*, 15200–15216. [CrossRef]
63. da Silva, J.C.G.; de Albuquerque, J.G.; de Araujo Galdino, W.V.; de Sena, R.F.; Andersen, S.L.F. Single-Step and Multi-Step Thermokinetic Study—Deconvolution Method as a Simple Pathway for Describe Properly the Biomass Pyrolysis for Energy Conversion. *Energy Convers. Manag.* **2020**, *209*, 112653. [CrossRef]
64. Chen, H.; Liu, Z.; Chen, X.; Chen, Y.; Dong, Z.; Wang, X.; Yang, H. Comparative Pyrolysis Behaviors of Stalk, Wood and Shell Biomass: Correlation of Cellulose Crystallinity and Reaction Kinetics. *Bioresour. Technol.* **2020**, *310*, 123498. [CrossRef] [PubMed]
65. Xu, S.; Chen, J.; Peng, H.; Leng, S.; Li, H.; Qu, W.; Hu, Y.; Li, H.; Jiang, S.; Zhou, W.; et al. Effect of Biomass Type and Pyrolysis Temperature on Nitrogen in Biochar, and the Comparison with Hydrochar. *Fuel* **2021**, *291*, 120128. [CrossRef]
66. Rodriguez Franco, C.; Page-Dumroese, D.S.; Pierson, D.; Miller, M.; Miles, T. Policy and Regulations for Mobile Biochar Production in the United States of America. *Forests* **2024**, *15*, 192. [CrossRef]
67. Bahcivanji, L.; Gascó, G.; Paz-Ferreiro, J.; Méndez, A. The Effect of Post-Pyrolysis Treatment on Waste Biomass Derived Hydrochar. *Waste Manag.* **2020**, *106*, 55–61. [CrossRef]
68. Fakayode, O.A.; Wang, Z.; Wahia, H.; Mustapha, A.T.; Zhou, C.; Ma, H. Higher Heating Value, Exergy, Pyrolysis Kinetics and Thermodynamic Analysis of Ultrasound-Assisted Deep Eutectic Solvent Pretreated Watermelon Rind Biomass. *Bioresour. Technol.* **2021**, *332*, 125040. [CrossRef] [PubMed]
69. Şen, U.; Pereira, H. Pyrolysis Behavior of Alternative Cork Species. *J. Therm. Anal. Calorim.* **2021**, *147*, 4017–4025. [CrossRef]
70. Reinehr, T.O.; Ohara, M.A.; de Oliveira Santos, M.P.; Barros, J.L.M.; Bittencourt, P.R.S.; Baraldi, I.J.; da Silva, E.A.; Zanatta, E.R. Study of Pyrolysis Kinetic of Green Corn Husk. *J. Therm. Anal. Calorim.* **2021**, *143*, 3181–3192. [CrossRef]
71. Pang, Y.X.; Yan, Y.; Foo, D.C.Y.; Sharmin, N.; Zhao, H.; Lester, E.; Wu, T.; Pang, C.H. The Influence of Lignocellulose on Biomass Pyrolysis Product Distribution and Economics via Steady State Process Simulation. *J. Anal. Appl. Pyrolysis* **2020**, *158*, 104968. [CrossRef]
72. Chen, D.; Gao, D.; Huang, S.; Capareda, S.C.; Liu, X.; Wang, Y.; Zhang, T.; Liu, Y.; Niu, W. Influence of Acid-Washed Pretreatment on the Pyrolysis of Corn Straw: A Study on Characteristics, Kinetics and Bio-Oil Composition. *J. Anal. Appl. Pyrolysis* **2021**, *155*, 105027. [CrossRef]
73. Yu, Y.; Wu, J.; Ren, X.; Lau, A.; Rezaei, H.; Takada, M.; Bi, X.; Sokhansanj, S. Steam explosion of lignocellulosic biomass for multiple advanced bioenergy processes: A review. *Renew. Sustain. Energy Rev.* **2022**, *154*, 111871. [CrossRef]
74. Mielke, K.; Kolb, T.; Müller, M. Chemical Fractionation of Inorganic Constituents in Entrained Flow Gasification of Slurry from Straw Pyrolysis. *Biomass Bioenergy* **2020**, *141*, 105732. [CrossRef]
75. Chua, Y.W.; Wu, H.; Yu, Y. Effect of Cellulose-Lignin Interactions on Char Structural Changes during Fast Pyrolysis at 100-350 °C. *Proc. Combust. Inst.* **2021**, *38*, 3977–3986. [CrossRef]
76. Fermoso, J.; Stevanov, C.; Moghtaderi, B.; Arias, B.; Pevida, C.; Plaza, M.G.; Rubiera, F.; Pis, J.J. High-Pressure Gasification Reactivity of Biomass Chars Produced at Different Temperatures. *J. Anal. Appl. Pyrolysis* **2009**, *85*, 287–293. [CrossRef]
77. Hussain, R.; Ghosh, K.K.; Ravi, K. Impact of Biochar Produced from Hardwood of Mesquite on the Hydraulic and Physical Properties of Compacted Soils for Potential Application in Engineered Structures. *Geoderma* **2021**, *385*, 114836. [CrossRef]
78. Basile, L.; Tugnoli, A.; Stramigioli, C.; Cozzani, V. Influence of Pressure on the Heat of Biomass Pyrolysis. *Fuel* **2014**, *137*, 277–284. [CrossRef]
79. Shrivastava, P.; Khongphakdi, P.; Palamanit, A.; Kumar, A.; Tekasakul, P. Investigation of Physicochemical Properties of Oil Palm Biomass for Evaluating Potential of Biofuels Production via Pyrolysis Processes. *Biomass Convers. Biorefinery* **2021**, *11*, 1987–2001. [CrossRef]
80. Johansson, A.C.; Molinder, R.; Vikström, T.; Wiinikka, H. Particle Formation during Suspension Combustion of Different Biomass Powders and Their Fast Pyrolysis Bio-Oils and Biochars. *Fuel Process. Technol.* **2021**, *218*, 106868. [CrossRef]
81. Rollag, S.A.; Lindstrom, J.K.; Brown, R.C. Pretreatments for the Continuous Production of Pyrolytic Sugar from Lignocellulosic Biomass. *Chem. Eng. J.* **2020**, *385*, 123889. [CrossRef]
82. Magdziarz, A.; Wilk, M.; Wądrzyk, M. Pyrolysis of Hydrochar Derived from Biomass—Experimental Investigation. *Fuel* **2020**, *267*, 117246. [CrossRef]
83. Sobek, S.; Werle, S. Solar Pyrolysis of Waste Biomass: A Comparative Study of Products Distribution, in Situ Heating Behavior, and Application of Model-Free Kinetic Predictions. *Fuel* **2021**, *292*, 120365. [CrossRef]
84. Yu, J.; Wang, D.; Sun, L. The Pyrolysis of Lignin: Pathway and Interaction Studies. *Fuel* **2021**, *290*, 120078. [CrossRef]
85. Ringer, M.; Putsche, V.; Scahill, J. *Large-Scale Pyrolysis Oil Production and Economic Analysis*; Technical Report NREL/TP-510–37779; National Renewable Energy Laboratory: Cole Boulevard, CO, USA, 2006; pp. 1–93.

86. Suntivarakorn, R.; Treedet, W.; Singbua, P.; Teeramaetawat, N. Fast Pyrolysis from Napier Grass for Pyrolysis Oil Production by Using Circulating Fluidized Bed Reactor: Improvement of Pyrolysis System and Production Cost. *Energy Rep.* **2018**, *4*, 565–575. [CrossRef]
87. Wu, D.; Xiao, L.; Ba, Y.; Wang, H.; Zhang, A.; Wu, X.; Niu, M.; Fang, K. The Recovery of Energy, Nitrogen and Phosphorous from Three Agricultural Wastes by Pyrolysis. *Energy Procedia* **2017**, *105*, 1263–1269. [CrossRef]
88. Zhu, Z.; Liu, Z.; Zhang, Y.; Li, B.; Lu, H.; Duan, N.; Si, B.; Shen, R.; Lu, J. Recovery of Reducing Sugars and Volatile Fatty Acids from Cornstalk at Different Hydrothermal Treatment Severity. *Bioresour. Technol.* **2016**, *199*, 220–227. [CrossRef]
89. Cavalaglio, G.; Cotana, F.; Nicolini, A.; Coccia, V.; Petrozzi, A.; Formica, A.; Bertini, A. Characterization of Various Biomass Feedstock Suitable for Small-Scale Energy Plants as Preliminary Activity of Biocheaper Project. *Sustainability* **2020**, *12*, 6678. [CrossRef]
90. Lu, X.; Ma, X.; Chen, X. Co-Hydrothermal Carbonization of Sewage Sludge and Lignocellulosic Biomass: Fuel Properties and Heavy Metal Transformation Behaviour of Hydrochars. *Energy* **2021**, *221*, 119896. [CrossRef]
91. Saengsuriwong, R.; Onsree, T.; Phromphithak, S.; Tippayawong, N. Conversion of Tobacco Processing Waste to Biocrude Oil via Hydrothermal Liquefaction in a Multiple Batch Reactor. *Clean Technol. Environ. Policy* **2021**, *25*, 1–11. [CrossRef]
92. Khan, S.A.; Ali, I.; Naqvi, S.R.; Li, K.; Mehran, M.T.; Khoja, A.H.; Alarabi, A.A.; Atabani, A.E. Investigation of Slow Pyrolysis Mechanism and Kinetic Modeling of Scenedesmus Quadricauda Biomass. *J. Anal. Appl. Pyrolysis* **2021**, *158*, 105149. [CrossRef]
93. Khan, S.R.; Zeeshan, M.; Ahmed, A.; Saeed, S. Comparison of Synthetic and Low-Cost Natural Zeolite for Bio-Oil Focused Pyrolysis of Raw and Pretreated Biomass. *J. Clean. Prod.* **2021**, *313*, 127760. [CrossRef]
94. Zheng, A.; Xia, S.; Cao, F.; Liu, S.; Yang, X.; Zhao, Z.; Tian, Y.; Li, H. Directional Valorization of Eucalyptus Waste into Value-Added Chemicals by a Novel Two-Staged Controllable Pyrolysis Process. *Chem. Eng. J.* **2021**, *404*, 127045. [CrossRef]
95. Tian, B.; Wang, X.; Zhao, W.; Xu, L.; Bai, L. Pyrolysis Behaviors, Kinetics and Gaseous Product Evolutions of Two Typical Biomass Wastes. *Catal. Today* **2021**, *374*, 77–85. [CrossRef]
96. Lu, Y.; Zheng, Y.; He, R.; Zheng, Z. Selective Conversion of Lignocellulosic Biomass and Its Components into Value-Added Furans over Al-Based Bimetals: Analytical Py-GC × GC/MS. *J. Anal. Appl. Pyrolysis* **2022**, *163*, 105485. [CrossRef]
97. Dong, Y.; Mao, S.; Guo, F.; Shu, R.; Bai, J.; Qian, L.; Bai, Y. Coal Gasification Fine Slags: Investigation of the Potential as Both Microwave Adsorbers and Catalysts in Microwave-Induced Biomass Pyrolysis Applications. *Energy* **2022**, *238*, 121867. [CrossRef]
98. Kumar Mishra, R. Pyrolysis of Low-Value Waste Switchgrass: Physicochemical Characterization, Kinetic Investigation, and Online Characterization of Hot Pyrolysis Vapours. *Bioresour. Technol.* **2022**, *347*, 126720. [CrossRef] [PubMed]
99. Fernandez, E.; Santamaria, L.; Amutio, M.; Artetxe, M.; Arregi, A.; Lopez, G.; Bilbao, J.; Olazar, M. Role of Temperature in the Biomass Steam Pyrolysis in a Conical Spouted Bed Reactor. *Energy* **2022**, *238*, 122053. [CrossRef]
100. Duman, G.; Yanik, J. Two-Step Steam Pyrolysis of Biomass for Hydrogen Production. *Int. J. Hydrogen Energy* **2017**, *42*, 17000–17008. [CrossRef]
101. Maisyarah, A.; Shiun, J.; Nasir, F.; Hashim, H. Ultimate and Proximate Analysis of Malaysia Pineapple Biomass from MD2 Cultivar for Biofuel Application. *Chem. Eng. Trans.* **2018**, *63*, 127–132. [CrossRef]
102. Persson, H.; Yang, W. Catalytic Pyrolysis of Demineralized Lignocellulosic Biomass. *Fuel* **2019**, *252*, 200–209. [CrossRef]
103. Palamanit, A.; Khongphakdi, P.; Tirawanichakul, Y.; Phusunti, N. Investigation of Yields and Qualities of Pyrolysis Products Obtained from Oil Palm Biomass Using an Agitated Bed Pyrolysis Reactor. *Biofuel Res. J.* **2019**, *6*, 1065–1079. [CrossRef]
104. Jawad Kadhum, H.; Murthy, G.S. Novel System Design for High Solid Lignocellulosic Biomass Conversion. *Bioresour. Technol.* **2022**, *350*, 126897. [CrossRef]
105. Tahir, M.H.; Çakman, G.; Goldfarb, J.L.; Topcu, Y.; Naqvi, S.R.; Ceylan, S. Demonstrating the Suitability of Canola Residue Biomass to Biofuel Conversion via Pyrolysis through Reaction Kinetics, Thermodynamics and Evolved Gas Analyses. *Bioresour. Technol.* **2019**, *279*, 67–73. [CrossRef]
106. Mesfun, S.; Matsakas, L.; Rova, U.; Christakopoulos, P. Technoeconomic Assessment of Hybrid Organosolv-Steam Explosion Pretreatment of Woody Biomass. *Energies* **2019**, *12*, 4206. [CrossRef]
107. Jiang, G.; Nowakowski, D.J.; Bridgwater, A.V. Effect of the Temperature on the Composition of Lignin Pyrolysis Products. *Energy Fuels* **2010**, *24*, 4470–4475. [CrossRef]
108. Braz, W.C.N.C.E.M.; Ribeiro, S.A.C.A. Mixture of Biomass to Energy Reuse. *J. Therm. Anal. Calorim.* **2018**, *131*, 765–769. [CrossRef]
109. Gil, M.V.; Oulego, P.; Casal, M.D.; Pevida, C.; Pis, J.J.; Rubiera, F. Bioresource Technology Mechanical Durability and Combustion Characteristics of Pellets from Biomass Blends. *Bioresour. Technol.* **2010**, *101*, 8859–8867. [CrossRef] [PubMed]
110. Lajili, M.; Limousy, L.; Jeguirim, M. Physico-Chemical Properties and Thermal Degradation Characteristics of Agropellets from Olive Mill by-Products/Sawdust Blends. *Fuel Process. Technol.* **2014**, *126*, 215–221. [CrossRef]
111. Boumanchar, I.; Chhiti, Y.; Ezzahrae, F.; Alaoui, M.; El, A.; Sahibed-dine, A.; Bentiss, F.; Jama, C.; Bensitel, M. Effect of Materials Mixture on the Higher Heating Value: Case of Biomass, Biochar and Municipal Solid Waste. *Waste Manag.* **2016**, *61*, 78–86. [CrossRef]
112. Lynam, J.G.; Reza, M.T.; Yan, W.; Vásquez, V.R.; Coronella, C.J. Hydrothermal Carbonization of Various Lignocellulosic Biomass. *Biomass-Convers. Biorefinery* **2014**, *5*, 173–181. [CrossRef]
113. Pattiya, A. *Fast Pyrolysis*; Elsevier Ltd.: Amsterdam, The Netherlands, 2018; ISBN 9780081010297.
114. Di Blasi, C.; Branca, C.; D’Errico, G. Degradation Characteristics of Straw and Washed Straw. *Thermochim. Acta* **2000**, *364*, 133–142. [CrossRef]

115. Carrier, M.; Neomagus, H.W.; Görgens, J.; Knoetze, J.H. Influence of Chemical Pretreatment on the Internal Structure and Reactivity of Pyrolysis Chars Produced from Sugar Cane Bagasse. *Energy Fuels* **2012**, *26*, 4497–4506. [CrossRef]
116. Ryu, H.W.; Kim, D.H.; Jae, J.; Lam, S.S.; Park, E.D.; Park, Y.K. Recent Advances in Catalytic Co-Pyrolysis of Biomass and Plastic Waste for the Production of Petroleum-like Hydrocarbons. *Bioresour. Technol.* **2020**, *310*, 123473. [CrossRef]
117. Boateng, A.A.; Mullen, C.A. Fast Pyrolysis of Biomass Thermally Pretreated by Torrefaction. *J. Anal. Appl. Pyrolysis* **2013**, *100*, 95–102. [CrossRef]
118. Zheng, A.; Zhao, Z.; Chang, S.; Huang, Z.; Wang, X.; He, F.; Li, H. Effect of Torrefaction on Structure and Fast Pyrolysis Behavior of Corncobs. *Bioresour. Technol.* **2013**, *128*, 370–377. [CrossRef]
119. Pandey, K.K.; Pitman, A.J. FTIR Studies of the Changes in Wood Chemistry Following Decay by Brown-Rot and White-Rot Fungi. *Int. Biodeterior. Biodegrad.* **2003**, *52*, 151–160. [CrossRef]
120. Singh, D.; Zeng, J.; Laskar, D.D.; Deobald, L.; Hiscox, W.C.; Chen, S. Investigation of Wheat Straw Biodegradation by Phanerochaete Chrysosporium. *Biomass Bioenergy* **2011**, *35*, 1030–1040. [CrossRef]
121. Yang, X.; Zeng, Y.; Ma, F.; Zhang, X.; Yu, H. Effect of Biopretreatment on Thermogravimetric and Chemical Characteristics of Corn Stover by Different White-Rot Fungi. *Bioresour. Technol.* **2010**, *101*, 5475–5479. [CrossRef]
122. Charisteidis, I.; Lazaridis, P.; Fotopoulos, A.; Pachatouridou, E.; Matsakas, L.; Rova, U.; Christakopoulos, P.; Triantafyllidis, K. Catalytic Fast Pyrolysis of Lignin Isolated by Hybrid Organosolv—Steam Explosion Pretreatment of Hardwood and Softwood Biomass for the Production of Phenolics and Aromatics. *Catalysts* **2019**, *9*, 935. [CrossRef]
123. Li, X.; Su, L.; Wang, Y.; Yu, Y.; Wang, C.; Li, X.; Wang, Z. Catalytic Fast Pyrolysis of Kraft Lignin with HZSM-5 Zeolite for Producing Aromatic Hydrocarbons. *Front. Environ. Sci. Eng. China* **2012**, *6*, 295–303. [CrossRef]
124. Bridgwater, A.V. Principles and Practice of Biomass Fast Pyrolysis Processes for Liquids. *J. Anal. Appl. Pyrolysis* **1999**, *51*, 3–22. [CrossRef]
125. Bridgwater, A.V.; Bridge, S.A. A Review of Biomass Pyrolysis and Pyrolysis Technologies. In *Biomass Pyrolysis Liquids Upgrading and Utilization*; Springer: Berlin/Heidelberg, Germany, 1991; pp. 11–92. [CrossRef]
126. Mamphweli, N.S.; Meyer, E.L. Implementation of the Biomass Gasification Project for Community Empowerment at Melani Village, Eastern Cape, South Africa. *Renew. Energy* **2009**, *34*, 2923–2927. [CrossRef]
127. Bridgwater, A.V.; Meier, D.; Radlein, D. An Overview of Fast Pyrolysis of Biomass. *Org. Geochem.* **1999**, *30*, 1479–1493. [CrossRef]
128. Krishna, B.B.; Biswas, B.; Kumar, J.; Singh, R.; Bhaskar, T. Role of Reaction Temperature on Pyrolysis of Cotton Residue. *Waste Biomass Valorization* **2016**, *7*, 71–78. [CrossRef]
129. Demirbas, A. Effect of Temperature on Pyrolysis Products from Four Nut Shells. *J. Anal. Appl. Pyrolysis* **2006**, *76*, 285–289. [CrossRef]
130. López, A.; de Marco, I.; Caballero, B.M.; Laresgoiti, M.F.; Adrados, A. Influence of Time and Temperature on Pyrolysis of Plastic Wastes in a Semi-Batch Reactor. *Chem. Eng. J.* **2011**, *173*, 62–71. [CrossRef]
131. Angin, D. Effect of Pyrolysis Temperature and Heating Rate on Biochar Obtained from Pyrolysis of Safflower Seed Press Cake. *Bioresour. Technol.* **2013**, *128*, 593–597. [CrossRef] [PubMed]
132. Chen, D.; Li, Y.; Cen, K.; Luo, M.; Li, H.; Lu, B. Pyrolysis Polygeneration of Poplar Wood: Effect of Heating Rate and Pyrolysis Temperature. *Bioresour. Technol.* **2016**, *218*, 780–788. [CrossRef] [PubMed]
133. Zhang, X.; Zhang, P.; Yuan, X.; Li, Y.; Han, L. Effect of Pyrolysis Temperature and Correlation Analysis on the Yield and Physicochemical Properties of Crop Residue Biochar. *Bioresour. Technol.* **2020**, *296*, 122318. [CrossRef] [PubMed]
134. Zhang, Y.; Deng, N.; Ling, J.; Xu, C. A New Pyrolysis Technology and Equipment for Treatment of Municipal Household Garbage and Hospital Waste. *Renew. Energy* **2003**, *28*, 2383–2393. [CrossRef]
135. Demirbaş, A.; Arin, G. An Overview of Biomass Pyrolysis. *Energy Sources* **2002**, *24*, 471–482. [CrossRef]
136. Itoh, T.; Fujiwara, N.; Iwabuchi, K.; Narita, T.; Mendbayar, D.; Kamide, M.; Niwa, S.; Matsumi, Y. Effects of Pyrolysis Temperature and Feedstock Type on Particulate Matter Emission Characteristics during Biochar Combustion. *Fuel Process. Technol.* **2020**, *204*, 106408. [CrossRef]
137. Sharifzadeh, M.; Sadeqzadeh, M.; Guo, M.; Borhani, T.N.; Murthy, N.V.S.N.; Cortada, M.; Wang, L.; Hallett, J.; Shah, N.; Berkeley, L.; et al. The Multi-Scale Challenges of Biomass Fast Pyrolysis and Bio-Oil Upgrading: Review of the State of Art and Future Research Directions. *Prog. Energy Combust. Sci.* **2019**, *71*, 1–80. [CrossRef]
138. Zhou, S.; Liang, H.; Han, L.; Huang, G.; Yang, Z. The Influence of Manure Feedstock, Slow Pyrolysis, and Hydrothermal Temperature on Manure Thermochemical and Combustion Properties. *Waste Manag.* **2019**, *88*, 85–95. [CrossRef]
139. Acocke, G.V.C.; Dick, C.M.; Hague, R.A.; Cooke, L.A.; Bridgwater, A.V. Comparison of Ablative and Fluid Bed Fast Pyrolysis Products: Yields and Analyses. In *Biomass for Energy and the Environment*; Elsevier Ltd.: Amsterdam, The Netherlands, 1997; Volume 3, pp. 1632–1637.
140. Zabaniotou, A.; Rovas, D.; Delivand, M.K.; Francavilla, M.; Libutti, A.; Cammerino, A.R.; Monteleone, M. Conceptual Vision of Bioenergy Sector Development in Mediterranean Regions Based on Decentralized Thermochemical Systems. *Sustain. Energy Technol. Assess.* **2017**, *23*, 33–47. [CrossRef]
141. Venderbosch, R.H.; Biomass, B.T.G.; Group, T. Fast Pyrolysis Technology Development. *Biofuels Bioprod. Biorefin.* **2010**, *4*, 178–208. [CrossRef]
142. Świechowski, K.; Liszewski, M.; Babelewski, P.; Koziel, J.A.; Białowiec, A. Fuel Properties of Torrefied Biomass from Pruning of Oxytree. *Data* **2019**, *4*, 55. [CrossRef]

143. Demirbas, A. Effect of Temperature on Pyrolysis Products from Biomass. *Energy Sources, Part A Recover. Util. Environ. Eff.* **2007**, *29*, 329–336. [CrossRef]
144. Xu, W.C.; Tomita, A. The Effects of Temperature and Residence Time on the Secondary Reactions of Volatiles from Coal Pyrolysis. *Fuel Process. Technol.* **1989**, *21*, 25–37. [CrossRef]
145. Liu, C.; Wang, H.; Karim, A.M.; Sun, J.; Wang, Y. Catalytic Fast Pyrolysis of Lignocellulosic Biomass. *Chem. Soc. Rev.* **2014**, *43*, 7594–7623. [CrossRef] [PubMed]
146. Rogers, J.G.; Brammer, J.G. Estimation of the Production Cost of Fast Pyrolysis Bio-Oil. *Biomass Bioenergy* **2012**, *36*, 208–217. [CrossRef]
147. Wang, J.; Ku, X.; Lin, J.; Yang, S. Impact of the Reactor Structure on Biomass Pyrolysis in Fluidized-Bed Reactors: A Coarse-Grained CFD-DEM Study. *Energy Fuels* **2021**, *35*, 10035–10050. [CrossRef]
148. Dhyani, V.; Bhaskar, T. Pyrolysis of Biomass. In *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels*; Academic Press: Cambridge, MA, USA, 2019; pp. 217–244. [CrossRef]
149. Xu, B.; Li, A. Effect of High-Pressure on Pine Sawdust Pyrolysis: Products Distribution and Characteristics. In Proceedings of the International Conference on Green Energy and Sustainable Development (GESD 2017), Chongqing, China, 27–28 May 2017; Volume 1864, p. 020116. [CrossRef]
150. Meier, D.; Faix, O. State of the Art of Applied Fast Pyrolysis of Lignocellulosic Materials a Review. *Bioresour. Technol.* **1999**, *68*, 71–77. [CrossRef]
151. Fletcher, C. *Computational Techniques for Fluid Dynamics*; Springer: Berlin/Heidelberg, Germany, 2012; Volume 1, pp. 1–46. [CrossRef]

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Waheed A. Rasaq, Charles Odilichukwu R. Okpala, Chinenye Adaobi Igwegbe, and Andrzej Białowiec, 2024. "Navigating Pyrolysis Implementation—A Tutorial Review on Consideration Factors and Thermochemical Operating Methods for Biomass Conversion." Materials 17(3), 1 – 44 doi: 10.3390/ma17030725

My contribution included:

Developing the concept and design of the study. I prepared the entire text of the article as well as Figures. During the review process, I made corrections to the text of the manuscript and prepared responses to the reviewers. I obtained funding for the publication of the manuscript.

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My contribution included: I participated in the conceptualization, data curation, formal analysis, investigation process, methodology, as well as writing—reviewing and editing the manuscript. During the review process, I made corrections to the text of the manuscript and responses to the reviewers.

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My contribution included:

Developing the concept and design of the study. I participated in the revision and supervision of the manuscript. I participated in the review process and the related modifications to the manuscript. I was also the corresponding author.

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Research article

Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste

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ABSTRACT

This study employs response surface methodology and a central composite design (CCD) to optimize hydrothermal treatment (HTT) conditions for the valorization of food waste (FW). Lab-scale pressure reactor-based HTT processes are investigated to detect the effects of temperature (220–340 °C) and resident time (90–260 min) on elemental composition and fatty acid recovery in the hydrothermal liquid. Central to the study is the identification of temperature as the primary factor influencing food waste conversion during the HTT process, showcasing its impact on HTT product yields. The liquid fraction, rich in saturated fatty acids (SFA), demonstrates a temperature-dependent trend, with higher temperatures favoring SFA recovery. Specifically, HTT at 340 °C in 180 min exhibits the highest SFA percentages, reaching up to 52.5 wt%. The study establishes HTT as a promising avenue for nutrient recovery, with the liquid fraction yielding approximately 95% at optimized conditions. Furthermore, statistical analysis using response surface methodology predicts the optimal achievable yields for hydrochar and hydrothermal liquid at 6.15% and 93.85%, respectively, obtained at 320 °C for 200 min.

1. Introduction

The disposal of food waste constitutes a significant global environmental challenge, arising primarily from the organic fraction of municipal solid and industrial waste streams (Avagyan, 2017; Grandhi and Appaiah Singh, 2016; Uçkun Kiran et al., 2014). China is responsible for approximately 19% of global food waste, equivalent to around 1.15 billion tons annually (Sheng and Song, 2019). Food waste in Europe accounts annually about 88 million tons, of which Poland occupies more than 10% (Jedzenia, 2018; Valta et al., 2019). In addition to them, the European economic zone alone produces meat-derived waste in the amount of 18 million tons per year (Kowalski and Krupa-Zuczek, 2007). The sky-rocketed attention on global food waste remains exacerbated by economic developments and increasing population. Both the Food and Agricultural Organization (FAO) of the United Nations and the World Bank understand that waste generation levels annually and globally would likely attain 2.2 billion tons (Su et al., 2020). On one hand, appropriately managing global food waste is increasingly challenging given the larger amounts annually generated from the food industry (Bhatt et al., 2018). On the other hand, the perspective of climate change and energy shortages points towards the increasing need for new ways to provide clean and sustainable energy (Avagyan, 2017, 2018; Rasaq et al., 2021, 2024; Santos Dalólio et al., 2017). The 17 United Nations Sustainable Development Goals (SDGs), introduced in 2015 and expected to be achieved by the end of 2030, have some aspects directly aimed at clean renewable energy and increasing waste recycling levels (Rosa, 2017). Given that the managing food waste research focus is shifting toward eco-friendly methods. Consequently, FW disposal in landfills has already been controlled in many countries. Traditional food waste management can include anaerobic digestion, combustion/composting, as well as direct land spreading (Avagyan, 2017, 2018; Hejna et al., 2022; Połomka and Jedrczak, 2020). Besides, hydrothermal treatment (HTT) could find a suitable place in food waste management, given its environment-friendly context of atmospheric emissions

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compared to other processes (Zabaniotou et al., 2017). HTT could be a low-cost and feasible energy-efficient process to valorize the digestate, and synergistically maximize nutrient recovery (Taylor and Demirbas, 2007). In particular, the HTT process can comprise operating conditions that involve carbonization (HTC) and liquefaction (HTL). The application of HTT can be considered advantageous over other treatment types, especially in the effective management of organic waste characterized by high moisture values (Avagyan, 2018; Hoekman et al., 2011; Lachos-Perez et al., 2022). In addition, HTT may be considered as a pretreatment step before microbial lipid production (Gao et al., 2022; Ma et al., 2018; Sikarwar et al., 2021). Interestingly, Ma and Co-workers reported the importance of lipids in co-fermentation for useful lipid production using *Rhodosporidium toruloides* (Ma et al., 2018). The presence of oil increases the production of organic acids like lactic acids that play a coordinated role in organic food waste to lipid production using microorganisms. pH additionally plays a crucial role in elemental extraction and lower pH was found to enhance phosphorous recovery (Oliver-Tomas et al., 2019).

Consequently, HTT of food waste may be a source of fatty acids that can be applied in a variety of sectors and applications. This demonstrates the need for further research in the thermal transformation of food waste. Indeed, there is a paucity of research on HTT treatment of food waste, specifically the impact on the physiochemical properties of hydrochar and liquid fraction. It can add to studies where process kinetic determination would model the HTT's energy balance of organic waste to elucidate optimum conditions of the target parameters (Helmi et al., 2021; Lu et al., 2015; Stępień et al., 2019; Zhou et al., 2015). Response surface methodology (RSM) can help optimize HTT conditions for food waste as influenced by several independent variables, via central composite design (Chelladurai et al., 2020). In particular, central composite design (CCD) in combination with RSM is considered a powerful tool to study, develop, and optimize several engineering processes (Anfar et al., 2020). Indeed, it appears as the better version of Box–Behnken design (BBD) that CCD constitutes fewer experimental numbers, reduces experimental errors, and equally helps in understanding the mechanism of the process. CCD is often considered more efficient for estimating model parameters compared to BBD. This is particularly true when a quadratic response surface is expected, as CCD includes additional points that improve the precision of parameter estimates. It includes both factorial points and axial points, allowing for the exploration of a broader region of the independent variable space. By optimizing the process parameters, RSM would predict outcomes via regression equation(s) engaging the interactive effects of temperature, resident time, hydrochar energy densification ratio, and liquid/mass yield (Marzbali et al., 2021; Toptas Tag et al., 2018; Udaya Prakash et al., 2022). The selected parameters involved in this study considered key aspects such as eco-friendliness, waste management, and best operating process, with the aim of obtaining good quality end products. More so, food waste, especially meat, comprises organic compounds and mineral salts, including a significant concentration of phosphorus, nitrogen, and potassium as essential nutrients (Sarrion et al., 2021; Zhao et al., 2018). However, the scarcity of these nutrients from natural sources makes it necessary to find new recovery pathways, especially phosphorus shortage may disrupt the whole world economy (Smol, 2019; Zhao et al., 2018). To supplement existing information, therefore, this current work sought to understand the potential of lab-scale pressure reactor-based HTT process to valorize food waste using the design of experiment approach. This study also aims to bridge this conceptual gap by delving into the nexus between the global food waste epidemic and the transformative capabilities of HTT. The link is grounded in the premise that an innovative approach to food waste management, such as HTT, not only addresses the environmental repercussions of waste but also unlocks the latent value within these discarded organic materials. In particular, the specific objectives include: a) the determination of hydrochar and liquid fraction yields as valuable resources, thereby contributing to the development of a regenerative economy, b) to investigate and optimize the critical parameters of the HTT process, including the determination of the operating conditions (temperature, resident time) effects on the HTT performance based on optimization, to enhance the yield of valuable compounds, with a specific emphasis on fatty acids, and c) validation of energy balance determination. These objectives will guide our exploration and analysis, shedding light on the transformative potential of hydrothermal treatment in addressing the global food waste challenge while fostering sustainable and circular solutions.

2. Materials and methods

2.1. *Materials*

In this study, 10 kg of fresh ground pork belly (PB), 5 kg of potatoes, and 5 kg of pumpkins were procured from a local grocery store. The decision to exclude actual food waste aimed to tackle challenges related to variability in composition, ensuring reproducibility and generalizability. Actual food waste often contains contaminants, making isolation difficult due to its diverse composition within collection points. To overcome these challenges, we opted for a controlled laboratory environment. Subsequently, the potatoes and pumpkins were ground using an electric grinder (Royal Catering, RCMZ-800, Wuppertal, Germany). The PB, potatoes, and pumpkins were separately homogenized using a drill (Bosch, model Professional GSB 16 RE, Gerlingen, Germany) with a mortar stirrer to ensure uniformity. The homogenized feedstocks were then divided into samples weighing 230 g each and stored in a freezer (Electrolux, model EC5231A0W, Stockholm, Sweden) at a temperature of −27 °C until further experiments.

2.2. *Design of Experiment Setup for HTT process*

The design of the experiment (DOE) was carried out to understand the influence of independent parameters (temperature and resident time) on dependent parameters [hydrochar (HC) and hydrothermal liquid (HL) yield and fatty acids]. The central composite design constituted a two-level factorial design (2^2) of two blocks carried out using Statgraphics Centurion 19 (Statgraphics Technologies Inc., Virginia, USA). The matrix of design and levels of independent parameters are given in Table 1.

The HTT process generated hydrochar mixed with a liquid fraction under varying process parameters (temperature, stirring rate, and resident time). Energy consumption during the process was measured. Subsequently, HTT products were separated through vacuum filtration. All data were comprehensively analyzed to determine the optimal conditions for treating PB in the HTT process.

2.3. *HTT process*

A sample of 220g of PB, potatoes, and pumpkins, once thawed, was placed in the feedstock vessel of the high-temperature high-pressure reactor (HPHT) (Büchi AG, Uster, Switzerland), which was then placed in the heating jacket, closed, and sealed. The speed of the stirrer was set to 120 rpm and the desired temperature inside the vessel was set. The HTT processes were carried out at five different temperatures of 220, 240, 280, 320, and 340 °C. After reaching a temperature of 5 °C lower than the set value, the process continued for 90, 120, 180, 240, and 260

Table 1
Operating conditions of independent parameters employed during DOE.

HTT parameters	Variable levels				
	−1.14	−1	0	1	1.14
Temperature (°C)	220	240	280	320	340
Resident Time (min)	90	120	180	240	260

min, respectively, (it was because of the PID temperature controller, which needs more time to heat the reactor for the last 5 °C). Each temperature was combined with each resident's time according to DOE to ensure repeatability.

After the specified time was achieved, the reactor was set to cool down. During the process, the energy consumption was recorded using a single-phase digital energy meter (Model SK-410, Starmeter Instruments Co., Ltd., Shenzhen, China). Additionally, during the process, the pressure was generated autogenously. After reaching the temperature of 40 °C during cooling, the reactor was turned off, the valve was opened to release pressure and the sample was removed from the vessel quantitatively using a plastic spoon. The sample was then weighed using a laboratory scale (Radwag, MA 50.R, Morawica, Poland). Liquid and solid products were separated by vacuum filtration (Rocker, ROCKER 300, Kaohsiung, Taiwan) and weighted (Radwag, MA 50.R, Morawica, Poland). The liquid part was placed into a plastic container and placed in the freezer (Electrolux, model EC5231A0W, Stockholm, Sweden) at a temperature of −27 °C for further analysis.

2.4. *Detection of fatty acids*

The measurement of fatty acid composition was achieved by using GC-MS. Total lipid was extracted following the procedures as described previously (Fărcaş et al., 2015). Lipids were derivatized into fatty acid methyl esters (FAMEs) following procedures described in a previous study (Nowacki et al., 2017). After that, the fatty acid profile was analyzed by using a gas chromatograph (GC6890) coupled with a mass spectrometer 5983 MS (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a quadrupole mass detector. Separation was performed in a capillary column HP-88 (0.25 mm × 100 m) filled with an 88:12 cyanopropyl-aryl poly-siloxane bed with a grain size of 0.2 μm. Helium (flow rate 1 mL min^{-1}) was used as the mobile phase and the sample was injected in the split mode at 4:1. Thus, the program was set with an initial temperature of 60 °C for 2 min, heating at 20 °C min^{-1} to reach 180 °C and 3 °C min^{-1} to reach 220 °C. The temperature was held for 15 min. The heating continued to reach 250 °C at a rate of 5 °C min^{-1}, and the temperature was held for 8 min. The spectra were identified using the algorithm of searching the National Institute of Standards and Technology (NIST) library (2008 version) (Folch et al., 1957; Nowacki et al., 2017).

2.5. *Statistical analyses*

Independent groups were compared using the Students' t-test in Statgraphics Centurion 19 (Statgraphics Technologies Inc., Virginia, USA), with statistical significance set at $p \leq 0.05$.

3. Results and discussion

3.1. *Selection of organic food waste product for HTT process*

Firstly, the HTT process was conducted on potatoes, PB, and pumpkin at 220g under different temperatures at 200, 240, and 280 °C. During the process, the resident time of the HTT process was maintained at 60 min. The increasing change of temperature in the reactor until it reached the threshold value of the selected temperature and the consequent increase in pressure was monitored through a digital Cam scanner. After the process, the weight of the feedstock had a reduction between 5 and 10%. The main obtained products of the HTT process were Hydrochar (HC) and Hydrothermal liquid (HL). The ratio of weights between HC and HL was represented in percentage in Table 2. In accordance with HC and HL content, the amounts varied within different temperatures, the higher the temperature the higher the HL content among all food waste samples. In consideration, at this point of the experiment, 280 °C had produced the best quantity of HL content.

Among different food waste, the highest amount of lipid recovered was at 280 °C except for pumpkin (Table 2). At this temperature, the highest quantity of lipid recovered was 3.4 ± 0.2% from the PB samples. The PB samples used in this experiment contain 65.59 ± 2.65% moisture, which proves that it is a suitable material for the HTT process. Feedstock with moisture content ranging between 60 and 90% appears to be ideal for this process (Kumar and Ankaram, 2019). The lipid content of PB samples after the HTT process constitutes fatty acids such as myristic acid, palmitoleic acid, stearic acid, palmitic acid, oleic acid, and linoleic acid (Table 2). Whereas potato and pumpkin HTT products had no presence of myristic acid and palmitoleic acid. In addition to them, among all samples, the highest quantity of oleic acid was present in PB. Considering the possible recovery of several fatty acids, PB samples were further assessed for optimum yield of HC, HL, and free fatty acids. Whereas the center point temperature was maintained at 280 °C of the optimization using the design of experiments (DOE) approach in the next step.

3.2. *Optimization of the parameters for hydrothermal treatment of pork belly*

In order to optimize HC and HL by (maximum) quantity, the DOE approach was employed. The influence of temperature and resident time was evaluated on HC and HL mass yield (%). In the design, 10 experiments (4 factorial points, 4 axial points, and 2 center points) were repeated randomly in 2 blocks to improve the significance, and the obtained results are presented in Table 3.

Among them, the maximal HL obtained was 95% (R6 and R11) and the maximal HC obtained was 7.3% (R12). Analyses of the results are presented in Fig. 1 using Pareto's charts (Fig. 1A–and C) to indicate the significance of the effecting factors. Surface plots (Fig. 1B–and D) indicate changes in HC and HL yields with the changes in temperature and

Table 2
Effect of varying temperature on yield of hydrochar, hydrothermal liquid, and fatty acids.

Feedstock	Tem (°C)	RT (min)	HC (%)	HL (%)	Lipid [%]	Yield of different fatty acids (%)					
						MY	POA	SA	PA	OA	LA
Potatoes	200	60	8.00	92.00	0.11 ± 0.03	ab	ab	36.67	46.14	7.14	10.05
	240	60	7.00	93.00	0.2 ± 0.05	ab	ab	36.68	47.31	6.65	9.36
	280	60	6.00	94.00	0.35 ± 0.16	ab	ab	21.24	28.10	14.73	35.93
Pork belly	200	60	7.50	92.50	2.58 ± 0.04	1.24	1.63	20.19	26.35	44.00	6.59
	240	60	7.00	93.00	3.3 ± 0.10	1.37	2.31	18.58	26.2	43.10	8.44
	280	60	6.00	94.00	3.4 ± 0.20	1.36	3.42	17.45	26.23	45.30	6.24
Pumpkin	200	60	8.00	92.00	0.38 ± 0.01	ab	ab	11.18	19.79	29.93	39.1
	240	60	7.00	93.00	0.16 ± 0.03	ab	ab	39.09	45.07	9.18	6.66
	280	60	6.00	94.00	0.12 ± 0.01	ab	ab	19.97	25.42	26.44	28.17

*Tem – temperature, RT – resident time, HC- hydrochar, HL-hydrothermal liquid, ab – absent, MY: myristic acid, POA: palmitoleic acid, SA: stearic acid, PA: palmitic acid, OA: oleic acid, LA: linoleic acid.

Table 3
Coded and numerical variable levels of the experiment including the obtained results.

HTT	Block	Temperature		Resident time		HC (%)	HL (%)
Factorial Points		Levels	°C	Levels	Min		
R1	1	1	320	1	240	6.0	94.0
R2	1	−1	240	−1	120	7.0	93.0
R3	1	−1	240	1	240	7.0	93.0
R4	1	1	320	−1	120	6.5	93.5
R5	2	1	320	−1	120	6.0	94.0
R6	2	1	320	1	240	5.0	95.0
R7	2	−1	240	−1	120	6.8	93.2
R8	2	−1	240	1	240	6.7	93.3
Axial Points							
R9	1	0	280	−1.14	90	6.0	94.0
R10	1	1.14	340	0	180	6.0	94.0
R11	1	0	280	1.14	260	5.0	95.0
R12	1	−1.14	220	0	180	7.3	92.7
R13	2	0	280	−1.14	90	5.9	94.1
R14	2	1.14	340	0	180	5.5	94.5
R15	2	0	280	1.14	260	5.7	94.3
R16	2	−1.14	220	0	180	7.0	93.0
Center Points							
R17	1	0	280	0	180	7.0	93.0
R18	1	0	280	0	180	6.0	94.0
R19	2	0	280	0	180	6.5	93.5
R20	2	0	280	0	180	7.0	93.0

*R – experiment number, HC- hydrochar, and HL-hydrothermal liquid.

resident time across the experiments. Upon examining the Pareto chart, a distinct statistical relationship emerges notably a linear correlation with temperature and a quadratic association with resident time specific to hydrothermal liquid (HL) yield (Fig. 1C and D). Conversely, an equally robust yet negative correlation is observed for hydrochar (HC) yield (Fig. 1A and B). This intricate pattern sheds light on the interplay between temperature and resident time in the hydrothermal treatment (HTT) process, specifically in the formation of HC and HL. The observed dynamics align with prior research on HTT processes, revealing a temperature range of 180–300 °C and a corresponding resident time of 30–180 min. These parameters have been empirically linked to the production of quantifiable hydrochar (HC) in the range of 40–70% (Hejna et al., 2022). This substantiates the significance of temperature-resident time synergy in influencing the yield of HC and HL, providing valuable insights into optimizing HTT processes for enhanced outcomes.

The two-way interaction (X_{AB}) of temperature and resident time was not significant on either HC or HL yields (Fig. 1A–and C). Considering their level of significance, HC yield mass was modeled in a quadratic polynomial equation (R^2 value: 0.94; R^2 adjusted value: 0.91) corresponding to obtained correlation values (Eq. (1)). The model representation was further examined for HL yield mass, representing where quadratic interaction of time (X_B^2) and linear effect of temperature (X_A) and time (X_B) had significant impact on HL yield mass and the equation (R^2 value: 0.91; R^2 adjusted value: 0.89) is presented based on them (Eq. (2)).

$$HC\ (\%) = 2.4958 + 0.0070\ (X_A) + 0.0578\ (X_B) - 0.0001\ (X_B)^2 \qquad (1)$$

$$HL\ (\%) = 97.5042 - \ 0.0070\ (X_A)\ - 0.0578\ (X_B)\ + 0.0001\ (X_B)^2 \qquad (2)$$

The optimal yields for HC and HL were projected at 6.15% and 93.85%, respectively at 320 °C for 200 min. To validate these predictions, optimization was conducted in triplicate at above said temperature and resident time. Consequently, HC and HL were obtained at 6 ± 1% and 94 ± 1%, respectively. Most interestingly, to complete the HTT process, the PB was submitted to 340 °C temperature at 260 min resident time to digest HC and maximize HL yield. To recover and hydrolyze fatty acids, the obtained HL fractions were subsequently examined. Herein, the theoretical optimization or practical value based on software was very near to the experimental optimization value obtained for HL yield. This could be explained by the minor loss of volatile compounds exhibited in PB samples. Similar fluctuations in HL yield have been documented in previous studies (El Ouadrhiri et al., 2021). Thus, to define the main character changes during DOE experiments (R1 – 20) and to explain specific properties and degree of carbonization further analyses were carried out.

3.3. *Fatty acid recovery from pork belly during hydrothermal treatment process*

European economic zone alone produces meat-derived waste in the amount of 18 million tons per year (Kowalski and Krupa-Zuczek, 2007). Meat waste consists of beef, pig, and poultry which requires proper management as part of sustainability and circular economy development. Many organs in meats contain more fatty acids which could be utilized in pharmaceutical and chemical industry sectors (Chaiwang et al., 2012). Therefore, reducing meat losses and wastage is widely recognized as a way to solve the challenges of global warming, food

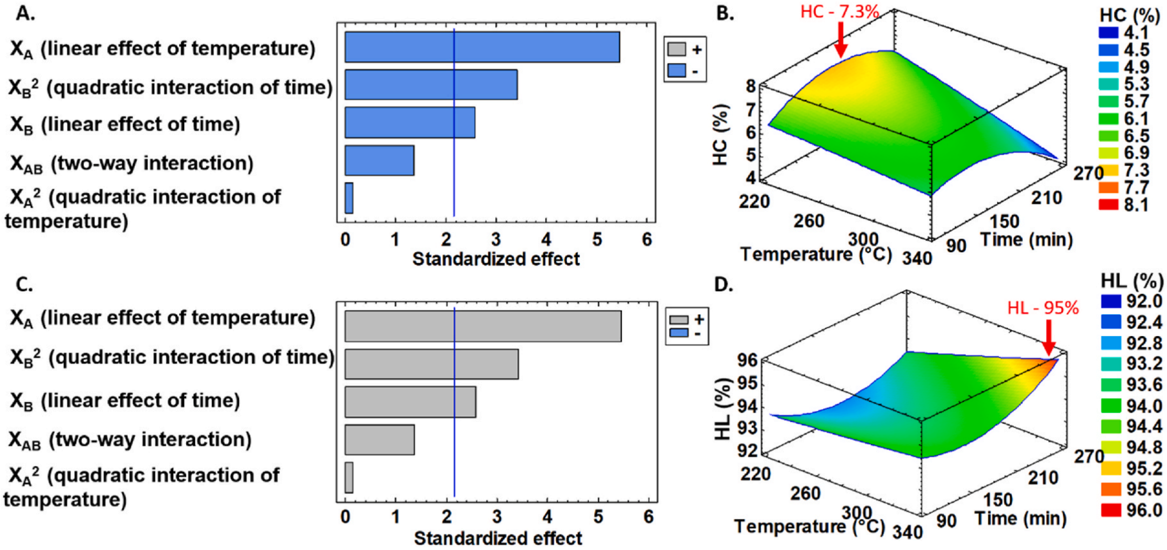

Fig. 1. Optimization of hydorchar (HC) and hydrothermal liquid (HL) fractions of HTT process. (A–B) Pareto chart and surface plot explaining the significant effecting factors and yields of HC. (C–D) Pareto chart and surface plot explaining the significant effecting factors and yields of HL.

security, access to food for those in need, and the protection of natural resources and ecosystems. Based on the variable levels (Table 3), 4 different factorial (R2 – 4, R6) and 4 axial (R9 – 12) points, and a center point (R17) were randomly selected to represent an all-optimization design. The resulting HL fatty acids profile is given in Table 4. Abundantly, they contain saturated fatty acids (SFA) including butyric (C4:0), caproic (C6:0) capric, caprylic (C8:0), lauric (C12:0), and palmitic (C16:0) acids.

As in Fig. 2. SFA in total, dominated with the highest percentages in all different operating conditions tested with 52.5, 45.8, and 32.5 wt% for HTT at (340, 280, and 220 °C in 180 min) respectively, this can be concluded that HTT at higher temperatures with 180 min were more favorable to SFA. Herein, unsaturated fatty acids (UFA) comprise polyunsaturated fatty acids (PUFA) with lower amounts compared to the other fatty acids type, containing about 2.1, 12.1, and 17.3 wt% concerning the above HTT conditions (Fig. 2). Therefore, this shows that the HTT process at low temperatures appears more favorable, and monounsaturated fatty acids (MUFA) were also present, including; oleic acid (C18:1 n-9) with 42.4, 49.6, and 47.5 wt% concerning the above selected HTT conditions. With this regard, MUFA quantity slightly decreased with increasing carbonization temperature. In order to maximize the SFA from the liquid fraction of the current study feedstock, higher HTT conditions such as temperature at 340 °C and resident time of 180 min are deemed suitable for PB.

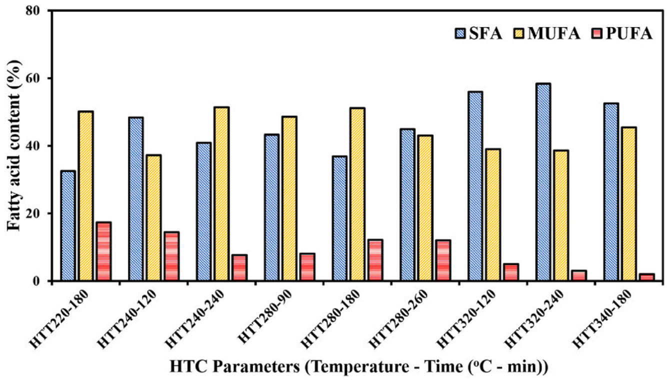

Fig. 2. Major fatty acid profile in the hydrothermal liquid fraction of the HTT process. SFA-saturated fatty acids; MUFA-monounsaturated fatty acids; and PUFA-polyunsaturated fatty acid.

3.4. *Hydrothermal carbonization performance and efficiency*

To understand the energy utilized in each experiment, HTT process energy usage was determined through the total electrical energy consumption (MJ) and relative electrical energy consumption (MJ x g^{-1}), as presented in Fig. 3. For emphasis, total electrical energy consumption (MJ) involves the direct measurement of electricity consumed by the HTT reactor, and its utilization per HL mass is further provided by the

Table 4
Fatty acid profile of selected hydrothermal liquid samples.

Fatty Acids	Selected hydrothermal liquid samples								
	R2 (240 °C/ 120 min)	R3 (240 °C/ 240 min)	R4 (320 °C/ 120 min)	R6 (320 °C/ 240 min)	R17 (280 °C/ 180 min)	R12 (220 °C/ 180 min)	R9 (280 °C/ 90 min)	R11 (280 °C/ 260 min)	R10 (340 °C/ 180 min)
C4:0	n.d	n.d	0.039	0.053	n.d	n.d	n.d	0.047	0.100
C6:0	n.d	n.d	0.052	0.076	n.d	n.d	n.d	0.104	0.166
C8:0	n.d	n.d	0.148	0.175	n.d	n.d	n.d	n.d	0.363
C10:0	n.d	n.d	0.065	0.068	n.d	0.051	n.d	0.057	0.091
C12:0	n.d	n.d	0.110	n.d	n.d	n.d	n.d	n.d	n.d
C12:1	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
C13:0	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
C14:0	2.528	1.338	1.764	2.791	1.415	2.550	5.823	4.406	2.780
C15:0	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
C16:0	25.419	22.987	31.731	31.883	22.877	17.810	25.840	24.832	28.470
C16:1 (n-7)	3.105	3.608	0.901	1.566	1.435	1.510	2.229	2.659	3.020
C17:0	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
C18:0	20.374	16.597	22.072	23.271	12.488	11.980	14.550	15.493	20.860
18:1 (n-9)	33.367	47.476	38.046	37.034	45.661	47.510	47.480	40.215	42.390
18:2 (n-6)	14.132	7.708	5.075	3.086	12.125	14.938	8.100	12.012	2.080
18:3 (n-3)	0.142	n.d	n.d	n.d	n.d	0.922	n.d	n.d	n.d
C20:0	n.d	n.d	n.d	n.d	n.d	0.120	n.d	n.d	n.d
20:1 (n-9)	0.777	0.289	n.d	n.d	n.d	1.141	n.d	0.177	n.d
20:2 (n-6)	0.159	n.d	n.d	n.d	n.d	0.732	n.d	n.d	n.d
20:4 (n-6)	n.d	n.d	n.d	n.d	n.d	0.739	n.d	n.d	n.d
20:5 (n-3)	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
22:6 (n-3)	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
SFA	48.320	40.922	55.979	58.316	n.d	32.510	43.300	44.938	52.510
MUFA	37.248	51.372	38.947	38.599	n.d	50.159	48.590	43.050	45.410
PUFA	14.432	7.708	5.075	3.086	n.d	17.330	8.100	12.012	2.090

*R2 (°C/min) – R17 (°C/min) - individual HTT process number with temperature and resident time; Butyric (C4:0); Caproic (C6:0); Caprylic (C8:0); Capric (C10:0); Lauric (C12:0); Lauroleic (C12:1); Tridecylic (C13:0); Myristic (C14:0); Pentadecylic (C15:0); Palmitic (C16:0); Palmitoleic (C16:1 (n-7); Margaric (C17:0); Stearic (C18:0); Oleic (18:1 (n-9); Linoleic (18:2 (n-6); Alpha-linolenic acid (ALA) (18:3 (n-3); Arachidic (C20:0); Eicosenoic (20:1 (n-9); Eicosadienoic (20:2 (n-6); Arachidonic (AA) (20:4 (n-6); Eicosapentaenoic acid (EPA, Timnodonic acid (20:5 (n-3); and, Docosahexaenoic (DHA, Cervonic (22:6 (n-3). SFAs-saturated fatty acids; MUFAs-monounsaturated fatty acids; PUFAs-polyunsaturated fatty acids; n.d (not detected).

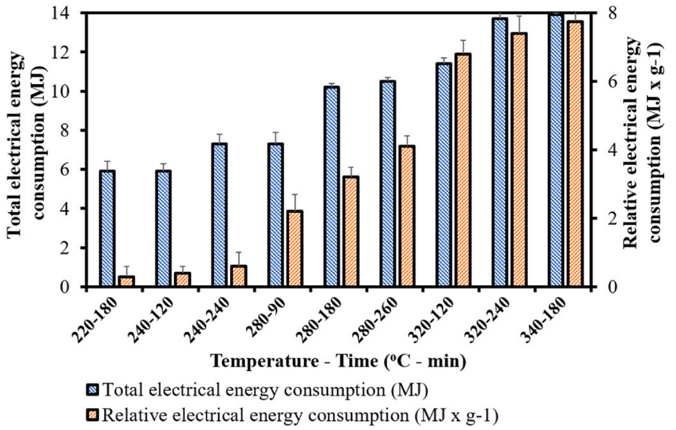

Fig. 3. Total electrical energy consumption (MJ) and relative electrical energy consumption of the HTT process in relation to the mass of liquid obtained after the process.

relative electrical energy consumption (MJ x g^{-1}). Results show electricity usage tends to increase with both temperature and resident time, reaching 7.7 MJ × g^{-1} for liquid fraction obtained at 340 °C in 180 min while the lowest electricity usage was observed at 220 °C in 180 min with 0.2 MJ × g^{-1}. More so, the electrical energy result showed a similar character, where 6 MJ × g^{-1} was observed at 220 °C in 180 min and maximum at 340 °C in 180 min with 14 MJ × g^{-1}. It is evident that the higher the operating parameters (temperature and resident time), the higher the energy consumption (Hejna et al., 2022). HL mass yield (MY), increased over time, for instance, 93.5% (R4) and 95% (R6) were observed at 320 °C in 120 and 240 min respectively, the MY increased with the process temperature in most cases, and the obtained result showed that 92.7% (R12) and 94.5% (R14) at 220 and 340 °C in 180 min respectively.

To highlight the dynamic changes in pressure under different HTT operating conditions, shedding light on the intricate relationship between temperature, resident time, and pressure during the process Fig. 4. These insights are invaluable for optimizing the process parameters to achieve the desired yield, quality, and efficiency in HTT products, all of which contribute to the sustainable management of food waste resources. The selected graphs were chosen based on CCD as follows: **(A):** 320 °C - 240 min, (**B**): 240 °C - 240 min, **(C):** 240 °C - 120 min, **(D):** 280 °C - 180 min, **(E):** 280 °C - 260 min, **(F):** 280 °C - 90 min. The pressure value depends on the set temperature point, which demonstrates that higher temperature led to higher generated pressure inside the HTT reactor, for instance, at 320 °C - 240 min with 115 bar, and 20 bar at 240 °C - 240 min while the amount of produced gas resulted from the decomposition of the processed material. Notably, the resident time did not lead to a considerable HC and HL yield change, which can be seen in Fig. 1. The liquid yield decreased at the low temperature and time by 2–2.5% while the solid increased. Herein, the HTT process at 320 and 340 °C with respective resident times 180, 240, and 260 min

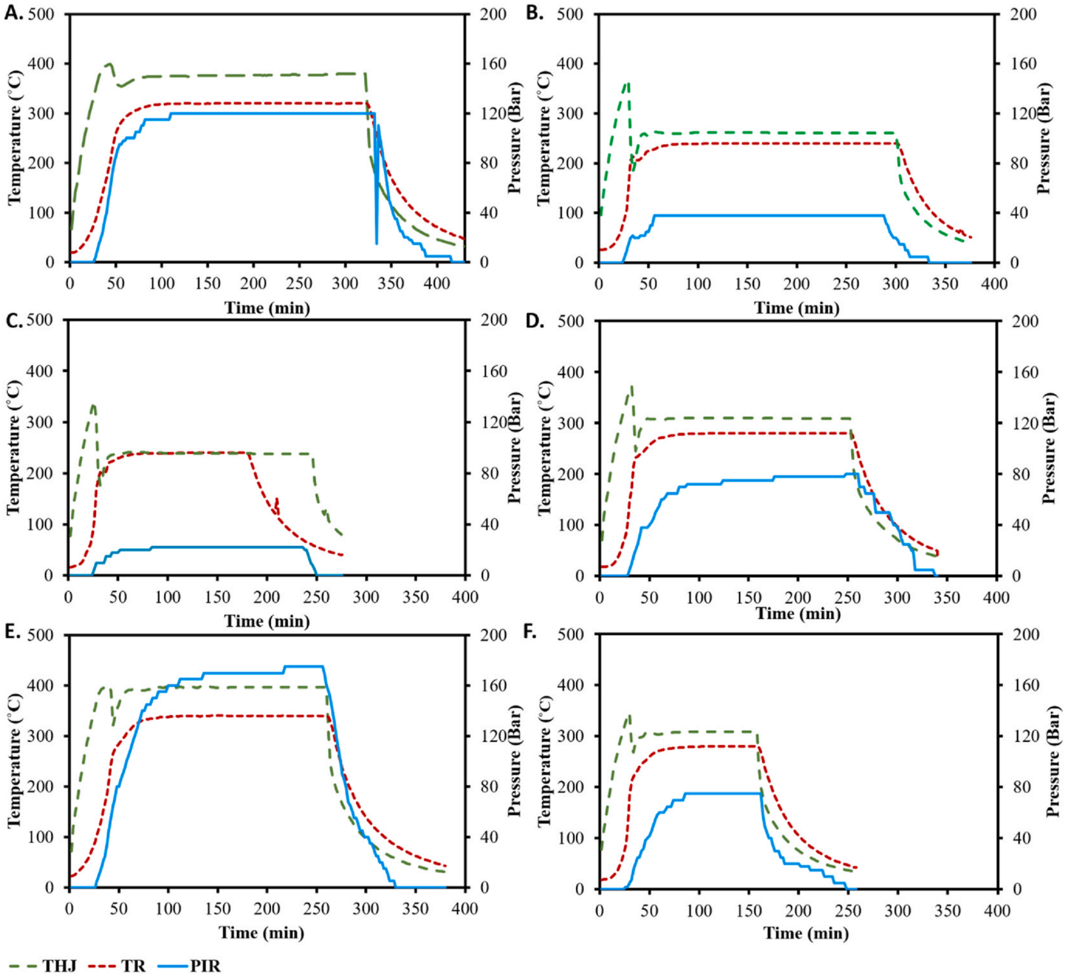

Fig. 4. (A–F) Change in pressure in connection with the main factors affecting the reactor during optimization. (A): R1 320 °C - 240 min, (B): R3 240 °C - 240 min, (C): R2 240 °C - 120 min, (D): R17 280 °C - 180 min, (E): R11 280 °C - 260 min, (F): R9 280 °C - 90 min respectively. THJ: temperature inside the heating jacket, TR: temperature of the reactor, and PIR: pressure inside the reactor.

showed the maximum liquid yield (best value = 95%), while the maximum solid yield (best value = 7.3%) observed at 220, 240, and 280 °C with respective resident time of 120, 180, 240 min. In this situation, both cases of increase and decrease are similar to some workers' findings (Hejna et al., 2022; Kantarli et al., 2016; Wilk et al., 2021). The observed yield may be induced by the decarboxylation process and the formation of organic compounds soluble in water.

4. Conclusion

The current study shows that both the process's temperature and resident time had varying impacts on HTT products. Briefly, regarding the liquid fraction, saturated fatty acids (SFA) in total, dominated with the highest percentages in all different operating conditions tested with 52.5, 45.8, and 32.5 wt% for HTT at (340, 280, and 220 °C in 180 min) respectively. This can be concluded that HTT at higher temperatures was more favorable for SFA recovery. Hence, the findings from this study strongly suggest that the liquid fraction produced through hydrothermal treatment possesses significant potential for effective utilization in chemical production applications such as biological treatment and biogas production.

Moreover, this research contributes to the broader understanding of hydrochar and liquid fraction production, which can be considered as vital components of a circular economy. Through systematic exploration and optimization of critical parameters, with a specific emphasis on fatty acids, the study advances the sustainable production of valuable resources. These resources hold promise for applications across various industries, promoting resource efficiency and reducing reliance on traditional raw materials. The findings of this current study reiterate the pivotal role of HTT in waste valorization, not only aligning with circular economy principles but also charting a sustainable course toward enhanced resource efficiency. Future research on a larger scale is recommended to delve deeper into energy consumption reduction and maximize the efficiency of food waste utilization in the HTT process, providing further insights that would contribute to a more sustainable and efficient circular economy.

While the hydrothermal liquid predominantly contains fatty acids, hydrochar, the solid fraction, also plays a role in the overall recovery process. The hydrochar obtained at different HTT conditions contributes to the overall yield of fatty acids. The connection between hydrochar and fatty acids lies in the initial organic composition of the food waste, which undergoes carbonization and transformation during the HTT process. The recovery and distribution of fatty acids within the hydrothermal liquid and hydrochar fractions illuminate the dynamic interplay between process parameters and product composition. This profound knowledge enriches the optimization strategies proposed in this study, reinforcing the potential of HTT as a sustainable solution for food waste valorization.

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CRediT authorship contribution statement

Waheed A. Rasaq: Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Vaikunthavasan Thiruchenthooran:** Writing – original draft, Validation, Formal analysis. **Paweł Telega:** Methodology. **Łukasz Bobak:** Writing – review & editing, Investigation, Data curation. **Chinenye Adaobi Igwegbe:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Formal analysis. **Andrzej Białowiec:** Writing – review & editing, Supervision, Project administration, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

Anfar, Z., Ait Ahsaine, H., Zbair, M., Amedlous, A., Ait El Fakir, A., Jada, A., El Alem, N., 2020. Recent trends on numerical investigations of response surface methodology for pollutants adsorption onto activated carbon materials: a review. Crit. Rev. Environ. Sci. Technol. 50, 1043–1084. https://doi.org/10.1080/10643389.2019.1642835.

Avagyan, A., 2018. Algae to Energy and Sustainable Development. Technologies, Resources, Economics and System Analyses. New Design of Global Environmental Policy and Live Conserve Industry. Amazon.

Avagyan, A.B., 2017. Environmental building policy by the use of microalgae and decreasing of risks for Canadian oil sand sector development. Environ. Sci. Pollut. Res. 24, 20241–20253. https://doi.org/10.1007/s11356-017-9864-x.

Bhatt, D., Shrestha, A., Dahal, R.K., Acharya, B., Basu, P., MacEwen, R., 2018. Hydrothermal carbonization of biosolids from Waste water treatment plant. Energies 11, 1–10. https://doi.org/10.3390/en11092286.

Chaiwang, N., Jaturasitha, S., Sringarm, K., Bunmee, T., Chomchai, N., Prakotrat, D., Pugdeethai, K., Chaichaum, W., Wicke, M., 2012. Comparison of fatty acid composition between white Lamphun and Brahman crossbred cattle raised with fresh pangola grass. Chiang Mai Univ. J. Nat. Sci. 11, 303–307.

Chelladurai, S.J.S., Murugan, K., Ray, A.P., Upadhyaya, M., Narasimharaj, V., Gnanasekaran, S., 2020. Optimization of process parameters using response surface methodology: a review. Mater. Today Proc. 37, 1301–1304. https://doi.org/10.1016/j.matpr.2020.06.466.

El Ouadrhiri, F., Elyemni, M., Lahkimi, A., Lhassani, A., Chaouch, M., Taleb, M., 2021. Mesoporous carbon from optimized date Stone hydrochar by catalytic hydrothermal carbonization using response surface methodology: application to dyes adsorption. Int. J. Chem. Eng. 2021 https://doi.org/10.1155/2021/5555406.

Fărcaş, A.C., Socaci, S.A., Dulf, F.V., Tofană, M., Mudura, E., Diaconeasa, Z., 2015. Volatile profile, fatty acids composition and total phenolics content of brewers' spent grain by-product with potential use in the development of new functional foods. J. Cereal Sci. 64, 34–42. https://doi.org/10.1016/j.jcs.2015.04.003.

Folch, J., Lees, M., Sloane Stanley, G.H., 1957. A simple method for the isolation and purification of total lipides from animal tissues. J. Biol. Chem. 226, 497–509. https://doi.org/10.1016/s0021-9258(18)64849-5.

Gao, Z., Ma, Y., Liu, Y., Wang, Q., 2022. Waste cooking oil used as carbon source for microbial lipid production: promoter or inhibitor. Environ. Res. 203, 111881 https://doi.org/10.1016/j.envres.2021.111881.

Grandhi, B., Appaiah Singh, J., 2016. What a waste! A study of food wastage behavior in Singapore. J. Food Prod. Market. 22, 471–485. https://doi.org/10.1080/10454446.2014.885863.

Hejna, M., Świechowski, K., Rasaq, W.A., Białowiec, A., 2022. Study on the effect of hydrothermal carbonization parameters on fuel properties of chicken manure hydrochar. Materials 15, 2022–2023. https://doi.org/10.3390/ma15165564.

Helmi, M., Tahvildari, K., Hemmati, A., Aberoomand azar, P., Safekordi, A., 2021. Phosphomolybdic acid/graphene oxide as novel green catalyst using for biodiesel production from waste cooking oil via electrolysis method: optimization using with response surface methodology (RSM). Fuel 287. https://doi.org/10.1016/j.fuel.2020.119528, 119528.

Hoekman, S.K., Broch, A., Robbins, C., 2011. Hydrothermal carbonization (HTC) of lignocellulosic biomass. Energy Fuel. 25, 1802–1810. https://doi.org/10.1021/ef101745n.

Jedzenia, N.I.E.M., 2018. Polskich Banków Żywności.

Kantarli, I.C., Kabadayi, A., Ucar, S., Yanik, J., 2016. Conversion of poultry wastes into energy feedstocks. Waste Manag. 56, 530–539. https://doi.org/10.1016/j.wasman.2016.07.019.

Kowalski, Z., Krupa-Zuczek, K., 2007. A model of the meat waste management. Pol. J. Chem. Technol. 9, 91–97. https://doi.org/10.2478/v10026-007-0098-4.

Kumar, S., Ankaram, S., 2019. Waste-to-energy model/tool presentation, Current Developments in Biotechnology and Bioengineering: Waste Treatment Processes for Energy Generation. Elsevier B.V. https://doi.org/10.1016/B978-0-444-64083-3.00012-9.

Lachos-Perez, D., César Torres-Mayanga, P., Abaide, E.R., Zabot, G.L., De Castilhos, F., 2022. Hydrothermal carbonization and Liquefaction: differences, progress, challenges, and opportunities. Bioresour. Technol. 343, 126084 https://doi.org/10.1016/j.biortech.2021.126084.

Lu, Y., Levine, R.B., Savage, P.E., 2015. Fatty acids for nutraceuticals and biofuels from hydrothermal carbonization of microalgae. Ind. Eng. Chem. Res. 54, 4066–4071. https://doi.org/10.1021/ie503448u.

Ma, X., Gao, Z., Gao, M., Ma, Y., Ma, H., Zhang, M., Liu, Y., Wang, Q., 2018. Microbial lipid production from food waste saccharified liquid and the effects of compositions. Energy Convers. Manag. 172, 306–315. https://doi.org/10.1016/j.enconman.2018.07.005.

Marzbali, M.H., Kundu, S., Halder, P., Patel, S., Hakeem, I.G., Paz-Ferreiro, J., Madapusi, S., Surapaneni, A., Shah, K., 2021. Wet organic waste treatment via hydrothermal processing: a critical review. Chemosphere 279, 130557. https://doi.org/10.1016/j.chemosphere.2021.130557.

Nowacki, D., Martynowicz, H., Skoczyńska, A., Wojakowska, A., Turczyn, B., Bobak, Ł., Trziszka, T., Szuba, A., 2017. Lecithin derived from ω-3 PUFA fortified eggs decreases blood pressure in spontaneously hypertensive rats. Sci. Rep. 7, 1–11. https://doi.org/10.1038/s41598-017-12019-w.

Oliver-Tomas, B., Hitzl, M., Owsianiak, M., Renz, M., 2019. Evaluation of hydrothermal carbonization in urban mining for the recovery of phosphorus from the organic fraction of municipal solid waste. Resour. Conserv. Recycl. 147, 111–118. https://doi.org/10.1016/j.resconrec.2019.04.023.

Połomka, J., Jedrczak, A., 2020. Potential ofmineral fraction in compost-like-output, methods of its obtaining and the possibility of using it in the context of circular economy. Materials 13. https://doi.org/10.3390/ma13133023.

Rasaq, W.A., Golonka, M., Scholz, M., Białowiec, A., 2021. Opportunities and challenges of high-pressure fast pyrolysis of biomass: a review. Energies 14, 1–20. https://doi.org/10.3390/en14175426.

Rasaq, W.A., Okpala, C.O.R., Igwegbe, C.A., Białowiec, A., 2024. Navigating pyrolysis implementation—a tutorial review on consideration factors and thermochemical operating methods for biomass conversion. Materials 17 (3), 725. https://doi.org/10.3390/ma17030725.

Transforming our world: The 2030 agenda for sustainable development. In A new era in global health, 2017, pp. 529–567. https://doi.org/10.1891/9780826190123.ap02.

Santos Dalólio, F., da Silva, J.N., Carneiro de Oliveira, A.C., Ferreira Tinôco, I. de F., Christiam Barbosa, R., Resende, M. de O., Teixeira Albino, L.F., Teixeira Coelho, S., 2017. Poultry litter as biomass energy: a review and future perspectives. Renew. Sustain. Energy Rev. 76, 941–949. https://doi.org/10.1016/j.rser.2017.03.104.

Sarrion, A., Diaz, E., de la Rubia, M.A., Mohedano, A.F., 2021. Fate of nutrients during hydrothermal treatment of food waste. Bioresour. Technol. 342, 125954 https://doi.org/10.1016/j.biortech.2021.125954.

Sheng, Y., Song, L., 2019. Agricultural production and food consumption in China: a long-term projection. China Econ. Rev. 53, 15–29. https://doi.org/10.1016/j.chieco.2018.08.006.

Sikarwar, V.S., Pohořelý, M., Meers, E., Skoblia, S., Moško, J., Jeremiáš, M., 2021. Potential of coupling anaerobic digestion with thermochemical technologies for waste valorization. Fuel 294. https://doi.org/10.1016/j.fuel.2021.120533.

Smol, M., 2019. The importance of sustainable phosphorus management in the circular economy (CE) model : the Polish case study. J. Mater. Cycles Waste Manag. 21, 227–238. https://doi.org/10.1007/s10163-018-0794-6.

Stępień, P., Pulka, J., Serowik, M., Białowiec, A., 2019. Thermogravimetric and calorimetric characteristics of alternative fuel in terms of its use in low-temperature pyrolysis. Waste and Biomass Valorization 10, 1669–1677. https://doi.org/10.1007/s12649-017-0169-6.

Su, Y., Liu, L., Zhang, S., Xu, D., Du, H., Cheng, Y., Wang, Z., Xiong, Y., 2020. A green route for pyrolysis poly-generation of typical high ash biomass, rice husk: effects on simultaneous production of carbonic oxide-rich syngas, phenol-abundant bio-oil, high-adsorption porous carbon and amorphous silicon dioxide. Bioresour. Technol. 295, 122243 https://doi.org/10.1016/j.biortech.2019.122243.

Taylor, P., Demirbas, A., 2007. Production of gasoline and diesel fuels from bio-materials 753–760. https://doi.org/10.1080/00908310500281288.

Toptas Tag, A., Duman, G., Yanik, J., 2018. Influences of feedstock type and process variables on hydrochar properties. Bioresour. Technol. 250, 337–344. https://doi.org/10.1016/j.biortech.2017.11.058.

Uçkun Kiran, E., Trzcinski, A.P., Ng, W.J., Liu, Y., 2014. Bioconversion of food waste to energy: a review. Fuel 134, 389–399. https://doi.org/10.1016/j.fuel.2014.05.074.

Udaya Prakash, J., Sivaprakasam, P., Jebarose Juliyana, S., Ananth, S., Sarala Rubi, C., Divya Sadhana, A., 2022. Multi-objective optimization using grey relational analysis for wire EDM of aluminium matrix composites. Mater. Today Proc. https://doi.org/10.1016/j.matpr.2022.09.415.

Valta, K., Sotiropoulos, A., Malamis, D., Kosanovic, T., Antonopoulou, G., Alexandropoulou, M., Jonuzay, S., Lyberatos, G., Loizidou, M., 2019. Assessment of the effect of drying temperature and composition on the biochemical methane potential of in-house dried household food waste. Waste Manag. Res. 37, 461–468.

Wilk, M., Śliz, M., Gajek, M., 2021. The effects of hydrothermal carbonization operating parameters on high-value hydrochar derived from beet pulp. Renew. Energy 177, 216–228. https://doi.org/10.1016/j.renene.2021.05.112.

Zabaniotou, A., Rovas, D., Delivand, M.K., Francavilla, M., Libutti, A., Cammerino, A.R., Monteleone, M., 2017. Conceptual vision of bioenergy sector development in Mediterranean regions based on decentralized thermochemical systems. Sustain. Energy Technol. Assessments 23, 33–47. https://doi.org/10.1016/j.seta.2017.09.006.

Zhao, X., Becker, G.C., Faweya, N., Correa, C.R., Yang, S., Xie, X., 2018. Fertilizer and Activated Carbon Production by Hydrothermal Carbonization of Digestate, pp. 423–436.

Zhou, H., Long, Y.Q., Meng, A.H., Li, Q.H., Zhang, Y.G., 2015. Thermogravimetric characteristics of typical municipal solid waste fractions during co-pyrolysis. Waste Manag. 38, 194–200. https://doi.org/10.1016/j.wasman.2014.09.027.

Appendix No. 3

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STATEMENT

I hereby declare that in the publication:

Waheed A. Rasaq, Vaikunthavasan Thiruchenthooran, Paweł Telega, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. "Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste". Journal of Environmental Management 357, 1 – 8 doi: 10.1016/j.jenvman.2024.120722

My contribution included:

Developing the concept and design of the study, in particular, the methodology of measurements. I prepared the text of the entire article, including the introduction part, description of the methodology, materials, analysis, and description of the results with discussion and conclusions. I participated in the preparation of the figures and tables included in the manuscript. I obtained funds for the publication of the article.

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Waheed A. Rasaq, Vaikunthavasan Thiruchenthooran, Paweł Telega, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. "Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste". Journal of Environmental Management 357, 1 – 8 doi: 10.1016/j.jenvman.2024.120722

My contribution included:

I participated in writing – review & editing, writing – original draft, validation, and formal analysis of the manuscript.

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STATEMENT

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Waheed A. Rasaq, Vaikunthavasan Thiruchenthooran, Paweł Telega, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. "Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste". Journal of Environmental Management 357, 1 – 8 doi: 10.1016/j.jenvman.2024.120722

My contribution included:
I participated in methodology and investigation during the experimental work of the manuscript.

24.05.2024 Paweł Telega
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Waheed A. Rasaq, Vaikunthavasan Thiruchenthooran, Paweł Telega, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. "Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste". Journal of Environmental Management 357, 1 – 8 doi: 10.1016/j.jenvman.2024.120722

My contribution included:

I participated in writing – reviewing & editing. Investigation, and Data curation analysis of fatty acids results in the manuscript.

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STATEMENT

I hereby declare that in the publication:

Waheed A. Rasaq, Vaikunthavasan Thiruchenthooran, Paweł Telega, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. "Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste". Journal of Environmental Management 357, 1 – 8 doi: 10.1016/j.jenvman.2024.120722

My contribution included:

I participated in writing – review & editing, writing – the original draft, visualization, validation, supervision, and formal analysis of the manuscript.

14.06.2024
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STATEMENT

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Waheed A. Rasaq, Vaikunthavasan Thiruchenthooran, Paweł Telega, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, 2024. "Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste". Journal of Environmental Management 357, 1 – 8 doi: 10.1016/j.jenvman.2024.120722

My contribution included:

Developing the concept and design of the study, including the selection of HTC parameters such as temperature and time. I participated in the revision and supervision of the manuscript. I participated in the review process. Also, I served as the corresponding author.

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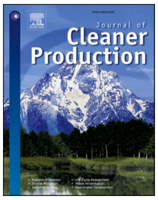

Food waste recycling to Yarrowia biomass due to combined hydrothermal carbonization and biological treatment

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ABSTRACT

Food waste (FW) to value-added application represents a demanding opportunity in the circular economy. As one of the approaches, FW hydrothermal carbonization (HTC) delivers an aqueous phase (HTC-AP), which would be suitable when applied to microbial growth and lipid production. In this context, this current work explored HTC-AP from FW obtained through HTC (temperatures 200 to 260 °C) for microbial growth of 14 different Yarrowia *species*. Among these strains, *Y.* lipolytica, Y. keelungensis, Y. porcina, and *Y.* galii showed the ability to utilize HTC-AP. In HTC from 200 °C high optical density (OD_{600}) reaching above 1.2 for the 4 species was observed. An increase in the temperature by 20 °C declined the growth of *Y. lipolytica, Y. porcina*, and *Y. galii* by 17%. However, *Y. keelungensis* showed good growth regardless of the HTC temperature. Further, the lipid produced better at higher biomass 240 °C compared to 260 °C during the HTC. Further, *Y. yakushimensis* showed the highest growth rate among all the analyzed media (0.12 – for medium 2 (0.45 NH_4^+ and 200 °C). Although the composition of HTC-AP is very diverse and often toxic, some analyzed yeast species can use the contained compounds as a carbon source for biomass and lipid biosynthesis. The presented possibilities are a very good starting point for developing processes on a larger scale.

1. Introduction

Food waste (FW) due to its organic characteristics and the mass scale of its production has a great potential for recycling. However, it requires novel management and treatment approaches. The global attention on food wastage has sky-rocketed, exacerbated by economic developments and increasing population. More than 1.33 billion tons of food are reportedly wasted annually, according to the Food and Agricultural Organization (FAO) (Uçkun Kiran et al., 2014). Factors that generate FW in one country would vary from another, which could be associated with agricultural conditions and policy constraints, etc. (Sridhar et al., 2021b). In many countries, these wastes are managed ineffectively; for example, with very high moisture content (MC), hence they are usually treated in mechanical biological treatment (MBT) plants, incinerated, and deposited in landfills. For instance, in Poland, there is a 27% chance of not recycling enough municipal waste and a 30% chance of not recycling enough packaging waste by 2025 (Zajemska and Korombel, 2024). The above-mentioned practices adversely affect environmental well-being because of cause nutrient-into-water contaminations and lead to the loss of valuable resources and greenhouse gas (GHG) emissions. Conventional FW disposals and their decomposition over a period in dump yards generate a significant amount of GHG, and release of chemicals that cause air and water pollution (Sridhar et al., 2021a). To make FW management effective requires a diligent practice of reduce, reuse, recycle, and recover strategy. Thermochemical treatment can, therefore, be exploited because the (thermal) decomposition process occurs without oxygen at temperatures 300 °C or even higher.

The ways of FW treatment, disposal, or management include anaerobic digestion (AD), which is the most favorable method, composting, combustion, and disposal in landfills (Cai et al., 2016; Isemin et al., 2021; Vigneshwar et al., 2022). Despite these applications, hydrothermal carbonization (HTC) can be considered a suitable approach to FW management because, it is more environmentally friendly among the different treatment techniques, particularly composting processes, in

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terms of emissions (International Energy Agency, 2006; Zabaniotou et al., 2017). It is cost-effective and able to maximize the recovery of water and nutrients while retaining carbon (Taylor and Demirbas, 2007). The hydrothermal treatment method typically including two categories; hydrothermal carbonization and liquefaction (HTC/L) (Abdalazeez et al., 2021; Taylor and Demirbas, 2007). HTC of FW appears a feasible process. Absence of pre-drying makes HTC efficient in managing organic waste with a high MC (Marzbali et al., 2021), such that the obtained final products are now of increasing interest to the food and food-related industries (Sridhar et al., 2021a). Based on the nature of FW which is rich in carbon (C) and hydrogen (H), offers the potential to be converted into other higher-value products (e.g., biofuels & biochemicals) using traditional thermochemical processes. The only drawback is that these processes are generally employed for feedstocks with low MC (Lachos-Perez et al., 2022a; SundarRajan et al., 2021; Swetha et al., 2021). For wet FW, pretreatment processes, such as washing, freezing, adding various minerals, and/or drying, become necessary for dewatering, making the whole system more complicated and energy-intensive (Lachos-Perez et al., 2022a). Conversion of wet biowastes via those traditional thermochemical processes is, therefore, less efficient, and environmentally harmful.

The hydrothermal process, which can be considered as the principle underscoring HTC, utilizes water at elevated temperatures in a pressurized vessel to eventually enable the conversion of wet feedstock into value-added products (Lachos-Perez et al., 2022b). As a thermal valorization process, the HTC not only gets implemented at temperatures of range 180 and 260 °C (Urbanowska et al., 2021), it operates effectively on biomass with high MC (70–90 %) compared to conventional thermal technologies like dry torrefaction and pyrolysis, doing away with pre-drying requirement considered energy costly (Lachos-Perez et al., 2022b). The energy requirements engaged within the production of hydrochar, which arises from the HTC process are much lower compared to those required for pyrolysis. The reason attributed to this is underpinned by the absence of feedstock drying, which renders the temperatures significantly lower compared to pyrolysis (500–1000 °C) (Rasaq et al., 2021; Swetha et al., 2021). Numerous studies have reported the successful microbial fermentation process used to convert FW into biofuels. This process breaks down mainly sugars into alcohols, however, also the nitrogenous compounds are sufficient for providing this element for microbial metabolism (Gao et al., 2022; Vigneshwar et al., 2022). However, biological treatment for wet FW valorization could help to achieve the goals of bioeconomy, circularity, and sustainability. FW with high water content could be converted into solid biofuels and valuable biochemicals effectively via combined HTC (Saengsuriwong et al., 2021) with biological treatment of the liquid condensate-hydrothermal aqueous phase (HTC-AP), resulting in the development of an energetically self-sufficient and zero waste technological system of FW recycling. The HTC-AP, a byproduct, is a marked limitation for developing hydrothermal technology on an industrial scale (Lachos-Perez et al., 2022a). It is rich in volatile fatty acids (VFAs) and nutrients, such as phosphorous P, nitrogen (N), and potassium (K), and consequently, a further treatment process is required to improve the qualities before returning it to the environment (Swetha et al., 2021). It provides the challenge to develop a cost-effective and energy-efficient system for FW recovery and recycling in line with the EU policy (Environmental Indicator Report, 2014) for renewables and sustainability (European Environment Agency, 2020; Jama-Rodzeńska et al., 2021). Using yeast species known for their abilities to utilize unconventional carbon courses, *e.g.* n-alkanes, provides significant improvement of processes proposed in the literature (Fukuda, 2023; Marzbali et al., 2021; Rasaq et al., 2024a). More interestingly, Ma and colleagues reported that, in the HTC conditions of organic biomass (especially at high temperatures), HTC-AP with VFAs of over 80% w/w concentration can be obtained (Ma et al., 2018). These Yarrowia species are known to use many alternative carbon sources, such as alkanes, fats, raw glycerol, or VFAs, and produce large quantities of intracellular lipids (Quarterman et al., 2017).

The microbiological treatment process of FW, after the production of the VFAs, entails such stages as microbial fermentation, isolation, and purification of intracellular lipids, which makes this process environmentally friendly and economically viable, as shown by previous studies (Gao et al., 2022; Lu et al., 2015, 2021; Ma et al., 2018; Vajpeyi and Chandran, 2015). For instance, Vajpeyi and Chandran (2015) showed that biochemical waste treatment could be linked to biofuel production by using VFA mixtures/substrates as key intermediates to accumulate lipids by oleaginous yeast *Cryptococcus albidus*. It was found that higher lipid accumulation using batch processes and synthetic VFA, occurred under nitrogen-limited conditions. During batch growth, a maximum intracellular lipid accumulation for *C. albidus* using VFA as the carbon source occurred with an initial COD:N ratio (25:1 mg COD: mg N), with no compromises on the growth kinetics. However, the batch cultures with the FW fermentation fed with VFA produced lower lipid content. With synthetic and FW-derived VFA, the lipid composition resembled those of commercial biodiesel feedstock. Recently, Gao et al. (2022) adopted variable pH strategies for microbial lipid production in studying the co-fermentation and lipid biosynthesis from FW. These Authors showed that lipid production by *Rhodosporidium toruloides* supplemented with FW cooking oil at a substitution rate range of 1.56–4.68 (based on waste cooking oil content in FW), owing to the better synergistic effect. When FW has been subject to merely HTC/HTL in the absence of nutritional supplementation under microbial-led lipid production, it may still be challenging to establish how the lipid-production substances get affected. In addition, to understand this better, Ma et al. (2018) used oleaginous yeasts for microbial lipids production from FW by removing oil residues. The extracted lipid can be used as raw material for biodiesel. The study conducted by Quarterman et al. (2017) where yeast from the *Yarrowia* sp. for lipid production on diluted acid pretreated biomass was investigated (Quarterman et al., 2017), and a similar study by Pereira et al. (2021) where the factor affecting the growth, lipid accumulation and bioconversion of VFAs into lipids by *Yarrowia lipolytica* were examined. These Authors reported that *Y. lipolytica's* growth on VFA-based media was improved as well as lipids production was enhanced by the addition of (glucose or glycerol) during batch cultures (Pereira et al., 2021).

The novelty of this study lies in its exploration of the utilization of HTC-AP derived from FW through the HTC process as a growth medium for yeast species, with a specific focus on lipid production. While previous research has primarily concentrated on converting FW into biofuels and biochar using HTC, limited attention has been given to the potential of HTC-AP as a nutrient-rich substrate for microbial biotechnology applications. By investigating the kinetics of yeast growth and lipid biosynthesis in HTC-AP-based media, this study offers new insights into the feasibility of using HTC-AP as a sustainable alternative to traditional growth media in microbial bioprocessing. Moreover, the comparative analysis of different HTC-AP processing parameters and their impact on yeast metabolism provides valuable information for optimizing waste valorization strategies and enhancing the efficiency of bio-recovery processes. By elucidating the relationship between HTC-AP composition, yeast growth kinetics, and lipid production, this study contributes to advancing our understanding of waste-to-value technologies and offers practical implications for sustainable waste management and bioprocessing industries.

Based on the above analysis, the study aims to: (a) propose a novel approach to FW recycling and their conversion to lipids using HTC combined with biological treatment by *Yarrowia* clade species, (b) the assessment of combining the HTC and fermentation of HTC-AP reach in VFA's with *Yarrowia* species for the production of the biomass as a method of the FW valorization and recycling, (c) evaluate the best *Yarrowia* clade species for biomass and lipid yield, and compare it as a nutrient, rich in lipid including essential fatty acids obtained from HTC-AP.

2. Materials and methods

2.1. Organic food waste collection and residual analysis

The collection/composition of food waste (FW) as previously explained elsewhere (Valta et al., 2019) represented a feedstock that modelled a household FW found in Europe. The FW mixture consists of 8.67% banana, 3.67% orange, 1.33% lemon, 7.33% apple, 24.33% potatoes, 4.67% onion, 3.33% of cabbage, 3.33% salad, 2.33% tomatoes, 6% pasta, 6% rice, 3% bread, 12% fish meat, 3% meat, and 11% cheese by fresh mass, the full description was given previously (Świechowski et al., 2022). The choice of not selecting domestic FW was made to ensure that specific composition various mixtures can be reproduced. Since domestic FW would vary by composition and easily contaminated, the use of a controlled laboratory setting helps to overcome these difficulties.

Therefore, the obtained fresh FW contents (raw and processed samples) were analyzed in three replicates for wet mass (WM), moisture content (MC), and dry matter (DM) The drying process took place at 105 °C for 24 h with the application of a laboratory dryer (WAMED, KBC-65W, Warsaw, Poland). The pre-mixed FW components were ground by laboratory mill (Testchem knife mill LMN100) to create a homogeneous material. The prepared (kitchen waste) mix was sieved using a sieve mesh of 5 mm diameter. The MC was determined following (Świechowski et al., 2019). Samples were also tested for the content of volatile solids (VS), according to the PNEN 15935:2022–01 standard (PN-EN 15935:2022–01 Standard, 2022).

2.2. Hydrothermal carbonization process

An hydrothermal carbonization (HTC) reactor (RBMT-2020-1.0) was used as previously explained elsewhere (Świechowski et al., 2022) to obtain a hydrothermal aqueous phase (HTC-AP). Briefly, the HTC-AP was produced using a prototype batch laboratory reactor (WUELS, RBMT2020–1.1, Wrocław, Poland). The reactor is steel-made, an air-tight vessel of 22.3 dm^3, wrapped in a 3 kW heating jacket and insulations. A full description of reactor design is available elsewhere (Matyjewicz et al., 2020). Inside the reactor is a special grill placed at 1/3 of the height of the reactor chamber. The grill is used for the placing of the processed materials. After the process, HTC-AP from the material and condensed water poured down under the grill, leaving solids residues on top of the grill. The prepared wet FW mixtures were divided into 5 portions and placed into aluminum trays that were placed on the grill (approximately 250 g of wet FW). Then the reactor was closed and filled with CO_2 inert gas. The reactor was operated at 4 different temperatures (200, 220, 240, and 260 °C) with a constant duration (60 min) to obtain four different HTC-AP products while the pressure was generated autogenously. After 60 min, the reactor's heating jacket was turned off and pressure was released (the reactor was depressurized). Additionally, a single-phase digital energy meter (Model SK-410, Starmeter Instruments Co., Ltd., Shenzhen, China) was used to record the energy consumption during the process. The released gas was cooled down and condensate was collected to form the first part of HTC-AP. After cooling down of the reactor, the condensate that stayed in the reactor chamber (below the grill) was collected and mixed with HTC-AP collected from released gas to form samples used as primary media for microbial growth. The difference between the initial feedstock and end mass of the HTC solid product was used to calculate the mass yield of the HTC-AP by the following Equation (1):

$$MY = \frac{Ms}{Mf}\ X\ 100 \tag{1}$$

Where:

MY—mass yield, %; Ms— wet mass of HTC of dry solid after hydrothermal carbonization, g, Mf—wet mass of the feedstock before hydrothermal carbonization, g.

2.3. *Yarrowia* clade species used for growth test on HTC-AP

Different yeast strains belonging to the *Yarrowia* clade were used during this study. The species were purchased from the CBS-KNAW culture collection, except for *Yarrowia lipolytica* A101 strain, which was obtained from the Department of Biotechnology and Food Microbiology, UPWr. The yeast species tested are present in Appendix E (Table A1). Yeast strains were kept at −80 °C in 25% glycerol stocks. Before use, the yeast was refreshed at YPD medium (glucose 20 g/L; peptone 20 g/L, yeast extract 10 g/L, agar 20 g/L) and grew for 24 h at room temperature.

2.4. Media composition and yeast growth determination

Nine different media types (labeled as M1, M2, M3, M4, M5, M6, M7, M8, and M9) were used in the present study to determine and identify the suitable conditions for the selected *Yarrowia* species' growth. These media were named based on the HTC operating conditions at 4 different temperatures and uniform residence time of 60 min shown in Appendix F (Table A2). For the *Yarrowia* species growth optimization, the C/N ratio was adjusted to the value of 60 by the addition of ammonium chloride – calculated according to the number of VFAs analyzed by HPLC (Rakicka et al., 2015). Before, the ammonium ions concentration in different medium types was analyzed using the standard ninhydrin method. Additionally, HTC's performance and efficiency are present in Table 1.

To verify the growth of the analyzed species on HTC-AP as a carbon source, an equal volume of sterile agar solution (4%) was added to the HTC-AP and the obtained plates were inoculated with different decimal dilutions of cell suspensions (10^0–10^{-5}). The initial optical density (OD_{600}) was equilibrated to 1 for each strain. The inoculum was prepared in a YPD liquid medium, where cells grew at room temperature at 180 rpm for 24 h (Lazar et al., 2017). Similarly, the yeast cell suspension was prepared from 24 h culture in a YPD medium with Yeast Nitrogen Base (without ammonium sulfate and amino acids) (Lazar et al., 2017). Furthermore, control plates with no biomass were also analyzed, to verify if the HTC-AP plates were sterile without heating or filtering it. The plates were incubated at room temperature for 48–72 h.

A similar experiment was conducted using microplate cultures and HTC-AP as carbon sources. In this experiment, species *YAPA* and *YABR* were included and analyzed along with all the other *Yarrowia* species. For that purpose, equilibrated cell suspension with optical density (OD_{600}) equal to 1 was introduced to the 96-well plate with twice diluted HTC-AP. The cultures were conducted for 72 h at 20 °C, and the obtained growth curves were further analyzed.

For the determination of biomass growth, the OD_{600} was measured to inoculate the flask cultures (50 mL) to initial OD_{600} 0,5. Yeast was grown for 72 h on a rotary shaker with 180 rpm at room temperature. After the

Table 1
Effect of varying temperature on yield of hydrothermal aqueous phase, and energy usage.

HTC condition		Energy consumption		HTC-AP yield (%)
Temperature (°C)	Time (min)	Total electrical energy consumption (MJ)	Relative electrical energy consumption (MJ x g^{-1})	
200	60	15.7 ± 0.70	1.3 ± 0.02	61.3 ± 0.20
220	60	16.8 ± 0.80	1.5 ± 0.05	64.9 ± 0.10
240	60	17.9 ± 0.50	1.7 ± 0.05	70.7 ± 1.50
260	60	19.1 ± 0.90	1.9 ± 0.03	74.9 ± 0.90

cultures were completed, the dry biomass of the cells was analyzed gravimetrically using a weight dryer.

2.5. Modelling of yeast growth kinetics

The *Yarrowia* species. cumulative growth in all prepared HTC-AP was fitted into the Gompertz equation (equation (1)) representing the kinetic growth of yeast (Tjørve and Tjørve, 2017).

$$G = G_0 * \exp\{-\exp[-k(t-\gamma)]\} \tag{2}$$

Where, G - *Yarrowia* clade growth value over time expressed as an optical density at the specific time, t – time, h, G_0 – the maximum *Yarrowia* clade growth potential (upper asymptote of the optical density), k – constant of the rate of growth, h^{-1}, and γ – time at an inflection, h. This Gompertz equation was fitted into Gauss-Newton estimation and the two-way analysis of variance (ANOVA) with post hoc Tukey tests was performed at the level of $\alpha = 0.05$ to find statistically significant differences of HTC temperatures effect on HTC-AP yield using Statistical 13.0 software (TIBCO Software Inc., Palo Alto, CA, USA). The representation of the model is considered based on the R^2 value.

2.6. Lipid production using Yarrowia species determination

The total lyophilized yeast biomass was processed for fatty acid extraction and derivatization to methyl esters (FAMEs), using the method described before (Browse et al., 1986). Briefly, 10 mg of freeze-dried biomass was mixed with 2 mL of solvent solution: 2.5% H_2SO_4, 97.5% methanol, as well as with or without 50 μg/mL of C17:0 as an internal standard for lipid quantification, in Pyrex glass tubes (Sigma-Aldrich, Saint Louis, MI, USA). All samples were thoroughly mixed and incubated at 80 °C overnight to form FAMEs. FAMEs were extracted by hexane and 0.9% NaCl and the organic phase was collected. FAME analysis was performed by gas chromatography on a GC-MS instrument (Shimadzu, Kyoto, Japan) equipped with a Zebron ZB-FAME capillary column (30 m × 0.25 mm × 0.20 μm). The samples (1 μL at 250 °C) were injected in splitless mode using helium (1 mL min^{-1}). The identification of fatty acids was carried out by the comparison of retention times with reference compounds (Supelco 37 Component FAME Mix, Sigma-Aldrich). Experiments were conducted in three biological replicates (see Fig. 1).

3. Results and discussion

3.1. HTC-AP yield and energy consumption

To understand the energy utilized in each experiment, hydrothermal carbonization (HTC) process energy usage was determined through total (MJ) and relative electrical energy consumption (MJ x g^{-1}), as presented

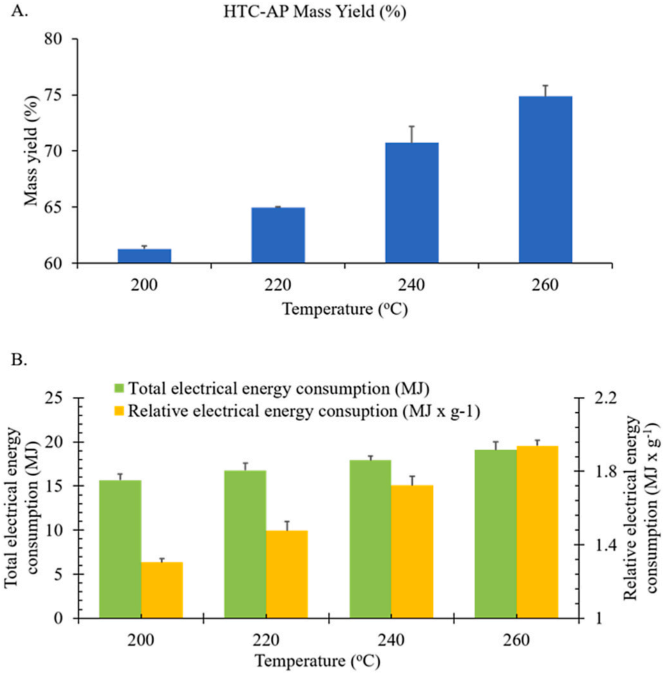

Fig. 2. A) The HTC-AP yield after the HTC process at different temperatures, and B) Total electrical energy consumption (MJ) and relative electrical energy consumption of the HTC process in relation to the mass of HTC-AP obtained after the process.

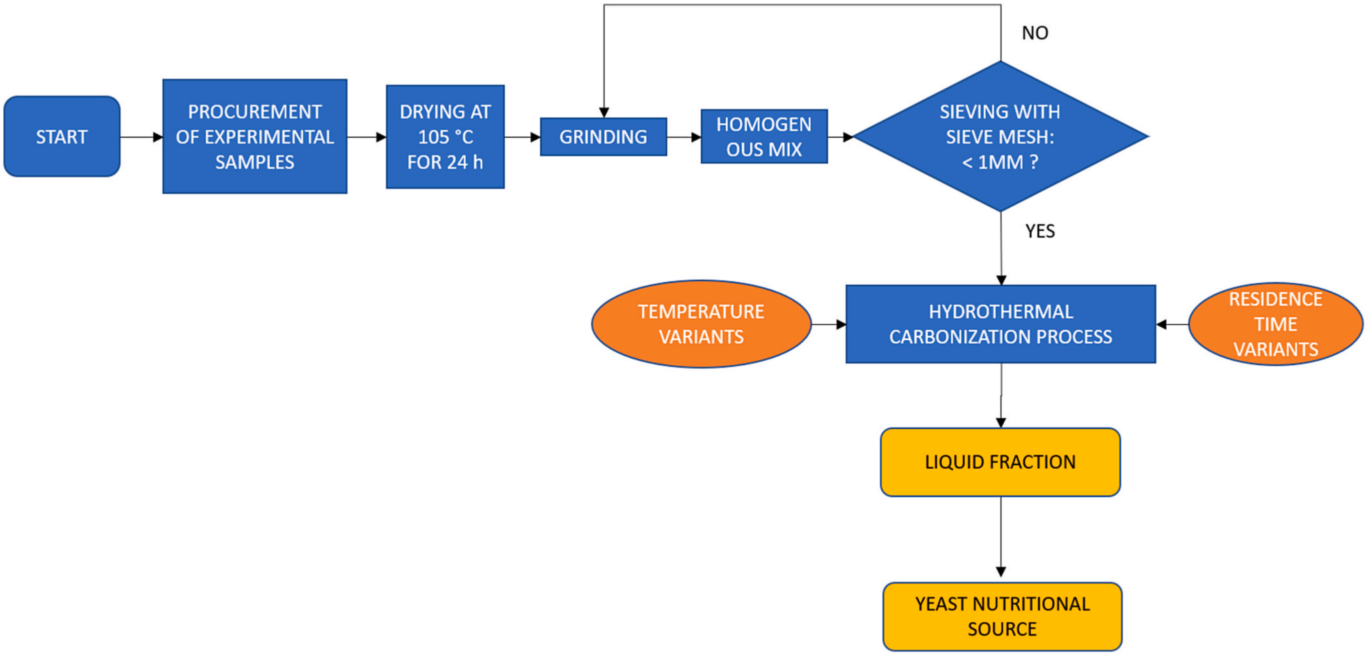

Fig. 1. Graphical representation of the overall work.

in Fig. 2B. For emphasis, the total involves the direct measurement of electricity consumed by the HTC reactor, and its utilization per hydrothermal aqueous phase (HTC-AP) mass is further provided by the relative electrical energy consumption. The result showed electricity usage tends to increase with temperature, reaching 1.9 ± 0.03 MJ x g^{-1} for the HTC-AP obtained at 260 °C, while the lowest electricity usage was observed at 200 °C with 1.3 ± 0.02 MJ x g^{-1}. The observed dynamics align with prior research on HTC processes, revealing a temperature range of 220–340 °C and a corresponding resident time of 90–260 min. These parameters have been empirically linked to energy usage in the range of 0.5–7.7 MJ x g^{-1} (Rasaq et al., 2024b). This is connected with the time needed for heating the material inside the HTC reactor to reach the desired temperatures. It is evident that the higher the set temperature point, the higher the energy consumption (Hejna et al., 2022; Rasaq et al., 2024b).

The mass yield (MY) of the HTC-AP is significantly affected by the temperature. Except between 200 and 220 °C and between 240 and 260 °C all temperatures significantly vary in MY (Appendix I; Table A5). Herein, the HTC-AP yield observed (61.3–74.9% of the total feedstock) was obtained across the tested HTC conditions Fig. 2A. The maximum HTC-AP yield (best value = 74.9 ± 0.9%) was observed at the HTC process at 260 °C, while the lowest value (61.3 ± 0.2%) was obtained at 200 °C temperatures. Both the increase and decrease situations as above mentioned tend to agree with the findings of previous reports (Hejna et al., 2022; Kantarli et al., 2016). Besides MY which shows a similar trend to the previous studies (Déniel et al., 2016; Swetha et al., 2021), HTC-AP yield would vary based on the HTC operating condition. Probably, the decarboxylation process and the formation of organic compounds soluble in water may have contributed to the observed yield.

3.2. Growth of Yarrowia species on HTC-AP

It is known that *YALI* can grow efficiently using VFA as a carbon source and convert it to lipids (Fontanille et al., 2012; Llamas et al., 2020). Naveira-Pazos et al. (2022) carried out a study to investigate the amounts of acids obtained during acidogenic fermentation, the only three VFAs present in such anaerobic fermentation generated via the Wood-Ljungdahl pathway as carbon sources for *Y. lipolytica* are acetic (C2), butyric (C4), and caproic (C6) (Naveira-pazos et al., 2022). A toxicity study for acetic, butyric, and caproic acid was conducted in five different flasks with different total acid concentrations ranging from 6 to 16 g/L and with acid ratios of 0.81:0.14:0.05, respectively (Naveira-pazos et al., 2022). However, in the analyzed studies, the VFAs were either pure acids or derived from the anaerobic fermentation of organic wastes. It was so far poorly analyzed if such a composed medium as HTC-AP can serve as a suitable carbon and nitrogen source for *YALI* growth and valuable product biosynthesis (Cordova et al., 2020). Among the compounds found in the HTC-AP, there can be various toxic substances whose presence inhibits the growth of many different groups of microorganisms. However, the natural abilities of the yeast *Y. lipolytica* to grow in substrates containing toxic compounds, such as polyethylene (Walker et al., 2023), poly(ethylene terephthalate) (PET) (da Costa et al., 2020),

high concentrations of VFA (Gao et al., 2020), or phenol (Balder-a-saavedra et al., 2024), suggest that these microorganisms will be well-equipped to handle the toxic compounds contained in HTC-AP. Herein, we further enlarged the study for the other *Yarrowia* species belonging to the *Yarrowia* clade, as some of these species could even more efficiently convert these toxic compounds into valuable products.

At first, a simple test of microbial growth on a solid medium based on the different HTC-AP, diluted twice with 4% agar solution was performed. Medium prepared this way became sterile, despite sterilizing only the agar solution (data not shown). Due to the presence of volatile fatty acids and their odor, as well as the avoidance of generating additional energy required for preparing the substrate based on HTC-AP, sterilization was not conducted (El Ouadrhiri et al., 2021). It was considered that substrates after the HTC process are inherently sterile, which was also experimentally verified.

The best media for the growth of *Yarrowia* species turned out to be 2, 3, 5, and 6, which were based on 4 different HTC-AP products concerning the HTC operating conditions and additional YBN supplementation (Table 2 and Appendix H (Table A4)). All analyzed yeasts grew well on these media (in most decimal dilutions analyzed). On the other hand, medium number 4, turned out to be so toxic that none of the yeast species was able to grow under these conditions. In turn, characterizing the growth of the analyzed strains the most efficient species growing on this toxic media were *YALI*, *YAKE*, *YAPO,* and *YAGA*. These species grew abundantly in most of the analyzed substrates, also at very high dilutions (Table 2 and Appendix H (Table A4)). However, because growth conditions in solid media, where the access to individual components of the medium and oxygen is different than in liquid media, it was also necessary to characterize the growth of yeast from the *Yarrowia* species using the microculture method.

3.3. Kinetic growth of yeast in media 2

Medium No. 2 was composed of the HTC-AP obtained from the HTC process, conducted at 200 °C and 60 min. Among the 14 tested yeast species (Table 1), the growth kinetics of well-grown species' are illustrated in (Table 3) and (Appendix A; Figures A1– A14). The fitted kinetic growth using the Gompertz equation expressed in descending order the best species to utilize the energy sources were *YAOS*, *YAKE*, *YAPA*, *YALI,* and *YAYA,* respectively. The best nutritional value for yeast growth and biomass production is selected based on the shortened lag phase associated with yeast adaptation, the lag phase associated with yeast concentration, the absence of exponential, death phases during this incubation period, and the value of the constant of the rate of individual species growth, h^{-1} (Table 3) and (Appendix A; Figures A1– A14). Medium 2 had shown commonly a higher concentration of biomass for *YABR, YAKE, YAOS,* and *YAPA* (Appendix A; Figures A6, A10, A13, and A14). It is shown that low-temperature treated HTC-AP contains compounds, suitable for several *Yarrowia* species growth that are not completely adapted to higher hydrophobic conditions (Cordova et al., 2020; Parchami et al., 2021). In this regard, the only species identified, that suit the above circumstances are *YAYA* and *YAPA*. In the context of growth kinetics, the *YAYA* strain showed the highest growth rate of 0.12 followed by *YAPA* at 0.04 in this medium. This indicates that *YAYA* and *YAPA* grow well in the HTC-AP.

3.4. Kinetic growth of yeast in media 3 and 5

In medium 3, the HTC-AP was prepared at temperature and time 220 °C and 60 min, respectively. It has given a continuous extension of yeast concentration of species namely, *YAHO, YALI, YAPO, YADI, YAKE, YAYA, YALI, YAOS,* and *OLHI* (Table 4) and (Appendix B; Figure B1-B14). However, the other tested species did not show a prominent utilization of these nutrients in this medium and had reached the exponential phase after 72 h of incubation. Furthermore, it is probably also a reason for the resistance of the remaining investigated species to toxic compounds present in the substrate, which may influence the prolongation of the adaptation phase as well as it may be influenced by the lack of other nutritional compounds required for efficient growth or due to insufficient aeration as the oxygen demand differs among the tested species. Oxygenation is crucial because many microorganisms use oxygen as an electron acceptor in the process of metabolizing organic compounds, including toxic ones. In the case of substances that are difficult to decompose, such as certain hydrocarbons or pesticides, proper oxygenation can significantly increase the efficiency of their biodegradation. An adequate amount of oxygen allows microorganisms to more effectively transform these compounds into less harmful decomposition products (Zou et al., 2018). Additionally, the mentioned *YAKE* initiated the death phase which had not been observed in medium

Table 2
Growth of different *Yarrowia* clade members in agar medium based on HTC-AP. The number of pluses/minuses corresponds to the dilution factor, which grew/not grew on the agar plate. One plus represents one decimal dilution of the cells growing on the corresponding medium (10^0–10^{-5}).

Yarrowia clade	Medium type								
	1	2	3	4	5	6	7	8	9
YAHO	+++	++++++	++++++	–	++++++	++++	+/–	–	–
YAKE	++++	+++++	++++	–	++++	++++	++++	+++++	+++
YALI	+++++	++++++	++++++	–	++++++	++++++	++++	++++	+++++
YAPO	+++++	++++++	++++++	–	+++++	++++++	++++	+++	+++
YADI	++	++++++	++++++	–	++++++	++++++	+/–	–	–
YAPH	+	+++++	++++++	–	++++++	++++++	+/–	–	–
YADE	+	+++++	++++++	–	++++++	++++++	+/–	+	–
YABU	++	+++++	++++++	–	++++++	+++++	+/–	+++	–
YAGA	+++++	++++++	++++++	–	++++++	++++++	+++++	++++	–
OLHI	+	++++++	++++++	–	++++++	+++++	+	+	+++
YAOS	++	+++++	++++	–	++++++	+++++	+	+++	–
YAYA	++	++++++	++++++	–	++++++	++++	+	–	+

Table 3
The kinetic parameters of *Yarrowia* clade member's growth on media 2 according to the Gompertz equation (1).

Yarrowia clade member	G_0 – the maximum *Yarrowia* clade growth potential	k – constant of the rate of growth, h^{-1}	γ – time at an inflection, h	R^2 – determination coefficient
OLHI	0.59	0.008	−124.10	0.996
YABU	53.86	0.002	777.93	0.997
YABR	1107.82	0.002	890.39	0.944
YADE	2.70	0.001	722.22	0.996
YADI	1.10	0.007	1.95	0.999
YAGA	117.29	0.002	858.04	0.987
YAHO	18.63	0.002	741.30	0.991
YALI	1.79	0.007	57.80	1.000
YAOS	357.61	0.002	925.80	0.978
YAPA	1.37	0.040	7.22	0.982
YAPH	0.56	0.006	−194.59	0.998
YAPO	288.63	0.002	937.91	0.970
YAYA	0.47	0.121	−23.29	0.874
YAKE	1.53	0.025	17.09	0.996

Table 4
The kinetic parameters of *Yarrowia* clade member's growth on media 3 according to the Gompertz equation (1).

Yarrowia clade member	G_0 – the maximum *Yarrowia* clade growth potential	k – constant of the rate of growth, h^{-1}	γ – time at an inflection, h	R^2 – determination coefficient
OLHI	0.48	0.020	−76.60	0.990
YABU	0.64	0.020	−29.90	1.000
YABR	4.17	0.000	171.00	0.970
YADE	3.18	0.000	155.00	0.970
YADI	1.73	0.010	79.30	1.000
YAGA	2.40	0.000	221.00	0.990
YAHO	1.42	0.000	103.00	0.920
YALI	11.50	0.010	239.00	0.990
YAOS	0.44	0.040	−45.60	0.990
YAPA	1.90	0.000	183.00	0.950
YAPH	4.10	0.000	121.00	0.980
YAPO	3.60	0.000	167.00	0.990
YAYA	0.42	0.100	−27.30	0.660
YAKE	1.27	0.080	9.58	0.940

Table 5
The kinetic parameters of *Yarrowia* clade member's growth on media 6 according to the Gompertz equation (1).

Yarrowia clade member	G_0 – the maximum *Yarrowia* clade growth potential	k – constant of the rate of growth, h^{-1}	γ – time at an inflection, h	R^2 – determination coefficient
OLHI	0.36	0.042	−38.30	0.983
YABU	0.57	0.005	−74.66	0.961
YABR	3.13	0.005	145.47	0.902
YADE	0.34	0.094	−13.63	0.995
YADI	0.35	0.033	−43.14	0.952
YAGA	1.07	0.003	112.48	0.970
YAHO	0.33	0.149	−10.71	0.941
YALI	0.34	0.032	−48.00	0.948
YAOS	4.33	0.004	233.92	0.979
YAPA	0.98	0.045	1.93	0.989
YAPH	0.36	0.074	−19.31	0.991
YAPO	0.42	0.008	−110.92	0.956
YAYA	0.40	5.572	−7.95	0.000
YAKE	1.32	0.002	229.46	0.901

2. Furthermore, a very similar microbial growth of *YAHO, YALI, YAPO, YAOS, YAYA*, and *YADI* was noted in medium 5 - HTC-AP prepared at 240 °C in 60 min present in (Appendix G (Table A3) and Appendix C, Figure C1 – C14)). In terms of growth kinetics, the *YAYA* strain showed the highest growth rate of 0.10 similar to *YAKE* reaching 0.08 in medium 3. The observed dynamics align with the study of Park et al. (2018), revealing growth of *Y. lipolytica* strain on propionate, and their result demonstrates a growth rate (0.16) (Park et al., 2018). This indicates that *YAYA* and *YAKE* grow well in the HTC-AP. Likewise, in media 5 (Appendix G (Table A3)) these two strains had the highest growth rate of 0.13 and 0.06 for *YAYA* and *YAKE*, respectively.

3.5. Kinetic growth of yeast in media 6

In medium 6, the HTC-AP was processed at a higher temperature and time of 260 °C and 60 min respectively. At this HTC-AP-based medium, a higher microbial concentration in the short term had been observed (Appendix D; Figures D1-D14). The composition of this medium has given a short-term yeast concentration of species namely, *YAHO, YADE, YAPA, YAPH*, and *OLHI* (Table 5). This indicates that a higher-temperature HTC process could break down complex carbohydrates, lipids, and proteins to short-chain simple readily available nutrients (Parchami et al., 2021). This early exponential stage indicates that medium No. 6 is unsuitable for long-term microbial growth. This phenomenon could be due to a lack of either nutrients or during growth the compounds present in this medium were transformed into other toxic chemicals, which reaching high concentrations became toxic to the yeast cells. This hypothesis was already tested, however, the huge number of compounds appearing in the chromatograms, different before and after the cultivation of microorganisms, did not allow for a clear conclusion as to which of the compounds present could cause growth inhibition (data not shown). The kinetic constant was highest at 5.57 at

YAYA followed by *YAHO* at 0.14. In this media, it shows that *YAYA* was able to grow fast which is the same in the previous medium.

Hu et al. (2022) adopted a different strategy using *E. coli* to pretreat the aqueous phase waste (AP) generated during the HTC of algae biomass. The microbiological pretreatment aimed to improve the biostructure of AP and recover nutrients. Through the action of *E. coli*, a large number of organic nitrogen compounds were transformed into ammonia nitrogen by degrading protein substances and deaminating nitrogenous heterocyclic compounds (Hu et al., 2022). In our strategy, growing yeast cells directly utilized available carbon and nitrogen compounds for growth and intracellular lipid biosynthesis. In turn, a similar to our strategy was employed by Cordova et al. (2020), who used *Y. lipolytica* to transform the acid- and other toxin-rich aqueous phase, a byproduct of the hydrothermal liquefaction (HTL) process. It was shown that *Y. lipolytica* can tolerate the presence of HTC-AP in culture media, up to 10% in defined media and 25% in rich media (Cordova et al., 2020). This allows the direct use of the toxic HTC-AP as a substrate in fermentation processes, particularly for producing esters, lipids, or itaconic acid. In our case, HTC-AP was only enriched with YNB or ammonium sulfate to establish the optimal C/N ratio for lipid biosynthesis. This strategy further reduces the costs of processing waste rich in toxic compounds into valuable products such as lipids.

3.6. Biomass and lipid production by Yarrowia clade species

The fatty acids composition of lipids is an additional crucial yeast biomass characterization parameter that serves as a macronutrient indicator for animal feeding. These substances are found in the triacylglycerols and sterol esters stored in lipid bodies and membranes inside the cells. GC-MS and a standard FAME mixture were used to analyze the fatty acid profiles and quantity among the tested strains including *YAKE, YAPA*, and *A101 (YALI)* in 4 media (Fig. 3). The total amount of lipids in the cells was evaluated with which the highest was observed in *YAKE* species in medium 6 (17.5%) as was already mentioned above. However, considering the entire analyzed media, medium 5 turned out to be the best among others, because all three analyzed species in this medium produced a high amount of lipids reaching 11%–14.5% of the dry biomass.

The composition of the fatty acid fraction consisted mostly of C18:1 (oleic acid) and C16:0 (palmitic acid) for all strains in all media (Fig. 4), which accounted for 20–35% of the lipid fraction. Around 15% of the lipid fraction was C18:0 (stearic acid). The rest of the analyzed fatty acids were composed of C16:1, C17:0, C17:1, and C18:2. The existence of the C17:0 and C17:1 fatty acids confirms the presence of propionic acid in the media, as the metabolic pathway of this acid in the yeast cells converts it into odd chain fatty acids (Park et al., 2018, 2021).

As the last step in the analysis of the microbial conversion of HTC-AP into a valuable product, lipid biosynthesis using *Yarrowia* species was analyzed. This experiment was performed in a shake flask, where the access to oxygen was higher, which is a required parameter for all *Yarrowia* species as they are aerobic microorganisms. For that experiment, only strains growing well in the previous stages of this study were chosen: *YALI, YAPA,* and *YAKE.* As it is already known, lipid biosynthesis requires nitrogen limitation to inhibit the activity of isocitrate dehydrogenase and to direct the citric acid into the cytoplasm to initiate lipid biosynthesis and accumulation (Beopoulos et al., 2009; Pomraning et al., 2016). Due to the high degree of different compounds in the HTC-AP, we mostly calculated the VFA content, which was a carbon source for the yeast. As mentioned above, the vast number of different compounds did not allow us to specify, if any other compound was used for growth or if they were only transformed into other chemicals (data not shown). The determined concentration of nitrogen (NH_4^+ ions) allowed us to select the necessary amount of ammonium chloride to create conditions for nitrogen limitation – C/N = 60. All three analyzed strains showed good growth in medium number 2 (Fig. 5). The amount of biomass obtained was from 4.5 to 6.5 g/L. The amount of biomass obtained in the other two media (5 and 6) was lower and ranged from 2.3 to 4.6 g/L. Unfortunately, the *YAKE* strain that had the highest growth in medium 2 produced the least biomass in medium 6.

In the course of the research, taking into account both the growth and the percentage of lipid content in the cell, the *Y. lipolytica* species turned out to be the best (Fig. 5). The A101 strain grew well on all media and was characterized by a stable amount of lipids (8.8–13.9%). Although *Y. keelungensis* showed the highest lipid content in the biomass (17.4%), it was characterized by the lowest growth in medium number 6. In the previous research by Fontanille et al. (2012), the final amount of lipids reached nearly 41%, however, the strategy of conducting the culture was different – a bioreactor culture with glucose feeding at the beginning of the process. However, when authors analyzed pure VFA in a shake flask they obtained from 3.4 to 6 g/L of dry biomass with a lipid content of 25–31% (Fontanille et al., 2012). Thus, several studies have concentrated on the comparative evaluation of various species within the *Yarrowia* clade. Consider Michely et al., who experimented with comparing growth parameters and lipid content using nine different

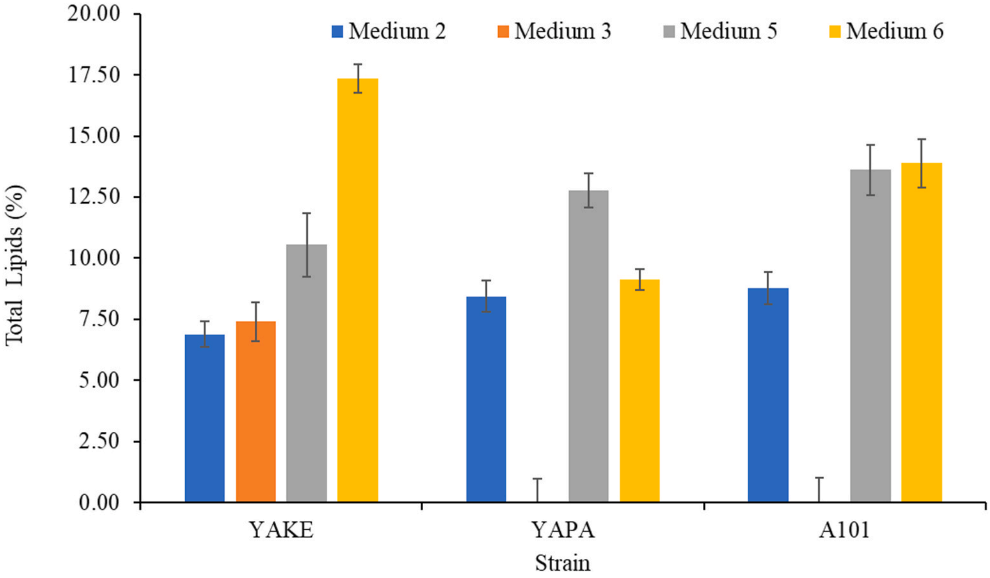

Fig. 3. The total lipids quantity among the tested strains.

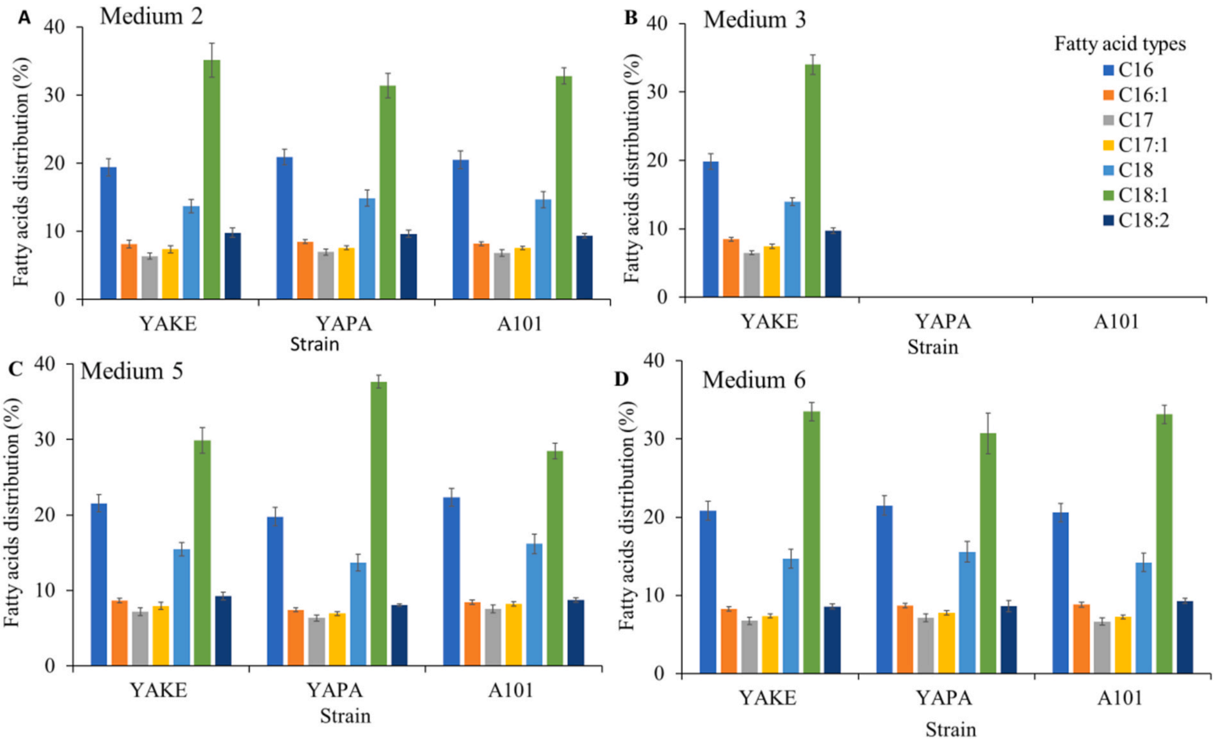

Fig. 4. (A–D). The distribution of fatty acid in HTC-AP among media 2, 3, 5, and 6.
*Palmitic (C16:0); Palmitoleic (C16:1) Margaric (C17:0); heptadecenoic (C17:1); Stearic (C18:0); Oleic (C18:1); and Linoleic (C18:2).

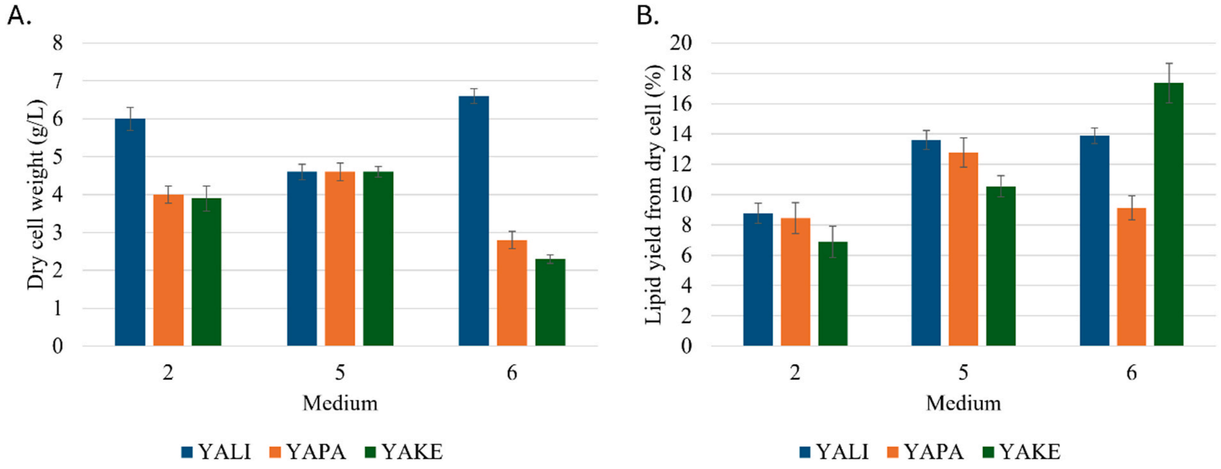

Fig. 5. Biomass production (A) and lipid yield (B) among HTC-AP media.

Yarrowia species in defined media containing either glucose or oleic acid. The maximum lipid content on oleic acid for all tested strains ranged from 30 to 67% DW, but only 4–7% DW on glucose (Michely et al., 2013). A similar study was conducted by (Rakicka et al., 2016) to assess the ability of 12 species of the *Yarrowia* clade to produce sugar alcohol in a minimal media with fructose, glycerol, or glucose. They obtained up to 69.8 g/L total polyols for *Candida oslonensis* and also to be the best producers of erythritol and mannitol compared to the other tested species (Rakicka et al., 2016).

4. Conclusion

Food waste (FW) was subjected to hydrothermal carbonization (HTC) at various temperatures (ranging from 200 to 260 °C). The hydrothermal aqueous phase (HTC-AP) produced during HTC was utilized as a growth medium for 14 different yeast strains. Among the tested yeast strains, four *Yarrowia* species, namely *Y. lipolytica*, *Y. keelungensis*, *Y. porcina*, and *Y. galii*, showed promise for utilizing HTC-AP for lipid production. Moreover, the HTC-AP-based media obtained at different temperatures highlighted the relationship between HTC-AP processing temperature and the bio-recovery process, which delivered promising yeast growth, biomass yield, and lipid production. For instance in lipid biosynthesis, *Y. lipolytica*, *Y. parophonii*, and *Y. keelungensis* produced approximately 4.5 g/L of dry biomass containing 10–14% lipids. Lipid recovery by HTC-AP-based media that combined HTC and biological treatment of FW appears a feasible process. Notably, HTC-AP obtained at 240 °C for 60 min would effectively support the growth and lipid biosynthesis of *Y. lipolytica, Y. parophonii,* and *Y. keelungensis*.

For emphasis, domestic FW would vary by composition, hence the collected samples (fresh FW) of various mixtures would ensure generalizability/reproducibility. As FW compositions vary regionally and temporally, translating laboratory-scale findings into large-scale industrial applications could pose challenges in achieving consistent outcomes. The HTC-AP processing temperature on bio-recovery, yeast growth, biomass yield, and lipid production from FW suggests a strong potential for cleaner and more sustainable production practices. Quantitative assessments, such as comparing energy consumption between traditional methods and the proposed process, or estimating emission reductions, could further support these potential improvements measurably.

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CRediT authorship contribution statement

Waheed A. Rasaq: Writing – review & editing, Writing – original draft, Visualization, Methodology, Data curation, Conceptualization. **Bartosz Matyjewicz:** Project administration, Investigation, Conceptualization. **Kacper Świechowski:** Writing – original draft, Methodology. **Zbigniew Lazar:** Validation, Supervision, Methodology. **Patryk Kupaj:** Investigation. **Tomasz Janek:** Data curation. **Marvin Valentin:** Writing – original draft, Visualization, Formal analysis. **Andrzej Białowiec:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2024.142385.

References

Abdalazeez, A., Li, T., Wang, W., Abuelgasim, S., 2021. A brief review of CO2utilization for alkali carbonate gasification and biomass/coal co-gasification: reactivity, products and process. J. CO2 Util. 43, 101370 https://doi.org/10.1016/j.jcou.2020.101370.

Baldera-saavedra, J., Quiñones-cerna, C.E., Sánchez-vásquez, S., Arévalo-gonzales, Y., Terrones-rodríguez, N., Rodríguez-soto, J.C., Robles-castillo, H.M., Cruz-noriega, La, M.D., 2024. Isolation and characterization of Yarrowia lipolytica YQ22 from diesel samples for phenol biodegradation. Environ. Res. Eng. Manag. 80, 32–38. https://doi.org/10.5755/j01.erem.80.1.33931.

Beopoulos, A., Chardot, T., Nicaud, J.M., 2009. Yarrowia lipolytica: a model and a tool to understand the mechanisms implicated in lipid accumulation. Biochimie 91, 692–696. https://doi.org/10.1016/j.biochi.2009.02.004.

Browse, J., McCourt, P.J., Somerville, C.R., 1986. Fatty acid composition of leaf lipids determined after combined digestion and fatty acid methyl ester formation from fresh tissue. Anal. Biochem. 152, 141–145. https://doi.org/10.1016/0003-2697(86)90132-6.

Cai, J., He, P., Wang, Y., Shao, L., Lü, F., 2016. Effects and optimization of the use of biochar in anaerobic digestion of food wastes. Waste Manag. Res. 34, 409–416. https://doi.org/10.1177/0734242X16634196.

Cordova, L.T., Lad, B.C., Ali, S.A., Schmidt, A.J., Billing, J.M., Pomraning, K., Hofstad, B., Swita, M.S., Collett, J.R., Alper, H.S., 2020. Valorizing a hydrothermal liquefaction aqueous phase through co-production of chemicals and lipids using the oleaginous yeast Yarrowia lipolytica. Bioresour. Technol. 313, 123639 https://doi.org/10.1016/j.biortech.2020.123639.

da Costa, A.M., de Oliveira Lopes, V.R., Vidal, L., Nicaud, J.M., de Castro, A.M., Coelho, M.A.Z., 2020. Poly(ethylene terephthalate) (PET) degradation by Yarrowia lipolytica: investigations on cell growth, enzyme production and monomers consumption. Process Biochem. 95, 81–90. https://doi.org/10.1016/j.procbio.2020.04.001.

Déniel, M., Haarlemmer, G., Roubaud, A., Weiss-Hortala, E., Fages, J., 2016. Energy valorisation of food processing residues and model compounds by hydrothermal liquefaction. Renew. Sustain. Energy Rev. 54, 1632–1652. https://doi.org/10.1016/j.rser.2015.10.017.

El Ouadrhiri, F., Elyemni, M., Lahkimi, A., Lhassani, A., Chaouch, M., Taleb, M., 2021. Mesoporous carbon from optimized date stone hydrochar by catalytic hydrothermal carbonization using response surface methodology: application to dyes adsorption. Int. J. Chem. Eng. 2021 https://doi.org/10.1155/2021/5555406.

European Environment Agency, 2014. 2014. Environmental Indicator Report 2014, 20 Oct 2014.

Fontanille, P., Kumar, V., Christophe, G., Nouaille, R., Larroche, C., 2012. Bioconversion of volatile fatty acids into lipids by the oleaginous yeast Yarrowia lipolytica. Bioresour. Technol. 114, 443–449. https://doi.org/10.1016/j.biortech.2012.02.091.

Fukuda, R., 2023. Utilization of n-alkane and roles of lipid transfer proteins in Yarrowia lipolytica. World J. Microbiol. Biotechnol. 39, 1–11. https://doi.org/10.1007/s11274-023-03541-3.

Gao, R., Li, Z., Zhou, X., Bao, W., Cheng, S., Zheng, L., 2020. Enhanced lipid production by Yarrowia lipolytica cultured with synthetic and waste-derived high-content volatile fatty acids under alkaline conditions. Biotechnol. Biofuels 13, 1–16. https://doi.org/10.1186/s13068-019-1645-y.

Gao, Z., Ma, Y., Liu, Y., Wang, Q., 2022. Waste cooking oil used as carbon source for microbial lipid production: promoter or inhibitor. Environ. Res. 203, 111881 https://doi.org/10.1016/j.envres.2021.111881.

Hejna, M., Świechowski, K., Rasaq, W.A., Białowiec, A., 2022. Study on the effect of hydrothermal carbonization parameters on fuel properties of chicken manure hydrochar. Materials 15. https://doi.org/10.3390/ma15165564.

Hu, Z.Y., Jiang, S.F., Shi, X.Y., Jiang, H., 2022. Simultaneous recovery of nutrients and improving the biodegradability of waste algae hydrothermal liquid. Environ. Pollut. 307, 1–7. https://doi.org/10.1016/j.envpol.2022.119556.

International Energy Agency, 2006. Annual Report 2006 IEA Bioenergy Pyrolysis of Biomass. Paris, France.

Isemin, R., Muratova, N., Kuzmin, S., Klimov, D., Kokh-Tatarenko, V., Mikhalev, A., Milovanov, O., Dalibard, A., Ibitowa, O.A., Nowotny, M., Brulé, M., Tabet, F., Rogge, B., 2021. Characteristics of hydrochar and liquid products obtained by hydrothermal carbonization and wet torrefaction of poultry litter in mixture with Wood sawdust. Processes 9, 1–10. https://doi.org/10.3390/pr9112082.

Jama-Rodzeńska, A., Białowiec, A., Koziel, J.A., Sowiński, J., 2021. Waste to phosphorus: a transdisciplinary solution to P recovery from wastewater based on the TRIZ approach. J. Environ. Manag. 287 https://doi.org/10.1016/j.jenvman.2021.112235.

Kantarli, I.C., Kabadayi, A., Ucar, S., Yanik, J., 2016. Conversion of poultry wastes into energy feedstocks. Waste Manag. 56, 530–539. https://doi.org/10.1016/j.wasman.2016.07.019.

Lachos-Perez, D., César Torres-Mayanga, P., Abaide, E.R., Zabot, G.L., De Castilhos, F., 2022a. Hydrothermal carbonization and Liquefaction: differences, progress, challenges, and opportunities. Bioresour. Technol. 343, 126084 https://doi.org/10.1016/j.biortech.2021.126084.

Lachos-Perez, D., César Torres-Mayanga, P., Abaide, E.R., Zabot, G.L., De Castilhos, F., 2022b. Hydrothermal carbonization and Liquefaction: differences, progress, challenges, and opportunities. Bioresour. Technol. 343 https://doi.org/10.1016/j.biortech.2021.126084.

Lazar, Z., Neuvéglise, C., Rossignol, T., Devillers, H., Morin, N., Robak, M., Nicaud, J.M., Crutz-Le Coq, A.M., 2017. Characterization of hexose transporters in Yarrowia lipolytica reveals new groups of Sugar Porters involved in yeast growth. Fungal Genet. Biol. 100, 1–12. https://doi.org/10.1016/j.fgb.2017.01.001.

Llamas, M., Tomás-Pejó, E., González-Fernández, C., 2020. Volatile fatty acids from organic wastes as novel low-cost carbon source for Yarrowia lipolytica. N. Biotech. 56, 123–129. https://doi.org/10.1016/j.nbt.2020.01.002.

Lu, X., Ma, X., Chen, X., 2021. Co-hydrothermal carbonization of sewage sludge and lignocellulosic biomass: fuel properties and heavy metal transformation behaviour of hydrochars. Energy 221, 119896. https://doi.org/10.1016/j.energy.2021.119896.

Lu, Y., Levine, R.B., Savage, P.E., 2015. Fatty acids for nutraceuticals and biofuels from hydrothermal carbonization of microalgae. Ind. Eng. Chem. Res. 54, 4066–4071. https://doi.org/10.1021/ie503448u.

Ma, X., Gao, Z., Gao, M., Ma, Y., Ma, H., Zhang, M., Liu, Y., Wang, Q., 2018. Microbial lipid production from food waste saccharified liquid and the effects of compositions. Energy Convers. Manag. 172, 306–315. https://doi.org/10.1016/j.enconman.2018.07.005.

Marzbali, M.H., Kundu, S., Halder, P., Patel, S., Hakeem, I.G., Paz-Ferreiro, J., Madapusi, S., Surapaneni, A., Shah, K., 2021. Wet organic waste treatment via hydrothermal processing: a critical review. Chemosphere 279, 130557. https://doi.org/10.1016/j.chemosphere.2021.130557.

Matyjewicz, B., Swiechowski, K., Koziel, J.A., Białowiec, A., 2020. Proof-of-concept of high-pressure torrefaction for improvement of pelletized biomass fuel properties and process cost reduction. Energies 13. https://doi.org/10.3390/en13184790.

Michely, S., Gaillardin, C., Nicaud, J.M., Neuvéglise, C., 2013. Comparative physiology of oleaginous species from the Yarrowia clade. PLoS One 8, 1–10. https://doi.org/10.1371/journal.pone.0063356.

Naveira-pazos, C., Veiga, M.C., Kennes, C., 2022. Bioresource Technology Accumulation of lipids by the oleaginous yeast Yarrowia lipolytica grown on carboxylic acids simulating syngas and carbon dioxide fermentation. Bioresour. Technol. 360, 127649 https://doi.org/10.1016/j.biortech.2022.127649.

Parchami, M., Ferreira, J.A., Taherzadeh, M.J., 2021. Starch and protein recovery from brewer's spent grain using hydrothermal pretreatment and their conversion to edible filamentous fungi – a brewery biorefinery concept. Bioresour. Technol. 337, 125409 https://doi.org/10.1016/j.biortech.2021.125409.

Park, Y.K., Bordes, F., Letisse, F., Nicaud, J.M., 2021. Engineering precursor pools for increasing production of odd-chain fatty acids in Yarrowia lipolytica. Metab. Eng. Commun. 12, e00158 https://doi.org/10.1016/j.mec.2020.e00158.

Park, Y.K., Dulermo, T., Ledesma-Amaro, R., Nicaud, J.M., 2018. Optimization of odd chain fatty acid production by Yarrowia lipolytica. Biotechnol. Biofuels 11, 1–12. https://doi.org/10.1186/s13068-018-1154-4.

Pereira, A.S., Miranda, S.M., Lopes, M., Belo, I., 2021. Factors affecting microbial lipids production by Yarrowia lipolytica strains from volatile fatty acids: effect of co-substrates, operation mode and oxygen. J. Biotechnol. 331, 37–47. https://doi.org/10.1016/j.jbiotec.2021.02.014.

PN-EN 15935:2022-01 Standard, 2022. Waste Characteristics. Determination of Loss on Ignition of Sludge, Treated Biowaste, Soil and Waste.

Pomraning, K.R., Kim, Y.M., Nicora, C.D., Chu, R.K., Bredeweg, E.L., Purvine, S.O., Hu, D., Metz, T.O., Baker, S.E., 2016. Multi-omics analysis reveals regulators of the response to nitrogen limitation in Yarrowia lipolytica. BMC Genom. 17, 1–18. https://doi.org/10.1186/s12864-016-2471-2.

Quarterman, J., Slininger, P.J., Kurtzman, C.P., Thompson, S.R., Dien, B.S., 2017. A survey of yeast from the Yarrowia clade for lipid production in dilute acid pretreated lignocellulosic biomass hydrolysate. Appl. Microbiol. Biotechnol. 101, 3319–3334. https://doi.org/10.1007/s00253-016-8062-y.

Rakicka, M., Kieroń, A., Hapeta, P., Neuvéglise, C., Lazar, Z., 2016. Sweet and sour potential of yeast from the Yarrowia clade. Biomass Bioenergy 92, 48–54. https://doi.org/10.1016/j.biombioe.2016.06.004.

Rakicka, M., Lazar, Z., Dulermo, T., Fickers, P., Nicaud, J.M., 2015. Lipid production by the oleaginous yeast Yarrowia lipolytica using industrial by-products under different culture conditions. Biotechnol. Biofuels 8, 1–11. https://doi.org/10.1186/s13068-015-0286-z.

Rasaq, W.A., Golonka, M., Scholz, M., Białowiec, A., 2021. Opportunities and challenges of high-pressure fast pyrolysis of biomass: a review. Energies 14, 1–20. https://doi.org/10.3390/en14175426.

Rasaq, W.A., Okpala, C.O.R., Igwegbe, C.A., Białowiec, A., 2024a. Navigating pyrolysis implementation—a tutorial review on consideration factors and thermochemical operating methods for biomass conversion. Materials 17. https://doi.org/10.3390/ma17030725.

Rasaq, W.A., Thiruchenthooran, V., Telega, P., Bobak, Ł., Igwegbe, C.A., Białowiec, A., 2024b. Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste. J. Environ. Manag. 357, 3–10. https://doi.org/10.1016/j.jenvman.2024.120722.

Saengsuriwong, R., Onsree, T., Phromphithak, S., Tippayawong, N., 2021. Conversion of tobacco processing waste to biocrude oil via hydrothermal liquefaction in a multiple batch reactor. Clean Technol. Environ. Policy. https://doi.org/10.1007/s10098-021-02132-w.

Sridhar, A., Kapoor, A., Senthil Kumar, P., Ponnuchamy, M., Balasubramanian, S., Prabhakar, S., 2021a. Conversion of food waste to energy: a focus on sustainability and life cycle assessment. Fuel 302, 121069. https://doi.org/10.1016/j.fuel.2021.121069.

Sridhar, A., Ponnuchamy, M., Kumar, P.S., Kapoor, A., 2021b. Food preservation techniques and nanotechnology for increased shelf life of fruits, vegetables, beverages and spices: a review. Environ. Chem. Lett. 19, 1715–1735. https://doi.org/10.1007/s10311-020-01126-2.

SundarRajan, P., Gopinath, K.P., Arun, J., GracePavithra, K., Adithya Joseph, A., Manasa, S., 2021. Insights into valuing the aqueous phase derived from hydrothermal liquefaction. Renew. Sustain. Energy Rev. 144, 111019 https://doi.org/10.1016/j.rser.2021.111019.

Swetha, A., ShriVigneshwar, S., Gopinath, K.P., Sivaramakrishnan, R., Shanmuganathan, R., Arun, J., 2021. Review on hydrothermal liquefaction aqueous phase as a valuable resource for biofuels, bio-hydrogen and valuable bio-chemicals recovery. Chemosphere 283, 131248. https://doi.org/10.1016/j.chemosphere.2021.131248.

Świechowski, K., Liszewski, M., Babelewski, P., Koziel, J.A., Białowiec, A., 2019. Fuel properties of torrefied biomass from pruning of oxytree. Data 4, 2–11. https://doi.org/10.3390/data4020055.

Świechowski, K., Matyjewicz, B., Telega, P., Białowiec, A., 2022. The influence of low-temperature food waste biochars on anaerobic digestion of food waste. Materials 15. https://doi.org/10.3390/ma15030945.

Taylor, P., Demirbas, A., 2007. Production of gasoline and diesel fuels from bio-materials 753–760. https://doi.org/10.1080/00908310500281288.

Tjørve, K.M.C., Tjørve, E., 2017. The use of Gompertz models in growth analyses, and new Gompertz-model approach: an addition to the Unified-Richards family. PLoS One 12, 1–17. https://doi.org/10.1371/journal.pone.0178691.

Uçkun Kiran, E., Trzcinski, A.P., Ng, W.J., Liu, Y., 2014. Bioconversion of food waste to energy: a review. Fuel 134, 389–399. https://doi.org/10.1016/j.fuel.2014.05.074.

Urbanowska, A., Kabsch-Korbutowicz, M., Aragon-Briceño, C., Wnukowski, M., Pożarlik, A., Niedzwiecki, L., Baranowski, M., Czerep, M., Seruga, P., Pawlak-Kruczek, H., Bramer, E., Brem, G., 2021. Cascade membrane system for separation of water and organics from liquid by-products of htc of the agricultural digestate—evaluation of performance. Energies 14. https://doi.org/10.3390/en14164752.

Vajpeyi, S., Chandran, K., 2015. Microbial conversion of synthetic and food waste-derived volatile fatty acids to lipids. Bioresour. Technol. 188, 49–55. https://doi.org/10.1016/j.biortech.2015.01.099.

Valta, K., Sotiropoulos, A., Malamis, D., Kosanovic, T., Antonopoulou, G., Alexandropoulou, M., Jonuzay, S., Lyberatos, G., Loizidou, M., 2019. Assessment of the effect of drying temperature and composition on the biochemical methane potential of in-house dried household food waste. Waste Manag. Res. 37, 461–468.

Vigneshwar, S.S., Swetha, A., Gopinath, K.P., Goutham, R., Pal, R., Arun, J., SundarRajan, P., Bhatnagar, A., Lan Chi, N.T., Pugazhendhi, A., 2022. Bioprocessing of biowaste derived from food supply chain side-streams for extraction of value added bioproducts through biorefinery approach. Food Chem. Toxicol. 165, 113184 https://doi.org/10.1016/j.fct.2022.113184.

Walker, C., Jr, M.M., Poudel, B., Cotter, C., Myers, R., Okekeogbu, I.O., Ryu, S., Khomami, B., Giannone, R.J., Laursen, S., Trinh, C.T., 2023. Biological upcycling of polyethylene into high-value chemicals. Am. Soc. Microbiol. 8, 1–23.

Zabaniotou, A., Rovas, D., Delivand, M.K., Francavilla, M., Libutti, A., Cammerino, A.R., Monteleone, M., 2017. Conceptual vision of bioenergy sector development in Mediterranean regions based on decentralized thermochemical systems. Sustain. Energy Technol. Assessments 23, 33–47. https://doi.org/10.1016/j.seta.2017.09.006.

Zajemska, M., Korombel, A., 2024. Risk factors for Poland to achieve the European commission ' s recycling and landfill targets and their effects on waste-to-energy conversion. A Review 17.

Zou, S., Zhang, B., Yan, N., Zhang, C., Xu, H., Zhang, Y., Rittmann, B.E., 2018. Competition for molecular oxygen and electron donor between phenol and quinoline during their simultaneous biodegradation. Process Biochem. 70, 136–143. https://doi.org/10.1016/j.procbio.2018.04.015.

Appendix No. 3

Waheed A. Rasaq
(Name and surname)

Wroclaw, Poland, 07.06.2024
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STATEMENT

I hereby declare that in the publication:

Waheed A. Rasaq, Bartosz Matyjewicz, Kacper Świechowski, Zbigniew Lazar, Patryk Kupaj, Tomasz Janek, Marvin Valentin, Andrzej Białowiec, 2024. "Food waste recycling to Yarrowia biomass due to combined hydrothermal carbonization and biological treatment". Journal of Cleaner Production 456, 1 – 10 doi:10.1016/j.jclepro.2024.142385

My contribution included:

I participated in the methodology of measurements of hydrothermal carbonization conditions. I participated in the text of the entire article, including the introduction part, description of the methodology, materials, analysis, and description of the results with discussion and conclusions. I participated in the preparation of the figures and tables included in the manuscript. I obtained funds for the publication of the article.

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Podpisano przez:

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Bartosz Matyjewicz
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Wroclaw, Poland, 23.05-2024
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Waheed A. Rasaq, Bartosz Matyjewicz, Kacper Świechowski, Zbigniew Lazar, Patryk Kupaj, Tomasz Janek, Marvin Valentin, Andrzej Białowiec, 2024. "Food waste recycling to Yarrowia biomass due to combined hydrothermal carbonization and biological treatment". Journal of Cleaner Production 456, 1 – 10 doi:10.1016/j.jclepro.2024.142385

My contribution included:

I participated in the developing design concept and methodology of measurements of the hydrothermal carbonization process experiment to obtain hydrothermal liquid for Yarrowia biomass analysis.

23.05.2024
Bartosz Matyjewicz
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Kacper Świechowski
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I hereby declare that in the publication:

Waheed A. Rasaq, Bartosz Matyjewicz, Kacper Świechowski, Zbigniew Lazar, Patryk Kupaj, Tomasz Janek, Marvin Valentin, Andrzej Białowiec, 2024. "Food waste recycling to Yarrowia biomass due to combined hydrothermal carbonization and biological treatment". Journal of Cleaner Production 456, 1 – 10 doi:10.1016/j.jclepro.2024.142385

My contribution included:

I participated in the developing concept and methodology of measurements of the hydrothermal carbonization process experiment.

03.06.2024 Świechowski
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Waheed A. Rasaq, Bartosz Matyjewicz, Kacper Świechowski, Zbigniew Lazar, Patryk Kupaj, Tomasz Janek, Marvin Valentin, Andrzej Białowiec, 2024. "Food waste recycling to Yarrowia biomass due to combined hydrothermal carbonization and biological treatment". Journal of Cleaner Production 456, 1 – 10 doi:10.1016/j.jclepro.2024.142385

My contribution included:
I participated in the validation, methodology, and analysis of the data of biological treatment results, and supervision of the manuscript preparation.

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Waheed A. Rasaq, Bartosz Matyjewicz, Kacper Świechowski, Zbigniew Lazar, Patryk Kupaj, Tomasz Janek, Marvin Valentin, Andrzej Białowiec, 2024. "Food waste recycling to Yarrowia biomass due to combined hydrothermal carbonization and biological treatment". Journal of Cleaner Production 456, 1 – 10 doi:10.1016/j.jclepro.2024.142385

My contribution included:

I participated in the biological treatment experiment process, and prepared tables during the manuscript preparation.

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Waheed A. Rasaq, Bartosz Matyjewicz, Kacper Świechowski, Zbigniew Lazar, Patryk Kupaj, Tomasz Janek, Marvin Valentin, Andrzej Białowiec, 2024. "Food waste recycling to Yarrowia biomass due to combined hydrothermal carbonization and biological treatment". Journal of Cleaner Production 456, 1 – 10 doi:10.1016/j.jclepro.2024.142385

My contribution included:

I participated in the biological treatment experiment process, and prepared tables during the manuscript preparation.

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My contribution included:

I participated in the description of the results and prepared tables in the manuscript.

10.06.2024
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Appendix No. 3

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Waheed A. Rasaq, Bartosz Matyjewicz, Kacper Świechowski, Zbigniew Lazar, Patryk Kupaj, Tomasz Janek, Marvin Valentin, Andrzej Białowiec, 2024. "Food waste recycling to Yarrowia biomass due to combined hydrothermal carbonization and biological treatment". Journal of Cleaner Production 456, 1 – 10 doi:10.1016/j.jclepro.2024.142385

My contribution included:

Developing the concept design of the study, including the selection of HTC parameters such as temperature and time. I participated in the writing – review & editing revision and supervision of the manuscript. Also, I served as the corresponding author.

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Review

Catalyst-Enhancing Hydrothermal Carbonization of Biomass for Hydrochar and Liquid Fuel Production—A Review

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Abstract: The research impact of catalysts on the hydrothermal carbonization (HTC) process remains an ongoing debate, especially regarding the quest to enhance biomass conversion into fuels and chemicals, which requires diverse catalysts to optimize bio-oil utilization. Comprehensive insights and standardized analytical methodologies are crucial for understanding HTC's potential benefits in terms of biomass conversion stages. This review seeks to understand how catalysts enhance the HTC of biomass for liquid fuel and hydrochar production, drawing from the following key sections: (a) catalyst types applied in HTC processes; (b) biochar functionality as a potential catalyst; (c) catalysts increasing the success of HTC process; and (d) catalyst's effect on the morphological and textural character of hydrochar. The performance of activated carbon would greatly increase via catalyst action, which would progress the degree of carbonization and surface modification, alongside key heteroatoms. As catalytic HTC technology advances, producing carbon materials for thermochemical activities will become more cost-effective, considering the ever-growing demands for high-performance thermochemical technologies.

Keywords: thermal conversion process; feedstock; hydrochar and bio-oil; catalyst; hydrothermal carbonization

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1. Introduction

Industrial output and economic growth are propelled by energy. The global quantity of energy consumption rises annually with population and intense urbanization. To meet global needs, especially in developing nations, global energy consumption is projected by the end of the century to exceed 84,000 metric tons [1,2]. In daily production processes, organic solid waste (OSW) as a potential resource loses its original value [2]. Since conventional fossil fuels still comprise a significant amount of the market today, finding substitutes for fossil fuels is essential. Thus, OSWs, as a fuel with a bright future, remain a significant energy conservation candidate [3]. Considered a waste product of human existence/production, OSWs are primarily separated into two groups as follows: (a) non-lignocellulosic wastes (such as sludge, manure, and digested food waste), and (b) lignocellulosic wastes (such as yard waste and agricultural waste) [4,5]. In urban areas, digested food waste would potentially be an OSW source of bio-renewable energy production [6,7], able to lessen environmental issues and fossil fuel reliance.

In general, biochemical and thermochemical processes can convert organic waste into energy. Anaerobic digestion is the most used biochemical approach for generating biogas for power plant purposes. High levels of volatile fatty acids and ammonia, however, can easily cause anaerobic digestion to become unstable and inefficient [8], and the release of biogas digestate with large volumes and high nutrient contents also poses a significant environmental risk. More crucially, because it can represent an unanticipated risk to humans through food chains, the proliferation of new pollutants, in particular antibiotics and antibiotic resistance genes, has sparked worry across the globe [9]. In contrast, thermochemical methods and biochemical methods, (gasification, pyrolysis, hydrothermal carbonization, and combustion) can efficiently convert biomass and manure into energy in a short time [4,10–12]. Previously, the most common thermal processes, like pyrolysis and incineration, appeared less effective in terms of energy recovery and value-added products, given the high moisture content of emergent organic waste. The presence of dangerous bacteria in waste presented certain challenges for technologies, including limited processing efficiency and the creation of secondary waste pollutants [13–15]. To successfully convert OSW into energy, one of the main priorities is to find a suitable method for OSW processing. Hydrothermal carbonization (HTC) technology is discovered to be an effective method for OSW treatment since HTC could reduce the need to dry the feedstock, providing a carbonized solid coupled with an aqueous phase rich in nutrition [13–16]. Biofuels and valuable chemicals can be produced from renewable resources like waste materials, woody and herbaceous biomass, forestry residues, crops, and algal biomass through HTC treatment [17]. A series of reactions known as decarboxylation, dehydration, condensation, and aromatization take place during HTC. According to earlier research, produced hydrochar can be used for energy storage, environmental remediation through the adsorption of heavy metals, CO_2 capture in the agriculture sector, and the production of alternative fuel feedstock for the steel and cement industries [18].

The research impact of catalysts on the HTC process remains an ongoing debate, especially the quest to enhance biomass conversion into fuels and chemicals, which requires diverse catalysts to optimize bio-oil utilization [19,20]. Different types of homogenous [21–23] and heterogeneous catalysts [24] employed in HTC would enhance the product yield and associated properties [25]. Furthermore, catalysts reducing tar and char formation would help progress the efficiency of the liquefaction process [26]. The water–gas shift reaction can be sped up through the use of catalysts, which can also increase the liquid yield [27,28]. Alkali catalysts also lessen the production of char and tar. Song and colleagues [29] reported that the yield of crude considerably increased from 33.4% to 47.2% when 1.0 wt% Na_2CO_3 was added to wood biomass, and other workers reported an increase in the oil yield from 17.88 wt% without a catalyst to 34.85 wt% with the addition of K_2CO_3 at 300 °C [30]. At 280 °C and concentrations of 0.235–0.94 M K_2CO_3, it was demonstrated that char formation was decreased while the liquid yield increased from 17.8% to 33.7% [31]. High-efficiency and inexpensive catalysts that undergo thermal conversion treatment must be viewed as an economically viable tactic that can successfully compete in the current energy market. Understanding, therefore, the foundation of catalysts, like magnesium oxide (MgO), is crucial. Calcium-based materials are considered another attractive and emerging aspect. These materials are thought by some to be reasonably priced catalysts that can provide catalytic HTC. Commercial lignocellulosic biomass could also be used in fast catalytic pyrolysis, which would involve a particular scale like a circulating fluid-bed reactor facility. Furthermore, the foundation sites of MgO would promote ketonization and aldol condensation reactions, resulting in an adequate production of hydrogen bio-oil [32]. For instance, Oliveira and colleagues reported that a bimetallic Pt/Rh catalyst, supported on carbon black and water, obtained at the lowest carbonization temperature, was eventually used to achieve a maximum H_2 yield of 98.7 mmol H_2 $gTOC^{-1}$ [33]. Rather than 250 °C to 300 °C, the temperature for the employed catalyst ranged from 150 °C to 180 °C. In this context, and given the thermodynamic constraints, lower process temperatures would favor a higher conversion of syngas into liquid fuels [34]. Furthermore, biochar-based catalysts, which are categorized as non-graphitizable, have drawn a lot of interest recently for their ability to produce biodiesel from microalgal lipids [35]. Moreso, the induction of chemical activation also played a major role in the context of thermal conversion products.

After impregnating biochar or hydrochar with one or more chemical agents (oxidizing agents, alkaline solutions, acids, etc.), an activation process in a fixed-bed reactor with a nitrogen flow rate is carried out [36]. However, phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), zinc chloride ($ZnCl_2$), potassium hydroxide (KOH), and potassium carbonate (K_2CO_3) are the most-used chemical activating agents for the chemical activation process [37–39]. At low temperatures, $ZnCl_2$ can penetrate the inner of the biomass and can remain liquid during the entire thermal process below 700 °C. Consequently, $ZnCl_2$ is dispersed uniformly throughout the biochar's matrix. $ZnCl_2$ could be eliminated to produce a well-developed microporous biochar. Additionally, given that $ZnCl_2$ has a strong capacity to dehydrate at high temperatures, it may lower the carbonization temperature of biomass components. Moreover, $ZnCl_2$ inhibits the formation of tar and modifies the pathways by which biomass decomposes [40]. Tevfi and colleagues recently used a high-pressure (40 MPa) autoclave reactor at three different temperatures (255, 275, and 355 °C) to liquefy Syrian mesquite stem in order to produce bio-oil in supercritical acetone and methanol with and without (zinc chloride, sodium hydroxide) a catalyst. They discovered that the peaked conversion of 77.96% and the liquid yield of 49.67% were attained in acetone at 295 °C with zinc chloride present [41]. Furthermore, biological catalyst systems which include free lipase, traditional immobilized lipase, and lipase immobilized on magnetic nanoparticles are of growing interest in the research. Although free enzyme catalysts in biological catalyst systems offer many advantages over chemical catalysts, the high cost of the enzymes and their non-reusability contribute to the high cost of biodiesel production. Considering that immobilized enzymes can be recycled, more favorable attention is required because they aggregate well, and, like silica-coated magnetic nanoparticles, are the ideal carrier for immobilizing enzymes [42]. Overall, the current kinetics reaction and statistical methods are significantly affected by the experimental data used for the calibration. Indeed, there could be proposed relationships between the HTC operating conditions and the properties of emergent phases.

A summary of reviews involving hydrothermal treatment and biomass conversion, along with catalysts/catalytic processes within the recent decade is shown in Table 1. Most reviews appear to focus on the catalyst as an enhancement tool of HTC products like biochar (solid from other thermal conversion process), hydrochar (solid from HTC), and bio-oil [37,43–45], including how catalyst types and their mechanisms determine the bio-oil yield [19,46–48]. There are some reviews that have shown activated biochar as a catalyst, and how the types favor the process that leads to an emergent end product [49–51]. While many reviews focus on the applications, the physical and chemical properties of the products, and the chemistry of the process, they also present the general knowledge of HTC [52–55]. Given the rapid development of experimental studies into the influence of catalysts in HTC, continued efforts using literature synthesis are necessary to highlight the strengths (of catalysts) and the generation of fuels, including value-added chemicals from different feedstock. In addition to enhancing the potential benefits of the HTC of biomass conversion stages, the corresponding standard analytical methodologies are crucial for understanding the HTC's potential benefits in terms of biomass conversion stages. To supplement existing information, therefore, this current review seeks to understand how catalysts enhance the HTC of biomass for liquid fuel and hydrochar production, drawing from the following key sections: (a) catalyst types applied in HTC processes; (b) biochar functionality as a potential catalyst; (c) catalyst increasing the success of the HTC process; and (d) the catalyst's effect on the morphological and textural character of hydrochar. To provide a pictorial viewpoint of this work, key stages in the application of catalysts in the thermal conversion process, from feedstock selection, catalyst types, treatment methods, and analytical methods of output, are presented in Figure 1.

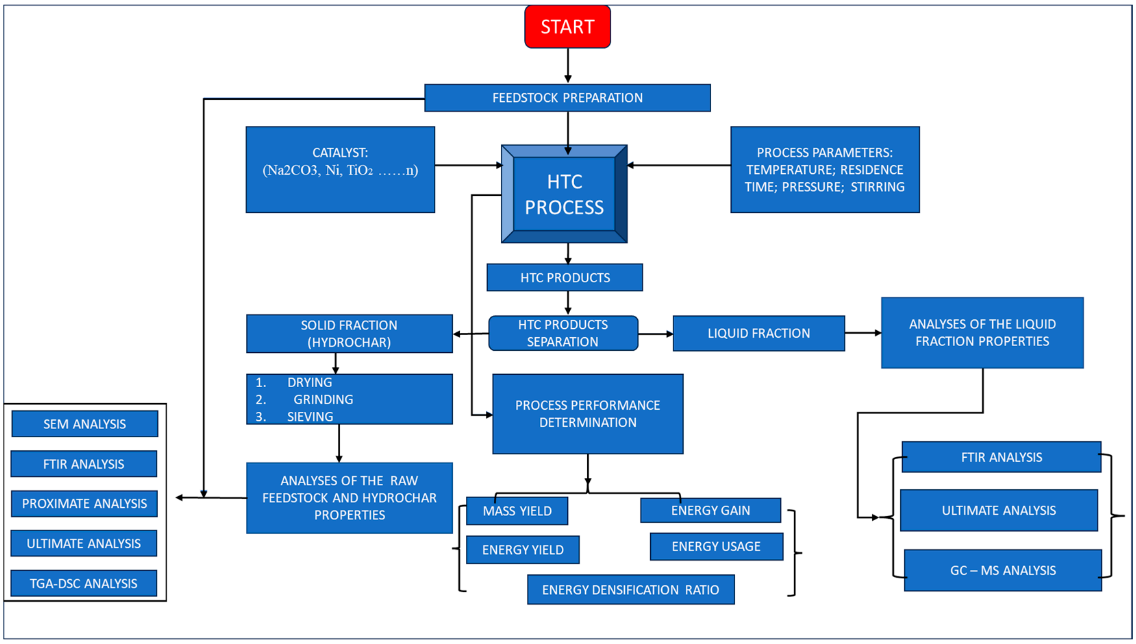

Figure 1. Key stages in the application of catalysts in the thermal conversion process, from feedstock selection, catalysts types, treatment methods, and analytical methods of output.

Table 1. Summary of reviews involving hydrothermal treatment, biomass conversion, and catalysts/catalytic processes from the past decade.

Review Objective	Key Sections	References
Reviewed biochar value of catalysts in biofuel production, alongside the processes utilized/various biomass sources	- Methods of biochar production - Biochar composition - Biochar-based catalysts - Biochar as a catalyst for fuel production	[43]
Review summarized/critically discussed catalyst types/catalytic mechanisms, as well as process parameters	- Impact of process parameters on hydrothermal carbonization - Reaction pathways that the feedstock compounds take during hydrothermal carbonization - Progress of catalytic hydrothermal carbonization - Hydrochar application/catalyst selection - Environmental/techno-economic features of catalytic hydrothermal carbonization - Challenges/future prospects of catalytic hydrothermal carbonization	[46]
Reviewed biochar as a catalyst for biomass conversion via thermolysis (pyrolysis)/hydrothermolysis (liquefaction/gasification).	- Biochar - Use of biochar in catalysis - Biochar-based catalytic biomass conversion processes	[44]
Reviewed whether biochar and hydrochar are sustainable catalysts for persulfate(PS) activation	- PS activation mechanism - Properties desired in hydrochar/biochar for PS activation - Strategies for desired char properties - Whether biochar/hydrochar is a sustainable catalyst for persulfate activation	[45]

Table 1. *Cont.*

Review Objective	Key Sections	References
Reviewed catalysts for high bio-oil yields with improved quality/factors that influence the catalytic hydrothermal liquefaction (HTL), mechanisms of catalytic-HTL reaction, HTL products	- Catalytic effect on bio-oil yield - Use of catalysts in HTL - Mechanism - Physicochemical properties of catalytic bio-oil - Effect of catalysts on the aqueous phase extract of HTL - Effect of catalyst on the gas fraction of HTL - Effect of catalyst on HTL biochar	[47]
Reviewed hydrochar characteristics/reaction mechanisms for char production technology, e.g., hydrothermal carbonization, hydrochar activation and functionalization	- Hydrochar versus biochar - Hydrochar production technologies - Activation and functionalization of hydrochar - Applications of activated hydrochar	[37]
Reviewed conversion techniques that transform lignocellulosic biomass waste into biochar (gasification and pyrolysis), compared conversion techniques in terms of benefits, drawbacks, and limitations	- Biomass conversion techniques - Biochar modification techniques - Applications of biochar-derived catalysts - Impacts of industrial revolution 4.0 on biomass industry	[49]
Reviewed biochar-based catalysts for fuel production, thermochemical routes and their yield, composition/production, and choice for fuel production	- Techniques for biochar production - Composition of biochar - Why biochar-based catalysts? - Biochar catalysts utilized to produce fuel	[35]
Reviewed two strategies to convert biomass into functional catalysts (Photocatalytic/Nonirradiant application of biomass)	- Biomass conversion to hydrothermal carbonation carbon (HTCC) catalysts - Biomass conversion to a biochar catalyst - Differences between biochar and HTCC	[50]
Reviewed catalysts' effects on thermochemical conversion research/development involving biomass/thermochemical conversion processes	- Torrefaction - Pyrolysis - Liquefaction - Gasification	[28]
Review summarized preparation/modification/catalytic application of biochar in biofuel production, from biomass hydrolysis to tar reduction	- Biochar synthesis - Biochar characteristics - Biochar modifications - Biochar-based catalysts to produce biofuel	[40]
Reviewed HTL catalytic upgrade/catalytic performances on algae (HTL/biocrude) upgrade	- Catalytic HTL involving algae - Catalytic upgrade involving biocrude - Reaction mechanism in algae HTL/biocrude upgrading	[48]
Reviewed the research progress of heterogeneous catalysts for biodiesel production/low grade feedstocks	- Problems of currently used catalysts for biodiesel - Advantages of solid acid catalysts - Effects of some reaction parameters for biodiesel production	[19]
Reviewed versatile applications of biochars as catalysts that upgrade biomass	- Thermochemical degradation to form biomass/biochar - Activation/functionality of biochars as catalysts/catalyst support - Biochar-based catalysts that upgrade biomass	[51]

2. Catalyst Types Applied in the HTC Process

Catalysts play a crucial role in either the thermal conversion process or ex situ upgrading via impacting the overall multiscale design of these processes [56,57]. To ensure the best catalyst combination and process design, the catalytic upgrading of HTC necessitates a thorough understanding of the chemical reactions that result in the desired products, as well as the identification of the catalyst species that would favor these transformations at various process configurations [57,58]. This is a complex challenge due to the three following reasons: (A) There are many components present in the product, derived from the sequential reactions happening during the biomass thermal conversion process. For instance, a typical bio-oil contains more than 300 oxygenated compounds [58]. Selecting a catalyst that can convert these species selectively into the desired products with minimal by-product formation is challenging. (B) The feedstock composition is frequently liable to large variations because of non-homogeneities in the material feed and process conditions. It is difficult to find a catalyst that can tolerate these alterations, but it is crucial for the various thermal and upgrading processes [56]. (C) Finally, the most advantageous combination of operating conditions and catalyst type is a significant difficulty in the development of multi-scale processes, largely due to the catalyst's "apparent" performance being reliant on the kind of operating parameters and reactor. The first part of this section provides a thorough overview of the state of our understanding regarding various upgrading catalysts and the kinetic pathways they are associated with. Different catalyst impacts and associated operating conditions are then reviewed [56]. Generally, a variety of fuels including methane, hydrogen, ethanol, and chemicals such as fructose, sorbitol, glucose, lactic, and levulinic acid can be obtained from the catalytic conversion of organic material [58].

Reactions involving catalytic transesterification can employ biological or chemical catalysts. Two catalytic routes are recognized for improving the properties and yield of the HTC products, including (a) the application of homogenous catalysts, such as alkali or organic acid catalysts, and (b) the application of heterogeneous catalysts, such as supported metals, molecular sieves, altered molecular sieves, insoluble inorganic salts, transition metal oxide, and others. The homogeneous catalysts are comprised of acid and alkali catalysts. Solid acid, base, biomass waste-based, acid-base bifunctional, and nanocatalysts are all included in the heterogeneous catalyst [59].

2.1. Homogeneous Catalysts

Homogeneous catalysts with a broad range of applications that have been investigated for the HTC include (1) alkaline compounds like carbonates and hydroxides with K, Na, and Ca forms; (2) organic acids like acetic and formic acid; and (3) inorganic acids like sulfuric acid. The homogenous catalysts used in the HTC are soluble in water at room temperature. In certain situations, homogeneous catalysts can process liquids without experiencing coking, making them cost-effective [60].

Nevertheless, homogenous catalysts have certain disadvantages as well. When employing homogeneous catalysts [61], the catalyst recovery process requires energy-intensive and expensive separation stages. Another drawback is that the homogeneous catalysts are corrosive, which is an important factor to consider when choosing the materials for the HTC reactor design [62]. Since the catalyst selection can reduce production costs, it plays a significant role in the synthesis of HTC products. The amount of free fatty acids (FFAs) in the feedstock oils determines the type of catalyst that should be used. The use of homogeneous catalysts is the first conventional technique for producing biodiesel. Homogeneous catalysts exist in the same phase as their reactants. On the other hand, homogeneous catalysts can be classified into two categories: homogeneous acid catalysts and homogeneous alkali catalysts. Since the reaction is fast and the reaction conditions are moderate, homogeneous alkali catalysts such as CH_3ONa, CH_3KO, KOH, and NaOH are the most widely used industrial catalysts in the industrial transesterification process for the production of biodiesel [63]. When extra-pure virgin oils are used, with FFA contents and acid values, respectively, of less than 0.5% and 1 mg KOH/g, homogeneous alkali catalysts should offer superior purity/yield, which is why enhancing the quality and, at the same time, maximizing the bio-oil yield has been crucial in catalysts' performance. In HTC, a variety of heterogeneous [21,22,64–67] and homogeneous [58,68] catalysts have been employed to enhance the yield and characteristics of bio-oil. Previously, a homogenous catalyst like Na_2CO_3 seems to dominate in the majority of HTC studies of lignocellulosic biomass to increase the bio-oil yield. But, while some studies found the yield to decrease [69], in the report of Long and colleagues, the HTC of bagasse in subcritical water $MgMnO_2$ was assessed. The intensification effect of the $MgMnO_2$ was investigated, where the product distribution and composition of volatiles and residue were compared. The result demonstrated the relative content of furfural of 2-methyl-2-cyclopenten-1-one, (250 °C in 5.02 min), 2-hydroxy-3-methyl-2-cyclopenten-1-one (250 °C in 7.67 min), and the significant increase in their derivatives. These compounds generally come from the Aldol condensation of the bagasse carbohydrate HTC product, which can be enhanced by the alkali catalyst [67]; others reported that adding Na_2CO_3 to various algal strains would increase the bio-oil yield [23,70]. Shakya and colleagues studied the bio-oil yield of *Nannochloropsis* with Na_2CO_3, and found this to be considerably lower at 250 °C than it was at higher temperatures. This kind of algal strain's high protein content was most likely the cause of this. Peptide bonds in proteins and glycosidic bonds in carbohydrates are more stable at lower temperatures. As a result, proteins hydrolyze slowly at low temperatures. However, proteins hydrolyze more readily at temperatures between 300 and 350 °C, which increases the amount of bio-oil produced. Because of the higher protein conversion at 350 °C, *Nannochloropsis* produced a larger yield. Additionally, this demonstrates that, at higher temperatures, the relative abundance of nitrogenous compounds increases [25]. The different ways that lipids, proteins, and carbohydrates liquefy when Na_2CO_3 is present could account for this discrepancy in the results [25]. To further elaborate the above discourse, Table 2 shows the catalyst (homogeneous and heterogeneous) types by feedstock, HTC operating conditions, and product yield [28,65,67,68,71–82]. The homogeneous catalysts like KOH, Na_2CO_3, CH_3COOH, and others display significant variability in product yields, underscoring the influence of the catalyst type and feedstock compatibility. Therefore, understanding the catalyst choice/type, the selection of feedstock, and the corresponding parameters involved in HTC treatment helps in achieving higher quality products.

Table 2. Catalyst (homogeneous and heterogeneous) types by feedstock, HTC operating conditions, and product yield.

Catalyst	Type	Feedstock	HTC Operating Conditions	Products Yield (%)			Reference
				Bio-Oil	Char	Gas	
Heterogeneous Catalyst Systems							
H-ZSM−5	Acidic catalyst	Algae	70 mL water, 7 g algae, catalyst of 0.35 g, at 300 °C for 20 min	34	24	42	[80]
H-ZSM−5		Wheat straw	350 °C for 60 min, catalyst to biomass—0.1:1	28	37	35	[28]
H-ZSM−5		Wheat husk	350 °C, catalyst to biomass—0.1:1, 1 h	26	31	43	[74]
Ce/H-ZSM−5		Algae	70 mL water, 7 g algae, catalyst of 0.35 g, at 300 °C for 20 min	50	18	32	[80]
CaO	Basic catalyst	Fruit bunch	390 °C for 30 min, water used was at a ratio of 1:10 of biomass and 1 wt% catalyst	63	-	-	[73]

Table 2. *Cont.*

Catalyst	Type	Feedstock	HTC Operating Conditions	Products Yield (%)			Reference
				Bio-Oil	Char	Gas	
Heterogeneous Catalyst Systems							
Pd/C	Metallic catalyst	Algae	87.5% water volume, at 350 °C for 60 min, 15 mg of catalyst	38	-	-	[81]
CoMo/Al_2O_3		Algae	95% water volume, at 350 °C for 60 min, 0.38 g of catalyst	55	-	-	[68]
Ni/SiO_2-Al_2O_3		Algae	95% water volume, at 350 °C for 60 min, 0.384 g of catalyst	55	-	-	[68]
Ni/TiO_2		Algae	480 g of water, at 300 °C for 30 min, and a catalyst of 10% of algae of 120 g	31	-	-	[71]
Pt/C		Algae	350 °C for 60 min, 95% water volume, and 0.38 g of catalyst	49	-	-	[68]
Ni		Cellulose	300 °C for 10 min, cellulose (1 g), water (5 g) and Ni (0.1 g)	25	6	13	[72]
Zeolite	Neutral catalyst	Algae	95% water volume, at 350 °C for 60 min, 0.38 g of catalyst	48	-	-	[68]
$MgMnO_2$		Bagasse	250 °C in 1 to 15 min, catalyst 2 g, and 20 g of biomass	60	12	28	[67]
Homogeneous Catalytic Systems							
KOH	Basic catalyst	Algae	350 °C, 3 g algae with 27 mL of catalyst	15	5	10	[65]
Na_2CO_3		Algae	300 °C for 30 min, 20 g algae with 150 mL water, 5 wt% catalyst	21	20	30	[75]
Na_2CO_3		Algae	250 °C for 60 min, 10 g of algae with 1:6 of biomass-to-water	38	25	8	[25]
K_2CO_3		Sewage sludge	350 °C, 7 g of sludge, 2% weight of sludge	45	7	-	[77]
CH_3COOH	Acidic catalyst	Algae	350 °C, 3 g algae, and 27 mL of catalyst	17	5	25	[65]
H_2SO_4		Algae	290 °C for 20 min, algae 30 g with 1:3 of biomass-to-water	28	12	60	[76]
HNO_3		Food waste mixture	250 °C for 120 min, feedstock 35 g, 350 mL water, catalyst 10% of biomass	-	47	-	[79]
$FeSO_4$		Sewage sludge	300 °C for 40 min sludge to water 1:5, catalyst, and 5 wt.% of dry Sludge	48	-	-	[78]
$FeSO_4$		Pine wood	350 °C for 40 min, 1 g of wood, 2% weight of wood	63	-	10	[82]

2.2. Heterogeneous Catalysts

Typically, heterogeneous acid catalysts exist in a solid state and function at distinct stages within the liquid reaction mixture. A wide range of solid catalysts have been used to produce biodiesel during the past ten years. The benefits of heterogeneous catalysts' resistance to water and the amount of FFA in feedstock are making them more important for the production of biodiesel [19,83]. Heterogeneous acid catalysts can overcome the primary issues related to toxic effects and vessel corrosion when compared to homogeneous acid catalysts [19]. These catalysts allow biodiesel production from inexpensive low-quality feedstocks without acid pretreatment because they are insensitive to the high FFA and water content in the feedstock oils [19]. Though BaO is toxic and easily soluble in methanol or ethanol, CaO and BaO are typically stronger than MgO [84]. Given its superior availability, activity, selectivity, and low solubility in methanol, calcium oxide (CaO) is considered an affordable, easily accessible, and highly effective heterogeneous catalyst that requires moderate reaction conditions [83]. Furthermore, when producing industrial biodiesel, it remains extremely stable for longer periods. Das and colleagues [85] generated biodiesel with the oil of *Scenedesmus quadricauda* algae and a cobalt-doped CaO catalyst.

Metal catalysts are useful in the manufacturing of jet fuel, diesel, oil, and other fuels, but they also hold promise for the next wave of green energy technologies. For instance, liquid hydrazine (N_2H_4) decomposes at an ambient temperature to form N_2, H_2, and NH_3 over a commercial Ir/-Al_2O_3 catalyst, which is already utilized as a propellant to modify the satellite orbit and attitude [86]. Solid catalysts such as silica-alumina, zeolites, and supported metals are so far preferred as catalytic materials for improving associated hydrocarbon fuels and bio-oil yields, as mentioned in the section of the list of catalyst types [87]. Feedstock algae or other biomass types can involve both homogeneous and heterogeneous catalyst types, which might differ in terms of HTC operating conditions and product yield. Table 2 also reveals that there are instances where char and gas were not analyzed after HTC [28,68,71,72,75,80,81]. Heterogeneous catalysts such as Ce/H-ZSM−5, H-ZSM−5, and others exhibit diverse bio-oil, char, and gas yields, emphasizing the sensitivity of the outcomes to catalyst composition and operating conditions. Xu and colleagues study the HTC of *Chlorella pyrenoidosa* with the addition of Ce/HZSM-5 and HZSM-5 to analyze the chemical groups and components of *C. pyrenoidosa* bio-oil. The results showed that the effects of Ce/HZSM-5 were superior to that of HZSM-5 due to its highly dispersed Ce_4O_7 with trivalent and tetravalent cerium in the zeolite skeleton channel, smaller particle size, larger specific surface, and significantly enhanced Lewis acid active center when compared with HZSM-5. The components of the bio-oils revealed that feedstock contains organic compounds with C4–C16 oxygen, such as aldehyde, ketone, acid, ester, and some chemicals that contain nitrogen, which originate from the protein in *C. pyrenoidosa.* Additionally, it has a higher heating value, which may be explained by the presence of more hydrocarbons such as cyclane derivatives, benzene derivatives, and alkene derivatives. Their findings demonstrate Ce/HZSM-5's strong catalytic properties and potential applications [80]. Furthermore, other reports discuss the production of biodiesel using heterogeneous acid catalysts. However, since the heterogeneous acid catalyst is typically hydrophilic, the water that is created during the esterification of fatty acids will reduce its activity. This is because the acid catalysis of these inorganic oxide solid acids takes place in the acidic hydroxyl groups (-OH), which function as potent Brönsted acid sites. In the presence of water, the hydration of -OH would lessen the acid strength of these [88–90]. Additionally, the low acid site concentration, microporosity, and the hydrophilic nature of the catalyst surface raise issues in terms of heterogeneous acid catalysts. It was recently reported that a novel class of solid acid catalyst based on sulfonated carbon showed promise in producing biodiesel [88].

In summary, Table 2 underscores the importance of tailored catalyst selection based on feedstock and operating parameters to achieve optimal outcomes in HTC processes, as evidenced by the distinct performances detailed for each catalyst across different works.

3. Biochar Functionality as a Potential Catalyst

Recently, a range of solid waste materials (including egg shells, fly ash, and fish bones) have been used as feedstocks for the preparation of hydrochar to be used as affordable catalysts to reduce the high cost of catalyst synthesis [91]. Biochar is a low-cost/carbon-rich material produced via thermochemical degradation. When compared to other commercially available solid-based catalysts, biochar is highly recommended due to its benefits over other catalysts involving enhancing the quality and yield of the thermal conversion process of several feedstock types [92]. The utilization of biochar as a carbonaceous catalyst or support in the production of biodiesel holds great potential, owing to its inexpensive cost, the presence of surface functional groups, and its relatively high surface-to-volume ratios [93]. Biochar is used as a heterogeneous catalyst or support because it is inexpensive, can be tailored to specific functional groups, has a large surface area, and is perfect for producing biodiesel, as shown in Figure 2. Moreso, it has an environmentally friendly nature, and good thermal, chemical, and mechanical stability [94]. Numerous scientists choose to investigate biochars because they are cheap, reusable, and environmentally friendly catalysts. According to Ormsby and colleagues, during the simultaneous reactions of transesterification and esterification of non-edible oils, recyclable biochar-based catalysts demonstrated better activity when compared with conventional acid catalysts [95]. Chang and colleagues demonstrated that the addition of inorganics (K and Fe) improves the catalytic activity of biochar [40], and the adsorption of metal precursors towards the synthesis of biochar-supported metal catalysts is facilitated by the presence of functional groups on the surface of biochar [51]. Furthermore, Chi and colleagues reported a study in which the biochar was treated with 10 M KOH, which resulted in catalysts with the highest catalyst activity for biodiesel production produced from canola oil due to their increased surface area and acid density [35]. Sulfonated biochar with ethanol at 60 °C demonstrated 77–88% fatty acids conversion from waste vegetable oil [96], which can be used directly/in combination with petroleum diesel in most diesel engines [51].

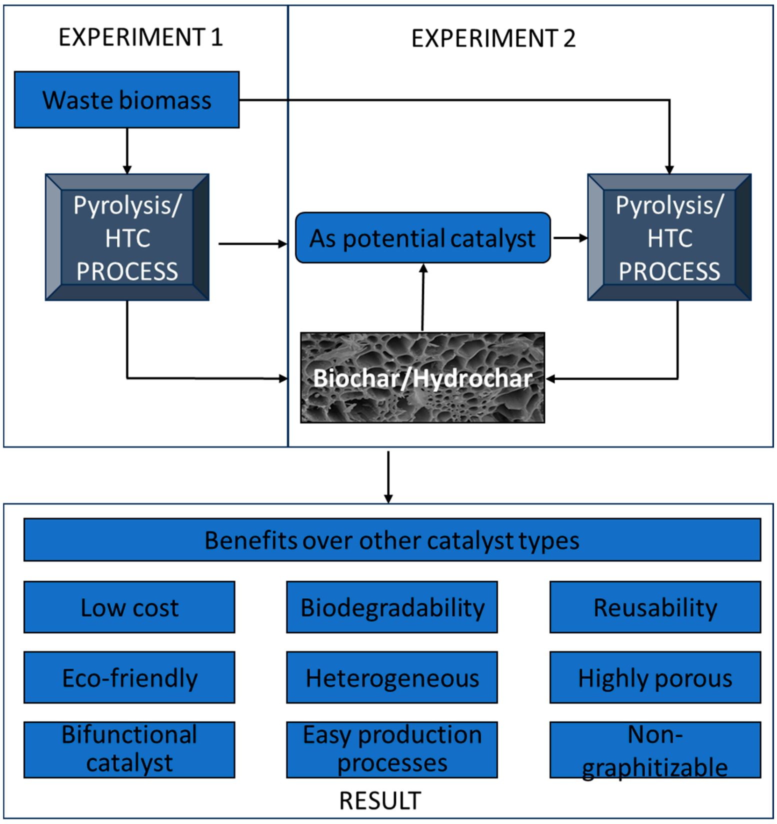

Figure 2. The benefit of the application of biochar as a potential catalyst.

The merits of biochar-based catalysts come from the production process, which makes it straightforward and profitable due to the availability of sustainable feedstock, and the physicochemical properties of biochar can be easily modified through different activation techniques. Essentially, surface functional groups, the presence of inorganic species, and the hierarchical structure derived from biomass are among the biochar features that make catalysts superior in diverse applications [35,40]. Due to those mentioned above, small-scale research on biochar as a catalyst remains scanty, and, to fully grasp its potential, particularly for long-term feasibility and economic viability, more extensive research is imperative. Furthermore, to make a significant advancement in the field of biochar-based catalysts, new technologies must be substituted for outdated ones, such as equipment, activation strategies, and conversion technology.

4. Catalyst Increasing the Success of the HTC Process

It is well-established that catalysts occupy crucial space in hydrothermal carbonization (HTC), providing numerous benefits, from enhancing bio-oil yield, improving biomass conversion, increasing biofuel flow properties, reducing biofuel heteroatom content, to lowering the required temperature for optimal biofuel yield [47]. Alkali, acids and metal salts, due to their cost-effectiveness, thrive in homogeneous catalysis during the hydrothermal liquefaction process. However, their recovery and corrosiveness challenges would limit their application, which might shift the focus towards heterogeneous catalysts [97] which are believed to offer high catalytic activity, low corrosion rate, and easy recovery compared to homogeneous catalysts [48]. Several homogeneous and heterogeneous catalysts have been shown to increase bio-oil yield during the hydrothermal liquefaction process, wherein heterogeneous catalysts revealed higher conversion efficiency over homogeneous catalysts [87,98]. An iron/nickel oxide nanocomposite resulted in a maximum bio-oil yield of 59.4 wt%, surpassing the 50.7 wt% achieved without the catalyst. At a temperature of 320 °C, 60 min of residence time, and 1.5 g of catalyst dosage, the maximum bio-oil yield was achieved [98]. HTC on various biomasses has enhanced the efficiency of liquefaction by catalysts, wherein alkali catalysts (such as KOH, NaOH, Na_2CO_3, and K_2CO_3) were particularly applied to wood [99,100], bark [101], EPFB (palm fruit bunch) [102], switchgrass [103], and algae [69]. Thus, alkali catalysts are crucial in enhancing biomass conversion, increasing bio-crude output, and improving bio-crude quality by elevating hydrogen content and decreasing oxygen concentration. Besides liquid yield and biomass conversion, where catalytic activity follows the order of K_2CO_3 > KOH > NaOH in some studies [100,102], Zhao and colleagues showed that the pore and surface area volume of the biochar increased significantly following chemical activation treatment with KOH [91]. Additionally, potassium carbonate has been shown to serve as the catalyst where hydroxides induce more severe equipment corrosion [58]. HTC product distribution, including bio-oil, gas, and char, has also received great interest. The total oil yields of cotton stalk, wheat straw, and corn stalk were less than 10%; the gas yield was 37–55% across the four tested feedstocks, while char covered 35–45% in the experiments performed using subcritical water without a catalyst by Wang and colleagues [104].

When rice straw was liquefied, however, a greater bio-crude yield of 21.1 wt% was attained in ethanol at 350 °C [66]. Gholizadeh and colleagues understood that biochar would support the hydrotreatment process through its unique structural properties [20]. To produce bio-oils, Wang and colleagues investigated the effects of solvents (water, ethanol, acetone, and carbon dioxide) on the liquefaction of pinewood sawdust. The experiment outcomes demonstrated that, by increasing the liquid yield and reducing the production of solid residue, both the catalyst and the solvent could significantly enhance the liquefaction process. The solvent had a significant impact on how the liquid products were distributed as well [105]. The direct liquefaction of woody feedstock using $Ba(OH)_2$ as a catalyst greatly increased the yield of heavy oils by 50% [105,106]; Lu and colleagues examined the effects of cellulose HTC with varying initial concentrations of basic and acidic conditions using H_2SO_4, HCl, $Ca(OH)_2$, and NaOH. Additives sped up the conversion of glucose as the concentrations increased and sped up the dissolution of the solid cellulose [107]. Additionally, acids promoted dehydration, which continued as the main carbonization mechanism with a lower oxygen content. Acid additives enhancing the production of CO_2 promoted the breakdown of organic acids through decarboxylation [107].

To further elaborate the above discourse, Table 3 provides a comprehensive characterization of hydrochar properties produced under different severity conditions of HTC, along with the use of various catalysts and feedstocks. Feedstock collection of interest included the likes of *Spirulina platensis*, *Nannochloropsis*, straw, *Dunaliella tertiolecta*, sludge (sewage), food waste, pig feces, *Nannochloropsis* sp., Spruce Lignin, Spirulina, *Ulva prolifera*, bagasse, and Sunflower oil [1,23,30,46,69,71,108]. The higher heating values (HHV), measured in MJ kg^{-1}, exhibit considerable variability, spanning from 15.5 to 39.6 MJ kg^{-1}. The elemental analyses (wt%) of C, H, N, S, and O content showcase significant differences based on the catalyst, feedstock, and temperature. Various catalysts, including NiO, $Ca_3(PO_4)_2$, Na_2CO_3, Fe, Mn, K_2CO_3, HCl, HNO_3, H_2SO_4, Pt/C, ZSM-5, CH_3COOH, $MgMnO_2$, and HCOOH, contribute distinct impacts to hydrochar properties, influencing the elemental composition and HHV. Examples such as NiO with *Spirulina platensis* at 350 °C, yielding an HHV of 38.4 MJ kg^{-1}, and Pt/C with *Nannochloropsis* sp. at 350 °C, producing a high HHV of 39.6 MJ kg^{-1}, showcase the diverse outcomes achievable.

Table 3. Characterization of hydrochar properties produced in the severity of HTC conditions.

Catalysts	**Feedstock**	**Temp. (°C)**	**HHV (MJ kg^{-1})**	**Elemental Analysis (wt%)**					**Reference**
				C	**H**	**N**	**S**	**O**	
NiO	*Spirulina platensis*	350	38.4	75	9	6	1.4	6.5	[23]
$Ca_3(PO_4)_2$			35.1	72	9	4	1.1	12.7	
Na_2CO_3			36.3	72	9	5	0.9	11.8	
Fe	Nannochloropsis	300	35.5	70	9.8	7	0.4	12.2	[71]
Mn			33.2	69	8.6	7.2	0.4	14.6	
K_2CO_3	Straw	300	17.2	53	4.3	0.9	0.7	40	[30]
Na_2CO_3	*Dunaliella tertiolecta*	360	30.7	63	7.7	3.7	-	25.1	[69]
HCl	Sludge	230	-	46	4.8	3.7	0.1	19.2	[46]
HNO_3	Food waste	250	-	57	5.8	1.6	0.5	23.4	
H_2SO_4	Pig feces	230	-	56	4.2	2.4	-	36.8	[1]
Pt/C	*Nannochloropsis* sp.	350	39.6	75.9	10.8	4.0	0.7	8.48	[71]
K_2CO_3	Straw	300	27.2	67.9	7.6	0.8	0.6	23.2	[30]
ZSM-5	Spruce lignin	-	-	64.7	6.3	0.5	0	28.6	[109]
CH_3COOH	*Spirulina*	-	35.1	71.7	9.7	6.1	0.9	11.6	[110]
H_2SO_4	*Ulva prolifera*	180	15.5	35.7	6.5	2	2.2	32.4	[111]
$MgMnO_2$	Bagasse	250	32.6	65.9	10.2	0.4	0.3	23.3	[67]
K_2CO_3	Sewage sludge	350	36.6	75.6	10.6	4.7	-	9.2	[77]
HCOOH	Sunflower oil	350	37.3	68.4	11	0.2	0	20.5	[22]

Wang and colleagues showed Ni/TiO_2 as a better catalyst, enhancing the yield, quality, and carbonization conversion of biocrude. Ni/TiO_2 was characterized by XRF, XPS, and XRD. The reaction temperature affected the HTL of microalgae Nano-chlorosis over Ni/TiO_2, as 300 °C produced the highest liquefaction conversion of 89.28% with a maximum biocrude yield of 48.23% [71]. More so, the metals Fe, Ni, and Zn added to biomass via HTC were investigated elsewhere. Fe demonstrated the greatest performance with increased bio-crude production from 17.4% of the blank test to 26.5%, and an increase in the higher heating value (HHV) from 27.0 MJ/kg to 29.7 MJ/kg. Also, Zn increased the number of water-soluble products by slightly increasing the amount of bio-crude. The H/C ratio and HHV of the resulting biocrude were dramatically increased with each of the evaluated transition metals [72]. Abdullah and colleagues used HTC to produce an activated carbon catalyst from renewable mesocarp fiber obtained from palm oil. In their investigation, they found that adding K_2CO_3 and $Cu(NO_3)_2$ created a bifunctional catalyst that could be used to convert spent cooking oil into biodiesel. The catalyst had a mesoporous structure with a BET surface area of 3909.33 m^2/g and an ideal treatment ratio of 4:1 (K_2CO_3:$Cu(NO_3)_2$). This resulted in elevated basic (5.52 mmol/g) and acidic (1.68 mmol/g) concentrations on the catalytic surface, which encouraged transesterification and esterification reactions [18]. Indeed, Table 4 provides a comprehensive overview of how different catalysts, including K_2CO_3, KOH, CaO, MnO, Na_2CO_3, TiO_2, ZrO_2, Na_2CO_3, Ni, among others [23,29–31,73,98,112,113], impact the HTC process, influencing product properties such as oil yield, gas yield, and chemical composition. Watanabe and colleagues studied the effects of the homogeneous and heterogeneous catalysts (H_2SO_4, NaOH and TiO_2, ZrO_2, respectively) on glucose in hot compressed water at 200 °C using a batch-type reactor. In their findings, the homogeneous catalyst demonstrated that the acid catalyst promoted dehydration, while the isomerization of glucose to fructose was catalyzed by alkali. Additionally, it was discovered that ZrO_2 functioned as a base catalyst to enhance the isomerization of glucose, whereas TiO_2 acted as an acid catalyst to promote the formation of 5-hydroxymethylfuraldehyde [27]; the application of K_2CO_3 on the HTC of wood biomass at 280 °C for 15 min decreased the hydrochar yield and the obtained oil contained mainly phenolic compounds [31]; Song and colleagues reported that bio-oil increased to 47.2% with 1.0 wt% of Na_2CO_3 from 33.4% without a catalyst in the conversion of corn stalk at 277–377 °C [29]. The importance of using catalysts in HTC is emphasized by their varied effects on different feedstocks and temperatures. For instance, K_2CO_3 and KOH at 550–600 °C favor a water–gas shift. Yim and colleagues investigated the effect of metal oxide catalysts like CaO, MgO, MnO, SnO, ZnO, CeO, NiO, AlO, and LaO on the supercritical HTC of empty fruit bunch (EFB) obtained from oil palm residues for the bio-oil yields and characteristics studied. EFB, water, and 1.0 wt% metal oxide were placed into a batch reactor and heated to 390 °C at a reaction time of 60 min. In their study, among the tested catalysts, the four most active metal oxides with lower electronegativity (CaO, MnO, La O, and CeO) provided a maximum relative yield of bio-oil, at 1.40 times that without catalyst [73]. The enumeration of a wide range of catalysts underscores their significance in tailoring the HTC process for sustainable biofuel and chemical production.

Table 4. List of catalyst types and effects in the HTC process on product properties.

Catalysts	Feedstock	Temperature °C	Effect	Reference
K_2CO_3 and KOH	Organic wastes and wet biomass	550–600	Water–gas shift	[114]
MnO, CaO, CeO_2, MgO, SnO, Al_2O_3, NiO, La_2O_3	Empty fruit bunch	390	Addition of CaO, CeO_2, MnO, and La_2O_3 catalysts maximized bio-oil yield	[73]
Na_2CO_3	Cornstalk	277–377	Oil yield increased	[29]
K_2CO_3	Wood biomass	280	Decreased the char yield	[31]
K_2CO_3	Barley straw	280–400	Oil yield increased	[30]
Ni, Na_2CO_3	Cellulose	200–350	Char decreased	[115]
Ni, K_2CO_3	Glucose	350–500	Water–gas shift	[113]
H_2SO_4, NaOH, ZrO_2, TiO_2	Glucose	200	Isomerization of glucose increased	[27]
Na_2CO_3 NiO	*Spirulina platensis microalgae*	300–350	Increased oil yield	[23]
NiO, $Ca_3(PO_4)_2$	*Spirulina platensis microalgae*	300–350	Increased gas yields	[23]
Ni/TiO_2	*Nannochloropsis microalgae*	300	Increased hydrocarbons in bio-oil and acids	[71]

Table 4. *Cont.*

Catalysts	Feedstock	Temperature °C	Effect	Reference
Pd/HZSM-5@meso-SiO_2	*Spirulina microalgae*	380	Oil yields increased and reduced coke yields	[116]
Co-Zn/HZSM-5	Pine sawdust	300	Hydrocarbon content and oil yields increased	[114]
Na_2CO_3	*Pavlova microalgae*	250–350	HHV and oil yields increased	[25]
$MgMnO_2$	Sugarcane bagasse	250	Degradation of lignin	[67]
Ni	Cellulose	350	Enhanced H_2 yield	[117]
H_2SO_4, zeolite, FeS	Wheat straw	100–180	Degradation of lignin	[118]
H_2SO_4	*Ulva prolifera*	180	Increased oil yields	[111]
K_2CO_3	Sewage sludge	350	Promote the hydrolysis of carbohydrate to increase the oil yield	[2]
Biochar at 875 °C + KOH	Woody biomass	-	Surface area of hydrochar increased	[35]
Biochar at 875 °C + KOH	Rice husk	-	Surface area of hydrochar increased	[119]
Biochar at 875 °C + KOH	Pomelo	-	Increase the surface area of hydrochar	[91]
Biochar + sulfonated with SO_3H	Wood	-	The porosity and surface area of the biochar increased	[96]
Ru/C	Oil from beech wood	350	High HHV of oil and low oxygen content	[120]
Ru/TiO_2	Oil from beech wood	350	It improves the oil yield	[120]
Pd/C	Oil from beech wood	250	Demonstrate a high oil yield and reduced oxygen content	[120]
Pt/C	Oil from beech wood	250	High oil yield, but oxygen content is relatively high	[120]
Fe	Cellulose	300	(HHV) increased from 27.0 to 29.7 MJ/kg of the blank test and the bio-oil yield from 17.4% to 26.5%	[72]
Zn	Cellulose	300	A slight increase in the bio-oil yield and water-soluble products also increased	[72]
Fe	Biomass	340	Less gas emission for obtained HTL bio-jet fuel and lower production costs	[121]

5. Catalyst Effect on the Morphological and Textural Character of Hydrochar

Investigating the changes in the specific surface area of HTC products, in particular hydrochar, could be achieved using the multi-point BET adsorption method [122]), while the structure, composition, and texture of the prepared catalysts and produced hydrochar were examined using scanning electron microscope (SEM). Numerous studies have investigated the impact of the addition of catalysts on the hydrochar properties of specific feedstock. According to Zhao and colleagues, the total surface area and pore volume of pure pomelo peel biochar were 6.7 m^2/g and 24.4 mm^3/g, respectively. With the addition of KOH as an activating agent, the surface area significantly increased (from 6.7 to 278.2 m^2/g), as well as the pore volume (from 24.4 to 154.2 mm^3/g) [91]. Elsewhere, four different kinds of activated carbons were employed, namely $FeCl_2$, $FeCl_3$, FeC_2O_4, and $FeC_6H_5O_7$. Thus, in the context of the external surface area and total pore volume, $FeC_6H_5O_7$-prepared activated carbon showed the highest results, while it was reported that $FeCl_3$ and $FeCl_2$ make promising substitutes for the production of high-quality activated carbon with a relatively high specific surface area and advantageous surface functional groups. The total surface area and micropore volume values were higher than those of the activated carbons obtained with FeC_2O_4 and $FeC_6H_5O_7$ [123].

SEM is typically used to examine the morphology of hydrochars under various HTC conditions, producing micrographs that display the material's physical characteristics and surface morphology [52]. Abdullah and colleagues' study used mesocarp fiber (MF), employing HTC for pretreatment in the presence of H_3PO_4. Thus, activated carbon undergoes a modification process with $Cu(NO_3)_2$ and K_2CO_3 after carbonization. Following that, they utilize SEM images captured at 20,000× to identify changes in the hydrochar surface morphology. Consequently, their results of raw MF and impregnated MF hydrochar indicated a dense surface with few variable pore sizes, and significant changes were observed. They concluded that the pretreatment with HTC in the presence of H_3PO_4 improved the degradation of MF by cleaving long-chain compounds [18]. Additionally, another finding reported that the number of surface pores gradually increased in the HTC conditions, especially the temperature, and a mesh structure appeared before transforming into a bar-like structure [124]. Furthermore, SEM images of biochar were also investigated elsewhere, where the morphology was heterogeneous, with particles ranging from a few micrometers to agglomerates higher than 100 µm. A single particle detail was noticed, revealing an increased porosity. The larger surface porosities were not very deep; however, they were formed by several small pores, according to their findings. The BET results are consistent with the conclusion that these micropores could help in the adsorbing properties of this material [125]. For example, Table 5 showcases the BET analyses of diverse feedstocks, such as corn straw, mesocarp fiber, sludge, tobacco stems, cattail leaves, arundo donax linn, wheat straw, cornstalk, manure, rice husk, pomelo peel, and bagasse of sugarcane [91,108,126–131]. This table details the HTC process, presenting crucial information, including temperature, BET surface area, SEM, pore volume, and citations for each catalyst–feedstock pairing. These data provide insights into the specific surface characteristics of feedstocks under various catalysts and temperatures, which is crucial for understanding and optimizing the HTC process. Recently, increasing evidence obtained via characterization techniques reveals that the structural evolution of catalysts caused by the interplay with electrolytes, electric fields, and reactants brings about the formation of real active sites. Therefore, key ideas related to structural evolution, such as stability, active sites, catalysts, and their significance, are presented in this review. Furthermore, previous studies indicated that the presence of hydrophilic functional groups on the surface of the biochar may aid in the adsorption of hydrophilic reactants like ethanol. Reactants can easily reach the active sites due to a large pore size. In some circumstances, the advantages of biochar's superior pore morphology may outweigh the drawbacks of its low $–SO_3H$ group density [40,88].

The hydrochar produced under various process conditions and from various feedstock types has a different structural characteristic. The majority of studies use FTIR techniques to examine the surface functional groups of raw biomass and hydrochar due to the complex composition of the hydrochar and the highly variable hydrothermal parameters and feedstock used in HTC. The Fourier infrared spectroscopy (FTIR) measurements were conducted to observe the changes in the functional groups of hydrochars' properties following HTC under different conditions [122]. The functional groups available on the hydrochar and feedstock are usually determined using FTIR, as presented in Table 6, including an asymmetry stretching vibration, aliphatic hydrocarbon chain stretching, and bending vibrations [18]. Indicators and their corresponding functional groups and vibrations can be seen in Table 6. The symmetrical and asymmetrical C–H stretching vibrations of the methyl and methylene groups are significant. The absorption at 1717 cm^{-1} is attributed to C-O stretching, which may originate from carboxylic, ketones, or aldehydes acids. However, the carbonyl in carboxylic acids absorbs much more intensely than those in ketones and aldehydes, which, combined with the presence of –OH, can confirm the existence of carboxylic acids rather than ketones or aldehydes. The vibrations of the aromatic ring breathing cause absorption at 1612 cm^{-1} [133].

Table 5. BET analyses of selected feedstock and different catalyst types.

Catalyst	Feedstock	Temp. (°C)	Surface Area (m^2/g)	SEM (nm)	Pore Volume (cm^3/g)	Reference
KOH	Pomelo peel	500	278.2	5000	154.2	[91]
$ZnCl_2$	Corn straw	200	110.2	10,000	0.6867	[126]
$2K_2CO_3/CuO$	Mesocarp fiber	200	678.8	5000	0.494	[18]
TiO_2	Sludge	-	-	500	-	[127]
K_2CO_3	Tobacco stems	450	255.7	-	1.647	[128]
H_2SO_4	Cattail leaves	200	423.0	20,000	0.286	[129]
$FeCl_3$	Arundo donax Linn	-	927.0	5000	0.509	[123]
$FeCl_2$	Arundo donax Linn	-	760	5000	0.466	[123]
$ZnCl_2$	Wheat straw	200	106.1	10	0.6195	[126]
SO_3H	Cornstalk	400	20.58	-	0.03	[131]
HCl	Manure	190	28.92	-	0.088	[130]
Ru	Rice husk	520	806	-	0.58	[119]
Biochar + SO_4	Wood	400	242	-	0.13	[95]
Citric acid	Pomelo peel	200	11.72	1000	0.06	[132]
Fe	Bagasse of sugarcane	200	75	-	-	[62]

Table 6. Functional groups associated with catalysts, their corresponding feedstock, and working parameters.

Catalyst	Feedstock	Temp (°C)	Wavenumber (cm^{-1})	Functional Group	Reference
SO_3H	Cornstalk	400	1177 and 1043	O=S=O asymmetric stretching	[131]
Graphene oxide	Tobacco		2800–3000	C–H aromatic structure and stretching vibration of aliphatic	[134]
$ZnCl_2$	Sunflower	600	3700 and 3000	C-H aliphatic stretching vibration	[38]
K_2CO_3	Switchgrass	235	1166	C-O-C asymmetry stretching of hemicelluloses and cellulose	[103]
Na_2CO_3	Microalgae	360	1269 and 967	C-O Stretching	[69]
KOH	Palm fruit bunch	270	1680–1570	C-C stretching of aromatic groups	[102]
$Ca(OH)_2$	Pine bark	300	1717	C=O stretching	[101]
Ni	Cellulose	300	3300	O–H stretching vibration of in phenols and alcohols	[72]
Fe	Paulownia wood	340	1700	Indicated the presence of ketone and C=O stretching vibration	[99]
K_2CO_3	Barley straw	300	1263, 1201, 1113 and 1032	The C-O stretching vibrations	[30]
Na_2CO_3	Spirulina	350	2935	Indicating C–H stretching vibrations bonds	[23]
$8K_2CO_3/CuO$	Mesocarp fiber		3102	V-OH stretching	[18]
Citric acid	Pomelo peel	220	2000–1000	Indicated the existence of C-C and C-O functional groups	[132]
H_2SO_4	Cattail leaves	200	2000–1000	OK group on the surface generated the -OH group	[129]
$ZnCl_2$	Prosopis farcta	295	3344	O-H stretching vibration bands	[41]

The functional groups associated with catalysts, their corresponding feedstock, and working parameters are shown in Table 6. Across the functional groups, there are single-and double-bond organic structures/stretched vibrations [38,41,69,91,102,131,134]. According to Sliz and Wilk's findings, bands in the 800–900 cm^{-1} range represent C–H in the plane bend. The comparison of the methyl band at 1380 cm^{-1} and the methylene band at about 1470 cm^{-1} indicates that, after Virginia mallow undergoes HTC treatment, the branched-chain tends to become a more linear structure [122]. Similar findings reported that the bagasse from sugarcane demonstrates a characteristic absorption of herbaceous biomass. The band at 3419 cm^{-1} represented the characteristic absorption of -OH stretching vibration. The peaking at 2922 cm^{-1} was assigned to the symmetric methyl group [67]. Absorption at 1464 cm^{-1} and 1424 cm^{-1} indicate the C–H stretching of alkanes. Primary, secondary, and tertiary alcohols' C–O stretching is the cause of absorption at 1121 cm^{-1} and 1099 cm^{-1}. However, in the case of bio-crudes derived from de-ashed barks, absorption at 1717 cm^{-1} is significantly weaker, suggesting that the bio-crude contains either no carboxylic acids or very little due to the direct liquefaction of the barks. Since alkali compounds (K_2CO_3 or $Ca(OH)_2$) are thought to catalyze the formation of carboxylic acids in the hydrothermal liquefaction of biomass, this result could be explained via the absence of alkali compounds in the bark ash [101], The bond vibrations corresponding to the C-H bending (1098 cm^{-1}), CH_2 rocking (719 cm^{-1}), and C=O stretching (1737 cm^{-1}) of hydrocarbons, free fatty acids, and esters are crucial [126]. Recently, research by Aysu and Halil demonstrated that the C-O stretching vibration bands at 1023.93 cm^{-1} and O-H stretching vibration bands at 3344.57 cm^{-1} disappeared in bio-chars [41], which could be attributed to the decomposition of raw feedstock and the removal of oxygen due to the thermal cracking of feedstock components producing carbonaceous hydrochar during the HTC process [108].

6. Areas of Future Research

Researchers who are new to thermal conversion technologies may consider this review as a foundation to rapidly deepen their understanding of catalyst applications/research. Moreover, areas of future research involving the application of catalysts in HTC treatment can be seen in Figure 3, which involve considerations like environmental, economical, analytical methods, feedstock/catalyst selection, as well as (HTC) operating conditions. Although several catalyst applications in thermal conversion technologies and approaches have been investigated in recent decades, the economic part of thermal technology does not seem thoroughly explored. Besides the economic aspect, there is a need for a broader scope of hydrochar-produced entities alongside catalyst functioning via HTC, especially for activated carbon production. Such studies should employ optimization operating/process conditions, which should allow for a combination of feedstock, HTC catalysts, and activation procedures—all of which are aimed at enhanced supercapacitor performance. In addition to the performance, the following environmental and recycling perspectives could be considered: (a) environmental impact and cost, which might necessitate the testing of novel activating agents and HTC catalysts with less environmental impact, and (b) the recycling of the activation agent and HTC liquid fraction where possible [35,135]. Feasibly, the massive body of scientific evidence regarding hydrochar reveals that the liquid/gas product needs additional attention. More detailed analyses of by-products that contain intermediate products would elevate the understanding of hydrothermal conversion, especially the formation of hydrochar. Moreso, the prior-treatment process is essential to the HTC liquid fraction and hydrochar for nutrient substances, such as P and N recovery. For emphasis, the distribution, transformation mechanism, recovery, and future initiatives should also seriously consider the relevant analysis and treatment [52,67]. From an environmental perspective, HTC products offer numerous benefits for their applications. However, the economic aspects need to be estimated based on the investments in the conversion technology and production costs [35]. This could be achieved through the addition of a suitable catalyst to a specific feedstock regarding the target product application.

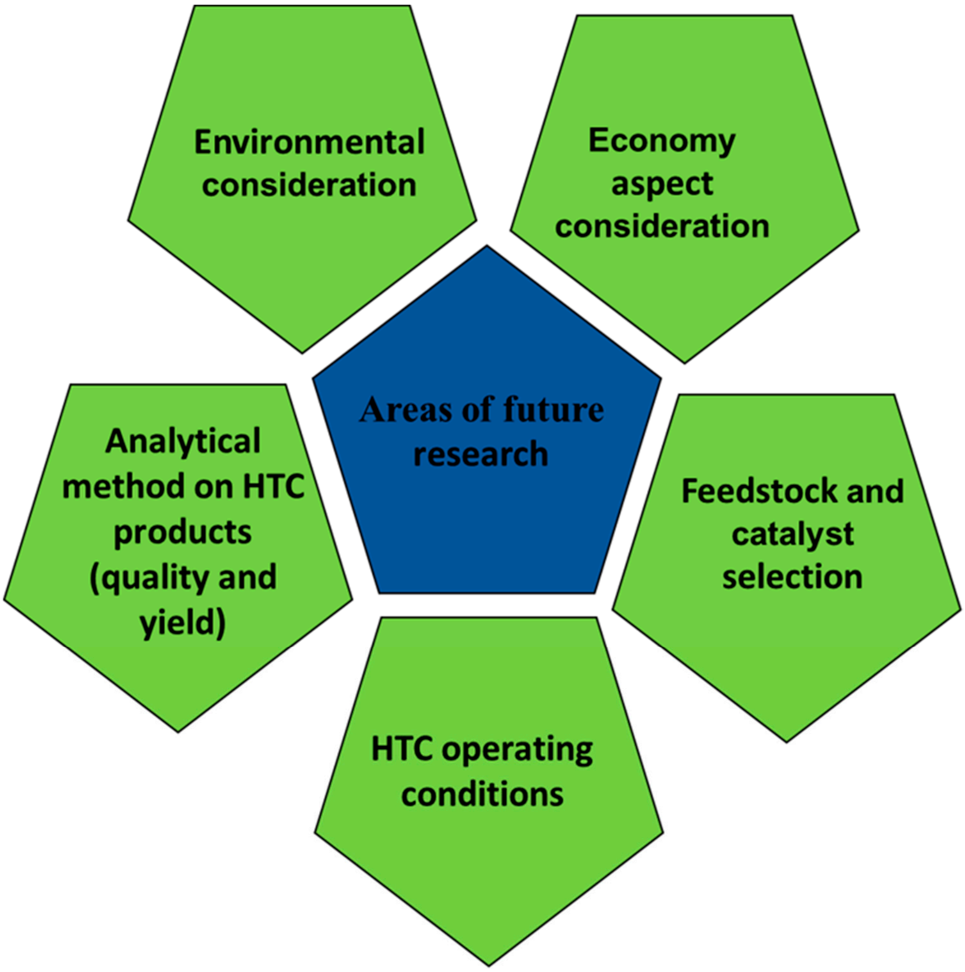

Figure 3. Areas of future research involving the application of catalysts in HTC treatment.

Again, as shown in Figure 3, areas of future research involving the application of catalysts in HTC treatment have a direct/indirect link to life cycle assessments (LCAs), which can assist in evaluating and comparing various scenarios of renewable process integrations, providing answers to concerns of society and decision makers. Biochar is used as a heterogeneous catalyst or support because it is inexpensive, has a large surface area, can be tailored to specific functional groups, and is perfect for producing biodiesel. Because of its stable structure, strong mechanical and thermal stability, and chemically hierarchical structure derived from biomass, biochar is regarded as a superior catalyst in a variety of catalytic applications [35]. When catalysts are applied in HTC, the water biomass mixture's properties are first affected, leading to the intended modifications in the process and end products. Consequently, the catalyst of choice is determined by the user's ultimate goal. For instance, the use of acid catalysts that promote hydrolysis can enhance the production of hydrochar. On the other hand, by using basic catalysts to promote the formation of liquid products, the formation of hydrochar can be reduced [136]. Furthermore, catalysts can also be used to reduce emissions like NOx that are produced during biomass combustion. In addition to the high-temperature thermal fixation of nitrogen in the combustion air, which contains excess oxygen, NOx is also produced by the fuel's chemically bound nitrogen being converted. Thus, the fuel's N content is one of the variables that influences the quantity of NOx generated. The behavior of N during the HTC treatment is related to the precombustion control of NOx, and it has been demonstrated that utilizing catalysts to switch from pure water to a more basic and acidic aqueous solution can enhance the removal of N [137]. Mumme and colleagues investigated the effects of cellulose and an agricultural digestate on natural zeolite in HTC. Zeolite significantly and marginally increased the energy and carbon content of the hydrochar that was produced from digestate and cellulose. Moreover, the catalytic HTC products had larger pore volumes and surface areas. The primary cause of the variations observed between the digestate and zeolite results is the zeolite layer's physical and chemical shielding of organic compounds such as cellulose. The fact that zeolite retained the digestate's cellulose fraction resulted in this [138]. According to research from Abd Hamid and colleagues, complete carbonization in HTC can occur at temperatures as low as 200 °C when Lewis acid catalysts ($FeCl_2$ and $FeCl_3$) are used. Prior research has examined the impact of catalysts, including acetic acid, KOH, KCl, Na_2CO_3, and NH_4Cl, on the hydrochar of HTC [139,140].

However, careful catalyst development is required to scale up the catalytic process. If premature deactivation is to be prevented, then a better understanding of the process design must be applied. Ahamed and colleagues carried out a comparable LCA through contrasting an incineration system and an AD system with a combined HTC system and oil refinery system (for the transesterification of the HTC liquid fraction with acid treatment, which produces glycerol and bio-diesel). In their study, they took into account one ton of food waste, the system boundary, which included collection, processing, waste conversion, and the disposal of food waste, as well as three outputs, namely electrical energy (using biodiesel with a 35% efficiency), hydrochar, and glycerol. According to their LCA results, when the feedstock's oil content exceeds 5%, the suggested HTC and refinery combination is more advantageous [53]. This review found that the addition of a catalyst in the hydrothermal process to enhance the process performs better technically and has a smaller environmental impact. Overall, it can be said that defining the boundaries of the scenarios while taking into account the difficulties is critical to take into account in a thorough LCA of the use of catalysts in HTC. This perimeter encompasses not only the stages of preparation and transformation, but also the post-treatment problems brought on by HTC, like waste management and expensive energy requirements.

7. Concluding Remarks

Critically, there are competing variables of influence involving HTC products, like gas formation, hydrochar, and liquid fraction. Also, the physicochemical components of the analysis can include ultimate or proximate analysis, aromatic structure, surface functional groups, and morphological aspects emanating from catalyst additives. Understanding how biomass behaves under hydrothermal conditions helped by various alkaline/transition metals is an essential first step to the complicated liquefaction mechanism of lignocellulosic biomass, as well as how it affects the products' quality and yield. Indeed, multiple catalysts and thermal operating conditions would allow for the production of lignocellulosic HTC products, most of which have been primarily empirical with an emphasis on rapid commercial process development. Fundamentally, biomass conversion should project a high-quality yield and by-products including proteins, lipids, residual carbohydrates, fibers, fat, and other biopolymers that are efficiently transformed into biofuels and biochemicals through waste-to-energy technologies.

For emphasis, the application of catalysts should enhance the degree of carbonization and surface modification, alongside the introduction of better heteroatoms, which should substantially improve the effectiveness of activated carbon. Overall, the addition of catalysts to the HTC, with a secondary treatment stage if necessary, would potentially resolve the existing barriers and produce activated carbon with special qualities that go above and beyond the current standards. To establish the use of homogeneous catalysts in HTC would be crucial in promoting the success of bio-oil production, which can be attributed to the decrease in tar and char formation, with K_2CO_3 and NaOH being the most and least effective catalysts, respectively. On the contrary, heterogeneous catalysts have unstable effects, while alkali and alkaline earth metals tend to increase the reaction rate in gasification. Nickel is the most effective catalyst for tar reduction in the gasification process. The direction of future work should look at the challenges associated with low-cost catalysts, as well as those of the best quality, being employed in thermochemical conversion technologies.

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References

1. Wang, Q.; Wu, S.; Cui, D.; Zhou, H.; Wu, D.; Pan, S.; Xu, F.; Wang, Z. Co-Hydrothermal Carbonization of Organic Solid Wastes to Hydrochar as Potential Fuel: A Review. *Sci. Total Environ.* **2022**, *850*, 158034. [CrossRef] [PubMed]
2. Li, J.; Li, L.; Suvarna, M.; Pan, L.; Tabatabaei, M.; Ok, Y.S.; Wang, X. Wet Wastes to Bioenergy and Biochar: A Critical Review with Future Perspectives. *Sci. Total Environ.* **2022**, *817*, 152921. [CrossRef]
3. Cui, D.; Li, J.; Zhang, X.; Zhang, L.; Chang, H.; Wang, Q. Pyrolysis Temperature Effect on Compositions of Basic Nitrogen Species in Huadian Shale Oil Using Positive-Ion ESI FT-ICR MS and GC-NCD. *J. Anal. Appl. Pyrolysis* **2021**, *153*, 104980. [CrossRef]
4. Lang, Q.; Liu, Z.; Li, Y.; Xu, J.; Li, J.; Liu, B.; Sun, Q. Combustion Characteristics, Kinetic and Thermodynamic Analyses of Hydrochars Derived from Hydrothermal Carbonization of Cattle Manure. *J. Environ. Chem. Eng.* **2022**, *10*, 106938. [CrossRef]
5. Liu, Y.; Sun, Y.; Wan, Z.; Jing, F.; Li, Z.; Chen, J.; Tsang, D.C.W. Tailored Design of Food Waste Hydrochar for Efficient Adsorption and Catalytic Degradation of Refractory Organic Contaminant. *J. Clean. Prod.* **2021**, *310*, 127482. [CrossRef]
6. Dutta, S.; He, M.; Xiong, X.; Tsang, D.C.W. Sustainable Management and Recycling of Food Waste Anaerobic Digestate: A Review. *Bioresour. Technol.* **2021**, *341*, 125915. [CrossRef] [PubMed]
7. Rasaq, W.A.; Thiruchenthooran, V.; Telega, P.; Bobak, Ł.; Igwegbe, C.A.; Białowiec, A. Optimizing Hydrothermal Treatment for Sustainable Valorization and Fatty Acid Recovery from Food Waste. *J. Environ. Manag.* **2024**, *357*, 3–10. [CrossRef] [PubMed]
8. Zhang, W.; Lang, Q.; Pan, Z.; Jiang, Y.; Liebetrau, J.; Nelles, M.; Dong, H.; Dong, R. Performance Evaluation of a Novel Anaerobic Digestion Operation Process for Treating High-Solids Content Chicken Manure: Effect of Reduction of the Hydraulic Retention Time at a Constant Organic Loading Rate. *Waste Manag.* **2017**, *64*, 340–347. [CrossRef]
9. Lu, Y.; Li, J.; Meng, J.; Zhang, J.; Zhuang, H.; Zheng, G.; Xie, W.; Ping, L.; Shan, S. Long-Term Biogas Slurry Application Increased Antibiotics Accumulation and Antibiotic Resistance Genes (ARGs) Spread in Agricultural Soils with Different Properties. *Sci. Total Environ.* **2021**, *759*, 143473. [CrossRef] [PubMed]
10. Sikarwar, V.S.; Pohořelý, M.; Meers, E.; Skoblia, S.; Moško, J.; Jeremiáš, M. Potential of Coupling Anaerobic Digestion with Thermochemical Technologies for Waste Valorization. *Fuel* **2021**, *294*, 120533. [CrossRef]
11. Zheng, H.; Song, C.; Bao, C.; Liu, X.; Xuan, Y.; Li, Y.; Ding, Y. Dark Calcium Carbonate Particles for Simultaneous Full-Spectrum Solar Thermal Conversion and Large-Capacity Thermochemical Energy Storage. *Sol. Energy Mater. Sol. Cells* **2020**, *207*, 110364. [CrossRef]
12. Rasaq, W.A.; Okpala, C.O.R.; Igwegbe, C.A.; Białowiec, A. Navigating Pyrolysis Implementation—A Tutorial Review on Consideration Factors and Thermochemical Operating Methods for Biomass Conversion. *Materials* **2024**, *17*, 725. [CrossRef] [PubMed]
13. Su, H.; Zhou, X.; Zheng, R.; Zhou, Z.; Zhang, Y.; Zhu, G.; Yu, C.; Hantoko, D.; Yan, M. Hydrothermal Carbonization of Food Waste after Oil Extraction Pre-Treatment: Study on Hydrochar Fuel Characteristics, Combustion Behavior, and Removal Behavior of Sodium and Potassium. *Sci. Total Environ.* **2021**, *754*, 142192. [CrossRef] [PubMed]
14. Son Le, H.; Chen, W.H.; Forruque Ahmed, S.; Said, Z.; Rafa, N.; Tuan Le, A.; Ağbulut, Ü.; Veza, I.; Phuong Nguyen, X.; Quang Duong, X.; et al. Hydrothermal Carbonization of Food Waste as Sustainable Energy Conversion Path. *Bioresour. Technol.* **2022**, *363*, 127958. [CrossRef] [PubMed]
15. Liu, Z.; Quek, A.; Kent Hoekman, S.; Balasubramanian, R. Production of Solid Biochar Fuel from Waste Biomass by Hydrothermal Carbonization. *Fuel* **2013**, *103*, 943–949. [CrossRef]
16. Rasaq, W.A.; Matyjewicz, B.; Lazar, Z.; Kupaj, P.; Janek, T.; Valentin, M.; Białowiec, A. Food Waste Recycling to Yarrowia Biomass Due to Combined Hydrothermal Carbonization and Biological Treatment. *J. Clean. Prod.* **2024**, *456*, 142385. [CrossRef]

17. Cheng, J.J.; Timilsina, G.R. Status and Barriers of Advanced Biofuel Technologies: A Review. *Renew. Energy* **2011**, *36*, 3541–3549. [CrossRef]
18. Abdullah, R.F.; Rashid, U.; Ibrahim, M.L.; NolHakim, M.A.H.L.; Moser, B.R.; Alharthi, F.A. Bifunctional Biomass-Based Catalyst for Biodiesel Production via Hydrothermal Carbonization (HTC) Pretreatment–Synthesis, Characterization and Optimization. *Process Saf. Environ. Prot.* **2021**, *156*, 219–230. [CrossRef]
19. Mansir, N.; Taufiq-Yap, Y.H.; Rashid, U.; Lokman, I.M. Investigation of Heterogeneous Solid Acid Catalyst Performance on Low Grade Feedstocks for Biodiesel Production: A Review. *Energy Convers. Manag.* **2017**, *141*, 171–182. [CrossRef]
20. Gholizadeh, M.; Hu, X.; Liu, Q. Progress of Using Biochar as a Catalyst in Thermal Conversion of Biomass. *Rev. Chem. Eng.* **2021**, *37*, 229–258. [CrossRef]
21. Anastasakis, K.; Ross, A.B. Hydrothermal Liquefaction of the Brown Macro-Alga Laminaria Saccharina: Effect of Reaction Conditions on Product Distribution and Composition. *Bioresour. Technol.* **2011**, *102*, 4876–4883. [CrossRef] [PubMed]
22. Biller, P.; Ross, A.B. Potential Yields and Properties of Oil from the Hydrothermal Liquefaction of Microalgae with Different Biochemical Content. *Bioresour. Technol.* **2011**, *102*, 215–225. [CrossRef] [PubMed]
23. Jena, U.; Das, K.C.; Kastner, J.R. Comparison of the Effects of Na_2CO_3, $Ca_3(PO_4)_2$, and NiO Catalysts on the Thermochemical Liquefaction of Microalga Spirulina Platensis. *Appl. Energy* **2012**, *98*, 368–375. [CrossRef]
24. 98/02824 Liquefaction Behavior of Point of Ayr Coal. *Fuel Energy Abstr.* **1998**, *39*, 261. [CrossRef]
25. Shakya, R.; Whelen, J.; Adhikari, S.; Mahadevan, R.; Neupane, S. Effect of Temperature and Na_2CO_3 Catalyst on Hydrothermal Liquefaction of Algae. *Algal Res.* **2015**, *12*, 80–90. [CrossRef]
26. Toor, S.S.; Rosendahl, L.; Rudolf, A. Hydrothermal Liquefaction of Biomass: A Review of Subcritical Water Technologies. *Energy* **2011**, *36*, 2328–2342. [CrossRef]
27. Watanabe, M.; Aizawa, Y.; Iida, T.; Aida, T.M.; Levy, C.; Sue, K.; Inomata, H. Glucose Reactions with Acid and Base Catalysts in Hot Compressed Water at 473 K. *Carbohydr. Res.* **2005**, *340*, 1925–1930. [CrossRef]
28. Ong, H.C.; Chen, W.H.; Farooq, A.; Gan, Y.Y.; Lee, K.T.; Ashokkumar, V. Catalytic Thermochemical Conversion of Biomass for Biofuel Production: A Comprehensive Review. *Renew. Sustain. Energy Rev.* **2019**, *113*, 109266. [CrossRef]
29. Song, C.; Hu, H.; Zhu, S.; Wang, G.; Chen, G. Nonisothermal Catalytic Liquefaction of Corn Stalk in Subcritical and Supercritical Water. *Energy Fuels* **2004**, *18*, 90–96. [CrossRef]
30. Zhu, Z.; Toor, S.S.; Rosendahl, L.; Yu, D.; Chen, G. Influence of Alkali Catalyst on Product Yield and Properties via Hydrothermal Liquefaction of Barley Straw. *Energy* **2015**, *80*, 284–292. [CrossRef]
31. Karagöz, S.; Bhaskar, T.; Muto, A.; Sakata, Y. Hydrothermal Upgrading of Biomass: Effect of K_2CO_3 Concentration and Biomass/Water Ratio on Products Distribution. *Bioresour. Technol.* **2006**, *97*, 90–98. [CrossRef] [PubMed]
32. Rasaq, W.A.; Golonka, M.; Scholz, M.; Białowiec, A. Opportunities and Challenges of High-pressure Fast Pyrolysis of Biomass: A Review. *Energies* **2021**, *14*, 5426. [CrossRef]
33. Oliveira, A.S.; Sarrión, A.; Baeza, J.A.; Diaz, E.; Calvo, L.; Mohedano, A.F.; Gilarranz, M.A. Integration of Hydrothermal Carbonization and Aqueous Phase Reforming for Energy Recovery from Sewage Sludge. *Chem. Eng. J.* **2022**, *442*, 136301. [CrossRef]
34. Muthu Dinesh Kumar, R.; Anand, R. *Production of Biofuel from Biomass Downdraft Gasification and Its Applications*; Elsevier Ltd.: Amsterdam, The Netherlands, 2019; ISBN 9780081027912.
35. Chi, N.T.; Anto, S.; Ahamed, T.S.; Kumar, S.S.; Shanmugam, S.; Samuel, M.S.; Mathimani, T.; Brindhadevi, K.; Pugazhendhi, A. A Review on Biochar Production Techniques and Biochar Based Catalyst for Biofuel Production from Algae. *Fuel* **2021**, *287*, 119411. [CrossRef]
36. Ao, W.; Fu, J.; Mao, X.; Kang, Q.; Ran, C.; Liu, Y.; Zhang, H.; Gao, Z.; Li, J.; Liu, G.; et al. Microwave Assisted Preparation of Activated Carbon from Biomass: A Review. *Renew. Sustain. Energy Rev.* **2018**, *92*, 958–979. [CrossRef]
37. Masoumi, S.; Borugadda, V.B.; Nanda, S.; Dalai, A.K. Hydrochar A Review on Its Production Technologies. *Catalysts* **2021**, *11*, 939. [CrossRef]
38. Moralı, U.; Demiral, H.; Şensöz, S. Optimization of Activated Carbon Production from Sunflower Seed Extracted Meal: Taguchi Design of Experiment Approach and Analysis of Variance. *J. Clean. Prod.* **2018**, *189*, 602–611. [CrossRef]
39. Sulaiman, N.S.; Hashim, R.; Mohamad Amini, M.H.; Danish, M.; Sulaiman, O. Optimization of Activated Carbon Preparation from Cassava Stem Using Response Surface Methodology on Surface Area and Yield. *J. Clean. Prod.* **2018**, *198*, 1422–1430. [CrossRef]
40. Cheng, F.; Li, X. Preparation and Application of Biochar-Based Catalysts for Biofuel Production. *Catalysts* **2018**, *8*, 346. [CrossRef]
41. Aysu, T.; Durak, H. Bio-Oil Production via Catalytic Supercritical Liquefaction of Syrian Mesquite (Prosopis Farcta). *J. Supercrit. Fluids* **2016**, *109*, 26–34. [CrossRef]
42. Thangaraj, B.; Solomon, P.R.; Muniyandi, B.; Ranganathan, S.; Lin, L. Catalysis in Biodiesel Production—A Review. *Clean Energy* **2019**, *3*, 2–23. [CrossRef]
43. Kumar, S.; Soomro, S.A.; Harijan, K.; Uqaili, M.A.; Kumar, L. Advancements of Biochar-Based Catalyst for Improved Production of Biodiesel: A Comprehensive Review. *Energies* **2023**, *16*, 644. [CrossRef]
44. Kang, K.; Nanda, S.; Hu, Y. Current Trends in Biochar Application for Catalytic Conversion of Biomass to Biofuels. *Catal. Today* **2022**, *404*, 3–18. [CrossRef]

45. Gasim, M.F.; Lim, J.W.; Low, S.C.; Lin, K.Y.A.; Oh, W. Da Can Biochar and Hydrochar Be Used as Sustainable Catalyst for Persulfate Activation? *Chemosphere* **2022**, *287*, 132458. [CrossRef] [PubMed]
46. Djandja, O.S.; Liew, R.K.; Liu, C.; Liang, J.; Yuan, H.; He, W.; Feng, Y.; Lougou, B.G.; Duan, P.G.; Lu, X.; et al. Catalytic Hydrothermal Carbonization of Wet Organic Solid Waste: A Review. *Sci. Total Environ.* **2023**, *873*, 162119. [CrossRef] [PubMed]
47. Nagappan, S.; Bhosale, R.R.; Nguyen, D.D.; Chi, N.T.L.; Ponnusamy, V.K.; Woong, C.S.; Kumar, G. Catalytic Hydrothermal Liquefaction of Biomass into Bio-Oils and Other Value-Added Products—A Review. *Fuel* **2021**, *285*, 119053. [CrossRef]
48. Xu, D.; Lin, G.; Guo, S.; Wang, S.; Guo, Y.; Jing, Z. Catalytic Hydrothermal Liquefaction of Algae and Upgrading of Biocrude: A Critical Review. *Renew. Sustain. Energy Rev.* **2018**, *97*, 103–118. [CrossRef]
49. Low, Y.W.; Yee, K.F. A Review on Lignocellulosic Biomass Waste into Biochar-Derived Catalyst: Current Conversion Techniques, Sustainable Applications and Challenges. *Biomass Bioenergy* **2021**, *154*, 106245. [CrossRef]
50. He, X.; Zheng, N.; Hu, R.; Hu, Z.; Yu, J.C. Hydrothermal and Pyrolytic Conversion of Biomasses into Catalysts for Advanced Oxidation Treatments. *Adv. Funct. Mater.* **2021**, *31*, 2006505. [CrossRef]
51. Cao, X.; Sun, S.; Sun, R. Application of Biochar-Based Catalysts in Biomass Upgrading: A Review. *RSC Adv.* **2017**, *7*, 48793–48805. [CrossRef]
52. Wang, T.; Zhai, Y.; Zhu, Y.; Li, C.; Zeng, G. A Review of the Hydrothermal Carbonization of Biomass Waste for Hydrochar Formation: Process Conditions, Fundamentals, and Physicochemical Properties. *Renew. Sustain. Energy Rev.* **2018**, *90*, 223–247. [CrossRef]
53. Heidari, M.; Dutta, A.; Acharya, B.; Mahmud, S. A Review of the Current Knowledge and Challenges of Hydrothermal Carbonization for Biomass Conversion. *J. Energy Inst.* **2019**, *92*, 1779–1799. [CrossRef]
54. Antero, R.V.P.; Alves, A.C.F.; de Oliveira, S.B.; Ojala, S.A.; Brum, S.S. Challenges and Alternatives for the Adequacy of Hydrothermal Carbonization of Lignocellulosic Biomass in Cleaner Production Systems: A Review. *J. Clean. Prod.* **2020**, *252*, 119899. [CrossRef]
55. Ischia, G.; Fiori, L. Hydrothermal Carbonization of Organic Waste and Biomass: A Review on Process, Reactor, and Plant Modeling. *Waste Biomass Valorization* **2021**, *12*, 2797–2824. [CrossRef]
56. Sharifzadeh, M.; Sadeqzadeh, M.; Guo, M.; Borhani, T.N.; Murthy, N.V.S.N.; Cortada, M.; Wang, L.; Hallett, J.; Shah, N.; Berkeley, L.; et al. The Multi-Scale Challenges of Biomass Fast Pyrolysis and Bio-Oil Upgrading: Review of the State of Art and Future Research Directions. *Prog. Energy Combust. Sci.* **2019**, *71*, 1–80. [CrossRef]
57. Yang, B.; Dai, J.; Zhao, Y.; Wang, Z.; Wu, J.; Ji, C.; Zhang, Y.; Pu, X. Synergy Effect between Tetracycline and Cr(VI) on Combined Pollution Systems Driving Biochar-Templated $Fe_3O_4@SiO_2/TiO_2/g\text{-}C_3N_4$ Composites for Enhanced Removal of Pollutants. *Biochar* **2023**, *5*, 1. [CrossRef]
58. Zhou, C.H.; Xia, X.; Lin, C.X.; Tong, D.S.; Beltramini, J. Catalytic Conversion of Lignocellulosic Biomass to Fine Chemicals and Fuels. *Chem. Soc. Rev.* **2011**, *40*, 5588–5617. [CrossRef] [PubMed]
59. Mandari, V.; Devarai, S.K. Biodiesel Production Using Homogeneous, Heterogeneous, and Enzyme Catalysts via Transesterification and Esterification Reactions: A Critical Review. *Bioenergy Res.* **2022**, *15*, 935–961. [CrossRef] [PubMed]
60. Elhalil, A.; Elmoubarki, R.; Farnane, M.; Machrouhi, A.; Sadiq, M.; Mahjoubi, F.Z.; Qourzal, S.; Barka, N. Photocatalytic Degradation of Caffeine as a Model Pharmaceutical Pollutant on Mg Doped $ZnO\text{-}Al_2O_3$ Heterostructure. *Environ. Nanotechnol. Monit. Manag.* **2018**, *10*, 63–72. [CrossRef]
61. Elhalil, A.; Elmoubarki, R.; Machrouhi, A.; Sadiq, M.; Abdennouri, M.; Qourzal, S.; Barka, N. Photocatalytic Degradation of Caffeine by ZnO-ZnAl2O4 Nanoparticles Derived from LDH Structure. *J. Environ. Chem. Eng.* **2017**, *5*, 3719–3726. [CrossRef]
62. Diaz De Tuesta, J.L.; Saviotti, M.C.; Roman, F.F.; Pantuzza, G.F.; Sartori, H.J.F.; Shinibekova, A.; Kalmakhanova, M.S.; Massalimova, B.K.; Pietrobelli, J.M.T.A.; Lenzi, G.G.; et al. Assisted Hydrothermal Carbonization of Agroindustrial Byproducts as Effective Step in the Production of Activated Carbon Catalysts for Wet Peroxide Oxidation of Micro-Pollutants. *J. Environ. Chem. Eng.* **2021**, *9*, 105004. [CrossRef]
63. Abelniece, Z.; Laipniece, L.; Kampars, V. Biodiesel Production by Interesterification of Rapeseed Oil with Methyl Formate in Presence of Potassium Alkoxides. *Biomass Convers. Biorefinery* **2022**, *12*, 2881–2889. [CrossRef]
64. Xu, S.; Chen, J.; Peng, H.; Leng, S.; Li, H.; Qu, W.; Hu, Y.; Li, H.; Jiang, S.; Zhou, W.; et al. Effect of Biomass Type and Pyrolysis Temperature on Nitrogen in Biochar, and the Comparison with Hydrochar. *Fuel* **2021**, *291*, 120128. [CrossRef]
65. Ross, A.B.; Biller, P.; Kubacki, M.L.; Li, H.; Lea-Langton, A.; Jones, J.M. Hydrothermal Processing of Microalgae Using Alkali and Organic Acids. *Fuel* **2010**, *89*, 2234–2243. [CrossRef]
66. Huang, H.-j.; Yuan, X.-z.; Zhu, H.-n.; Li, H.; Liu, Y.; Wang, X.-l.; Zeng, G.-m. Comparative Studies of Thermochemical Liquefaction Characteristics of Microalgae, Lignocellulosic Biomass and Sewage Sludge. *Energy* **2013**, *56*, 52–60. [CrossRef]
67. Long, J.; Li, Y.; Zhang, X.; Tang, L.; Song, C.; Wang, F. Comparative Investigation on Hydrothermal and Alkali Catalytic Liquefaction of Bagasse: Process Efficiency and Product Properties. *Fuel* **2016**, *186*, 685–693. [CrossRef]
68. Duan, P.; Savage, P.E. Hydrothermal Liquefaction of a Microalga with Heterogeneous Catalysts. *Ind. Eng. Chem. Res.* **2011**, *50*, 52–61. [CrossRef]
69. Shuping, Z.; Yulong, W.; Mingde, Y.; Kaleem, I.; Chun, L.; Tong, J. Production and Characterization of Bio-Oil from Hydrothermal Liquefaction of Microalgae Dunaliella Tertiolecta Cake. *Energy* **2010**, *35*, 5406–5411. [CrossRef]
70. Yang, Y.F.; Feng, C.P.; Inamori, Y.; Maekawa, T. Analysis of Energy Conversion Characteristics in Liquefaction of Algae. *Resour. Conserv. Recycl.* **2004**, *43*, 21–33. [CrossRef]

71. Wang, W.; Xu, Y.; Wang, X.; Zhang, B.; Tian, W.; Zhang, J. Hydrothermal Liquefaction of Microalgae over Transition Metal Supported TiO_2 Catalyst. *Bioresour. Technol.* **2018**, *250*, 474–480. [CrossRef]
72. de Caprariis, B.; Scarsella, M.; Bavasso, I.; Bracciale, M.P.; Tai, L.; De Filippis, P. Effect of Ni, Zn and Fe on Hydrothermal Liquefaction of Cellulose: Impact on Bio-Crude Yield and Composition. *J. Anal. Appl. Pyrolysis* **2021**, *157*, 105225. [CrossRef]
73. Yim, S.C.; Quitain, A.T.; Yusup, S.; Sasaki, M.; Uemura, Y.; Kida, T. Metal Oxide-Catalyzed Hydrothermal Liquefaction of Malaysian Oil Palm Biomass to Bio-Oil under Supercritical Condition. *J. Supercrit. Fluids* **2017**, *120*, 384–394. [CrossRef]
74. Krishna, B.B.; Singh, R.; Bhaskar, T. Effect of Catalyst Contact on the Pyrolysis of Wheat Straw and Wheat Husk. *Fuel* **2015**, *160*, 64–70. [CrossRef]
75. Zhou, D.; Zhang, L.; Zhang, S.; Fu, H.; Chen, J. Hydrothermal Liquefaction of Macroalgae Enteromorpha Prolifera to Bio-Oil. *Energy Fuels* **2010**, *24*, 4054–4061. [CrossRef]
76. Yang, W.; Li, X.; Liu, S.; Feng, L. Direct Hydrothermal Liquefaction of Undried Macroalgae Enteromorpha Prolifera Using Acid Catalysts. *Energy Convers. Manag.* **2014**, *87*, 938–945. [CrossRef]
77. Shah, A.A.; Toor, S.S.; Conti, F.; Nielsen, A.H.; Rosendahl, L.A. Hydrothermal Liquefaction of High Ash Containing Sewage Sludge at Sub and Supercritical Conditions. *Biomass Bioenergy* **2020**, *135*, 105504. [CrossRef]
78. Malins, K.; Kampars, V.; Brinks, J.; Neibolte, I.; Murnieks, R.; Kampare, R. Bio-Oil from Thermo-Chemical Hydro-Liquefaction of Wet Sewage Sludge. *Bioresour. Technol.* **2015**, *187*, 23–29. [CrossRef] [PubMed]
79. He, M.; Zhu, X.; Dutta, S.; Khanal, S.K.; Lee, K.T.; Masek, O.; Tsang, D.C.W. Catalytic Co-Hydrothermal Carbonization of Food Waste Digestate and Yard Waste for Energy Application and Nutrient Recovery. *Bioresour. Technol.* **2022**, *344*, 126395. [CrossRef] [PubMed]
80. Xu, Y.; Zheng, X.; Yu, H.; Hu, X. Hydrothermal Liquefaction of Chlorella Pyrenoidosa for Bio-Oil Production over Ce/HZSM-5. *Bioresour. Technol.* **2014**, *156*, 1–5. [CrossRef]
81. Yang, L.; Li, Y.; Savage, P.E. Catalytic Hydrothermal Liquefaction of a Microalga in a Two-Chamber Reactor. *Ind. Eng. Chem. Res.* **2014**, *53*, 11939–11944. [CrossRef]
82. Xu, C.; Etcheverry, T. Hydro-Liquefaction of Woody Biomass in Sub- and Super-Critical Ethanol with Iron-Based Catalysts. *Fuel* **2008**, *87*, 335–345. [CrossRef]
83. Islam, A.; Taufiq-Yap, Y.H.; Chan, E.S.; Moniruzzaman, M.; Islam, S.; Nabi, M.N. Advances in Solid-Catalytic and Non-Catalytic Technologies for Biodiesel Production. *Energy Convers. Manag.* **2014**, *88*, 1200–1218. [CrossRef]
84. Corma, A. From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis. *Chem. Rev.* **1997**, *97*, 2373–2419. [CrossRef]
85. Trong On, D.; Desplantier-Giscard, D.; Danumah, C.; Kaliaguine, S. Perspectives in Catalytic Applications of Mesostructured Materials. *Appl. Catal. A Gen.* **2003**, *253*, 545–602. [CrossRef]
86. Ma, Z.; Zaera, F. Heterogeneous Catalysis by Metals. *Encycl. Inorg. Chem.* **2006**. [CrossRef]
87. Galadima, A.; Muraza, O. Hydrothermal Liquefaction of Algae and Bio-Oil Upgrading into Liquid Fuels: Role of Heterogeneous Catalysts. *Renew. Sustain. Energy Rev.* **2018**, *81*, 1037–1048. [CrossRef]
88. Shu, Q.; Gao, J.; Nawaz, Z.; Liao, Y.; Wang, D.; Wang, J. Synthesis of Biodiesel from Waste Vegetable Oil with Large Amounts of Free Fatty Acids Using a Carbon-Based Solid Acid Catalyst. *Appl. Energy* **2010**, *87*, 2589–2596. [CrossRef]
89. Ramos, M.J.; Casas, A.; Rodríguez, L.; Romero, R.; Pérez, Á. Transesterification of Sunflower Oil over Zeolites Using Different Metal Loading: A Case of Leaching and Agglomeration Studies. *Appl. Catal. A Gen.* **2008**, *346*, 79–85. [CrossRef]
90. Shu, Q.; Yang, B.; Yuan, H.; Qing, S.; Zhu, G. Synthesis of Biodiesel from Soybean Oil and Methanol Catalyzed by Zeolite Beta Modified with La^{3+}. *Catal. Commun.* **2007**, *8*, 2159–2165. [CrossRef]
91. Zhao, C.; Lv, P.; Yang, L.; Xing, S.; Luo, W.; Wang, Z. Biodiesel Synthesis over Biochar-Based Catalyst from Biomass Waste Pomelo Peel. *Energy Convers. Manag.* **2018**, *160*, 477–485. [CrossRef]
92. Yu, J.T.; Dehkhoda, A.M.; Ellis, N. Development of Biochar-Based Catalyst for Transesterification of Canola Oil. *Energy Fuels* **2011**, *25*, 337–344. [CrossRef]
93. Liu, W.J.; Jiang, H.; Yu, H.Q. Development of Biochar-Based Functional Materials: Toward a Sustainable Platform Carbon Material. *Chem. Rev.* **2015**, *115*, 12251–12285. [CrossRef]
94. Chen, B.; Chen, Z.; Lv, S. A Novel Magnetic Biochar Efficiently Sorbs Organic Pollutants and Phosphate. *Bioresour. Technol.* **2011**, *102*, 716–723. [CrossRef]
95. Ormsby, R.; Kastner, J.R.; Miller, J. Hemicellulose Hydrolysis Using Solid Acid Catalysts Generated from Biochar. *Catal. Today* **2012**, *190*, 89–97. [CrossRef]
96. Dehkhoda, A.M.; West, A.H.; Ellis, N. Biochar Based Solid Acid Catalyst for Biodiesel Production. *Appl. Catal. A Gen.* **2010**, *382*, 197–204. [CrossRef]
97. Tian, C.; Li, B.; Liu, Z.; Zhang, Y.; Lu, H. Hydrothermal Liquefaction for Algal Biorefinery: A Critical Review. *Renew. Sustain. Energy Rev.* **2014**, *38*, 933–950. [CrossRef]
98. Aturagaba, G.; Egesa, D.; Mubiru, E.; Tebandeke, E. Catalytic Hydrothermal Liquefaction of Water Hyacinth Using Fe_3O_4/NiO Nanocomposite: Optimization of Reaction Conditions by Response Surface Methodology. *J. Sustain. Bioenergy Syst.* **2023**, *13*, 73–98. [CrossRef]
99. Sun, P.; Heng, M.; Sun, S.; Chen, J. Direct Liquefaction of Paulownia in Hot Compressed Water: Influence of Catalysts. *Energy* **2010**, *35*, 5421–5429. [CrossRef]

100. Karagöz, S.; Bhaskar, T.; Muto, A.; Sakata, Y.; Oshiki, T.; Kishimoto, T. Low-Temperature Catalytic Hydrothermal Treatment of Wood Biomass: Analysis of Liquid Products. *Chem. Eng. J.* **2005**, *108*, 127–137. [CrossRef]
101. Feng, S.; Yuan, Z.; Leitch, M.; Xu, C.C. Hydrothermal Liquefaction of Barks into Bio-Crude–Effects of Species and Ash Content/Composition. *Fuel* **2014**, *116*, 214–220. [CrossRef]
102. Akhtar, J.; Kuang, S.K.; Amin, N.A.S. Liquefaction of Empty Palm Fruit Bunch (EPFB) in Alkaline Hot Compressed Water. *Renew. Energy* **2010**, *35*, 1220–1227. [CrossRef]
103. Kumar, S.; Gupta, R.B. Biocrude Production from Switchgrass Using Subcritical Water. *Energy Fuels* **2009**, *23*, 5151–5159. [CrossRef]
104. Wang, C.; Pan, J.; Li, J.; Yang, Z. Comparative Studies of Products Produced from Four Different Biomass Samples via Deoxy-Liquefaction. *Bioresour. Technol.* **2008**, *99*, 2778–2786. [CrossRef] [PubMed]
105. Wang, Y.; Wang, H.; Lin, H.; Zheng, Y.; Zhao, J.; Pelletier, A.; Li, K. Effects of Solvents and Catalysts in Liquefaction of Pinewood Sawdust for the Production of Bio-Oils. *Biomass Bioenergy* **2013**, *59*, 158–167. [CrossRef]
106. Qian, Y.; Zuo, C.; Tan, J.; He, J. Structural Analysis of Bio-Oils from Sub-and Supercritical Water Liquefaction of Woody Biomass. *Energy* **2007**, *32*, 196–202. [CrossRef]
107. Lu, X.; Flora, J.R.V.; Berge, N.D. Influence of Process Water Quality on Hydrothermal Carbonization of Cellulose. *Bioresour. Technol.* **2014**, *154*, 229–239. [CrossRef]
108. Yuan, H.; Lu, T.; Wang, Y.; Huang, H.; Chen, Y. Influence of Pyrolysis Temperature and Holding Time on Properties of Biochar Derived from Medicinal Herb (Radix Isatidis) Residue and Its Effect on Soil CO_2 Emission. *J. Anal. Appl. Pyrolysis* **2014**, *110*, 277–284. [CrossRef]
109. Charisteidis, I.; Lazaridis, P.; Fotopoulos, A.; Pachatouridou, E.; Matsakas, L.; Rova, U.; Christakopoulos, P.; Triantafyllidis, K. Catalytic Fast Pyrolysis of Lignin Isolated by Hybrid Organosolv—Steam Explosion Pretreatment of Hardwood and Softwood Biomass for the Production of Phenolics and Aromatics. *Catalysts* **2019**, *9*, 935. [CrossRef]
110. Yeh, T.M.; Dickinson, J.G.; Franck, A.; Linic, S.; Thompson, L.T.; Savage, P.E. Hydrothermal Catalytic Production of Fuels and Chemicals from Aquatic Biomass. *J. Chem. Technol. Biotechnol.* **2013**, *88*, 13–24. [CrossRef]
111. Zhuang, Y.; Guo, J.; Chen, L.; Li, D.; Liu, J.; Ye, N. Microwave-Assisted Direct Liquefaction of Ulva Prolifera for Bio-Oil Production by Acid Catalysis. *Bioresour. Technol.* **2012**, *116*, 133–139. [CrossRef]
112. Schmieder, H.; Abeln, J.; Boukis, N.; Dinjus, E.; Kruse, A.; Kluth, M.; Petrich, G.; Sadri, E.; Schacht, M. Hydrothermal Gasification of Biomass and Organic Wastes. *J. Supercrit. Fluids* **2000**, *17*, 145–153. [CrossRef]
113. Sinag, A.; Kruse, A.; Schwarzkopf, V. Key Compounds of the Hydropyrolysis of Glucose in Supercritical Water in the Presence of K_2CO_3. *Ind. Eng. Chem. Res.* **2003**, *42*, 3516–3521. [CrossRef]
114. Cheng, S.; Wei, L.; Rabnawaz, M. Catalytic Liquefaction of Pine Sawdust and In-Situ Hydrogenation of Bio-Crude over Bifunctional Co-Zn/HZSM-5 Catalysts. *Fuel* **2018**, *223*, 252–260. [CrossRef]
115. Minowa, T.; Zhen, F.; Ogi, T. Cellulose Decomposition in Hot-Compressed Water with Alkali or Nickel Catalyst. *J. Supercrit. Fluids* **1998**, *13*, 253–259. [CrossRef]
116. Liu, C.; Kong, L.; Wang, Y.; Dai, L. Catalytic Hydrothermal Liquefaction of Spirulina to Bio-Oil in the Presence of Formic Acid over Palladium-Based Catalysts. *Algal Res.* **2018**, *33*, 156–164. [CrossRef]
117. Duman, G.; Yanik, J. Two-Step Steam Pyrolysis of Biomass for Hydrogen Production. *Int. J. Hydrogen Energy* **2017**, *42*, 17000–17008. [CrossRef]
118. Ouyang, X.; Zhu, G.; Huang, X.; Qiu, X. Microwave Assisted Liquefaction of Wheat Straw Alkali Lignin for the Production of Monophenolic Compounds. *J. Energy Chem.* **2015**, *24*, 72–76. [CrossRef]
119. Zhu, L.; Yin, S.; Yin, Q.; Wang, H.; Wang, S. Biochar: A New Promising Catalyst Support Using Methanation as a Probe Reaction. *Energy Sci. Eng.* **2015**, *3*, 126–134. [CrossRef]
120. Wildschut, J.; Mahfud, F.H.; Venderbosch, R.H.; Heeres, H.J. Hydrotreatment of Fast Pyrolysis Oil Using Heterogeneous Noble-Metal Catalysts. *Ind. Eng. Chem. Res.* **2009**, *48*, 10324–10334. [CrossRef]
121. Tzanetis, K.F.; Posada, J.A.; Ramirez, A. Analysis of Biomass Hydrothermal Liquefaction and Biocrude-Oil Upgrading for Renewable Jet Fuel Production: The Impact of Reaction Conditions on Production Costs and GHG Emissions Performance. *Renew. Energy* **2017**, *113*, 1388–1398. [CrossRef]
122. Śliz, M.; Wilk, M. A Comprehensive Investigation of Hydrothermal Carbonization: Energy Potential of Hydrochar Derived from Virginia Mallow. *Renew. Energy* **2020**, *156*, 942–950. [CrossRef]
123. Fu, K.; Yue, Q.; Gao, B.; Sun, Y.; Wang, Y.; Li, Q.; Zhao, P.; Chen, S. Physicochemical and Adsorptive Properties of Activated Carbons from Arundo Donax Linn Utilizing Different Iron Salts as Activating Agents. *J. Taiwan Inst. Chem. Eng.* **2014**, *45*, 3007–3015. [CrossRef]
124. Jia, Y.; Shi, S.; Liu, J.; Su, S.; Liang, Q.; Zeng, X.; Li, T. Applied Sciences Study of the Effect of Pyrolysis Temperature on the Cd^{2+} Adsorption Characteristics of Biochar. *Appl. Sci.* **2018**, *8*, 1019. [CrossRef]
125. Scapin, E.; Lazzari, E.; Benvenutti, E.V.; Falcade, T. Activated Carbon from Rice Husk Biochar with High Surface Area. *Biointerface Res. Appl. Chem.* **2021**, *11*, 10265–10277.
126. Xing, X.; Jiang, W.; Li, S.; Zhang, X.; Wang, W. Preparation and Analysis of Straw Activated Carbon Synergetic Catalyzed by $ZnCl_2$-H_3PO_4 through Hydrothermal Carbonization Combined with Ultrasonic Assisted Immersion Pyrolysis. *Waste Manag.* **2019**, *89*, 64–72. [CrossRef] [PubMed]

127. Zhou, Z.; Zhang, Y.; Wang, H.; Chen, T.; Lu, W. Enhanced Photodegradation of Pentachlorophenol in a Soil Washing System under Solar Irradiation with TiO_2 Nanorods Combined with Municipal Sewage Sludge. *Microporous Mesoporous Mater.* **2015**, *201*, 99–104. [CrossRef]
128. Li, W.; Zhang, L.-b.; Peng, J.-h.; Li, N.; Zhu, X.-y. Preparation of High Surface Area Activated Carbons from Tobacco Stems with K_2CO_3 Activation Using Microwave Radiation. *Ind. Crops Prod.* **2008**, *27*, 341–347. [CrossRef]
129. Longprang, T.; Jaruwat, D.; Udomsap, P.; Chollacoop, N.; Eiad-Ua, A. Influence of Acid Additive on Nanoporous Carbon Materials via HTC for Catalyst Support. *Mater. Today Proc.* **2020**, *23*, 762–766. [CrossRef]
130. Dai, L.; Yang, B.; Li, H.; Tan, F.; Zhu, N.; Zhu, Q.; He, M.; Ran, Y.; Hu, G. A Synergistic Combination of Nutrient Reclamation from Manure and Resultant Hydrochar Upgradation by Acid-Supported Hydrothermal Carbonization. *Bioresour. Technol.* **2017**, *243*, 860–866. [CrossRef]
131. Liu, Z.; Liu, Z. Comparison of Hydrochar- and Pyrochar-Based Solid Acid Catalysts from Cornstalk: Physiochemical Properties, Catalytic Activity and Deactivation Behavior. *Bioresour. Technol.* **2020**, *297*, 122477. [CrossRef]
132. Ma, R.; Fakudze, S.; Shang, Q.; Wei, Y.; Chen, J.; Liu, C.; Han, J.; Chu, Q. Catalytic Hydrothermal Carbonization of Pomelo Peel for Enhanced Combustibility of Coal/Hydrochar Blends and Reduced CO_2 Emission. *Fuel* **2021**, *304*, 121422. [CrossRef]
133. Jezierska-Thöle, A.; Rudnicki, R.; Kluba, M. Development of Energy Crops Cultivation for Biomass Production in Poland. *Renew. Sustain. Energy Rev.* **2016**, *62*, 534–545. [CrossRef]
134. Liang, M.; Zhang, K.; Lei, P.; Wang, B.; Shu, C.M.; Li, B. Fuel Properties and Combustion Kinetics of Hydrochar Derived from Co-Hydrothermal Carbonization of Tobacco Residues and Graphene Oxide. *Biomass Convers. Biorefinery* **2020**, *10*, 189–201. [CrossRef]
135. MacDermid-Watts, K.; Pradhan, R.; Dutta, A. Catalytic Hydrothermal Carbonization Treatment of Biomass for Enhanced Activated Carbon: A Review. *Waste Biomass Valorization* **2021**, *12*, 2171–2186. [CrossRef]
136. Nizamuddin, S.; Baloch, H.A.; Griffin, G.J.; Mubarak, N.M.; Bhutto, A.W.; Abro, R.; Mazari, S.A.; Ali, B.S. An Overview of Effect of Process Parameters on Hydrothermal Carbonization of Biomass. *Renew. Sustain. Energy Rev.* **2017**, *73*, 1289–1299. [CrossRef]
137. Zhao, P.; Shen, Y.; Ge, S.; Chen, Z.; Yoshikawa, K. Clean Solid Biofuel Production from High Moisture Content Waste Biomass Employing Hydrothermal Treatment. *Appl. Energy* **2014**, *131*, 345–367. [CrossRef]
138. Mumme, J.; Titirici, M.M.; Pfeiffer, A.; Lüder, U.; Reza, M.T.; Mašek, O. Hydrothermal Carbonization of Digestate in the Presence of Zeolite: Process Efficiency and Composite Properties. *ACS Sustain. Chem. Eng.* **2015**, *3*, 2967–2974. [CrossRef]
139. Lynam, J.G.; Coronella, C.J.; Yan, W.; Reza, M.T.; Vasquez, V.R. Acetic Acid and Lithium Chloride Effects on Hydrothermal Carbonization of Lignocellulosic Biomass. *Bioresour. Technol.* **2011**, *102*, 6192–6199. [CrossRef]
140. Rather, M.A.; Khan, N.S.; Gupta, R. Catalytic Hydrothermal Carbonization of Invasive Macrophyte Hornwort (Ceratophyllum Demersum) for Production of Hydrochar: A Potential Biofuel. *Int. J. Environ. Sci. Technol.* **2017**, *14*, 1243–1252. [CrossRef]

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STATEMENT

I hereby declare that in the publication:

Waheed A. Rasaq, Charles Odilichukwu R. Okpala, Chinenye Adaobi Igwegbe, and Andrzej Białowiec, 2024. " Catalyst-Enhancing Hydrothermal Carbonization of Biomass for Hydrochar and Liquid Fuel Production—A Review." Materials 17(11), 1 – 25 doi: 10.3390/ma17112579

My contribution included:

Developing the concept and design of the study. I prepared the entire text of the article as well as Figures. During the review process, I made corrections to the text of the manuscript and prepared responses to the reviewers. I obtained funding for the publication of the manuscript.

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My contribution included: I participated in the data curation, investigation process, as well as writing—reviewing and editing the manuscript. During the review process, I made corrections to the text of the manuscript and responses to the reviewers.

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My contribution included:

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My contribution included:
Developing the concept and design of the study. I participated in the revision and supervision of the manuscript. I participated in the review process and the related modifications to the manuscript. I was also the corresponding author.

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Waste Management

Hydrothermal carbonization of combined food waste: A critical evaluation of emergent products

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Abstract:	Hydrothermal carbonization (HTC) increasingly appears as an eco-friendly method for managing food waste (FW). In this current work, a combination of FW was subjected to HTC, and emergent products were critically evaluated. This involved a lab-scale pressure reactor and optimization of HTC conditions: temperature (220-340 °C) and residence time (90-260 min) via central composite design type of response surface methodology (CCD-RSM). Results showed varying temperatures and residence time to impact the hydrochar (HC) and hydrothermal liquid (HTL) properties. Although HC produced through HTC exhibited lower ash content (<2%) despite higher fixed carbon (>55%), the heating value of HC ranged from 19.2 to 32.5 MJ/kg. Temperature primarily influenced FW conversion, affecting carbonaceous properties. Saturated fatty acids (SFA) were found to be predominant in the HTL under all tested operating conditions (77.3, 48.4, and 37.1 wt% for HTC at 340, 280, and 220 oC in 180 min, respectively). Total phosphorus recovery in HC and HTL respectively peaked at 340°C and 220°C in 180 min. The study concludes that HTC holds promise for energy-dense biofuel production, nutrient recovery, and fostering a circular economy.
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The Editor-in-Chief,

Waste Management Journal

Dear Sir,

Submission of Original Manuscript

I undertake to submit the manuscript titled, '**Hydrothermal carbonization of combined food waste: A critical evaluation of emergent products**' which belongs to the authors stated as follows:

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Hydrothermal carbonization (HTC) as a sustainable and environmentally friendly method for valorizing food waste while mitigating atmospheric emissions and promoting a greener future aligns with the environmental focus of the Journal of **Waste Management**. With this innovative technology, HTC also has the potential to reduce the burden on landfills, making it an eco-conscious alternative to traditional waste disposal methods. HTC provides an opportunity to harness the energy potential of waste materials. The resulting hydrochar can serve as a renewable and energy-dense solid biofuel, supporting industrial and energy sector needs while reducing reliance on fossil fuels.

The main objective of this work is to optimize the HTC of food waste, considering the following: a) Characterization of raw FW/feedstock and fuel properties of HC from HTC; b) Optimization and efficiency of the HTC parameters (temperature and residence time); c) Examination of fatty acid content in both FW and the resulting HTL and HC, alongside phosphorus recovery generated through HTC.

The HTC appears to be a promising process (in managing food waste sustainably and contributing to a greener future) to produce energy-dense solid biofuel, nutrient recovery, and contribute to the circular economy development, while also reducing reliance on fossil fuels. These elements further emphasize the relevance of the study to the journal's scope. Therefore optimizing the HTC process will improve the above merits.

We confirm that this work is original and has not been published elsewhere, nor is it currently under consideration for publication elsewhere. The APC is financed by the Wrocław University of Environmental and Life Sciences. All co-authors have approved the manuscript and there is no conflict of interest. Thank you very much for your consideration.

Sincerely,

prof. dr hab. inż. Andrzej Białowiec

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Highlights

- The FW valorization is a potential source of HC due to HTC/L
- HTC/L converted FW into HC with C (>55%), AC (<2%), and HHV (19.2-32.5 MJ/kg)
- HC produced better at high 320 and 340 ^{o}C over 220 ^{o}C
- The DOE approach offered the optimization of solid and liquid fractions
- Household FW was converted to energy, fatty acid, and P via HTC/L

Hydrothermal carbonization of combined food waste: A critical evaluation of emergent products

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Abstract

Hydrothermal carbonization (HTC) increasingly appears as an eco-friendly method for managing food waste (FW). In this current work, a combination of FW was subjected to HTC, and emergent products were critically evaluated. This involved a lab-scale pressure reactor and optimization of HTC conditions: temperature (220-340 °C) and residence time (90-260 min) via central composite design type of response surface methodology (CCD-RSM). Results showed varying temperatures and residence time to impact the hydrochar (HC) and hydrothermal liquid (HTL) properties. Although HC produced through HTC exhibited lower ash content (<2%) despite higher fixed carbon (>55%), the heating value of HC ranged from 19.2 to 32.5 MJ/kg. Temperature primarily influenced FW conversion, affecting carbonaceous properties. Saturated fatty acids (SFA) were found to be predominant in the HTL under all tested operating conditions (77.3, 48.4, and 37.1

wt% for HTC at 340, 280, and 220 ºC in 180 min, respectively). Total phosphorus recovery in HC and HTL respectively peaked at 340°C and 220°C in 180 min. The study concludes that HTC holds promise for energy-dense biofuel production, nutrient recovery, and fostering a circular economy.

Keywords: Hydrothermal carbonization, Hydrochar, Fatty acid and phosphorus recovery, Liquid fraction, Food waste, Process optimization

1. Introduction

Food waste (FW) has emerged as a pressing environmental and societal challenge, with significant implications for resource management and sustainability. It makes up one of the biggest portions of the global waste stream [1]. In Europe alone, about 88 million tons of food is wasted annually, of which Poland occupies more than 10% [2,3]. The global attention on food wastage has sky-rocketed, caused by population growth and economic development. Over 1.33 billion tons of food are lost or wasted annually worldwide, contributing to 2.2 billion tons of waste annually, according to the Food and Agricultural Organization (FAO) and the World Bank of the United Nations [4]**.** The amount of generated FW, which is the main industrial waste from food production and the organic solid part of municipal waste, shows an annual exponential growth, becoming one of the main global environmental problems [5]. On the one hand, the larger amounts of FW produced annually by the food industry, such as expired food and droppings that pose a risk to human health, make it more difficult to manage globally [6]. However, the perspective of energy scarcity and climate change indicates that new approaches to supplying clean, sustainable energy are becoming more and more necessary [7,8]. The traditional disposal methods of FW not only contribute to greenhouse gas emissions but also burden landfills, exacerbating environmental degradation. Therefore, an urgent need to explore innovative and eco-friendly solutions for FW management. The 17 Sustainable Development Goals (SDGs) introduction were meant to be accomplished by the year 2030, and are specifically focused on boosting the amount of waste recycled and using clean, renewable energy [9]. Given that, the emphasis of the research is moving toward environmentally friendly FW management techniques, as a result, many countries have already implemented controls on the disposal of FW in landfills. Various methods for FW management exist, encompassing hydrothermal carbonization (HTC)/anaerobic digestion, combustion, composting, and direct land spreading [10,11]. Among these methods, HTC, particularly when used as a prelude to anaerobic digestion, stands out as the most favorable approach. Its versatile applications make it a promising solution for managing FW, offering an opportunity to extract energy from waste materials [12,13], before subjecting the HTC liquid waste to anaerobic digestion. Notably, HTC demonstrates significant environmental friendliness by reducing emissions, particularly in contrast to processes like composting. This advantage lies in the diminished gas release during HTC, establishing it as a more sustainable FW treatment option [11,14,15]. Moreover, its cost-effectiveness and feasibility position HTC as a practical method, aiding in valorizing digestate energy while optimizing nutrient recovery and carbon use efficiency [16]. All these benefits led to the increased interest in HTC by researchers. Generally speaking, there are two categories of hydrothermal treatment depending on the operational conditions: hydrothermal carbonization and liquefaction (HTC/L) [17–19]. This study focuses on the application of HTC/L due to its advantages over other treatment methods, particularly its efficiency in managing any study-selected feedstock with high moisture content (MC) without necessitating pre-drying.

The lipid composition for the phosphorus (P) recovery process, using synthetic and FW-derived VFA, resembled those of commercial biodiesel feedstock. Variable pH strategies for microbial lipid production using FW for co-fermentation [20]. The study demonstrated that, as a result of the improved synergistic effect, lipid production from *Rhodosporidium toruloides* increased with FW cooking oil at a substitution rate range of 1.56–4.68 (based on waste cooking oil content in FW) [20]. A similar report found that phosphorus is fixed in hydrochar (HC), that is, the total phosphorus (TP) present in the wet raw material is recovered in dry HC (obtained from the HTC process) and, its concentration is increased [21]. Other findings showed a significant decrease of TP content in the hydrothermal liquid (HTL) with increasing HTC temperature. They reported that the TP content in HTL decreased from 1.66 mg/L to 0.37 mg/L for olive (increased by 77.71%) [22]. Additionally, green diesel, also known as biodiesel, is frequently made using palmitic acid [12,23]. Consequently, the HTC of FW could be a source of valuable fatty acids that can find diverse applications across various sectors. These fatty acids can be harnessed for a wide range of uses, opening up new possibilities and avenues for their utilization.

Despite the growing interest in HTC, there remains a research gap concerning the specific impact of process parameters, such as residence time and temperature, on the properties of HC and

HTL obtained from FW. To address this gap, we employed the response surface methodology (RSM) with a central composite design for optimizing HTC conditions for FW as demonstrated by [24]. This endeavor focuses on enhancing fuel quality, exploring fatty acid distribution, enabling phosphorus recovery, and assessing combustion behavior and thermal characteristics. RSM was employed to systematically optimize a response that is influenced by several independent variables to enhance the quality of HC and HTL obtained from FW. Regression equations involving the interactive effects of residence time, temperature, HTL/mass yield, and HC energy densification ratio would used by RSM to predict outcomes through process parameter optimization [25–27]. The results of the current work provide reference values for the interaction between process parameters on responses including energy densification ratio and mass yield of the resulting products. In doing so, our study aims to contribute to a more comprehensive understanding of the efficiency of the HTC process and its potential for sustainable FW management.

Consequently, more research is required on the thermal transformation of waste given the paucity of research on HTC treatment of FW, particularly how it affects the chemical and physical characteristics of the HTL and HC. Further, there is a need to determine process kinetics, simulate the energy balance of HTC of waste, and identify the HTC ideal condition of the desired parameters [28–31]. To supplement existing literature, this current work therefore assembled a combination of FW that was subject to HTC, and the emergent products were critically evaluated. The specific objectives included: a) Characterization of raw FW/feedstock and fuel properties of HC from HTC; b) Optimization and efficiency of the HTC parameters (temperature and residence time); c) Examination of fatty acid content in both FW and the resulting HTL and HC, alongside phosphorus recovery generated through HTC. This current study involved a lab-scale pressure reactor, and optimization of HTC conditions: temperature (220-340 °C) and residence time (90-260 min) via central composite design type of response surface methodology (CCD-RSM). Specifically, CCD-RSM was selected for optimization given its suitability for systematically exploring complex processes with multiple variables. Data-driven optimization is facilitated by RSM, while variable interactions are captured by CCD, making it ideal for the study's goal of optimizing HTC conditions for FW valorization. Notably, the combination of CCD and RSM proved to be a robust and effective tool for studying, developing, and optimizing various engineering processes [32].

2. Materials and Methods

2.1. Feedstock preparation

The food waste (FW) used in the current study was purchased from a grocery store in Wroclaw - Poland, and its preparation was performed as explained elsewhere [2]. FW as a potential feedstock for HTC demonstrates exceptional quality features such as stable and comprehensive combustion behavior, as well as energy recovery (22.7 MJ kg–^{1}) [33]. This ensures morphological similarity and percentage of individual FW components to ensure reproducibility. Obtained FW contents at fresh state included quantified proportions of dry matter (DM), moisture content (MC), and wet mass (WM), which were analyzed as follows. Grinding and drying of FW: Using a laboratory dryer WAMED, KBC-65 r (WAMED, KBC-65W, Warsaw, Poland), the drying procedure was carried out at 105 °C for 24 hours. To produce a homogenous material, the pre-mixed FW components were ground in a laboratory mill (Testchem knife mill LMN100). After the FW mixture was prepared, it was shredded and sieved through a 5 mm diameter sieve mesh. Three replicates of the raw FW and obtained samples were examined. The MC was determined as previously reported [34]. The AC samples were incinerated in a muffle furnace (Snol 8.1/1100, Utena, Lithuania) by PN-Z-15008-04:1993 standard [35]. Volatile matter (VM) content was determined using a tubular furnace and the thermogravimetric method (Czylok, RST 40 × 200/100, Jastrzębie-Zdrój, Poland) [36]. The difference between AC and VM was calculated to determine fixed carbon (FC). The volatile solids (VS) content of the samples was also examined by the PNEN 15935:2022-01 standard [37]. **Table A1** (Appendix A) presents the FW's properties, including mixture composition according to dry, fresh, and volatile solids percentage share bases, total solids (TS), MC, AC, and volatile solids of used FW**.**

2.2. Methods

2.2.1. Design of HTC process experiment setup

The design of the experiment (DOE) was implemented to ascertain how independent variables (temperature and residence time) affected dependent variables (HC and HTL yield, elements, HC fuel property, fatty acid, and phosphorous recovery). The CCD was created as a two-level factorial design (2^2) of two blocks using Statgraphics 18. **Table A2** (Appendix A) presents the independent parameter levels.

2.2.1. HTC Process

The Waste and Biomass Valorization Group Laboratory's high-temperature high-pressure reactor (HPHT) (Büchi AG, Uster, Switzerland) was used to implement the HTC process. A sample of 285.71 g was added to the feedstock vessel, which consisted of 100 g of dry FW and 185.71 g of water added to obtain 65% MC [38]. After that, the mixture was put inside the heating jacket, sealed, and closed. The vessel operated at a set desired temperature with a stirrer's speed of 120 RPM. The HTC experimental runs were carried out according to Table A3 (Appendix A). At five different temperatures 220, 240, 280, 320, and 340 °C the HTC processes were conducted. The process proceeded for 90, 120, 180, 240, and 260 min after the temperature dropped by 5°C from the predetermined value. The PID temperature controller was the reason for this, as it takes some time to heat the reactor to the final 5°C. Following DOE, each temperature was paired with each retention time. After allowing the reactor to cool, the energy consumption was recorded using an energy meter (Energy meter, Starmeter Instruments Co., Ltd., SK-410, Shenzhen, China). At a cooling temperature of 40 °C, the reactor was switched off and pressure was released by opening the valve. Following that, the sample was taken out of the vessel. After that, a laboratory scale was used to weigh the sample (Radwag, MA 50.R, Morawica, Poland). The liquid from the solid products was separated with the aid of vacuum filtration (Rocker, ROCKER 300, Kaohsiung, Taiwan), and then the weighing (Weighing instrument, Radwag, MA 50. R, Morawica, Poland) was performed. Following its transfer to a plastic container, the liquid portion was kept for additional analysis in an Electrolux freezer (model EC5231A0W, Stockholm, Sweden) maintained at -27°C.

2.2.2 Hydrochar Properties Analyses

The current study's feedstock was examined for VS, AC, and TS. A laboratory dryer (WAMED, model KBC-65W, Warsaw, Poland) was used to determine the VS and TS according to PN-EN 14346:2011 [39]. A Muffle furnace (SNOL, model 8.1/1100, Utena, Lithuania) was used to determine the AC by PN-EN 15169:2011 standard [40]. The proximate analysis VM and (fixed carbon (FC)) were measured by the thermogravimetric method described elsewhere [36] with the aid of a tubular furnace (RST 40 × 200/100, Czylok, Jastrzębie-Zdrój, Poland). HHV was measured by a calorimeter (IKA, C200, Staufen, Germany) by PN-EN ISO 18125:2017-07 standards [41]. An elemental analyzer was used (PerkinElmer, 2400 CHNS/O Series II, Waltham, MA, USA) for ultimate analysis (hydrogen (H), sulfur (S), carbon (C), and nitrogen (N) content) determination was performed by PN-EN ISO 16948:2015-07 standard [42]. Equation (1) was utilized to calculate the content of oxygen [43].

$$O = 100\% - C - H - N - S - AC \quad (1)$$

Equation (2) was used to calculate the fuel ratio [44]. Additionally, the FW mixture and HC were subjected to thermogravimetric analysis (TGA) under isothermal conditions (950 °C) and 7 min. The process was performed with the use of the TGA equipment available [45]. The change in mass during the TGA operation was measured and recorded in a data logger.

$$FR = \frac{FC}{VM} \quad (2)$$

where: FR = the fuel ratio; VM = the volatile matter (%); and FC = the fixed carbon (%). Equation (3) was used to determine the low heating value [46].

$$LHV = HHV - 2441.8 \times \left(9 \times \frac{H}{100}\right) - 24.41 \times \left(\frac{MC}{100}\right) \times \left(100 - \frac{MC}{100}\right) \quad (3)$$

Where: LHV represents the low heating value (J × g−1).; HHV represents the high heating value; MC = moisture content (%); and H = hydrogen content. The O/C and H/C ratios were also determined using Equations (4) and (5) [45].

$$H/C = \frac{H12}{C} \quad (4)$$

$$O/C = 0.75\frac{O}{C} \quad (5)$$

2.2.3. Hydrothermal Carbonization Performance

Equations (6), (7), and (8) were used to determine the mass yield (*MY*), energy densification ratio (*EDr*), and (energy) yield (*EY*), respectively [45].

$$MY = \frac{m_h}{m_r} \times 100 \quad (6)$$

$$EDr = \frac{HHV_h}{HHV_r} \times 100 \quad (7)$$

$$EY = MY \times EDr \quad (8)$$

where: MY = mass yield (%); m_h= the mass of dry hydrochar after the HTC process (g); m_r = the dry raw material mass before the HTC process (g); ED_r =the energy densification ratio (%); HHV_h = the high heating value of HC (J × g^{-1}); HHV_r = the high heating value of raw material before the

HTC process (J × g^{-1}); and EY = the energy yield (%). Equation (9) was also used to determine the energy gain (EG) in percent to ascertain the optimal process conditions [47].

$$EG = \frac{(HHV_h - HHV_r)/HHV_r}{(m_r - m_h)/m_r} \times 100 \quad (9)$$

2.2.4 Combustion behavior and thermal characteristics

The kinetic parameters of the raw FW and HC were calculated from the Gompertz model [48]. It was fitted into the developed model representing the sample degradation during the TGA analyses in the following equation below:

$$m = a * \exp(-k * \mathrm{t})) + b \quad (10)$$

$$p = a * \exp(-k * \mathrm{t})) + b \quad (11)$$

Where: m = *mass* value over time; t = time; a is represents the upper asymptote; b = sample initial mass; k = kinetic constant; and p =predicted model

2.2.5 Lipids analyses

GC-MS was used to measure the composition of fatty acids. Total lipid was extricated utilizing the techniques reported [49]. As previously reported, lipids were converted into FAMEs [50]. Next, a gas chromatograph (GC6890) connected to a mass spectrometer 5983 MS (Agilent Technologies Inc., Santa Clara, CA, USA) with a quadrupole mass detector was used to analyze the fatty acid profile. A capillary column HP-88 (0.25 mm × 100 m) filled with an 88:12 cyanopropyl-aryl poly-siloxane bed with 0.2 µm grain size was used in the separation process. The mobile phase used in the experiment was helium (flow rate 1 mL min$-^{1}$), and the sample was injected in split mode at a ratio of 4:1. As a result, the program was configured to start at 60 °C for 2 min, then heat at 20 °C√min$-^{1}$ to reach 180 °C and 3 °C·min$-^{1}$ to reach 220 °C. A 15-minute hold was placed on the temperature, at the rate of 5°C per minute, the heating continued until it reached 250°C, and it was maintained there for 8 min. The National Institute of Standards and Technology (NIST) library search algorithm was used to identify the spectra (2008 version) [50,51].

2.2.6. Phosphorous content analyses

The mass yield, the coefficient concentration of phosphorus in the HC and liquid fraction, as well as the efficiency of phosphorus in the HC and liquid fraction of each variant were calculated based on equations (10)-(15), respectively.

$$MY = \frac{m_b}{m_a} x100 \tag{12}$$

Where: MY represents mass efficiency (%); Ma represents a mass of dry substrate before hydrothermal carbonization (g); and mb – a mass of dry substrate after hydrothermal carbonization (g).

$$PDh = \frac{Cp_s}{Cp_i} x100\% \tag{13}$$

Where PDh is the phosphorus density factor in hydrochar (%); Cps is phosphorus concentration in the hydrochar (g 100g^{-1}); and Cpi is the concentration of phosphorus in the substrate (g·100g^{-1}).

$$PDl = \frac{Cp_l}{Cp_{i+w}} \cdot 100\% \tag{14}$$

PDl is the phosphorus density factor in liquid fraction (%); Cpl is phosphorus concentration in liquid fraction (g 100g^{-1}); and Cpi+w is the concentration of phosphorus in the substrate (g·100g^{-1}).

$$PYh = MY \cdot PDh \tag{15}$$

Where PY is the efficiency of phosphorus in hydrochar (%); MY is mass efficiency (%); and PDh is the phosphorus density factor in hydrochar (%).

$$PYl = MY \cdot PDl \tag{16}$$

Where: PY is the efficiency of phosphorus in the liquid fraction (%); MY is mass efficiency (%); PDl is the phosphorus density factor in the liquid fraction (%).

3. Results and discussion

3.1 Characterization of raw food waste

Table A1 (Appendix A) presents the properties of the raw food waste (FW) used in this study, which predominantly comprised vegetables, fruits, meat, and other processed products [2].

The experimental FW mixture had a moisture content (MC) of 66.32 ± 2.65%, aligning well with the ideal MC range of 64% to 90% recommended for hydrothermal carbonization (HTC) [38,52]. The FW mixture by fresh mass consisted of such components as orange (3%), banana (10%), apple (5%), lemon (2%), potatoes (24%), onion (3%), lettuce (3%), cabbage (3%), tomatoes (2%), rice (10%), pasta (10%), bread (5%), meat (5%), fish (5%), and cheese (10%) (**Table A1**). The fresh FW mixture exhibited a volatile solids (VS) constituting 84.76% of dry mass, MC of 66.32%, and an ash content (AC) of 15.24%.

Comparatively, the volatile matter (VM) content in FW at 84.18% is higher than other reported results. The AC at 13.90% is comparable to values found elsewhere [53]. Although the fixed carbon (FC) value in this study was 1.92% lower than in other fuel sources, it signifies potential as an alternative to conventional fossil fuels [54]. Carbon (C) and hydrogen (H) contents align with literature values, while nitrogen (N) content is higher, likely due to elevated protein and uric acid levels, resulting in a higher N:P ratio compared to other digestates [53,55]. The notable S and N content should be considered, as high levels of these elements may contribute to emissions of SOx and NOx, impacting fuel suitability [56]. The HHV of the raw FW mixture was measured as 19193 ± 1.53 J x g^{-1}, exceeding values reported in a similar study (15.4 MJ/kg) [12] as shown in **Appendix A (Table A5)**, but falling within the general range of 14.5 MJ/kg to 23 MJ/kg found in most FW studies [54].

3.2 Optimization of the HTC parameters

To obtain the desired quantity of hydrochar (HC) and hydrothermal liquid (HTL), at their maximal quantity, the DOE was carried out. The impact of temperature and residence time on the yield of HC and HTL was assessed. To increase the significance of the approach, 10 experiments (consist 4 axial points, 4 factorial points, and 2 center points) were randomly repeated in two blocks. The results are given in **Table A3** (Appendix A).

The obtained results were analyzed and presented in **Figure 1**. From Pareto’s chart of HC (**Figure 1**, A), its visible effect of independent variables (temperature and resident time) has statistical significance on HC yield. Furthermore, their individual effects have a significant negative impact on the yielding mass of HC (**Figure 1**, A-B). However, HTL yield mass was significantly affected by rising temperature. Though an equal quantity of HTL could be obtained at either, lower resident time with higher temperature or low temperature with prolonged resident time (**Figure 1**, C-D). In contrast, resident time had no statistical impact on the produced HTL yield mass.

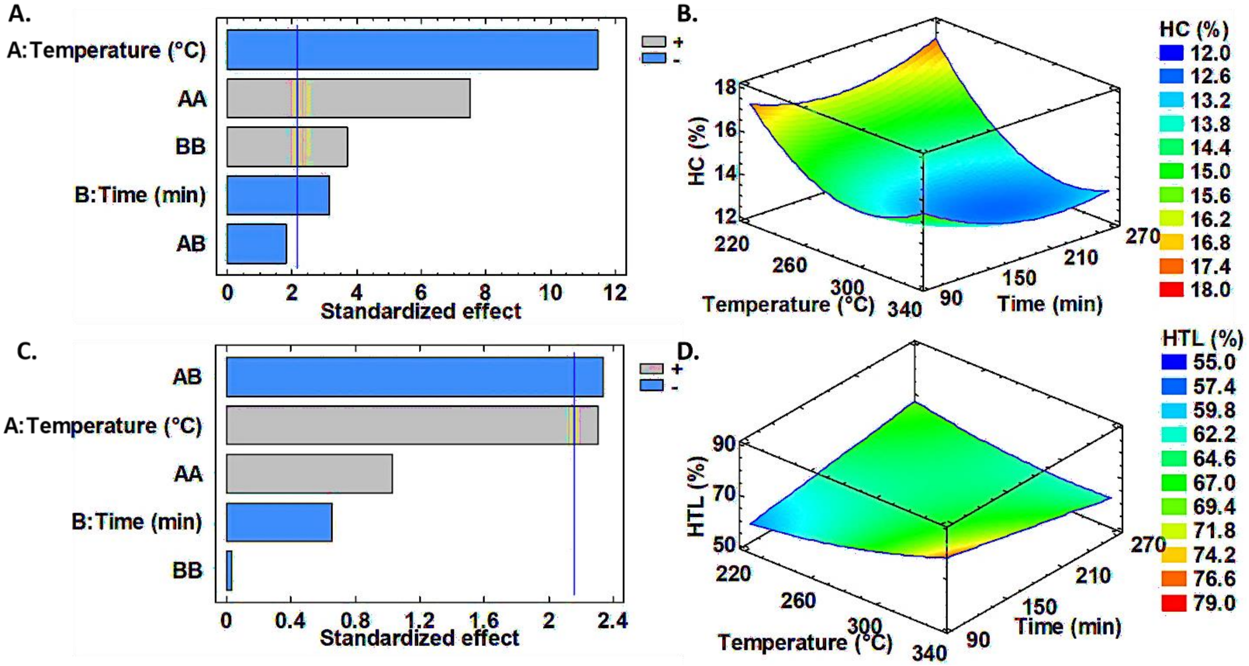

Figure 1. A - C: Pareto chart explaining the positive and negative influence, and significance of mathematical equation of the quadratic model on HC and HTL yield mass, respectively; B - D: Surface response plot for HC and HTL yield mass, respectively.

Temperature (A) and resident time (B) had a two-way interaction (X_{AB}) that had no significant effect on HC yield (**Figure 1, A**). As a result of their significant level, HC yield mass was modeled in a quadratic polynomial equation (R^2 value: 0.94; R2 adjusted value: 0.91) to correlate with the obtained values (Eq. 17), taking into account their level of significance. The model representation was further investigated for HTL yield mass; it was found that the linear effect (X_B) of time and the quadratic interaction (X_{A2} and X_{B2}) had no significant effects on the yield mass. Based on these findings, an equation (Eq. 18) with an R^2 value of 0.91 (and an R^2 adjusted value of 0.89) is presented.

$$HC\ (\%) = 61.786 - 0.3078\ (X_A) - 0.0209\ (X_B) + 0.0005(X_A)^2 + 0.0001(X_B)^2 \qquad (17)$$

$$HTL\ (\%) = 49.8346 - 0.1435\ (X_A) + 0.0012\ (X_{AB}) \tag{18}$$

The maximum achievable yields for HC and HTL were projected at 19.19% and 89.5%, respectively. An optimization run was carried out with the temperature and time set at 220°C and 270 min to verify these predictions. Consequently, HC and HTL were obtained as 18.9 ± 1.2% and 78.2 ± 2.2%, respectively. The observed decrease in experimental HTL yield compared to the predicted values can be attributed to the moisture and volatile compound losses during the process [57]. Therefore, additional analyses were done with caution to define the key character changes that occurred during DOE experiments (R1–R20) and to explain particular properties and the degree of carbonization.

3.3 Key features of feedstock and hydrochar from HTC

The obtained elemental analysis of HC presented in **Appendix A** (**Table A4)** indicates a significant increase in C content during the rise of temperature. This property is known to constitute several industrial scale-up processes using active materials. During this study, food waste HC constitutes maximal C content at 72.52 ± 1.06% in temperature and time at 320°C and 240 min, respectively. According to serval others, the higher C content is known to provide better adsorption and textural properties to activated materials [57,58]. In contrast, the percentage of oxygen (**Figure 2**, B - C) and hydrogen (**Figure 2**, D - E) decreases with the rise of temperature during the HTC process. This decrease is commonly concluded in the HTC process among others [13,59]. In addition, the nitrogen content is significantly affected by rising temperature (**Figure 2**, G). More interestingly, the Sulfur content of HC appeared not significantly affected by temperature or resident time **(Figure 2**, I). In common, acid-assisted HTC is known to obtain heteroatomic HC materials with S- and N-dopped surfaces and this study constitutes food waste-derived HC treatment at varying temperatures and time to result in an adequate quantity of N and S [59]. The obtained HC products (R1 – R20) constituted N (**Figure 2**, H) and S (**Figure 2**, J) content between 3 – 9 and 0.18 – 1.02 %, respectively.

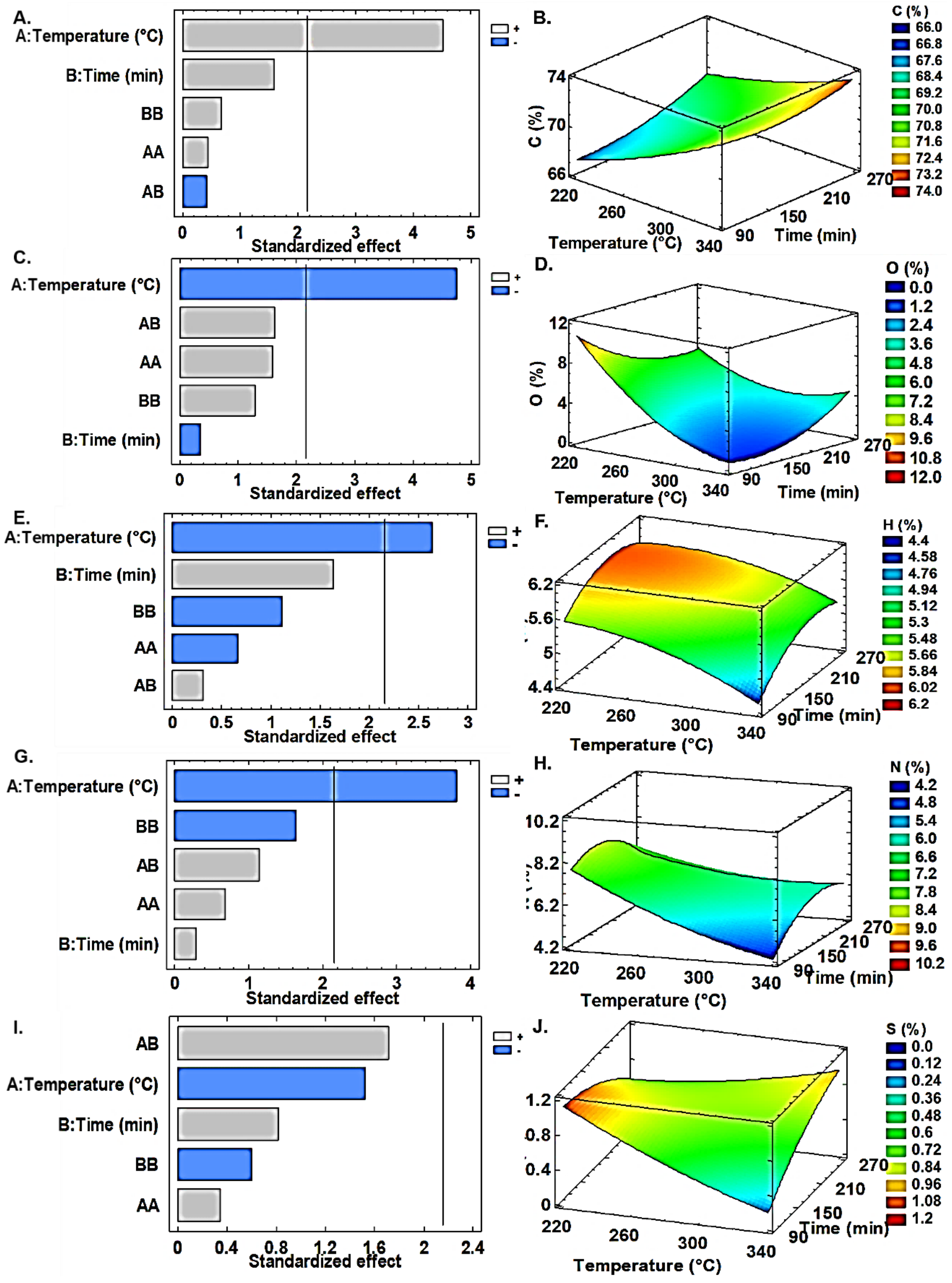

Figure 2. (A – J) Elemental variation during the HTC process. A, C, E, G and I: Pareto chart of C, O, H, N and S contents in HC material; B, D, F, H, and J: surface response plot of C, O, H, N and S contents throughout varying temperature and resident time.

Furthermore, to evaluate the fuel properties of FW treated with HTC and the resulting HC for energy application, it is crucial to consider the O/C and H/C atomic ratios. [60]. In particular, higher O/C and H/C indicated a more stable HC which could be achieved by acid pre-treatment [61]. To explain them, the Van Krevelen diagram **(Figure A17)** is presented using obtained atomic H/C and O/C ratios from elemental analysis [62]. The results were compared with other materials to explain the degree of decarboxylation. As the process temperature increased, both H/C and O/C ratio values dropped. Whereas the HCs obtained at higher parameters (residence time and temperature) resembled those of lignite and coal, the HCs obtained at lower parameters positioned on the diagram resembled those of biomass and peat. The fuels with lower O/C and H/C ratios would, therefore, be beneficial as they reduce water vapor, smoke, and energy loss during the combustion process [63].

3.4 Hydrochar Fuel Properties

The current study results indicate that the fuel quality of hydrochar is improved compared to the respective feedstock/FW. This is due to the reduced volatiles, oxygen, increased fixed carbon, and carbon content. The HTC process conditions also have an impact on the ash, fixed carbon, moisture, and volatile matter content of hydrochars. Herein, FC increased with process temperature, whereas the VM content reduced as AC slightly increased with temperature. HC produced at 340 ºC in 180 min demonstrated the highest FC content (31.69 ± 0.01%) comparison to (1.92 ± 0.21%) input feedstock (Table A4). It is implied that some of the compounds were moved to a liquid fraction by a decrease in VM content [64]. The HTC-tested parameters showed a difference in FC content ($p < 0.05$), and VM content showed the same trend (**Table A4**). The highest VM content observed in HC produced at (220 °C, 180 min) with 69.58 ± 0.11% compared to HC produced at peak temperature with the same duration (340 °C, 180 min) with 53.66 ± 0.09%. The remaining volatile matter contained a large amount of solid carbon due to the high temperature-induced increase in FC content, which in turn caused the devolatilization of organic matter [65,66]. The AC in derived HC of FW increased with temperature owed to inorganic compounds in the feedstock that remained in the solid part after the HTC process, the AC observed in this study increased from 11.59 ± 0.12% to 14.65 ± 0.10% in HC derived from 220 and 340 °C at 180 min respectively, resembling those result previously reported elsewhere [67].

The peak energy that can be released during the complete oxidation of a single fuel unit is referred to as the HHV [7]. The HHV of HC increased with temperature and residence time **(Figure 3)**. With rising temperatures, the HHV of HC found in this study gradually rose to a value 1.69 times greater than that of the raw FW. The highest HHV was observed at (340 °C in 180 min) with (32.49 ± 2.92 MJ/kg) and feedstock was (19.19 ± 0.2MJ/kg) (**Figure 3**). The HHV value appears to corroborate the data reported by Engin et al. (2019) and other reports on the HTC of FW (20.8-31.1 MJ/kg at 200 –300 ◦C) [68,69]. Moreover, the current study values are higher than other biomass feedstock reported. For instance, 20.4 and 19.3 MJ × kg$-^{1}$ were found in spruce and beech wood, respectively [70]. More so, the LHV value of the current study, which makes it possible the determine the actual energy potential of biomass [71], which would increase with higher HTC process parameters in **Appendix A (Table A5**), is probably associated with the amount of hydrochar produced. For instance, the HC was produced at 220 °C and 340 °C in 180 min with LHV of 27.81 ± 3.7 MJ/kg and 31. 92.64 ± 42.1 MJ/kg. In addition, the LHV value for raw FW was 18.98.91 ±6.01 MJ/kg.

3.4.1 Hydrothermal Carbonization Performance and Efficiency

As for the mass yield (MY), decreased over time, the increased temperature tends to reduce the MY in most cases, for instance, it was observed at 45.50 ± 3.23% and 36.50 ± 3.13% at 280 and 320 °C respectively and this represents the lowest and highest MY in the current study **Figure 3 and Appendix A (Table A5)**. The observed reduction of MY could be caused by the formation of water-soluble organic compounds and the decarboxylation process**.** A similar report on decreasing cases can be found in the literature [72,73]. Consequently, hydrothermal carbonization appears to be a viable substitute for producing solid fuels from high-moisture waste biomass that can be potentially combusted in existing coal-fired power plants due to its high hydrochar yields and lower operating temperatures [74].

The energy densification ratio (EDr) and (energy) yield (EY) of the produced HC were also evaluated in the current study **(Figure 3)**. Previous workers calculated the EDr by dividing the energy content of the biochar by the energy content of the raw biomass. Meanwhile, the energy yield would emerge from multiplying the EDr by the biochar yield [63,74]. In general, as shown in (**Figure 3**), the EDr increased with temperature, increasing from 1.47% to 1.69% at (220 and 340 °C for 180 min) respectively. As for the EY, it is a crucial parameter that indicates the remaining energy in HC, the increase of temperature resulting in decreased EY was observed for most cases in this study with values of 63.83 and 67.11% at (220 and 340 °C for 180 min). However, when the temperature increased, the EY of HC and the biochar made from chicken manure and FW decreased [63,66]. Consequently, samples with high organic matter content had lower MY, higher EY, and higher decomposition, EDr, and EG than samples with higher ash content. Additionally, process temperature and time impact the fuel ratio (FR) of produced HC as it is shown in **Figure 3**, this observed in obtained samples with a value of 0.29 and 0.67 at 220 °C for 180 min and 320 °C for 240 min in contrast to untreated FW with 0.02. Based on published research, FW typically has a low fuel ratio FC/VM unless a suitable pre-treatment is applied. FW fuel ratios have been found to range from 0.014 to 0.27 [54]. Consequently, it can be deduced that all derived HC showed sufficient combustion performance for burning pulverized fuel.

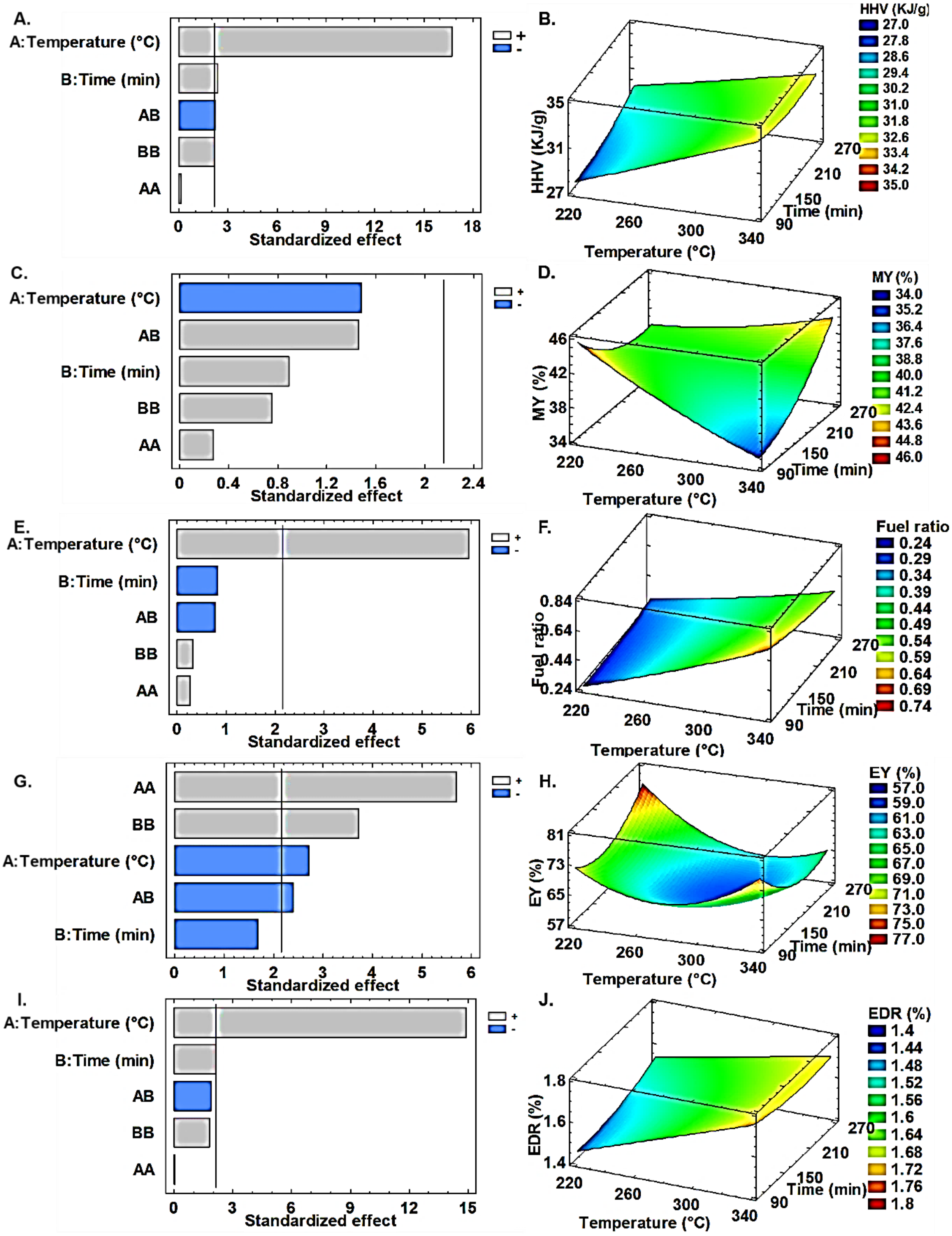

Figure 3. (A – J) Fuel Properties of food waste used in HTC process. A, C, E, G, and I: Pareto chart explaining negative and positive influence, level of significance of components in the quadratic polynomial model on higher heating value (HHV), mass yield (MY), fuel ratio, energy

yield (EY) and energy densification ratio (EDR), respectively. B, D, F, H, J: Surface response plot of HHV, MY, fuel ratio, EY, and EDR.

Figure 4 provides a visual representation of pressure and temperature patterns observed during various HTC processes: (A) 320°C for 240 min (R1), (B) 240°C for 120 min (R2), (C) 280°C for 90 min (R9), and (D) 280°C for 180 min (R17). **Appendix B1** (**Figures A1-A4**) has additional graphs that show pressure and temperature patterns with varying parameters during the HTC process. The value of generated pressure would depend on the amount of produced gas and set temperature point, while the decomposition of the processed material determined the amount of produced gas. Notably, the retention time did not significantly affect the HC yield as as evident from the data presented in **Figure 3.** Additionally, **Figure 4** sheds light on the complex relationship between HTC parameters including (temperature, residence time, and gas evolution) during the process by highlighting the dynamic changes in pressure under various HTC conditions. These insights are crucial for maximizing the process parameters to produce HC and HTL with the appropriate quality, yield, and system efficiency, all of which support the long-term sustainable management of FW assets.

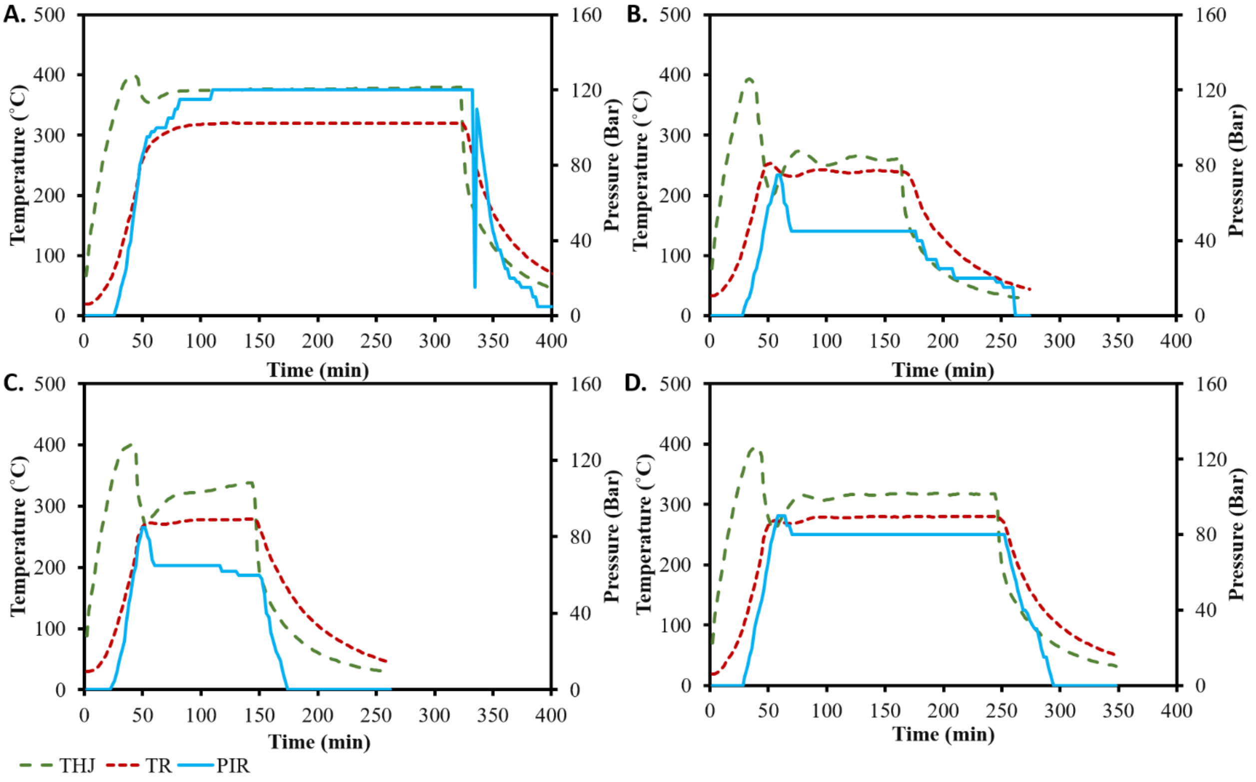

Figure 4. Change in pressure at different HTC operating temperatures and residence time; A) 320°C - 240 min; B) 240°C - 120 min; C) 280°C - 90 min; D) and 280°C - 180 min.

3.4.2 Energy balance

As seen in **Figure 5**, the process's energy consumption tends to rise with retention time and temperature, reaching 11.4 MJ with an HHV of 32.5 MJ/kg for HC produced at 340 °C in 180 min. The MY decreased over time, the increased temperature tends to reduce the MY in most cases, for instance, it was observed at 45.50 ± 3.23% and 36.50 ± 3.13% at 280 and 320 °C respectively. Conversely, the energy densification ratio exhibited an upward trend with increasing temperature. Thus, chemical energy was calculated using the high heating values obtained in the received hydrochar i.e. (mass of dry hydrochar x HHV), and the electrical energy and energy usage to prepare the liquid fraction of examined samples present in **Appendix B2** (**Figure A5)**. There is much higher energy input than there is potential output. Interestingly, the energy consumption in 180 min at 220 ^{o}C is approximately five times greater than the energetic effect that the HC combustion can produce. Similar trends were reported by other researchers where 200 ^{o}C in 4h showed 17 times higher energy usage than combustion energy that could be achieved from the obtained HC [64]. Therefore other, than HC burning, options for the HTC products' valorization should be investigated. Another way may be an intensification of volatile fatty acids content in liquid fraction or an increase in the phosphorous content in the solid phase.

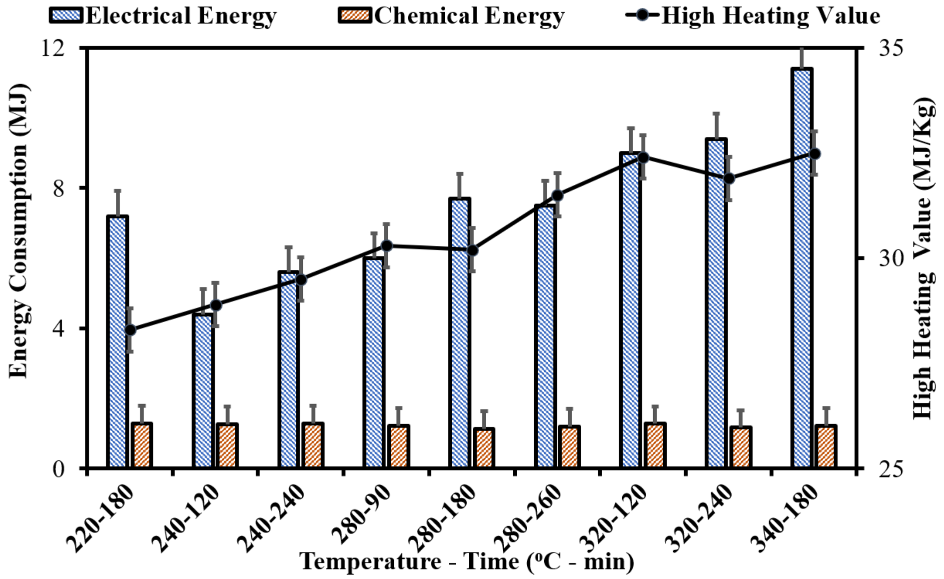

Figure 5. Chemical energy bound in samples, high heating value of tested samples, and electrical energy used to prepare HC.

3.5 Fatty acids composition in food waste and HTC products

3.5.1 Composition of fatty acids in food waste mixture

Lipids and fatty acids (FA) are additional crucial FW macronutrients. These substances are found as parts of spherosomes (small oil droplets), and intercellular membrane bodies throughout the FW material. GC-MS and a standard FAME mixture to analyze the FA profiles and quantity were used. FW was well-off in saturated fatty acids (SFA) with (45.9 wt% of the total) comprised of palmitic (C16:0), myristic (C14:0), stearic (C18:0), lauric (C12:0), and capric (C10:0) being the most abundant at 27.1, 7.5, 5.2, 2.2, and 1.6 wt% respectively. The remaining SFA were all 2.5 wt% or less (**Figure 6** and **Appendix A, Table A8**). Unsaturated fatty acids (UFA) are divided into polyunsaturated fatty acids (PUFA) consist about 33 wt%, comprising omega-3 (n-3 PUFA); eicosapentaenoic (C20:5 n-3) with 0.7 wt%, docosahexaenoic acid (C22:6 n-3) with 5.9 wt%, α-linolenic (C18:3 n-3) with 6.2 wt%, and omega-6 (n-6 PUFA); arachidonic acid (C20:4 n-6) with 0.3 wt%, linoleic acid (C18:2 n-6) with 19.8 wt%, and monounsaturated fatty acids (MUFA) contain about 20 wt%, including; palmitoleic acid (C16:1 n-7) with 2.9 wt%, oleic acid (C18:1 n-9) with 17.1 wt%. The total fatty acid present in the FW was about 98 wt%. For naming fatty acids, we employed the omega nomenclature system. The carbon atoms within the entire molecule are indicated by the first number in parentheses [75]. The second number indicates how many double bonds are present in the molecule, and the information in brackets indicates where each double bond is situated. Green diesel also known as biodiesel is frequently made using palmitic acid. Dietetic, nutritional, and medical uses all exist for capric acid [12,23]. As a result, HTC of FW might be a source of fatty acids used in numerous industries and applications.

3.5.2 Composition of fatty acids in hydrochar

The purpose of this part of the experiment was to ascertain the effect of HTC's operating condition on FA composition in the obtained products. About 80% of the lipids that were initially present in the FW are still present in the HC. The produced HC through HTC from FW composition was reported to be made up of SFA including capric (C10:0), lauric (C12:0), myristic (C14:0), stearic (C18:0), and palmitic (C16:0) being the most abundant. The remaining SFA were less as illustrated in (**Figure 6B and Appendix A, Table A8**). The obtained HC was rich in SFA in all different operating conditions tested with 77.2, 67.4, and 59.5 wt% for HTC at 320 ºC in 120 min, 280 ºC in 180 min, and 220 ºC in 180 min, respectively. It can assumed that HTC at higher parameters (320 ºC in 180 min) is favorable to SFA. Further, UFA consists of polyunsaturated fatty acids (PUFA) and monounsaturated fatty acids (MUFA). PUFA had lower amounts compared to the feedstock, containing about 1.1, 0.42, and 10.3 wt% demonstrating that HTC condition at low temperatures is more favorable, comprising omega-6 (n-6 PUFA); linoleic acid (C18:2 n-6) with 1.1, 0.4, and 9.2 wt% (320 ºC in 120 min; 280 ºC in 180 min; and 220 ºC in 180 min respectively, and omega-3 (n-3 PUFA); α- linolenic (C18:3 n-3) with 1.0 wt% at 220 ºC in 180 min. On the other hand, MUFA contained about 20 wt%, including; palmitoleic acid (C16:1 n-7) with 2.9 wt%, oleic acid (C18:1 n-9) with 19.3, 31.1, and 27.5 wt% concerning the above selected HTC conditions. In terms of oxidation and oligomerization, PUFAs with two or more double bonds are more prone. This makes the PUFAs difficult to recover after HTC [12,31]. At the various HTC process conditions, HTC at 220 °C and 180 min produced a fatty acids recovery, which appeared relatively coinciding with those under the higher HTC conditions. The majority of HTC researchers would prefer these less extreme conditions because they would use less energy. For the HTC processing of FW, a continuous process might be developed given the relatively 180 min or less reaction time that was demonstrated here in a batch process. The HTC at 220 ◦C seems to be the better temperature for keeping FA in the HC for each type of fatty acid. Overall, more total fatty acids (roughly 70%) were retained in the HC as a result of the higher HTC temperatures, which ranged from 220 to 320 ºC.

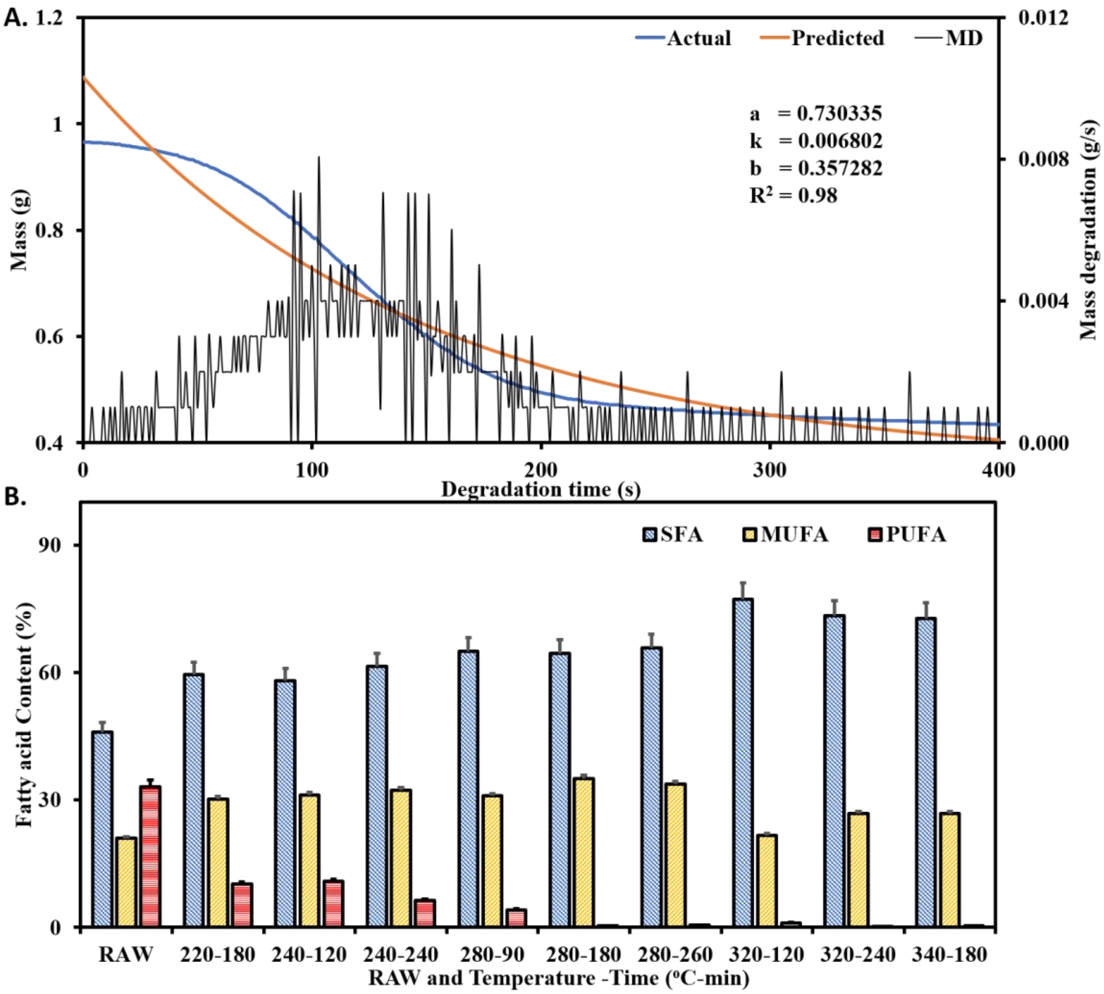

Figure 6. A) TGA for HC obtained with temperature and time at 340˚C and 180 min, respectively, and B) The distribution of fatty acid in HC after the HTC process with different parameters.

3.5.3 Composition of fatty acids in the liquid fraction

The produced fraction of water from FW composition appeared to include SFA including caproic (C6:0), butyric (C4:0), palmitic (C16:0), and caprylic (C8:0) being the most abundant. All other SFA were less as illustrated in **Figure 7 and Appendix A (Table A9)**. HTL samples obtained consist of the high content of SFA with 77.3, and 48.4 wt% for HTC at 340, and 280 ºC in 180 min respectively, this demonstrates that HTC at higher parameters was more favorable to SFA. More so, UFA is divided into PUFA with lower amounts compared to the feedstock, containing about 6.4, 10.5, and 14.4 wt% concerning the above HTC conditions, this shows that the process at low temperatures is more favorable, comprising omega-6 (n-6 PUFA); linoleic acid (C18:2 n-6) with 4.9, 10.5, and 12.2 wt% (340; 280, and 220 ºC in 180 min respectively and omega-3 (n-3 PUFA); α- linolenic (C18:3 n-3) with 1.5, 2.2 wt% at 220, and 340 ºC in 180 min respectively, and MUFA including; oleic acid (C18:1 n-9) with 16.3, 41.0, and 48.5 wt% respect to the above selected HTC conditions. As a result, the quantity of MUFA significantly decreased as HTC temperature increased. Higher HTC is thought to be appropriate for FW to maximize the SFA from the liquid fraction, such as temperature at 340 ºC and residence time of 180 min.

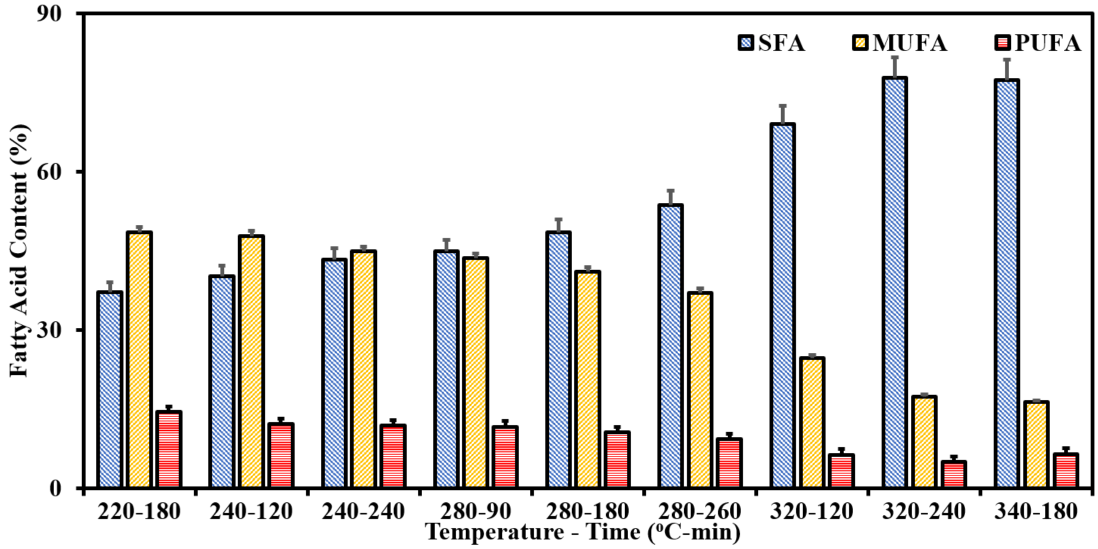

Figure 7. The distribution of fatty acid in liquid fraction after the HTC reaction of examined samples with different parameters.

3.6 Phosphorous recovery from hydrochar and liquid fractions

In the fertilizer industry, phosphorus is used to produce phosphate-based fertilizers. Phosphorus (P) is a non-renewable resource that is extracted from ores for commercial purposes [76]. Before and after the HTC, an effort was made to attain a total phosphorus mass balance (TP) in the FW mixture and HTC products. The content of phosphorus in food waste was 3.28 g·100g^{-1} of dry waste. On the other hand, in the hydrochar, it was 4.70 g·100g^{-1} on average, while the average P content in the liquid fraction was 0.51 g·100g^{-1} presented in (**Figure 7**) and **Appendix A** (**Tables A6 and A7**).

The TP in HC shows that the highest recovery of phosphorus took place at the HTC 340°C and 180 min (5.64 g·100 g^{-1}), while the lowest value at 240°C in 240 min of (4.76 g·100 g^{-1}). It is evident that temperature significantly affects P recovery by HTC, the study result is similar to findings by Malhotra and Garg, where the TP increased with HTC temperature [77]. Additionally, Azzaz et al., found that TP increased with process temperature [22]. More so, a longer period at an average temperature value also results in a greater P recovery in solid products. Furthermore, HTL generally contains a low phosphorus concentration, the highest value of TP was 0.83 g·100g^{-1}, which was obtained at (220 °C), the current result is similar to the previously reported literature [78]. For that reason, it can be said that P is fixed in HC, i.e. the entire P that was in the wet raw material is recovered in the dry HC [21], and TP content in the HTL of the research reported previously, the result showed a significant decrease with increasing HTC temperature. Azzaz and colleagues reported that the concentration of HTL decreased by 1.29 mg/L [22]. The shorter process duration as well as the HTC temperature, contributed to the advantage of obtaining a larger amount of phosphorus in the HTL. It is shown that, with the increase in process duration and temperature, the share of TP in the HC increased, while the HTL experienced a decrease, indicating a reduced concentration of liquids within the final product (**Figure 8** and **Appendix A, Table A5**).

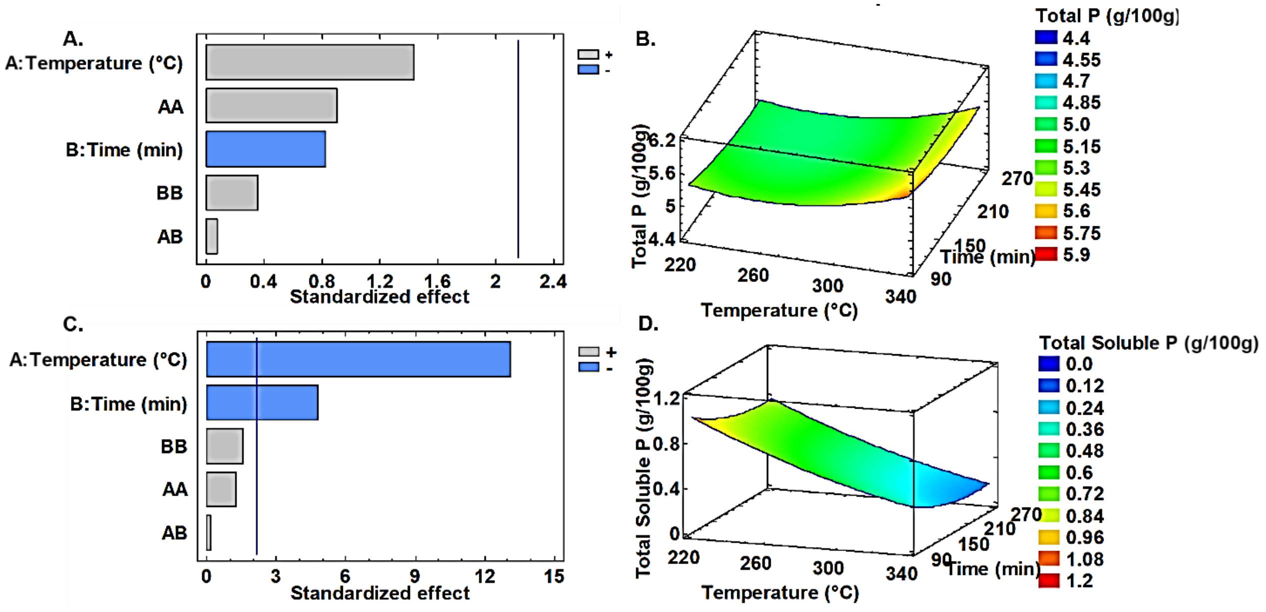

Figure 8. Food waste to phosphorous recovery in HTC process. A and C: Pareto chart explaining negative and positive influence, level of significance of components in a quadratic polynomial model of total P and soluble P, respectively; B and D: Surface response plot of total P and total soluble P, respectively.

3.8 Combustion behavior and thermal characteristics

Following the HTC process, samples of raw FW and HC thermal behavior were determined and compared with the aid of thermogravimetric analysis (TGA). The TGA analysis was performed on a thermo-gravimetric analyzer with a known sample mass (~1–2 g) in non-isothermal conditions to obtain complete thermal degradation data of the samples. The analyses were carried out in 7 min at a heating rate of 10˚C·min^{-1} at increasing temperatures (20 - 950˚C). Herein, the average initial mass of the samples at time zero before subjecting to TGA analysis was 1.020 grams, and after the TGA operation was 0.25 grams shown in **Appendix** (**Figure 6A** and **Figures A7-A15)**. However, there are significantly different degradation values over time between the feedstock and HC samples obtained in high HTC parameters, for instance, (0.10 and 0.40 g) in feedstock and 340 in 180 min respectively. The constant c was determined through the initial value condition while the kinetic constant k was determined based on non-linear regression through the Solver Tool-Pak of Microsoft Excel [79]. The minimum value for the predicted mass and the sum of squares of the actual values were considered. The developed model for the degradation of FW had a R^2 value ranging from 0.96 to 0.99. Substituting these values to Eq. (10) will give a predictive model for the volatile mass degradation of the FW at any time, $m_T(t)$ shown in Eq. 11. To describe the change in mass of the sample, the mass loss of the samples during the TGA operation (**Figure 6A**) was fitted using the developed model in Eq. 11. The DTA of the FW reflects that most of the mass that is easily degradable were lost between 40 to 100 seconds which explains the sudden drop of the TGA especially samples obtained at lower HTC operating conditions. The DTA was conducted at isobaric conditions (with a constant temperature of 950 ^{o}C). The proximate findings elsewhere [80] and the kinetic properties of biomass [81] corroborated our study. This concluded that HC derived from FW at higher operating HTC conditions characterized optimum degradation behaviors.

4. Conclusions

Successfully and for the first time to our best knowledge, a combination of food waste (FW) (which comprised orange (3%), banana (10%), apple (5%), lemon (2%), potatoes (24%), onion (3%), lettuce (3%), cabbage (3%), tomatoes (2%), rice (10%), pasta (10%), bread (5%), meat (5%), fish (5%), and cheese (10%)) subjected to hydrothermal carbonization (HTC) and emergent products were critically evaluated. Both temperature and residence time had an impact on HTC products. The hydrochar (HC) produced from high operating temperature and residence time (340˚C and 180 min) demonstrated promising fuel properties. The ash, fixed carbon, and volatile matter content were 14.65 ± 0.10, 31.69 ± 0.01, and 53.66 ± 0.09%, respectively. The H/C and O/C ratios were 0.90 ± 0.01 and 0.02 ± 0.01, respectively. The high and low heating values were 32496 ± 292.19 $J \times g^{-1}$, and 31915.64 ± 82.14 $J \times g^{-1}$, respectively. Saturated fatty acids (SFA) were the predominant constituent in the hydrothermal liquid (HTL), exhibiting the highest percentages across all tested operating conditions (77.3, 48.4, and 37.1 wt% for HTC at (340, 280, and 220 ^{o}C in 180 min), respectively). Similar conditions were observed in the context of hydrochars, SFA in total with 77.2, 67.4, and 59.5 wt% for HTC at (320 ^{o}C in 120 min; 280 ^{o}C in 180 min; and 220 ^{o}C in 180 min, respectively). Considering the total phosphorous (TP) on one hand, the hydrochar TP shows that the highest recovery of phosphorus took place at 340°C and 180 min (5.64 $g \cdot 100\ g^{-1}$). On the other hand, the liquid fraction generally contains a low phosphorus concentration, the highest value of TP was 0.83 $g \cdot 100g^{-1}$, which was obtained at the lowest temperature (220 °C). This finding implies that HTC was more conducive to SFA recovery at higher temperatures.

The study results reveal a substantial increase in the heating values and energy yield from hydrochar derived through HTC. This presents a notable potential for cleaner and more sustainable production. The increase in energy content indicates a promising avenue for reduced energy consumption in subsequent utilization. While the current study highlights promising outcomes of HTC of FW, certain limitations must be acknowledged. The variability in FW composition from diverse sources might influence the reproducibility and generalizability of these results. As FW compositions differ regionally and temporally, the direct translation of laboratory-scale findings to large-scale industrial applications could present challenges in achieving similar outcomes consistently. Therefore, the results of this study indicate that the HC generated via HTC has a great deal of potential for efficient use in energy production applications. In the future, it is imperative to research on a larger scale to comprehensively explore the benefits associated with maximizing the effectiveness and minimizing energy consumption of FW in the HTC process. Such studies would provide valuable insights into optimizing the efficiency and overall performance of HTC, paving the way for more sustainable and efficient utilization of FW resources.

Author contributions

Conceptualization: W.A.R and A.B; Methodology: W.A.R and A.B; Result analysis and validation: W.A.R, V.T, L.B, K.W; Project administration: W.A.R and A.B; writing – original draft: W.A.R, K.W,V.T, M.V and C.A.I; writing – review and editing: W.A.R, L.B, C.A.I , and A.B; Supervision: C.A.I and A.B

Conflicts of interest

There are no conflicts to declare.

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References

1. Grandhi, B.; Appaiah Singh, J. What a Waste! A Study of Food Wastage Behavior in Singapore. *J. Food Prod. Mark.* **2016**, *22*, 471–485, doi:10.1080/10454446.2014.885863.
2. Valta, K.; Sotiropoulos, A.; Malamis, D.; Kosanovic, T.; Antonopoulou, G.; Alexandropoulou, M.; Jonuzay, S.; Lyberatos, G.; Loizidou, M. Assessment of the Effect of Drying Temperature and Composition on the Biochemical Methane Potential of In-House Dried Household Food Waste. *Waste Manag. Res.* **2019**, *37*, 461–468.
3. Jedzenia, N.I.E.M. *Polskich Banków Żywności*; 2018;
4. Su, H.; Kanchanatip, E.; Wang, D.; Zheng, R.; Huang, Z.; Chen, Y.; Mubeen, I.; Yan, M. Production of H2-Rich Syngas from Gasification of Unsorted Food Waste in Supercritical

Water. *Waste Manag.* **2020**, *102*, 520–527, doi:10.1016/j.wasman.2019.11.018.

5. Uçkun Kiran, E.; Trzcinski, A.P.; Ng, W.J.; Liu, Y. Bioconversion of Food Waste to Energy: A Review. *Fuel* **2014**, *134*, 389–399, doi:10.1016/j.fuel.2014.05.074.

6. Bhatt, D.; Shrestha, A.; Dahal, R.K.; Acharya, B.; Basu, P.; MacEwen, R. Hydrothermal Carbonization of Biosolids from Waste Water Treatment Plant. *Energies* **2018**, *11*, 1–10, doi:10.3390/en11092286.

7. Santos Dalólio, F.; da Silva, J.N.; Carneiro de Oliveira, A.C.; Ferreira Tinôco, I. de F.; Christiam Barbosa, R.; Resende, M. de O.; Teixeira Albino, L.F.; Teixeira Coelho, S. Poultry Litter as Biomass Energy: A Review and Future Perspectives. *Renew. Sustain. Energy Rev.* **2017**, *76*, 941–949, doi:10.1016/j.rser.2017.03.104.

8. Rasaq, W.A.; Golonka, M.; Scholz, M.; Białowiec, A. Opportunities and Challenges of High-pressure Fast Pyrolysis of Biomass: A Review. *Energies* **2021**, *14*, 1–20, doi:10.3390/en14175426.

9. United Nation Transforming Our World: The 2030 Agenda for Sustainable Development. *A New Era Glob. Heal.* **2015**, 1–6, doi:10.1891/9780826190123.ap02.

10. Połomka, J.; Jedrczak, A. Potential Ofmineral Fraction in Compost-like-Output, Methods of Its Obtaining and the Possibility of Using It in the Context of Circular Economy. *Materials (Basel).* **2020**, *13*, doi:10.3390/ma13133023.

11. Hejna, M.; Świechowski, K.; Rasaq, W.A.; Białowiec, A. Study on the Effect of Hydrothermal Carbonization Parameters on Fuel Properties of Chicken Manure Hydrochar. *Materials (Basel).* **2022**, *15*, doi:10.3390/ma15165564.

12. Motavaf, B.; Dean, R.A.; Nicolas, J.; Savage, P.E. Hydrothermal Carbonization of Simulated Food Waste for Recovery of Fatty Acids and Nutrients. *Bioresour. Technol.* **2021**, *341*, 125872, doi:10.1016/j.biortech.2021.125872.

13. Yu, S.; Zhao, P.; Yang, X.; Li, Q.; Zhang, Y.; Zhou, H. Formation and Evolution of Pectin-Derived Hydrothermal Carbon from Pectin. *Fuel* **2022**, *326*, 10–15, doi:10.1016/j.fuel.2022.124997.

14. Zabaniotou, A.; Rovas, D.; Delivand, M.K.; Francavilla, M.; Libutti, A.; Cammerino, A.R.; Monteleone, M. Conceptual Vision of Bioenergy Sector Development in Mediterranean Regions Based on Decentralized Thermochemical Systems. *Sustain. Energy Technol. Assessments* **2017**, *23*, 33–47, doi:10.1016/j.seta.2017.09.006.

15. Rasaq, W.A.; Thiruchenthooran, V.; Telega, P.; Bobak, Ł.; Igwegbe, C.A.; Białowiec, A. Optimizing Hydrothermal Treatment for Sustainable Valorization and Fatty Acid Recovery from Food Waste. *J. Environ. Manage.* **2024**, *357*, 3–10, doi:10.1016/j.jenvman.2024.120722.

16. Taylor, P.; Demirbas, A. Production of Gasoline and Diesel Fuels from Bio- Materials. **2007**, 753–760, doi:10.1080/00908310500281288.

17. Hoekman, S.K.; Broch, A.; Robbins, C. Hydrothermal Carbonization (HTC) of Lignocellulosic Biomass. *Energy and Fuels* **2011**, *25*, 1802–1810, doi:10.1021/ef101745n.

18. Lachos-Perez, D.; César Torres-Mayanga, P.; Abaide, E.R.; Zabot, G.L.; De Castilhos, F. Hydrothermal Carbonization and Liquefaction: Differences, Progress, Challenges, and Opportunities. *Bioresour. Technol.* **2022**, *343*, 126084, doi:10.1016/j.biortech.2021.126084.

19. Yang, F.; Zhang, S.; Cheng, K.; Antonietti, M. A Hydrothermal Process to Turn Waste Biomass into Artificial Fulvic and Humic Acids for Soil Remediation. *Sci. Total Environ.* **2019**, *686*, 1140–1151, doi:10.1016/j.scitotenv.2019.06.045.

20. Gao, Z.; Ma, Y.; Liu, Y.; Wang, Q. Waste Cooking Oil Used as Carbon Source for Microbial Lipid Production: Promoter or Inhibitor. *Environ. Res.* **2022**, *203*, 111881, doi:10.1016/j.envres.2021.111881.

21. Oliver-Tomas, B.; Hitzl, M.; Owsianiak, M.; Renz, M. Evaluation of Hydrothermal Carbonization in Urban Mining for the Recovery of Phosphorus from the Organic Fraction of Municipal Solid Waste. *Resour. Conserv. Recycl.* **2019**, *147*, 111–118, doi:10.1016/j.resconrec.2019.04.023.

22. Azzaz, A.A.; Jeguirim, M.; Kinigopoulou, V.; Doulgeris, C.; Goddard, M.L.; Jellali, S.; Matei Ghimbeu, C. Olive Mill Wastewater: From a Pollutant to Green Fuels, Agricultural

and Water Source and Bio-Fertilizer – Hydrothermal Carbonization. *Sci. Total Environ.* **2020**, *733*, 139314, doi:10.1016/j.scitotenv.2020.139314.

23. Huang, D.; Li, T.; Li, X.; Zhang, L.; Sun, L.; He, X.; Zhong, X.; Jia, D.; Song, L.; Semenza, G.L.; et al. HIF-1-Mediated Suppression of Acyl-CoA Dehydrogenases and Fatty Acid Oxidation Is Critical for Cancer Progression. *Cell Rep.* **2014**, *8*, 1930–1942, doi:10.1016/j.celrep.2014.08.028.

24. Chelladurai, S.J.S.; Murugan, K.; Ray, A.P.; Upadhyaya, M.; Narasimharaj, V.; Gnanasekaran, S. Optimization of Process Parameters Using Response Surface Methodology: A Review. *Mater. Today Proc.* **2020**, *37*, 1301–1304, doi:10.1016/j.matpr.2020.06.466.

25. Udaya Prakash, J.; Sivaprakasam, P.; Jebarose Juliyana, S.; Ananth, S.; Sarala Rubi, C.; Divya Sadhana, A. Multi-Objective Optimization Using Grey Relational Analysis for Wire EDM of Aluminium Matrix Composites. *Mater. Today Proc.* **2022**, doi:10.1016/j.matpr.2022.09.415.

26. Shah, D.R.; Pancholi, N.; Gajera, H.; Patel, B. Investigation of Cutting Temperature, Cutting Force and Surface Roughness Using Multi-Objective Optimization for Turning of Ti-6Al-4 V (ELI). *Mater. Today Proc.* **2021**, *50*, 1379–1388, doi:10.1016/j.matpr.2021.08.285.

27. Toptas Tag, A.; Duman, G.; Yanik, J. Influences of Feedstock Type and Process Variables on Hydrochar Properties. *Bioresour. Technol.* **2018**, *250*, 337–344, doi:10.1016/j.biortech.2017.11.058.

28. Zhou, H.; Long, Y.Q.; Meng, A.H.; Li, Q.H.; Zhang, Y.G. Thermogravimetric Characteristics of Typical Municipal Solid Waste Fractions during Co-Pyrolysis. *Waste Manag.* **2015**, *38*, 194–200, doi:10.1016/j.wasman.2014.09.027.

29. Stępień, P.; Serowik, M.; Koziel, J.A.; Białowiec, A. Waste to Carbon Energy Demand Model and Data Based on the TGA and DSC Analysis of Individual MSW Components. *Data* **2019**, *4*, 1–6, doi:10.3390/data4020053.

30. Helmi, M.; Tahvildari, K.; Hemmati, A.; Aberoomand azar, P.; Safekordi, A.

Phosphomolybdic Acid/Graphene Oxide as Novel Green Catalyst Using for Biodiesel Production from Waste Cooking Oil via Electrolysis Method: Optimization Using with Response Surface Methodology (RSM). *Fuel* **2021**, *287*, 119528, doi:10.1016/j.fuel.2020.119528.

31. Lu, Y.; Levine, R.B.; Savage, P.E. Fatty Acids for Nutraceuticals and Biofuels from Hydrothermal Carbonization of Microalgae. *Ind. Eng. Chem. Res.* **2015**, *54*, 4066–4071, doi:10.1021/ie503448u.

32. Anfar, Z.; Ait Ahsaine, H.; Zbair, M.; Amedlous, A.; Ait El Fakir, A.; Jada, A.; El Alem, N. Recent Trends on Numerical Investigations of Response Surface Methodology for Pollutants Adsorption onto Activated Carbon Materials: A Review. *Crit. Rev. Environ. Sci. Technol.* **2020**, *50*, 1043–1084, doi:10.1080/10643389.2019.1642835.

33. He, M.; Zhu, X.; Dutta, S.; Khanal, S.K.; Lee, K.T.; Masek, O.; Tsang, D.C.W. Catalytic Co-Hydrothermal Carbonization of Food Waste Digestate and Yard Waste for Energy Application and Nutrient Recovery. *Bioresour. Technol.* **2022**, *344*, 126395, doi:10.1016/j.biortech.2021.126395.

34. Zhou, S.; Liang, H.; Han, L.; Huang, G.; Yang, Z. The Influence of Manure Feedstock, Slow Pyrolysis, and Hydrothermal Temperature on Manure Thermochemical and Combustion Properties. *Waste Manag.* **2019**, *88*, 85–95, doi:10.1016/j.wasman.2019.03.025.

35. PN-Z-15008-04:1993 Standard. *Municipal Solid Waste. Analysis of Combustible and Non-Combustible Content*; 1993; p. 15008;.

36. Torquato, L.D.M.; Crnkovic, P.M.; Ribeiro, C.A.; Crespi, M.S. New Approach for Proximate Analysis by Thermogravimetry Using CO2 Atmosphere: Validation and Application to Different Biomasses. *J. Therm. Anal. Calorim.* **2017**, *128*, 1–14, doi:10.1007/s10973-016-5882-z.

37. PN-EN 15935:2022-01 Standard *Waste Characteristics. Determination of Loss on Ignition of Sludge, Treated Biowaste, Soil and Waste*; 2022; p. 15935;.

38. Świechowski, K.; Matyjewicz, B.; Telega, P.; Białowiec, A. The Influence of Low-

Temperature Food Waste Biochars on Anaerobic Digestion of Food Waste. *Materials (Basel).* **2022**, *15*, doi:10.3390/ma15030945.

39. PN-EN14346:2011 Standard Characterization Of Waste - Determination Of Loss On Ignition/Https://Infostore.Saiglobal.Com/En- Au/Standards/PN-EN-14346-2011-932471_SAIG_PKN_PKN_2197939/ (Accessed on 20 June 2023). **2011**.

40. PN-EN15169:2011 Standard Characterization Of Waste - Determination Of Loss On Ignition. Available Online: Http://Sklep.Pkn.Pl/Pn-En-15169- 2011p.Html (Accessed on 20 June 2023). **2011**.

41. PN EN ISO 18125:2017-07 *Solid Biofuels—Determination of Calorific Value.*; 2021; p. 18125;.

42. PN-EN ISO 16948: 2015-07 Standard *Solid Biofuels - Determination of Total Carbon, Hydrogen and Nitrogen Content*; 2015; p. 16948;.

43. Bhatnagar, N.; Ryan, D.; Murphy, R.; Enright, A.M. A Comprehensive Review of Green Policy, Anaerobic Digestion of Animal Manure and Chicken Litter Feedstock Potential – Global and Irish Perspective. *Renew. Sustain. Energy Rev.* **2022**, *154*, 111884, doi:10.1016/j.rser.2021.111884.

44. Aich, S.; Behera, D.; Nandi, B.K.; Bhattacharya, S. Relationship between Proximate Analysis Parameters and Combustion Behaviour of High Ash Indian Coal. *Int. J. Coal Sci. Technol.* **2020**, *7*, 766–777, doi:10.1007/s40789-020-00312-5.

45. Świechowski, K.; Liszewski, M.; Babelewski, P.; Koziel, J.A.; Białowiec, A. Fuel Properties of Torrefied Biomass from Pruning of Oxytree. *Data* **2019**, *4*, 2–11, doi:10.3390/data4020055.

46. Tańczuk, M.; Junga, R.; Kolasa-Więcek, A.; Niemiec, P. Assessment of the Energy Potential of Chicken Manure in Poland. *Energies* **2019**, *12*, doi:10.3390/en12071244.

47. Cardona, S.; Gallego, L.J.; Valencia, V.; Martínez, E.; Rios, L.A. Torrefaction of Eucalyptus-Tree Residues: A New Method for Energy and Mass Balances of the Process with the Best Torrefaction Conditions. *Sustain. Energy Technol. Assessments* **2019**, *31*, 17–24, doi:10.1016/j.seta.2018.11.002.

48. Tjørve, K.M.C.; Tjørve, E. The Use of Gompertz Models in Growth Analyses, and New Gompertz-Model Approach: An Addition to the Unified-Richards Family. *PLoS One* **2017**, *12*, 1–17, doi:10.1371/journal.pone.0178691.

49. Fărcaş, A.C.; Socaci, S.A.; Dulf, F. V.; Tofană, M.; Mudura, E.; Diaconeasa, Z. Volatile Profile, Fatty Acids Composition and Total Phenolics Content of Brewers' Spent Grain by-Product with Potential Use in the Development of New Functional Foods. *J. Cereal Sci.* **2015**, *64*, 34–42, doi:10.1016/j.jcs.2015.04.003.

50. Nowacki, D.; Martynowicz, H.; Skoczyńska, A.; Wojakowska, A.; Turczyn, B.; Bobak, Ł.; Trziszka, T.; Szuba, A. Lecithin Derived from ω-3 PUFA Fortified Eggs Decreases Blood Pressure in Spontaneously Hypertensive Rats. *Sci. Rep.* **2017**, *7*, 1–11, doi:10.1038/s41598-017-12019-w.

51. Folch, J.; Lees, M.; Sloane Stanley, G.H. A Simple Method for the Isolation and Purification of Total Lipides from Animal Tissues. *J. Biol. Chem.* **1957**, *226*, 497–509, doi:10.1016/s0021-9258(18)64849-5.

52. Kumar, S.; Ankaram, S. *Waste-to-Energy Model/Tool Presentation*; Elsevier B.V., 2019; ISBN 9780444640833.

53. Sarrion, A.; Diaz, E.; de la Rubia, M.A.; Mohedano, A.F. Fate of Nutrients during Hydrothermal Treatment of Food Waste. *Bioresour. Technol.* **2021**, *342*, 125954, doi:10.1016/j.biortech.2021.125954.

54. Khan, M.A.; Hameed, B.H.; Siddiqui, M.R.; Alothman, Z.A.; Alsohaimi, I.H. Hydrothermal Conversion of Food Waste to Carbonaceous Solid Fuel—A Review of Recent Developments. *Foods* **2022**, *11*, 1–21, doi:10.3390/foods11244036.

55. Dutta, S.; He, M.; Xiong, X.; Tsang, D.C.W. Sustainable Management and Recycling of Food Waste Anaerobic Digestate: A Review. *Bioresour. Technol.* **2021**, *341*, 125915, doi:10.1016/j.biortech.2021.125915.

56. Kozak, M. Rozwój Metod Oznaczania Siarki w Paliwach i w Komponentach Paliw Technikami Spektrometrii Atomowej. *Nafta-Gaz* **2018**, *74*, 619–624, doi:10.18668/ng.2018.08.08.

57. El Ouadrhiri, F.; Elyemni, M.; Lahkimi, A.; Lhassani, A.; Chaouch, M.; Taleb, M. Mesoporous Carbon from Optimized Date Stone Hydrochar by Catalytic Hydrothermal Carbonization Using Response Surface Methodology: Application to Dyes Adsorption. *Int. J. Chem. Eng.* **2021**, *2021*, doi:10.1155/2021/5555406.

58. Kumar, A.; Jena, H.M. Preparation and Characterization of High Surface Area Activated Carbon from Fox Nut (Euryale Ferox) Shell by Chemical Activation with H3PO4. *Results Phys.* **2016**, *6*, 651–658, doi:10.1016/j.rinp.2016.09.012.

59. Zhang, S.; Sheng, K.; Yan, W.; Liu, J.; Shuang, E.; Yang, M.; Zhang, X. Bamboo Derived Hydrochar Microspheres Fabricated by Acid-Assisted Hydrothermal Carbonization. *Chemosphere* **2021**, *263*, 128093, doi:10.1016/j.chemosphere.2020.128093.

60. Li, J.; Pan, L.; Suvarna, M.; Tong, Y.W.; Wang, X. Fuel Properties of Hydrochar and Pyrochar: Prediction and Exploration with Machine Learning. *Appl. Energy* **2020**, *269*, 115166, doi:10.1016/j.apenergy.2020.115166.

61. Zhu, X.; He, M.; Xu, Z.; Luo, Z.; Gao, B.; Ruan, R.; Wang, C.H.; Wong, K.H.; Tsang, D.C.W. Combined Acid Pretreatment and Co-Hydrothermal Carbonization to Enhance Energy Recovery from Food Waste Digestate. *Energy Convers. Manag.* **2022**, *266*, 2022–2024, doi:10.1016/j.enconman.2022.115855.

62. Al Afif, R.; Anayah, S.S.; Pfeifer, C. Batch Pyrolysis of Cotton Stalks for Evaluation of Biochar Energy Potential. *Renew. Energy* **2020**, *147*, 2250–2258, doi:10.1016/j.renene.2019.09.146.

63. Liu, Z.; Quek, A.; Kent Hoekman, S.; Balasubramanian, R. Production of Solid Biochar Fuel from Waste Biomass by Hydrothermal Carbonization. *Fuel* **2013**, *103*, 943–949, doi:10.1016/j.fuel.2012.07.069.

64. Śliz, M.; Wilk, M. A Comprehensive Investigation of Hydrothermal Carbonization: Energy Potential of Hydrochar Derived from Virginia Mallow. *Renew. Energy* **2020**, *156*, 942–950, doi:10.1016/j.renene.2020.04.124.

65. Basu, P. Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory. In *Chapter 11*; 2018; pp. 393–413 ISBN 9780128129920.

66. Muthu Dinesh Kumar, R.; Anand, R. *Production of Biofuel from Biomass Downdraft Gasification and Its Applications*; Elsevier Ltd, 2019; ISBN 9780081027912.

67. Sarrion, A.; Diaz, E.; Rubia, M.A. De; Mohedano, A.F. Bioresource Technology Fate of Nutrients during Hydrothermal Treatment of Food Waste. *Bioresour. Technol.* **2021**, *342*, 125954, doi:10.1016/j.biortech.2021.125954.

68. Engin, B.; Atakül, H.; Ünlü, A.; Olgun, Z. CFB Combustion of Low-Grade Lignites: Operating Stability and Emissions. *J. Energy Inst.* **2019**, *92*, 542–553, doi:10.1016/j.joei.2018.04.004.

69. Saqib, N.U.; Sharma, H.B.; Baroutian, S.; Dubey, B.; Sarmah, A.K. Valorisation of Food Waste via Hydrothermal Carbonisation and Techno-Economic Feasibility Assessment. *Sci. Total Environ.* **2019**, *690*, 261–276, doi:10.1016/j.scitotenv.2019.06.484.

70. Demirbas, A. Higher Heating Values of Lignin Types from Wood and Non-Wood Lignocellulosic Biomasses. *Energy Sources, Part A Recover. Util. Environ. Eff.* **2017**, *39*, 592–598, doi:10.1080/15567036.2016.1248798.

71. Drudi, K.C.R.; Drudi, R.; Martins, G.; Antonio, G.C.; Leite, J.T.C. Statistical Model for Heating Value of Municipal Solid Waste in Brazil Based on Gravimetric Composition. *Waste Manag.* **2019**, *87*, 782–790, doi:10.1016/j.wasman.2019.03.012.

72. Velebil, J.; Malaták, J.; Bradna, J. Mass Yield of Biochar from Hydrothermal Carbonization of Sucrose. *Res. Agric. Eng.* **2016**, *62*, 179–184, doi:10.17221/73/2015-RAE.

73. Kantarli, I.C.; Kabadayi, A.; Ucar, S.; Yanik, J. Conversion of Poultry Wastes into Energy Feedstocks. *Waste Manag.* **2016**, *56*, 530–539, doi:10.1016/j.wasman.2016.07.019.

74. Mau, V.; Gross, A. Energy Conversion and Gas Emissions from Production and Combustion of Poultry-Litter-Derived Hydrochar and Biochar. *Appl. Energy* **2018**, *213*, 510–519, doi:10.1016/j.apenergy.2017.11.033.

75. Chaiwang, N.; Jaturasitha, S.; Sringarm, K.; Bunmee, T.; Chomchai, N.; Prakotrat, D.; Pugdeethai, K.; Chaichaum, W.; Wicke, M. Comparison of Fatty Acid Composition between White Lamphun and Brahman Crossbred Cattle Raised with Fresh Pangola Grass.

Chiang Mai Univ. J. Nat. Sci. **2012**, *11*, 303–307.

76. Jama-Rodzeńska, A.; Białowiec, A.; Koziel, J.A.; Sowiński, J. Waste to Phosphorus: A Transdisciplinary Solution to P Recovery from Wastewater Based on the TRIZ Approach. *J. Environ. Manage.* **2021**, *287*, doi:10.1016/j.jenvman.2021.112235.

77. Malhotra, M.; Garg, A. Hydrothermal Carbonization of Centrifuged Sewage Sludge: Determination of Resource Recovery from Liquid Fraction and Thermal Behaviour of Hydrochar. *Waste Manag.* **2020**, *117*, 114–123, doi:10.1016/j.wasman.2020.07.026.

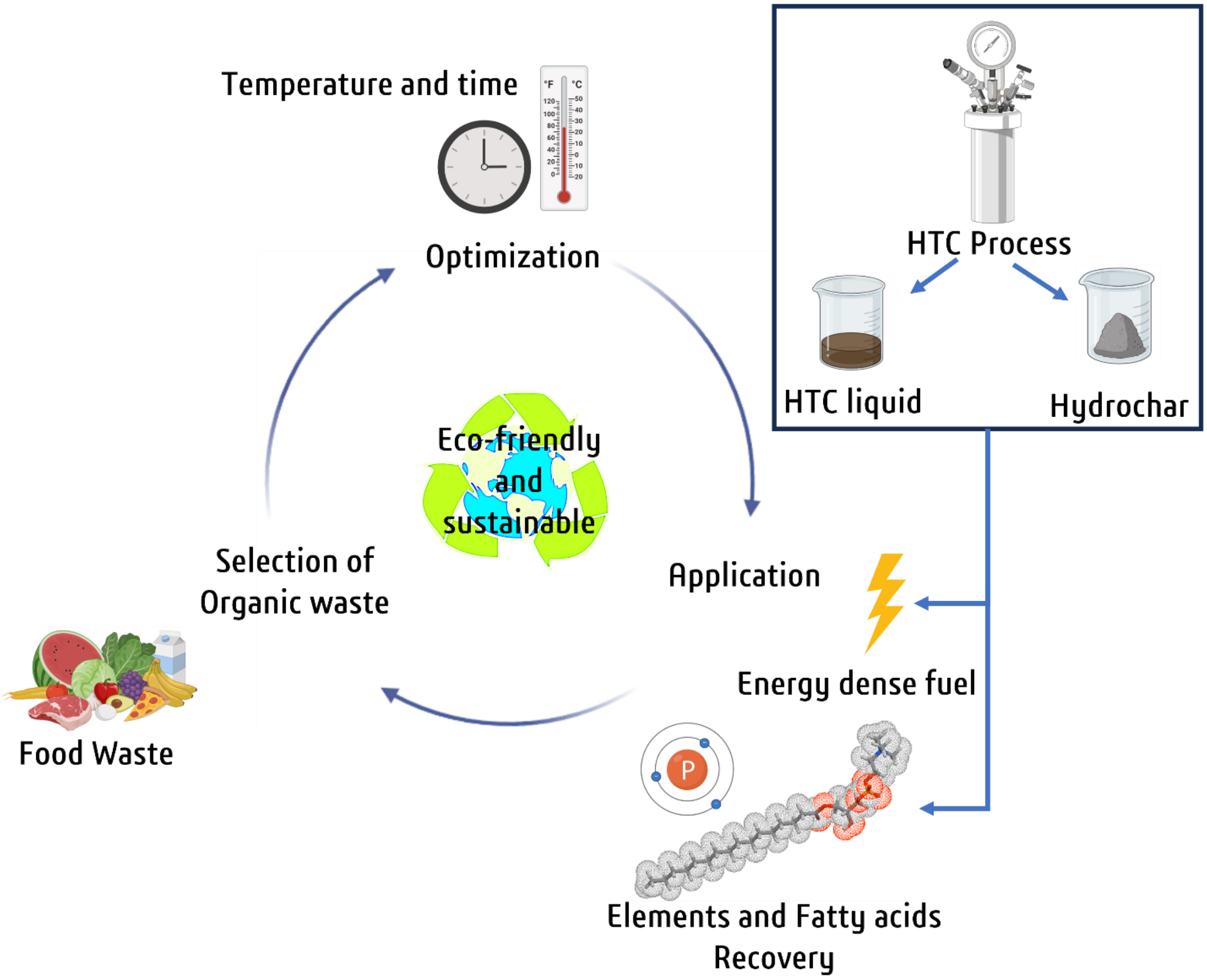
78. Idowu, I.; Li, L.; Flora, J.R.V.; Pellechia, P.J.; Darko, S.A.; Ro, K.S.; Berge, N.D. Hydrothermal Carbonization of Food Waste for Nutrient Recovery and Reuse. *Waste Manag.* **2017**, *69*, 480–491, doi:10.1016/j.wasman.2017.08.051.

79. Li, P.; Wang, Q.; He, X.; Yu, R.; He, C.; Shen, D.; Jiao, Y. Investigation on the Effect of Different Additives on Anaerobic Co-Digestion of Corn Straw and Sewage Sludge: Comparison of Biochar, Fe3O4, and Magnetic Biochar. *Bioresour. Technol.* **2022**, *345*, 126532, doi:10.1016/j.biortech.2021.126532.

80. Tanai, Y.S. Food Waste Energy Analysis: Characterizing Energy Content as a Function of Proximate Analysis Factors. **2016**, 2.

81. Song, G.; Huang, D.; Li, H.; Wang, X.; Ren, Q.; Jiang, L.; Wang, Y.; Su, S.; Hu, S.; Xiang, J. Pyrolysis Reaction Mechanism of Typical Chinese Agriculture and Forest Waste Pellets at High Heating Rates Based on the Photo-Thermal TGA. *Energy* **2022**, *244*, 123164, doi:10.1016/j.energy.2022.123164.

Graphical Abstract



Declaration of Interest Statement

Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Wroclaw, Poland, 07.06.2024
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STATEMENT

I hereby declare that in the publication:

Waheed A. Rasaq, Vaikunthavasan Thiruchenthooran, Katarzyna Wirkijowska, Marvin Valentin, Łukasz Bobak, Chinenye Adaobi Igwegbe, Andrzej Białowiec, "Hydrothermal carbonization of combined food waste: A critical evaluation of emergent products". Waste Management, is (under review)

My contribution included:

Preparation of a graphic abstract of the article. I prepared the text of the entire article, including the introduction part, description of the methodology, materials, and description of the results with discussion and conclusions. I prepared the figures and tables included in the manuscript. I obtained funds for the publication of the article.

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My contribution included:

I participated in writing – review & editing, writing – original draft, validation, and formal analysis of the manuscript.

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My contribution included:

I participated in methodology and investigation during the experimental work of the manuscript.

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My contribution included:

I participated in writing – reviewing & editing. Investigation, and data curation analysis of fatty acids results in the manuscript.

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My contribution included:

I participated in writing – review & editing, writing – the original draft, visualization, validation, supervision, and formal analysis of the manuscript.

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My contribution included:

Developing the concept design of the study, in particular, the methodology of HTC parameters and measurements. I participated in the revision and supervision of the manuscript preparation. Also, I served as the corresponding author.

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Renewable Energy

Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization

--Manuscript Draft--

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Abstract:	This study investigated the influence of hydrothermal carbonization (HTC) conditions and TiO2/biochar catalyst addition on the biochemical methane potential (BMP) from food waste (FW) hydrothermal carbonization liquid (HL) during anaerobic digestion (AD). Employing central composite design-response surface methodology, HTC conditions were optimized to produce different HL variants, and the impact of TiO2/biochar addition to the HTC system for HL BMP was examined. Variant 3 (T240, RT150, W200, C2) with the highest catalyst addition demonstrated the highest BMP (274.03 mL/gVS), while variant 5 (T240, RT150, W200, C0) without catalyst addition showed the lowest BMP (40.09 mL). The value of variant 5 was lower than the control suggesting inhibition of the AD process. The obtained results suggest that using TiO2/biochar catalyst during HTC is crucial for using HL for methane fermentation and biomethane production. The presented findings show a feasible approach for boosting BMP and the dual utilization of food waste.
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Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization

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Abstract

This study investigated the influence of hydrothermal carbonization (HTC) conditions and TiO_2/biochar catalyst addition on the biochemical methane potential (BMP) from food waste (FW) hydrothermal carbonization liquid (HL) during anaerobic digestion (AD). Employing central composite design-response surface methodology, HTC conditions were optimized to produce different HL variants, and the impact of TiO_2/biochar addition to the HTC system for HL BMP was examined. Variant 3 (T240, RT150, W200, C2) with the highest catalyst addition demonstrated the highest BMP (274.03 mL/gVS), while variant 5 (T240, RT150, W200, C0) without catalyst addition showed the lowest BMP (40.09 mL). The value of variant 5 was lower than the control suggesting inhibition of the AD process. The obtained results suggest that using TiO_2/biochar catalyst during HTC is crucial for using HL for methane fermentation and biomethane production. The presented findings show a feasible approach for boosting BMP and the dual utilization of food waste.

Keywords: Methane production; hydrothermal carbonization; hydrothermal liquid ;food waste; catalyst

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The Editor-in-Chief,

Renewable Energy

Dear Sir,

Submission of Original Manuscript

I am writing to submit the manuscript titled, '**Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization'** which belongs to the authors stated as follows:

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This study investigated the influence of hydrothermal carbonization (HTC) conditions and TiO_2/biochar catalyst addition on the biomethane potential (BMP) from food waste (FW) hydrothermal carbonization liquid (HL) during anaerobic digestion (AD). Through employing central composite design-response surface methodology, we optimized HTC conditions to produce different HL variants and examined the impact of TiO_2/biochar addition to the HTC system for HL BMP. Our findings demonstrated that incorporating TiO_2/biochar catalyst during HTC was crucial for enhancing BMP and utilizing FW for methane fermentation and biomethane production.

The research presented in our manuscript addresses pressing environmental and energy challenges by proposing a feasible approach for boosting BMP and promoting the dual utilization of food waste. Furthermore, it contributes to the understanding of HTC parameters, catalyst addition, and biomethane production, thereby advancing knowledge in waste valorization and renewable energy generation.

We believe that our manuscript aligns well with the scope and objectives of **Renewable Energy**, and it will be of significant interest to your readership. We have carefully followed the journal's guidelines for manuscript preparation and formatting.

The authors listed in this manuscript have all contributed substantially to the research and preparation of this manuscript. There are no conflicts of interest to disclose.

Thank you for considering our submission. We look forward to your favorable consideration.

Sincerely,

prof. dr hab. inż. Andrzej Białowiec

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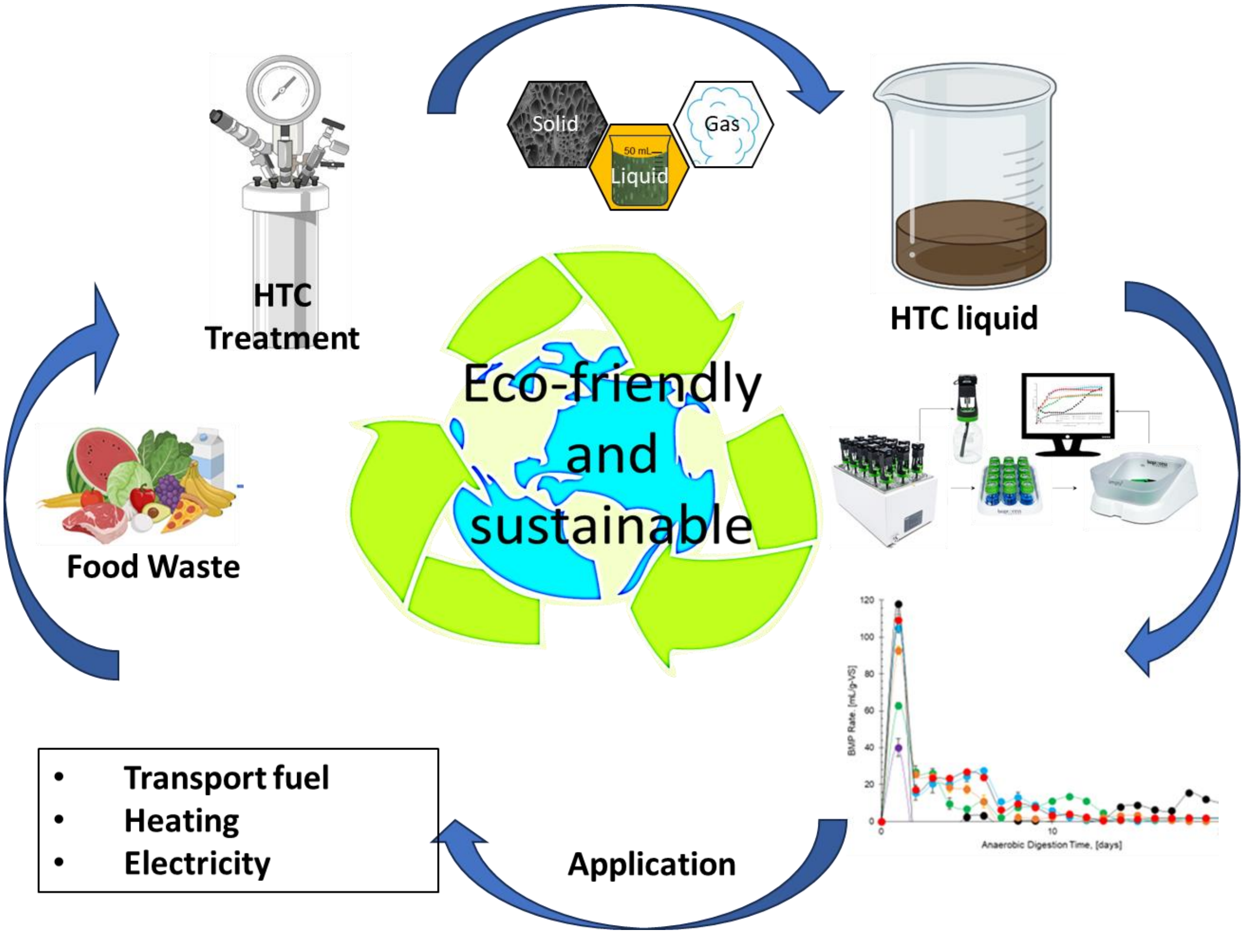
Graphical abstract



Highlights

- Optimize HTC conditions and catalyst for food waste (FW) biomethane potential.
- TiO_2/biochar catalyst enhances biomethane production from HTC liquid of FW.
- A feasible approach proposed for boosting biomethane potential from FW.
- HTC variant 3 with catalyst exhibited the highest biomethane potential yield.
- Variant 5 without catalyst shows inhibition of the anaerobic digestion process.

Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization

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Abstract

This study investigated the influence of hydrothermal carbonization (HTC) conditions and TiO_2/biochar catalyst addition on the biochemical methane potential (BMP) from food waste (FW) hydrothermal carbonization liquid (HL) during anaerobic digestion (AD). Employing central composite design-response surface methodology, HTC conditions were optimized to produce different HL variants, and the impact of TiO_2/biochar addition to the HTC system for HL BMP was examined. Variant 3 (T240, RT150, W200, C2) with the highest catalyst addition demonstrated the highest BMP (274.03 mL/gVS), while variant 5 (T240, RT150, W200, C0) without catalyst addition showed the lowest BMP (40.09 mL). The value of variant 5 was lower than the control suggesting inhibition of the AD process. The obtained results suggest that using TiO_2/biochar catalyst during HTC is crucial for using HL for methane fermentation and biomethane production. The presented findings show a feasible approach for boosting BMP and the dual utilization of food waste.

Keywords: Methane production; hydrothermal carbonization; hydrothermal liquid ;food waste; catalyst

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1. Introduction

Food waste (FW) has become a major environmental and social issue with profound effects on sustainability and resource management. It makes up one of the biggest portions of the global waste stream (Grandhi and Appaiah Singh, 2016). One of the primary environmental issues facing the world today is the quantity of generated FW, which is the primary organic part of industrial waste from food production and municipal solid waste. It exhibits an annual exponential development (Uçkun Kiran et al., 2014). On the one hand, given the higher quantities produced annually by the food industry, properly managing global FW is becoming more challenging which could be hazardous to human health (Bhatt et al., 2018). Concurrently, the imperatives of energy security and climate change underscore the pressing need for innovative approaches to sustainable energy production (Santos Dalólio et al., 2017).

Hydrothermal carbonization (HTC) appears to be a promising method for managing FW when taking its applications into account. HTC offers a chance to maximize waste materials' potential for energy production, including food waste. HTC involves subjecting organic biomass to high temperature and pressure in a water-rich environment, resulting in the formation of hydrochar and a liquid byproduct known as hydrothermal carbonization liquid (HL). The HL contains water-soluble organic compounds, which can then be used in anaerobic digestion (AD) to produce biogas. In terms of emissions, HTC is noteworthy for being environmentally friendly, especially when contrasted with other processes like composting. This benefit results from HTC's reduction of gases released into the atmosphere, which makes it a more environmentally friendly option for FW treatment (Hejna et al., 2022; Rasaq et al., 2021, 2024a; Zabaniotou et al., 2017). Even though HTC is becoming more and more popular, little is known about how particular process variables like temperature and residence time including catalyst addition affect the characteristics of hydrochar and hydrothermal liquid made from mixed food waste. This knowledge is crucial for maximizing energy recovery and promoting sustainable waste management practices.

Anaerobic digestion (AD) or methane fermentation has become a viable method for converting organic waste, including FW, into biogas, primarily composed of methane and carbon dioxide. It is the breakdown of organic matter by anaerobic microorganisms at 37 or 55 ◦C in an oxygen-free environment. Combustible biogas with a CO_2 to CH_4 ratio of roughly 1:1 and digestate residues that can be used as both solid fuel and fertilizer are the primary process products (Świechowski et al., 2022). Almost any sort of biological feedstock, including those from the key agricultural sectors and diverse organic waste streams from society at large, can be used to produce biogas (Holm-Nielsen et al., 2009). Despite extensive research on enhancing methane production through processes like biochar addition, the potential benefits of incorporating HTC-derived liquid fractions into AD remain underexplored (Valentin et al., 2023). The methane production rate of glucose was found to be 37% higher when hydrochar from sewage sludge was used. Nevertheless, the use of HTC-liquid fraction of mixed FW is not frequently discussed in the literature; the majority of the available data relates to its application to substrates like fish processing waste (Pagés-Díaz and Huiliñir, 2020). Lucian and colleagues reported an AD study testing the application of HTC liquid fraction produced from different waste biomasses including orange pomace, food waste, sewage sludge, and microalgae for biomethane potential (Fernandez et al., 2022; Lucian et al., 2020; Zhao et al., 2018).

TiO_2 nanoparticles have been recognized for their photocatalytic properties, which accelerate the degradation of organic compounds and enhance biochemical reactions (Chen et al., 2020). Incorporating TiO_2 into the HTC process catalyzes the breakdown of complex organic molecules in food waste into simpler compounds. This accelerates carbonization and increases the bioavailability of organic substrates for microbial metabolism during anaerobic digestion. By optimizing TiO_2 dosage and HTC conditions (such as temperature and residence time), this study aims to optimize TiO_2/biochar dosage and HTC conditions to maximize biomethane production (BMP) from FW. Understanding the interplay between HTC parameters, catalyst addition, and biomethane production is imperative. The research seeks to bridge this knowledge gap to contribute to the advancement of waste valorization and renewable energy generation.

Employing central composite design-response surface methodology (CCD-RSM), this study systematically evaluates the effects of HTC conditions (temperature and residence time) and TiO2/biochar catalyst addition on biomethane production from FW HL via AD. Through comprehensive experimentation and mathematical modeling, the aim is to optimize HTC parameters and quantify the catalyst's impact on biomethane yield. The outcomes of the research provide valuable insights into the factors influencing biomethane production during HTC and offer a promising avenue for advancing waste-to-energy conversion processes. RSM via CCD was used for optimization due to their suitability in exploring complex processes with multiple variables (Chung et al., 2022). This choice of methodology offers the advantage of requiring fewer experimental runs compared to traditional one-factor-at-a-time approaches (Igwegbe et al., 2023). RSM provides a systematic framework for designing experiments, analyzing data, and optimizing process parameters by establishing mathematical models that capture the relationship between independent variables and the desired response (Rasaq et al., 2024b).

Leveraging a laboratory-scale pressure reactor and the design of experiments (DOE) methodology, the study underscores the significance of optimizing process parameters to enhance biomethane potential (BMP) from FW HL during AD. This investigation not only enriches our understanding of FW valorization through HTC but also offers novel insights into sustainable biogas production from organic waste streams. Six different samples based on various HTC operating conditions using a systematic approach guided by RSM was investigated. In this manuscript, the results of the investigation, which involved systematic experimentation with various HTC operating conditions guided by RSM, are presented. The outcomes of the research contribute to a better understanding of FW valorization through HTC and offer insights into sustainable biogas production from organic waste streams. Through this research, a feasible approach for boosting biomethane potential and promoting the dual utilization of FW is proposed, thereby contributing to sustainable waste management and renewable energy generation.

2. Materials and Methods

The schematic diagram of the performed research is given in **Figure 1**. The research started with the preparation and analysis of the food waste mixture used for the hydrothermal carbonization process. Afterward, the optimization was carried out using the Design of Experiment (DOE) to investigate the intricate relationships among independent parameters: HTC temperature, residence time, added water (liquid), and catalyst dosage, assessing their collective impact on dependent variables, including hydrochar (HC) and hydrothermal liquid (HL) yields, as well as biomethane production. Then, the preparation of the composite catalyst, the TiO_2 nanoparticles with the addition of wheat-derived biochar was performed. Next, at different HTC process parameters (temperature, stirring rate, and process time), hydrochar combined with a liquid fraction was produced as a result of the HTC process. After the HTC process, HTC products were separated using vacuum filtration. After that, the liquid fraction was subjected to anaerobic digestion using AMPTS® II for the production of biomethane. Finally, all data were analyzed and the best conditions for the HTC treatment of the FW liquid fraction for the methane production process were determined. Further details are provided in the subsequent sections.

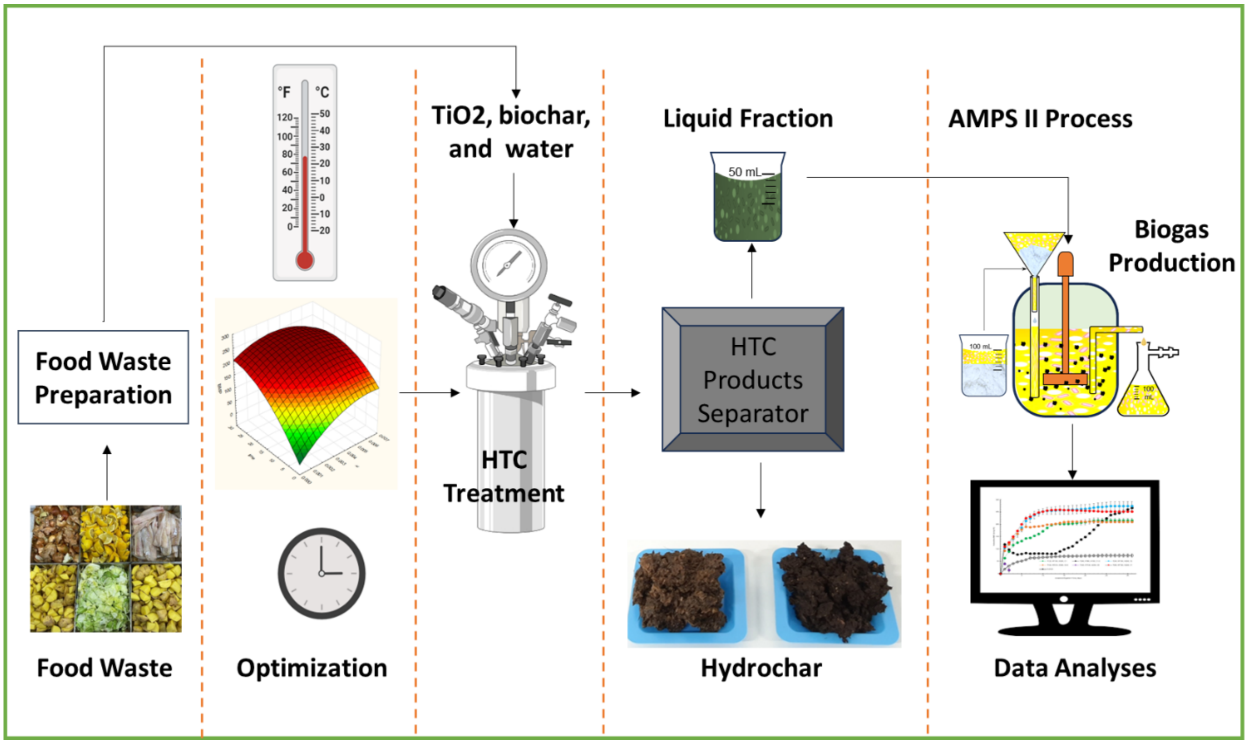

Figure 1. Schematic diagram of the HTC of food waste and anaerobic digestion of the liquid fraction.

2.1. Materials preparation

2.1.2. Food waste mixture

The food waste used in this study was made from food purchased in a grocery store (Wroclaw, Poland). The preparation of the food waste mixture was performed according to (Valta et al., 2019). The composition of the food waste mixture is presented in **Table 1**. Each food waste mixture component was analyzed for moisture content (MC), total solids (TS), volatile solids (VS), and ash content (AC). The MC and TS were determined using a laboratory dryer (WAMED, KBC-65W, Warsaw, Poland) at 105 °C for 24 h (Zhou et al., 2019). The VS and AC were determined using a muffle furnace (Snol 8.1/1100, Utena, Lithuania) at 550 °C and 3 h according to (PN-EN15169:2011 Standard, 2011). The pre-mixed food waste components were ground with the use of a laboratory knife mill (Testchem, LMN100, Pszów, Poland), to create a homogeneous material. The prepared FW mixture was shredded and sieved using a sieve mesh of 0.5mm diameter.

Table 1. Food waste properties and its share in food waste mixtures.

FW components	Component share, % *	MC, % *	TS, % *	VS, % **	AC, % **
Potatoes	15	83.09	16.91	92.9	7.1
Fish	2	78.93	21.07	94.81	5.91
Cheeses	10	38.30	61.70	94.22	5.78
Bananas	5	82.20	17.80	92.08	7.92
Apples	5	86.15	13.85	95.16	4.84
Rice	18	10.55	89.45	99.28	0.72
Pasta	20	11.70	88.30	99.41	0.59
Onions	1	89.94	10.06	92.54	7.46
Oranges	2	83.60	16.40	95.28	4.72
Lettuce	1	95.60	4.40	83.81	16.19
Cabbage	1	90.26	9.74	90.75	9.25
Bread	5	35.82	64.18	96.87	3.13
Meat	11	70.40	29.60	96.41	3.59
Tomatoes	2	91.82	8.18	81.72	18.28
Lemons	2	87.64	12.36	94.36	5.64
Mixture	-	67.22	32.78	85.25	14.75

* as received base, ** as dry base.

2.1.3. Catalyst preparation

TiO_2 nanoparticles (<100 nm particle size, 99.5%), acetic acid (≥99.7%), and ethanol (96%) were obtained from Sigma Aldrich, Germany. The same wheat-derived biochar produced, characterized and used for a study in the same laboratory (Igwegbe et al., 2024), was collected for the composite catalyst preparation. For preparation of the composite catalyst, the TiO_2 nanoparticles were initially subjected to a cleaning process by washing with ethanol, aiming to eliminate impurities and surface contaminants. A solution of 10% acetic acid was then prepared by dissolving acetic acid in deionized water, with subsequent mixing of 10 mL of acetic acid with 90 mL of deionized water to achieve a total volume of 100 mL. The TiO_2 nanoparticles were combined with the solution of the functionalizing agent, ensuring a thorough mixing process to facilitate interaction between the functionalizing agent and the TiO_2 surface. The resulting mixture of TiO_2 nanoparticles and the functionalizing agent solution was allowed to sit for 24 hours, promoting adsorption. Following this, the functionalized TiO_2 nanoparticles underwent a washing process with deionized water to remove unreacted or loosely attached molecules, thereby eliminating excess reagents and impurities. The washing process was repeated until the pH reached a range between 6-7, ensuring the removal of any residual functionalizing agent. Subsequently, the functionalized TiO_2 nanoparticles were dried at 120 °C in an oven (WAMED, KBC-65W, Warsaw, Poland) for 4 – 6 hours. In the next step of the composite catalyst preparation, the functionalized TiO_2 nanoparticles were mixed with biochar in a specified proportion of 1:10 by mass. Emphasis was placed on the thorough mixing of biochar and TiO_2 nanoparticles to attain a uniform distribution, thereby homogenizing the composite.

2.1.4. Inoculum preparation

Digestate from the 1 MWel commercial agricultural biogas plant (Bio-Wat Sp. z o.o., Świdnica, Poland) was used as an inoculum for biomethane potential tests. The biogas plant is running in mesophilic (37 °C) and wet conditions (dry mass less than 10%). After being collected into plastic canisters, the digestate was brought to the lab and left to stand at room temperature for roughly 24 hours. The digestate was filtered through gauze the next day to remove solid particles, such as plastics and unprocessed substrate, from the liquid portion. After that, the liquid digestate was kept in a climate chamber (Pollab, model 140/40, Wilkowice, Poland) at 4 °C until the biomethane potential test was conducted.

2.2. Experimental methods

2.2.1. Experimental design for HTC process for biomethane production

In this study, a thorough DOE was carefully conducted to investigate the intricate relationships among independent parameters: temperature, residence time, added water (liquid), and catalyst dosage, assessing their collective impact on dependent variables, including hydrochar (HC) and hydrothermal liquid (HL) yields, as well as biomethane production. The experimental design followed a Response surface rotatable Central Composite Design (CCD) framework with 5-level (-α, -1, 0, +1, +α) factors, comprising 30 experimental runs (**Table S1,** refer to supplementary material) generated through Design Expert software (Stat-Ease, version 13.0.1.0) to unravel the complex interactions among these variables. Each run represented a unique combination of the specified independent parameters, facilitating an in-depth analysis of their influences on key outcomes. This design incorporated 8 axial points, 16 factorial points, and 6 replicates at the center points, all aimed at optimizing the HTC process. A comprehensive set of operating conditions, outlined in **Table 2**, was thoughtfully devised to encompass a designated range of actual and coded variables for the full factorial experiment. The factors included HTC temperature (A), resident time (B), the weight of the liquid (C), and catalyst dosage (D).

Following the HTC experiments, the HL component was utilized for biomethane production. For the biomethane experiments, specific runs (7, 10, 17, 18, 23, and 24, identified with * in **Table S1**) were randomly selected for the bioprocess experiments, and subsequent measurements were recorded for biomethane yields and other relevant parameters.

Table 2. Experimental operating conditions and levels.

Factor	Name	Units	Range of actual and coded variables				
			-α	-1	0	+1	+α
A	HTC temperature	°C	120	180	240	300	360
B	Resident time	min	30	90	150	210	270
C	Weight of the liquid	g	100	150	200	250	300
D	Catalyst dosage	g	0	0.5	1	1.5	2

2.2.2. HTC process

A high-temperature high-pressure reactor (HTHP) was used to carry out the HTC process (Büchi AG, Uster, Switzerland). A sample volume depends on moisture content and catalyst dosage concerning DOE experimental runs (**Table S1,** refer to supplementary material), which consist of 100 g of dry FW for each sample and water added to obtain the targeted moisture content. After that, the mixture was put inside the reactor vessel. The vessel was sealed and placed in the heating jacket. The desired temperature inside the vessel was set, and the stirrer's speed was adjusted to 120 RPM. The HTC processes were carried out at five different temperatures and residence times of 120, 180, 240, 300, and 360 °C; and 30, 90, 150, 210, and 270 min respectively, while the pressure was generated autogenously. Each temperature was combined with each resident time by DOE. Throughout the HTC process, a single-phase digital energy meter (Model SK-410, Starmeter Instruments Co., Ltd., Shenzhen, China) was used to record the energy consumption. At a cooling temperature of 40 °C, the reactor was switched off and pressure was released by opening the valve. Following that, the sample was taken out of the vessel. After that, a laboratory scale was used to weigh the sample (Radwag, MA 50.R, Morawica, Poland). The vacuum filtration (Rocker, ROCKER 300, Kaohsiung, Taiwan) helped to separate the liquid from solid products followed by weighing (weighing instrument, Radwag, MA 50.R, Morawica, Poland). Following its transfer to a plastic container, the liquid portion was kept for additional analysis in a freezer (Electrolux, model EC5231A0W, Stockholm, Sweden) set to a temperature of -27°C.

2.2.3. Biomethane potential test experimental setup

The experimental setup adhered to the protocol that had been previously described in the lab by (Świechowski et al., 2022). The (BPC Instruments AB, AMPTS® II, Lund, Sweden) automated methane potential test system was used. The AD experiment was carried out at a mesophilic temperature of 37 °C in 500 mL glass reactors with an agitation (Lin et al., 2017, 2013). The experiment was conducted in a single batch. The working volume of the reactor was set to (123.9 – 236.0 mL. To ensure homogeneity throughout the AD process, the automatic mixer was operated every hour for three minutes on the AMPTS's default mixing setting (Lin et al., 2017). The produced biomethane was automatically measured and recorded by the AMPTS equipment. The biomethane potential test took 30 days. The matrix of the BMP experiment is shown in

Table 3. Each variant consists of two reactors filled with inoculum and hydrothermal liquid. The control variant contained only inoculum. The amount of inoculum placed into the specific reactor was selected so that the inoculum-to-substrate ratio (ISR) by volatile solids was 2.0. Thus, 32–60 g of HL were added to each reactor (apart from control). Consequently, the reactors' total solids ranged from 2.2 to 7.5%. Tested experimental conditions were labeled by HTC operating conditions of selected HL samples as variant 1 (T120-RT150-W200-C1); variant 2 (T300-RT90-W150-C1.5); variant 3 (T240-RT150-W200-C2); variant 4 (T180-RT210-W250-C0.5); variant 5 (T240-RT150-W200-C0); and variant 6 (T360-RT150-W200-C1), respectively **(Table 3)**.

Table 3. Selected samples for biomethane production among others

Variants	HTC conditions				MC, %	TS, %	VS, %	Subs, g	Inoc, g	ISR	Total, g
	T, °C	RT, min	W, g	C, g							
T120-RT150-W200-C1	120	150	200	1	94.8	5.2	82.3	40.0	155.4	2.0	195.4
T300-RT90-W150-C1.5	300	90	150	1.5	96.1	3.9	62.6	40.0	87.7	2.0	127.7
T240-RT150-W200-C2	240	150	200	2	95.0	5.0	76.6	40.0	138.0	2.0	178.0
T180-RT210-W250-C0.5	180	210	250	0.5	94.0	7.5	93.9	32.0	203.0	2.0	236.0
T240-RT150-W200-C0	240	150	200	0	94.2	5.8	83.5	40.0	176.5	2.0	216.5
T360-RT150-W200-C1	360	150	200	1	97.8	2.2	56.3	60.0	66.9	2.0	126.9

*T – temperature; RT – resident time; C – catalyst dosage; W – added water; MC – moisture content; TS – total solid; VS – volatile solid; Subs – substrate (HL); Inoc – inoculum; ISR – inoculum to substrate ratio, Total – sum of inoculum and substrate

2.3. Data analysis

The specific methane production from the anaerobic digestion of the hydrothermal liquid fraction from the food waste mixture was calculated using Eq. 1 (Valentin et al., 2023).

$$SMP(t) = \frac{MP_M - VS_{DM}\ x\ ASMP_D}{S} \qquad (1)$$

Where $SMP(t)$ = specific methane production (mL/gVS) from AD of HL at any time, MP_M = methane production from the mixture of HL and inoculum (mL), VS_D = the concentration of volatile solid of the inoculum in the mixture (gVS), $ASMP_D$ = average specific methane production of the inoculum from the control reactor (mL/gVS); and S = amount of VS of the HL added into the specific reactor (gVS). The SMP was fitted in the Modified Gompertz (Lin et al., 2017; Namal, 2020) (Eq. 2). Python was used to estimate the model's variables, and Statistica 13.0 (TIBCO Software Inc., Palo Alto, CA, USA) was used to validate the results. The Python code for the calculation was prepared in the Jupyter Notebook.

$$M(t) = P * \; exp\left[-exp\left(\frac{R_{max} * \; e}{P} \; x \; (\lambda - t) + 1\right)\right] \tag{2}$$

Where $M(t)$ = represents the cumulative methane production in $mL/(gVS)$ at time t; P = represents the maximum methane production in $mL/(gVS)$; R_{max} = represents the maximum methane production rate in $mL/(gVS.day)$; λ = represents the duration of lag phase (day); t = represents the digestion time in day; and e = represents the mathematical constant (2.718282). To characterize the hydrolytic process of AD, the first-order kinetic model was used under different conditions (De Gioannis et al., 2009).

3. Results and Discussion

3.1. Effect of hydrothermal carbonization conditions on the biomethane production

The hydrothermal carbonization liquid (HL) of food waste produced at different HTC operating conditions was subjected to an anaerobic digestion test for 30 days. The accumulated BMP from the anaerobic digestion AD of the HL is shown in **Figure 2**. The biomethane production started from the first day of AD in all reactors, which demonstrated the microbial community's quick response to the feedstock (Lucian et al., 2020; Valentin et al., 2023). The current study findings showed that among the tested variants, biomethane productions were statistically different ($p < 0.05$). Herein, the highest BMP was observed in variant 3 (T240, RT150, W200, C2), which shows that the maximum amount (2g) of catalyst added to the HTC treatment of food waste enhanced HL for biomethane production. The cumulative BMP for variant 3 (T240, RT150, W200, C2) was 274.03 mL, followed by 266.19 mL and 251.31 mL for variant 2 (T300, RT90, W150, C1.5) and variant 6 (T360, RT150, W200, C1), respectively, compared to the control reactor of 73.77 mL. The lowest BMP (40.09 mL) was obtained in variant 5 (T240, RT150, W200, C0) where the HL was produced without the addition of a catalyst. Therefore, the result of the current study demonstrates that the HL of food waste produced with the addition of catalysts (TiO_2 with biochar) appears more favorable for biomethane production enhancement. The variations in biomethane production observed show the positive impact of HL obtained under various operating conditions. The positive observation regarding the impact of HTC process conditions is in line with earlier research that has been published elsewhere (Aragón-Briceño et al., 2017; Lucian et al., 2020; Zhao et al., 2018).

The observed enhancement in BMP due to catalyst addition can be attributed to several key mechanisms. Catalysts facilitate the breakdown of complex organic compounds in food waste, leading to enhanced hydrolysis and solubilization (Liu et al., 2023; Wu et al., 2023) TiO2, with its photocatalytic activity, promotes the degradation of recalcitrant organic matter (Chen et al., 2020), while biochar enhances the adsorption of organic molecules, increasing their accessibility to microbial enzymes; this process results in a higher concentration of fermentable substrates available for microbial metabolism, ultimately boosting biomethane production (Igwegbe et al., 2024). Additionally, catalysts influence microbial community dynamics within the HTC liquid by providing a conducive environment for microbial growth and activity. Biochar acts as a habitat for microbial colonization and fosters the proliferation of anaerobic microorganisms involved in methanogenesis (Igwegbe et al., 2024). Moreover, TiO2 nanoparticles may stimulate microbial metabolism by acting as electron acceptors or donors, thereby enhancing the efficiency of metabolic pathways involved in methane production. Furthermore, catalysts can mitigate the inhibitory effects of certain compounds present in food waste, such as phenolic compounds and heavy metals, which can impede microbial activity and methanogenic pathways. TiO2 nanoparticles have been demonstrated to adsorb and degrade various organic pollutants, thereby reducing their concentrations in the HTC liquid and alleviating the inhibition of methanogenic bacteria.

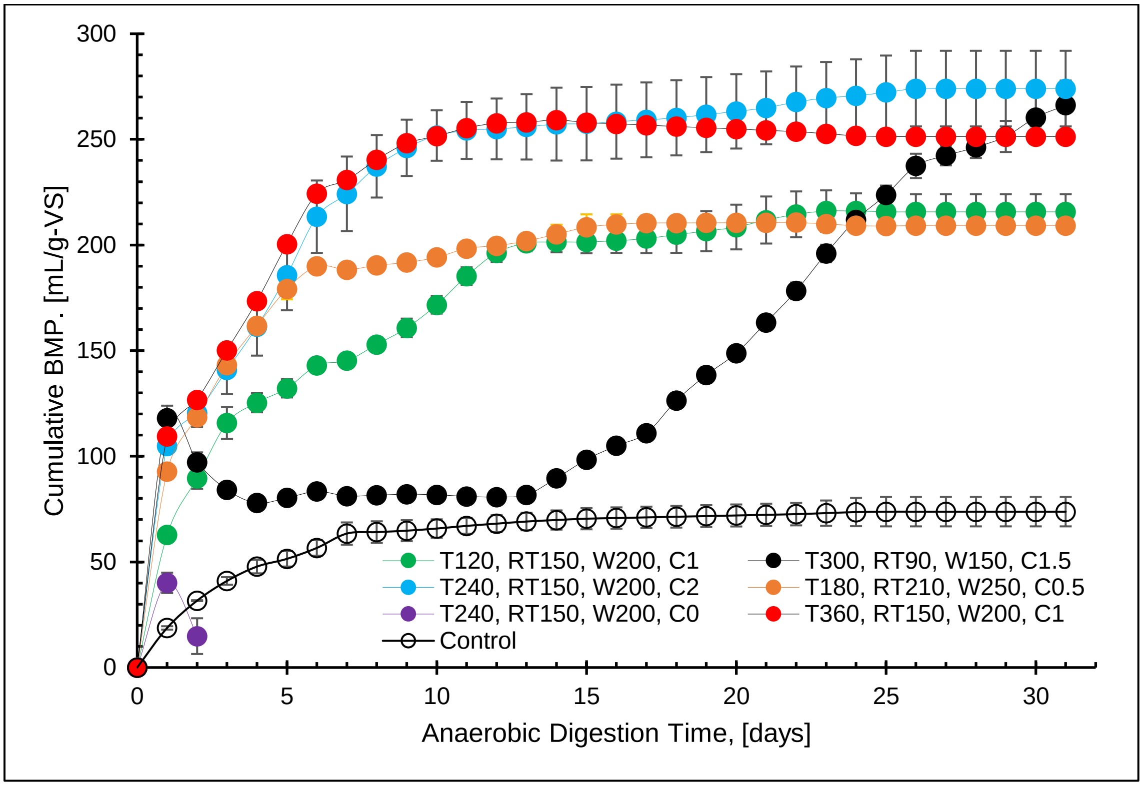

Figure 2. The cumulative biomethane production of the anaerobic digestion of hydrothermal carbonization liquid, (biomethane production from the control was subtracted).

3.2. Model parameters

The parameters of the models obtained from the modified Gompertz equation and the fitness criterion are summarized, and after the test, a pH meter (Electron, CPC-411, Zabrze, Poland) was used to measure the pH **Table 4**. The maximum biomethane production of the current study was obtained in variant 3 (T240, RT150, W200, C2) with values of 270.27 mL/gVS, while the control variant is 164.07 mL. This indicates that, in comparison to the other treatments, the catalyst added resulted in a higher potential for biomethane production. Furthermore, the fitted data showed a high R^2 values, which is within the acceptable range (0.75 – 1.0) (Ma et al., 2021), and low RMSE suggesting a good fit in the modified Gompertz model. At variant 5 (T240, RT150, W200, C0), the methane production stopped after day 2 due to acidification which gave insufficient data points reason why its RSME was high (34.86). Similarly, at variant 2 (T300, RT90, W150, C1.5), the methane production declined on day 2 and was constant until day 13 but recovered afterward giving a poor fitting with the model.

Table 4. Kinetics parameters of the modified Gompertz equation of the predicted methane production of anaerobic digestion of the HL produced from HTC of food waste under various conditions.

Variants	BMP yield, mL		P	R_{max}	λ	RMSE	pH	R^2	k
	Measured	Predicted							
T120, RT150, W200, C1	215.71	215.88	216.57	0.65	-3.40	6.38	8.0	0.980	0.003
T300, RT90, W150, C1.5	266.19	282.19	18732	3.61	71	19.46	8.4	0.948	0.000
T240, RT150, W200, C2	279.04	270.27	270.36	1.12	-2.57	6.25	8.2	0.985	0.004
T180, RT250, W200, C0.5	209.24	207.90	207.90	1.24	-2.01	4.57	8.3	0.981	0.006
T240, RT150, W200, C0	4.76	0.00	42.83	-1.37	2.48	34.86	8.2	0.983	0.032
T360, RT150, W200, C1	251.31	255.91	255.92	1.39	-1.92	5.96	8.4	0.982	0.005
Control	73.77	72.23	164.07	0.88	-1.56	3.84	8.4	0.984	0.005

*T – HTC temperature; RT – HTC resident time; C – catalyst dosage; W – added water; BMP – biomethane production; P – biomethane production (ml/g-VS); R_{max} – maximum methane production rate (mL/day); λ - lag phase (day); RMSE – root mean square error; k-biodegradability constant (day^{-1}).

3.3. Cumulative biomethane production

A cumulative biomethane violin plot that shows both the box plot and kernel density of the impact of the hydrothermal carbonization conditions across the variants during the process is presented in **Figure 3**. Based on the distinct shape of the violin plot, the mean value was highest in variant 3 with (233) and the lowest obtained in variant 5 with (1.7). What is more, the violin width corresponds to the density of the measured biomethane. Notably, in the case of variant 3, the plot exhibits a pronounced density of accumulated biomethane quantity primarily at the interquartile range of 227.49 to 270.40 mL/g-VS. More so, the median value of variant 3 (257.90) is the highest among the tested variants. Furthermore, the control reactor continued to accumulate methane but at an insignificant rate with a maximum production of only 12.64 mL/g-VS. This emphasizes the significant effect of HTC operating conditions, especially in the context of catalyst dosage in the hydrothermal liquid subjected to the biomethane process.

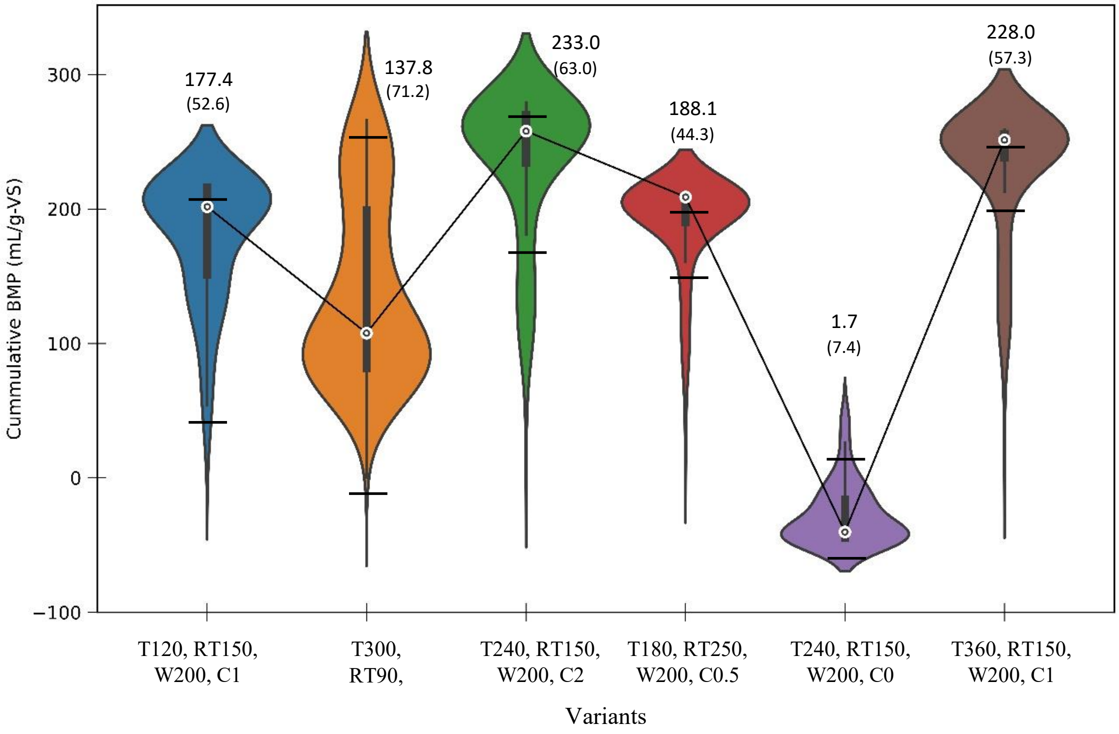

Figure 3. The Violin plot and *Box and whisker plot* of the specific biomethane potential yield from the AD of the HL of the HTC of food waste under various conditions (The group median is represented by the central line, the 75th and 25th percentiles by the top and bottom lines, and the 1.5 times difference between the 75th and 25th percentiles by the top and bottom whiskers. Above each box are the average values and standard deviations (in parenthesis) for each sample group.

3.4. The 3D Surface Plot of Biomethane Production

To understand the biodegradation process during the anaerobic digestion process, a 3D surface plot that relates the biodegradability at the different variants and the BMP over the digestion time is presented in **Figure 4**. The 3D surface is described by a quadratic equation and was determined using the Statistica software. The quadratic equation describing the model is given in **Eq. 3** with a root mean square error (RMSE) of 27.149 and a coefficient of determination (R^2) of 0.86. Based on the model, the BMP was significantly affected by the biodegradability of the substrate. Reactors that had higher biodegradability such as 0.005 showed significant differences in the BMP starting in the early days of the experiment.

$$BM = -10.62 + 45465.22k + 0.58t - 3.68E6k^2 - 28.46kt - 0.0004t^2 \quad (3)$$

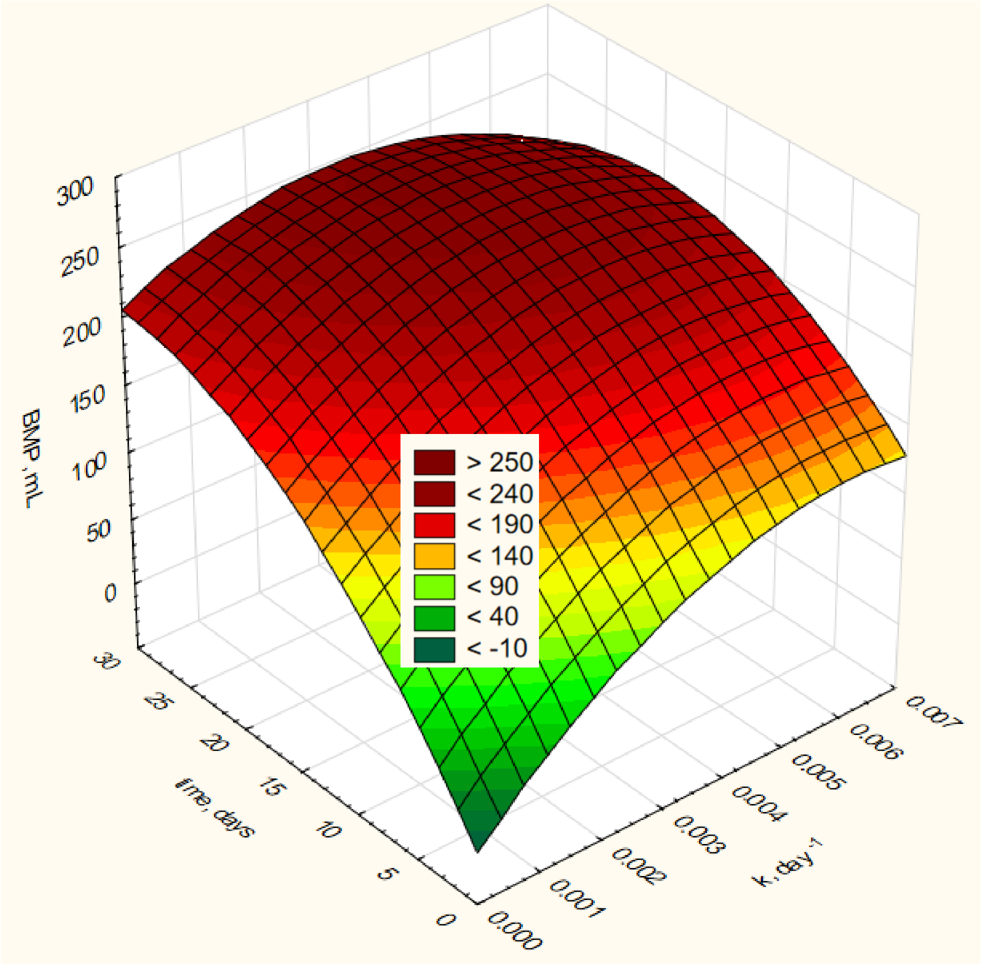

Figure 4. The 3D surface plot relating the biomethane potential as affected by time and biodegradability.

3.5. Methane production rate

The daily biomethane production of HTC liquid's anaerobic digestion process under various conditions is present in **Figure 5**. The effect of hydrothermal carbonization conditions at higher parameters including temperature, resident time, and catalyst dosage is evident on day 1, where the peak biomethane production rate observed in all the reactors with variant 2 (T300, RT90, W150, C1.5) being the highest, with 117.99 mL/g-VS/day, followed by variant 6 (T360, RT150, W200, C1) with 109.42 mL/g-VS/day, the current result is similar to the previously reported works (Codignole Luz et al., 2018; Lucian et al., 2020). The results indicate that, for all reactors other than variant 5, which stops producing biomethane further, the biomethane production rate gradually decreases until day 5, at which point a slight rise that appears to be an attempt to approach a second peak is seen between days 5 and 6. Li and colleagues observed a similar pattern, with the exception that peak production started on day 6 (Li et al., 2022). In the current study, the low yield of methane production in some variants could be explained by the existence of some refractory substances that are toxic to the anaerobic microbial community during the HTC process of reducing sugars and amino acids present in the food waste (Pagés-Díaz and Huiliñir, 2020).

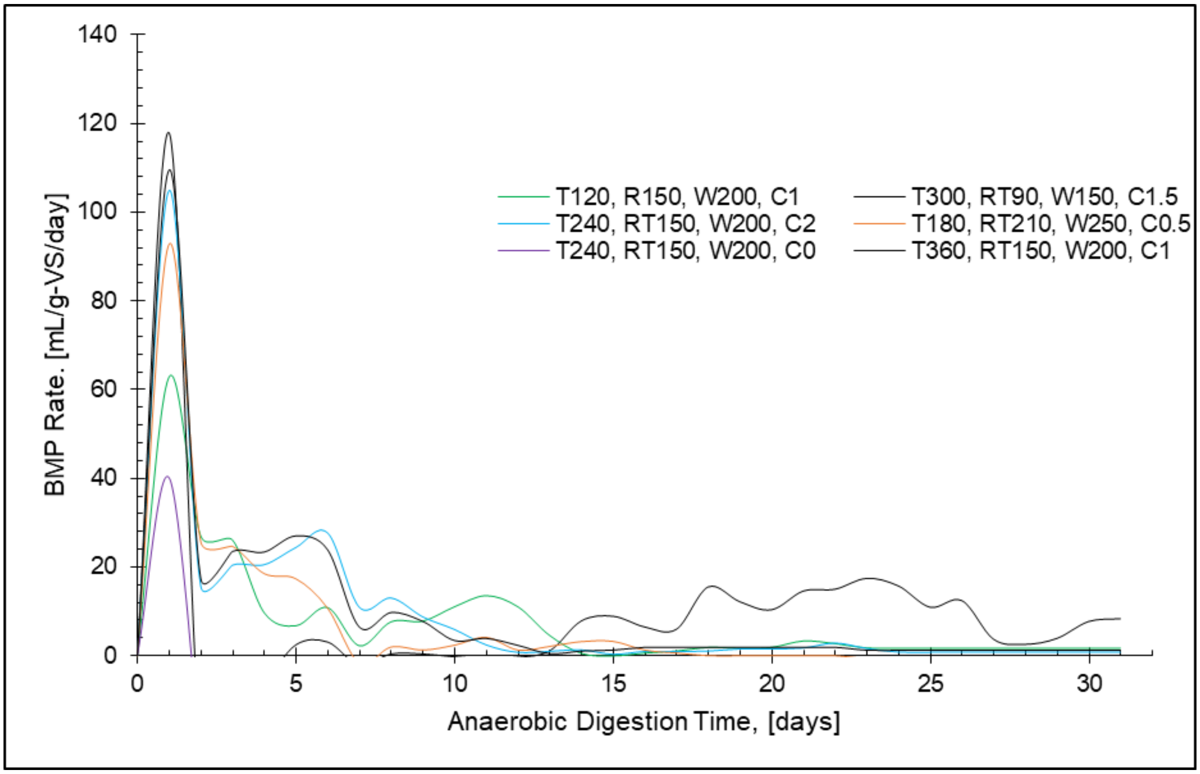

Figure 5. Methane production rate (mL/g-VS/day) of the anaerobic digestion of hydrothermal carbonization liquid.

Conclusion

The investigation underscores the considerable potential of utilizing HL derived from food waste to amplify biomethane production within anaerobic digestion systems. Through systematic optimization, coupled with the strategic integration of a TiO_2/biochar catalyst, the efficiency of biomethane generation was enhanced effectively. Notably, variant 3 (T240, RT150, W200, C2) emerged as the most effective configuration amongst other test scenarios, indicating the crucial role of catalyst addition in maximizing biomethane output. Beyond experimental findings, our research fills key knowledge gaps in sustainable waste management and renewable energy production by elucidating the complex relationships between HTC parameters, catalyst use, and biomethane production.

Author contributions

Conceptualization: W.A.R., C.A.I. and A.B.; Methodology: W.A.R., C.A.I. and A.B.; Result analysis and validation: W.A.R., M.V., K.Ś. and C.A.I.; Project administration: W.A.R. and A.B.; writing – original draft: W.A.R, C.A.I, and M.V; Visualization: W.A.R. and M.V.; writing – review and editing: W.A.R., M.V., K.Ś., C.A.I., and A.B.; Supervision: C.A.I. and A.B.

Conflicts of interest

There are no conflicts to declare.

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References

Aragón-Briceño, C., Ross, A.B., Camargo-Valero, M.A., 2017. Evaluation and comparison of product yields and bio-methane potential in sewage digestate following hydrothermal treatment. Appl. Energy 208, 1357–1369. https://doi.org/10.1016/j.apenergy.2017.09.019

Bhatt, D., Shrestha, A., Dahal, R.K., Acharya, B., Basu, P., MacEwen, R., 2018. Hydrothermal carbonization of biosolids from Waste water treatment plant. Energies 11, 1–10. https://doi.org/10.3390/en11092286

Chen, D., Cheng, Y., Zhou, N., Chen, P., Wang, Y., Li, K., Huo, S., Cheng, P., Peng, P., Zhang, R., Wang, L., Liu, H., Liu, Y., Ruan, R., 2020. Photocatalytic degradation of organic pollutants using TiO2-based photocatalysts: A review. J. Clean. Prod. 268, 121725. https://doi.org/10.1016/j.jclepro.2020.121725

Chung, N.T., Choi, S.-R., Kim, J.-G., 2022. Comparison of Response Surface Methodologies and Artificial Neural Network Approaches to Predict the Corrosion Rate of Carbon Steel in Soil. J. Electrochem. Soc. 169, 051503. https://doi.org/10.1149/1945-7111/ac700d

Codignole Luz, F., Cordiner, S., Manni, A., Mulone, V., Rocco, V., 2018. Biochar characteristics and early applications in anaerobic digestion-a review. J. Environ. Chem. Eng. 6, 2892–2909. https://doi.org/10.1016/j.jece.2018.04.015

De Gioannis, G., Muntoni, A., Cappai, G., Milia, S., 2009. Landfill gas generation after mechanical biological treatment of municipal solid waste. Estimation of gas generation rate constants. Waste Manag. 29, 1026–1034. https://doi.org/10.1016/j.wasman.2008.08.016

Fernandez, E., Santamaria, L., Amutio, M., Artetxe, M., Arregi, A., Lopez, G., Bilbao, J., Olazar, M., 2022. Role of temperature in the biomass steam pyrolysis in a conical spouted bed reactor. Energy 238, 122053. https://doi.org/10.1016/j.energy.2021.122053

Grandhi, B., Appaiah Singh, J., 2016. What a Waste! A Study of Food Wastage Behavior in Singapore. J. Food Prod. Mark. 22, 471–485. https://doi.org/10.1080/10454446.2014.885863

Hejna, M., Świechowski, K., Rasaq, W.A., Białowiec, A., 2022. Study on the Effect of Hydrothermal Carbonization Parameters on Fuel Properties of Chicken Manure Hydrochar. Materials (Basel). 15, 2022–2023. https://doi.org/10.3390/ma15165564

Holm-Nielsen, J.B., Al Seadi, T., Oleskowicz-Popiel, P., 2009. The future of anaerobic digestion and biogas utilization. Bioresour. Technol. 100, 5478–5484. https://doi.org/10.1016/j.biortech.2008.12.046

Igwegbe, C.A., Kozłowski Kozłowski, Wasowicz, J., Edyta, P., Białowiec, A., 2024. Nitrogen Removal from Landfill Leachate Using Biochar Derived from Wheat Straw. Materials (Basel). 928, 20. https://doi.org//doi.org/10.3390/ma17040928

Igwegbe, C.A., Obi, C.C., Ohale, P.E., Ahmadi, S., Onukwuli, O.D., Nwabanne, J.T., Białowiec, A., 2023. Modelling and optimisation of electrocoagulation/flocculation recovery of effluent from land-based aquaculture by artificial intelligence (AI) approaches. Environ. Sci. Pollut. Res. 30, 70897–70917. https://doi.org/10.1007/s11356-023-27387-2

Li, P., Wang, Q., He, X., Yu, R., He, C., Shen, D., Jiao, Y., 2022. Investigation on the effect of different additives on anaerobic co-digestion of corn straw and sewage sludge: Comparison of biochar, Fe3O4, and magnetic biochar. Bioresour. Technol. 345, 126532. https://doi.org/10.1016/j.biortech.2021.126532

Lin, R., Cheng, J., Zhang, J., Zhou, J., Cen, K., Murphy, J.D., 2017. Boosting biomethane yield and production rate with graphene: The potential of direct interspecies electron transfer in anaerobic digestion. Bioresour. Technol. 239, 345–352. https://doi.org/10.1016/j.biortech.2017.05.017

Lin, Y., Lü, F., Shao, L., He, P., 2013. Influence of bicarbonate buffer on the methanogenetic pathway during thermophilic anaerobic digestion. Bioresour. Technol. 137, 245–253. https://doi.org/10.1016/j.biortech.2013.03.093

Liu, X., Shen, J., Guo, Y., Wang, S., Chen, B., Luo, L., Zhang, H., 2023. Technical progress and perspective on the thermochemical conversion of kitchen waste and relevant applications: A comprehensive review. Fuel 331, 1–7. https://doi.org/10.1016/j.fuel.2022.125803

Lucian, M., Volpe, M., Merzari, F., Wüst, D., Kruse, A., Andreottola, G., Fiori, L., 2020. Hydrothermal carbonization coupled with anaerobic digestion for the valorization of the organic fraction of municipal solid waste. Bioresour. Technol. 314, 123734.

https://doi.org/10.1016/j.biortech.2020.123734

Ma, J., Chen, F., Xue, S., Pan, J., Khoshnevisan, B., Yang, Y., Liu, H., Qiu, L., 2021. Improving anaerobic digestion of chicken manure under optimized biochar supplementation strategies. Bioresour. Technol. 325, 124697. https://doi.org/10.1016/j.biortech.2021.124697

Namal, O.O., 2020. Investigation of the effects of different conductive materials on the anaerobic digestion. Int. J. Environ. Sci. Technol. 17, 473–482. https://doi.org/10.1007/s13762-019-02498-x

Pagés-Díaz, J., Huiliñir, C., 2020. Valorization of the liquid fraction of co-hydrothermal carbonization of mixed biomass by anaerobic digestion: Effect of the substrate to inoculum ratio and hydrochar addition. Bioresour. Technol. 317, 123989. https://doi.org/10.1016/j.biortech.2020.123989

PN-EN15169:2011 Standard, 2011. Characterization Of Waste - Determination Of Loss On Ignition. Available online: http://sklep.pkn.pl/pn-en-15169- 2011p.html (accessed on 20 June 2023).

Rasaq, W.A., Golonka, M., Scholz, M., Białowiec, A., 2021. Opportunities and challenges of high-pressure fast pyrolysis of biomass: A review. Energies 14, 1–20. https://doi.org/10.3390/en14175426

Rasaq, W.A., Okpala, C.O.R., Igwegbe, C.A., Białowiec, A., 2024a. Navigating Pyrolysis Implementation—A Tutorial Review on Consideration Factors and Thermochemical Operating Methods for Biomass Conversion. Materials (Basel). 17. https://doi.org/10.3390/ma17030725

Rasaq, W.A., Thiruchenthooran, V., Telega, P., Bobak, Ł., Igwegbe, C.A., Białowiec, A., 2024b. Optimizing hydrothermal treatment for sustainable valorization and fatty acid recovery from food waste. J. Environ. Manage. 357, 3–10. https://doi.org/10.1016/j.jenvman.2024.120722

Santos Dalólio, F., da Silva, J.N., Carneiro de Oliveira, A.C., Ferreira Tinôco, I. de F., Christiam Barbosa, R., Resende, M. de O., Teixeira Albino, L.F., Teixeira Coelho, S.,

2017. Poultry litter as biomass energy: A review and future perspectives. Renew. Sustain. Energy Rev. 76, 941–949. https://doi.org/10.1016/j.rser.2017.03.104

Świechowski, K., Matyjewicz, B., Telega, P., Białowiec, A., 2022. The Influence of Low-Temperature Food Waste Biochars on Anaerobic Digestion of Food Waste. Materials (Basel). 15. https://doi.org/10.3390/ma15030945

Uçkun Kiran, E., Trzcinski, A.P., Ng, W.J., Liu, Y., 2014. Bioconversion of food waste to energy: A review. Fuel 134, 389–399. https://doi.org/10.1016/j.fuel.2014.05.074

Valentin, M.T., Świechowski, K., Białowiec, A., 2023. Influence of Pre-Incubation of Inoculum with Biochar on Anaerobic Digestion Performance. Materials (Basel). 16, 1–13. https://doi.org/10.3390/ma16206655

Valta, K., Sotiropoulos, A., Malamis, D., Kosanovic, T., Antonopoulou, G., Alexandropoulou, M., Jonuzay, S., Lyberatos, G., Loizidou, M., 2019. Assessment of the effect of drying temperature and composition on the biochemical methane potential of in-house dried household food waste. Waste Manag. Res. 37, 461–468.

Wu, S., Wang, Q., Fang, M., Wu, D., Cui, D., Pan, S., Bai, J., Xu, F., Wang, Z., 2023. Hydrothermal carbonization of food waste for sustainable biofuel production: Advancements, challenges, and future prospects. Sci. Total Environ. 897, 1–8. https://doi.org/10.1016/j.scitotenv.2023.165327

Zabaniotou, A., Rovas, D., Delivand, M.K., Francavilla, M., Libutti, A., Cammerino, A.R., Monteleone, M., 2017. Conceptual vision of bioenergy sector development in Mediterranean regions based on decentralized thermochemical systems. Sustain. Energy Technol. Assessments 23, 33–47. https://doi.org/10.1016/j.seta.2017.09.006

Zhao, K., Li, Y., Zhou, Y., Guo, W., Jiang, H., Xu, Q., 2018. Characterization of hydrothermal carbonization products (hydrochars and spent liquor) and their biomethane production performance. Bioresour. Technol. 267, 9–16. https://doi.org/10.1016/j.biortech.2018.07.006

Zhou, S., Liang, H., Han, L., Huang, G., Yang, Z., 2019. The influence of manure feedstock, slow pyrolysis, and hydrothermal temperature on manure thermochemical and combustion properties. Waste Manag. 88, 85–95. https://doi.org/10.1016/j.wasman.2019.03.025

Supplementary

Table S1. The operating conditions of independent parameters employed during DOE.

Run	Temperature (°C)	Resident time (Min)	Weight of the liquid (g)	Catalyst dosage (g)
1	180	90	150	0.5
2	300	90	150	0.5
3	180	210	150	0.5
4	300	210	150	0.5
5	180	90	250	0.5
6	300	90	250	0.5
7*	180	210	250	0.5
8	300	210	250	0.5
9	180	90	150	1.5
10*	300	90	150	1.5
11	180	210	150	1.5
12	300	210	150	1.5
13	180	90	250	1.5
14	300	90	250	1.5
15	180	210	250	1.5
16	300	210	250	1.5
17*	120	150	200	1
18*	360	150	200	1
19	240	30	200	1
20	240	270	200	1
21	240	150	100	1
22	240	150	300	1
23*	240	150	200	0
24*	240	150	200	2
25	240	150	200	1
26	240	150	200	1
27	240	150	200	1
28	240	150	200	1
29	240	150	200	1
30	240	150	200	1

Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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STATEMENT

I hereby declare that in the publication:

Waheed A. Rasaq, Marvin Valentin, Kacper Świechowski, Chinenye Adaobi Igwegbe, Andrzej Białowiec. "Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization". Renewable Energy, is under review. Preprint: DOI: 10.2139/ssrn.4827691

My contribution included:

Developing the concept and design of the study, in particular, the methodology of measurements. I prepared the text of the entire article, including the introduction part, description of the methodology, materials, analysis, and description of the results with discussion and conclusions. I participated in the preparation of the figures and tables included in the manuscript. I obtained funds for the publication of the article.

Signed by /
Podpisano przez:

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STATEMENT

I hereby declare that in the publication:

Waheed A. Rasaq, Marvin Valentin, Kacper Świechowski, Chinenye Adaobi Igwegbe, Andrzej Białowiec. "Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization". Renewable Energy, is under review. Preprint: DOI: 10.2139/ssrn.4827691

My contribution included:

I participated in the analysis and description of the results with discussion. I participated in the preparation of the figures and tables included in the manuscript.

10.06.2024

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STATEMENT

I hereby declare that in the publication:

Waheed A. Rasaq, Marvin Valentin, Kacper Świechowski, Chinenye Adaobi Igwegbe, Andrzej Białowiec. "Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization". Renewable Energy, is under review. Preprint: DOI: 10.2139/ssrn.4827691

My contribution included:

I participated in the investigation and writing-editing of the manuscript.

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STATEMENT

I hereby declare that in the publication:

Waheed A. Rasaq, Marvin Valentin, Kacper Świechowski, Chinenye Adaobi Igwegbe, Andrzej Białowiec. "Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization". Renewable Energy, is under review. Preprint: DOI: 10.2139/ssrn.4827691

My contribution included:

Participated in developing the concept design of the study, including the selection of hydrothermal carbonization parameters such as temperature and time using the DOE approach. I participated in writing – reviewing & editing, and writing – the original draft.

14.06.2024
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I hereby declare that in the publication:

Waheed A. Rasaq, Marvin Valentin, Kacper Świechowski, Chinenye Adaobi Igwegbe, Andrzej Białowiec. "Enhancing Biomethane Production from Food Waste Hydrothermal Carbonization Liquid through Catalyst Addition and Process Optimization". Renewable Energy is (under review). Preprint: DOI: 10.2139/ssrn.4827691

My contribution included:
Developing the concept and design of the study, including the selection of hydrothermal carbonization process parameters such as temperature and time using the DOE approach. I supervised the preparation of the manuscript. Also, I served as the corresponding author.

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