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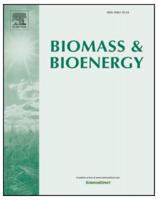

Advances and challenges on hydrothermal processes for biomass conversion: Feedstock flexibility, products, and modeling approaches

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ABSTRACT

Developing technologies to harness biomass energy is essential for the transition to a low-carbon economy. Emerging biorefineries, where biomass energy is converted via thermochemical processes like Hydrothermal Liquefaction (HTL), could be at the core of this transition. This review offers a comprehensive analysis of biomass Hydrothermal Processes (HTP), emphasizing HTL as a sustainable approach to convert high-moisture, heterogeneous biomass—including municipal solid waste, lignocellulosic residues, and microalgae—into biofuels and valuable bioproducts. This review examines the flexibility of feedstocks suitable for hydrothermal processes, including organic solid waste, food waste, and sludge, while critically assessing recent advances in reactor design, as well as kinetic and phenomenological modeling. Additionally, to the best of our knowledge, this work proposes the first strategies to model and simulate transport phenomena within HTL technology, capturing the structural effects generated by the chemical reactions involved. The analysis identifies existing challenges in understanding these processes, highlights research gaps, and proposes a roadmap for future studies. This roadmap integrates theoretical and experimental approaches aimed at accelerating the development of next-generation biorefineries and supporting the shift towards a circular bioeconomy.

1. Introduction

Planet Earth is experiencing accelerating global warming [1] due to the temperature rise caused by the greenhouse effect of emissions from human activities accumulating in the atmosphere. One of the most impactful activities is burning fossil fuels for energy, which releases mass quantities of carbon dioxide from outside the natural carbon cycle. As a result, the energy transition is an obligation as well as transforming the global energy sector from fossil fuels to zero-net-carbon renewable energy resources [2] and adopting sustainable practices. However, this is a highly challenging task given the lifestyles society is used to. The energy sector is one of the largest emitters of greenhouse gases at 33,904.36 $MtCO_2e$ [3].

Lignocellulosic biomass can be a carbon-neutral alternative as an energy source that enables the production of renewable hydrocarbon fuels, heat, and energy worldwide. As a subset of lignocellulosic biomasses, residual biomasses have significant potential because residues hold little economic value and, in many cases, are considered waste and contribute to environmental pollution. Nevertheless, they could serve as valuable feedstock for fuels via thermochemical, biochemical, chemical, physical, and/or biological conversion processes.

Biorefineries will be crucial in sustainable biomass processing into biofuels, biochemicals, and bioproducts. These facilities utilize advanced conversion technologies to transform biomass into a diverse range of valuable products, thus enhancing biomass utilization's economic viability and contributing environmental benefits [4]. Biorefineries integrate conversion processes to maximize biofuel and bioproduct production, yield, and efficiency. The importance of

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biorefineries lies in their ability to reduce dependency on fossil fuels, lower greenhouse (GHG) emissions, and contribute to a circular economy by converting waste materials into high-value products [5]. Developing and optimizing biomass conversion processes within biorefineries are critical for advancing renewable energy technologies and achieving global sustainability goals. The increasing number of publications on hydrothermal processes requires more rigorous analysis to understand more extensively the topics and critical factors being investigated.

1.1. Bibliometric analysis

Looking for a global panorama of biomass thermochemical processes, an analysis of the Scopus database engine was done. This bibliometric data was collected using this database from 1st Oct to Oct 11, 2024 and updated on January 1st, 2025. The initial search string was title, abstract, and keywords (*Biomass AND thermochemical AND processes*) in the last 20 years, resulting in 4316 documents. The search phrase was adjusted to exclude standard review articles and unrelated studies, targeting only original research articles. Additional terms like "review," "overview," and "bibliometric" were added to the query in the title, abstract, and keywords to filter out review articles that might be included in the research articles. From 2004 to 2024, 3297 research articles on biomass thermochemical processes were published. The number of papers published each year gradually increased, reaching 303 last year and 345 in 2024. The United States, China, and India lead the publication in this field.

More search strings were applied to limit the document types of the research field to *"hydrothermal," "carbonization," "liquefaction," "gasification," and "modeling and/or simulation."* Bibliometric maps were constructed using these additional search strings in the Scopus database through the VOSViewer software (version 1.6.20) [6]. In this study, specific settings in VOSViewer were adjusted to suit the scope and scale of the analysis, enabling the construction of network maps to visualize the author's keyword co-occurrence. This analysis, which included 5731 keywords, was streamlined by setting a minimum co-occurrence threshold of 12 for keywords, resulting in 126. Fig. 1a–b illustrates the keyword co-occurrence map based on occurrences; each node's size corresponds to the keyword's frequency, and the connecting lines, or links, indicate the extent of association between the terms [7]. This map provides a macroscopic view of the topics in the research field, allowing researchers to discern predominant areas of study and emergent trends.

In Fig. 1a, each cluster is represented by a distinct color: red, green, blue, yellow, purple, and cyan. Cluster 1 (red) emphasizes the keyword "pyrolysis" with a total strength of 1125, cluster 2 (green) focuses on "biomass" with a 1578 strength, and Cluster 3 (blue) focuses on "biofuel" with 278 total link strength. The keyword "thermochemical conversion" is highlighted with 500 strengths in cluster 4 (yellow), "biofuels" with 233 in cluster 5 (purple), and "bio-oil" with 351 strengths in cluster 6 (cyan). The prominence of "biomass" in the keyword analysis underscores the use of biomass as the primary feedstock in this hydrothermal process to transform into valuable products. These results are consistent with other studies on hydrothermal processes (HTP) [8]. There is strong potential for utilizing HTP as an alternative method for treating biomass with high moisture content.

Fig. 1b shows the overlay visualization model integrating a temporal dimension. It assigns color gradients based on the average year of occurrence for each keyword, as the recent trend in publications year of keywords labeled in yellow. This temporal overlay facilitates understanding the evolution of research focus over time. The keywords "hydrochar," "hydrothermal carbonization," and "numerical simulation" provide insights into emerging trends within this field. In addition, using keywords such as 'modeling' or 'simulation,' the search string found 39 articles related to modeling or simulation in this field, revealing a gap and possible challenges to overcome to study this process on a small scale.

Despite scientific and technological advances, the industrial scale-up of hydrothermal liquefaction (HTL) remains a work in progress. Pilot and demonstration plants dominate the field, and efforts are ongoing to address challenges such as ensuring high-pressure system stability and managing feedstock variability. Industrial players emphasize increased investment in reactor design, process optimization, and scalability to achieve commercial deployment.

Several challenges hinder large-scale adoption, including high initial capital costs for high-pressure reactors, corrosion issues caused by extreme operating conditions, and regulatory uncertainties that require consistent policy support [9]. From a scientific perspective, the complexity of chemical reactions, interactions, and phenomena under high-pressure conditions presents additional challenges. These complexities limit the ability to track and measure these processes, complicating efforts to build and validate models essential for scale-up.

Some pilot and semi-industrial HTL plants worldwide demonstrate the feasibility of this technology. The ***Licella™ Advanced Biofuels Plant*** (Australia) operates the Cat-HTR™ platform, efficiently converting biomass and plastic waste into biocrude and other valuable products [10]. ***Steeper Energy*** (Denmark/Canada) employs the patented Hydrofaction® process to process wood residues and agricultural waste into biofuels [11]. ***Genifuel Corporation*** (USA), in collaboration with Pacific Northwest National Laboratory (PNNL), has developed HTL systems for converting wastewater sludge into biocrude [12]. Additionally, the ***Sludge2Fuel*** plant (Fredericia, Denmark), stands as the first full-scale HTL facility, processing sewage sludge into 1400 tonnes of biocrude annually while addressing environmental challenges such as microplastics and nutrient recovery [13].

Moreover, supportive policies and frameworks, such as the EU Renewable Energy Directive and the Fit for 55 package [14], strongly influence these hydrothermal technologies. Advanced biofuels derived from hydrothermal processes are expected to play an important role in meeting EU energy demands for transport by 2050, particularly in the aviation and maritime sectors.

This review provides several novel contributions to the understanding and advancement of hydrothermal processes (HTP), especially hydrothermal liquefaction (HTL) technology. Unlike previous reviews, such as those by Usman et al. [15], that have addressed technological advancements in HTL, with a particular focus on catalysts, aqueous phase recycling, and the integration of machine learning to optimize biomass conversion into biocrude and enhance its refining process. Similarly, the review by Bao et al. [16] provides a detailed analysis of operational parameters, reaction mechanisms, and catalytic control methods in HTL, emphasizing their impact on product yields and characteristics. Furthermore, Guirguis et al. [17] contribute by evaluating and comparing predictive models for biocrude yields in HTL, identifying the most accurate models for various biomass types and suggesting improvements to enhance their applicability.

While all these studies are of high quality, they differ from our manuscript in several important aspects. Notably, one of the main distinctions lies in the modeling and simulation of the HTL process. E.g., Guirguis et al. [17], conducted an in-depth exploration of various chemical reaction models and mechanisms, focusing primarily on intrinsic kinetics. However, this approach did not account for the significant mass, energy, and momentum transport phenomena that are important at both the particle and reactor scales, nor did it consider the structural changes that occur during the process. In contrast, our manuscript proposes, to the best of our knowledge, the first strategies to model and simulate these transport phenomena within HTL technology and to capture the structural effects generated by the chemical reactions involved.

This work also highlights the flexibility of HTL and related hydrothermal processes, such as hydrothermal carbonization (HTC), in processing a wide variety of feedstocks. It includes an analysis of 102 feedstock types, detailing their characteristics and main product yields (as outlined in the supplementary information). Additionally, it

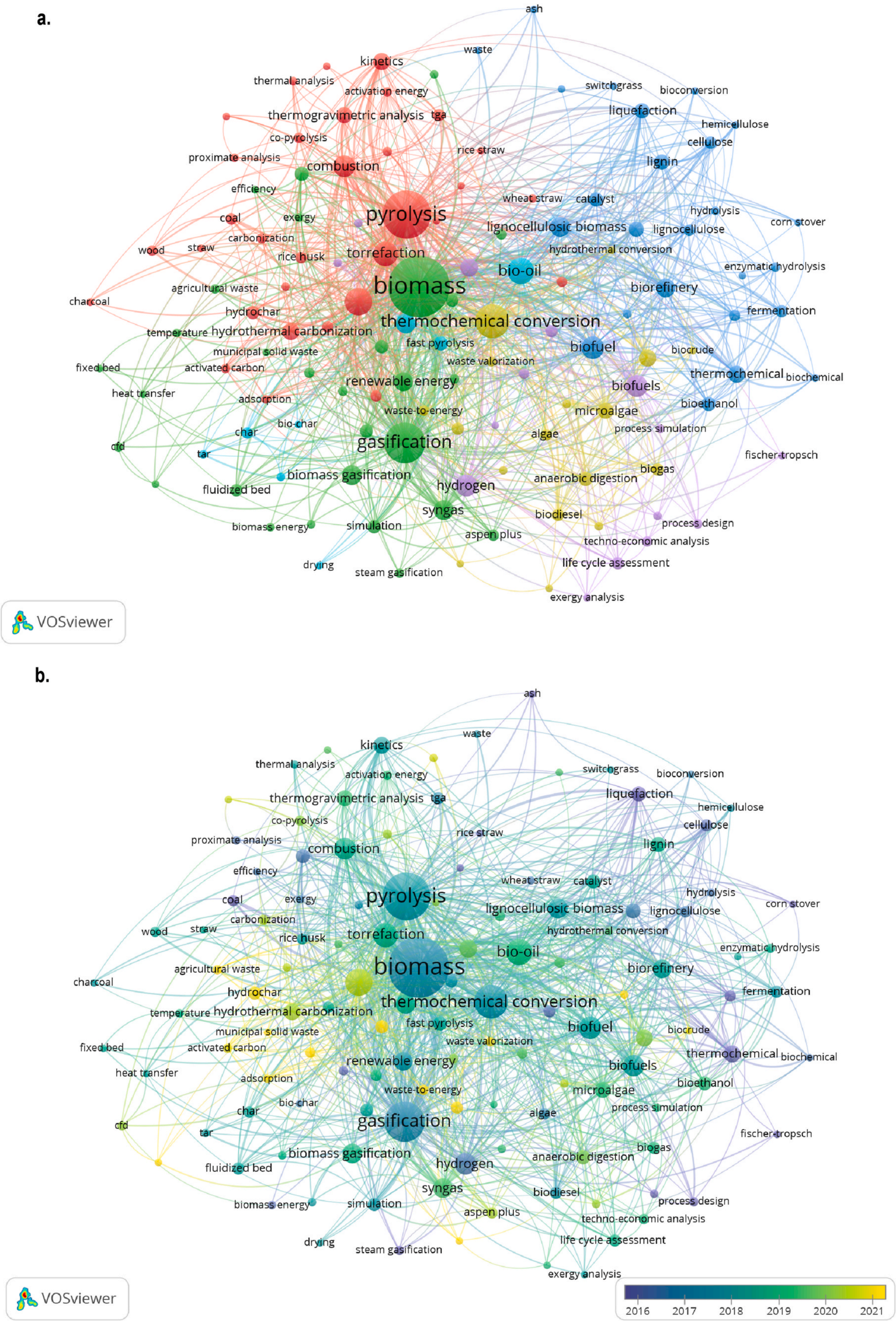


Fig. 1. Keywords co-occurrence map based on occurrences in **a**) network visualization clustered by keyword categories and **b**) overlay visualization mode based on average publication year.

evaluates advancements in reactor design and modeling, identifies key scientific and engineering challenges for optimizing hydrothermal conversion processes, and proposes a comprehensive roadmap for future research on integrating these technologies into biorefineries.

2. Feedstocks

HTP can handle a wider variety of feedstocks than pyrolysis because they can process wet material directly. Different feedstocks, such as lignocellulosic biomass from crops and waste, forestry residues, industrial residues, sewage, animal residues, algae, and municipal solid waste (MSW) [18] can be used in hydrothermal liquefaction because their high humidity does not affect the process since it leverages their water content (see Fig. 2).

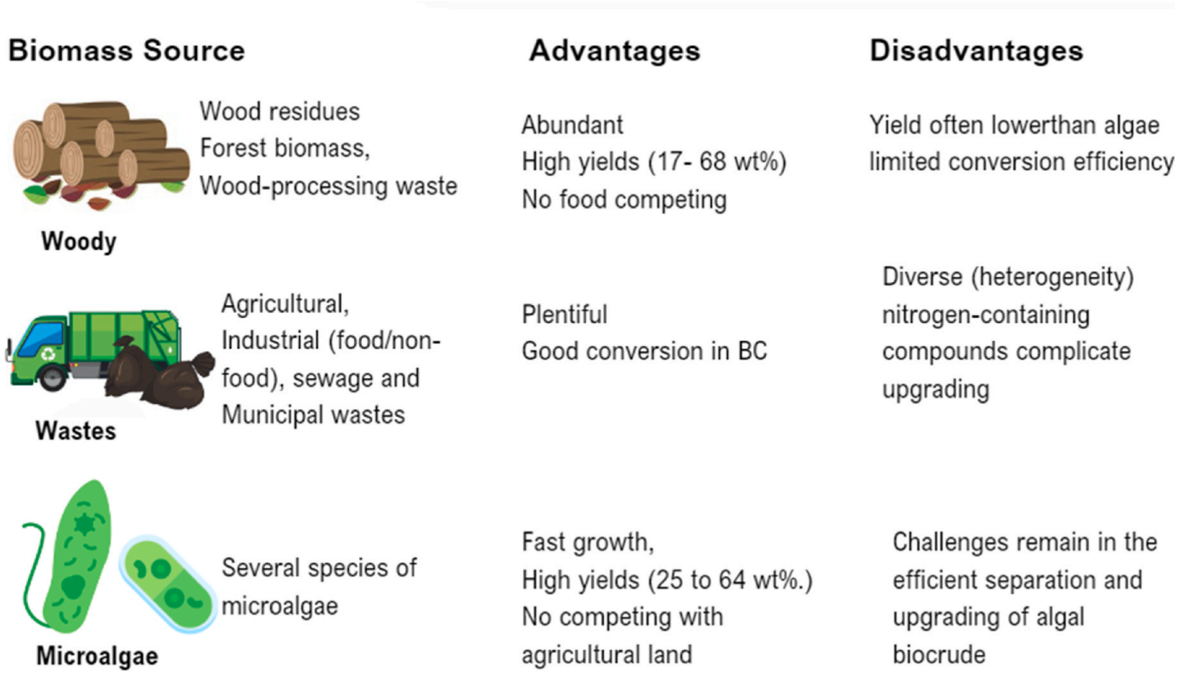
This work surveyed literature on 102 types of biomasses from various sources grouped as lignocellulosic – plants, organic solid waste – OSW, food, lignin, sludge, algae, and microorganisms – MO (Fig. 3). These biomasses show a wide variability in their initial moisture contents, ranging from 2.25 % to 95.7 % wt. (see Supplementary information). When comparing HTL performance of these feedstocks, no apparent correlation was identified between biocrude (BC) yield and initial moisture content. In many cases, total solids content is not reported, although available data range from 5 % to 95 %, in contrast to volatile matter content, which mostly exceeded 68 %. The ashes content in the evaluated biomasses was up to 37 %.

Variables such as fixed carbon, lignin, and protein present scattered data and do not show a defined relationship. Lipids, proteins, and carbohydrates are detailed only in a few studies, which makes data analysis difficult.

There is a very slight correlation between the initial heat value of biomass and BC yield (R^2 of 0.37 %, Root Mean Square Deviation (RMSD) of 13.3 % as shown in Fig. S1), but it is not clear enough to be used as a predictor with the data analyzed here. The calorific value of raw materials reaches up to approximately 27 MJ/kg, while the values in BC vary between 21.2 and 41.3 MJ/kg. Regarding the types of biomass, lignin shows better performance in BC production, and algae, due to their great diversity, show a wide range of performance (Fig. S3). The use of organic cosolvents also has a positive effect, mainly isopropanol-water mixtures (1:1) and acetone (Fig. S4). Water as a solvent also presents a wide range of BC yield, perhaps due to the influence of other process parameters. However, water and ethanol show better results in the BC heating value (Fig. S5).

The total solids content is not reported in all publications; a significant trend was determined between this variable and hydrochar yield (the higher the ST, the lower the hydrochar), with an R^2 of 0.641 and RMSD of 10.64 % (Fig. S2). No other characteristics or trends were found in biochar. Unfortunately, the available information on gas and Aqueous Phase (AP) yields are minimal compared to BC, which restricts the ability to identify trends or develop regression models that predict these yields based on the chemical characterization of biomasses. Regression Trees are a promising type of model to estimate BC and other primary product yields; these yields could be estimated based on carbon - C, hydrogen - H, nitrogen - N, oxygen - O, moisture, heating value, and ash content as input variables (predictors). Nevertheless, it collects much more data from the literature, so this model type is viable. Also, incorporating variables such as lipids, carbohydrates, and proteins could improve the estimates, especially in feedstocks such as algae or food waste rich in these components.

Other promising residual biomasses for hydrothermal processes include those found in agriculture, forests, and food processing, which are examples of low-value biomass sources. These biomass wastes come from a variety of plants such as sugar cane (bagasse, sugarcane leaves, and shoots), coconut (shells and fiber), rice (rice husk), corn (corn cob and leaves), oil palm (empty fruit bunches, shells, fiber, and liquid waste), wood (wood waste). These characteristics have been a focal point of attention in recent years. Food waste is a significant pollution problem and is difficult to manage today. The Food and Agriculture Organization of the United Nations (FAO) estimates that around 1.05 billion tons of food were wasted (just considering household, food service, and retail) in the world in 2022 [19]. Among these, the most complex are those with a high moisture content due to their rapid decomposition and generation of emissions; furthermore, water content makes their transportation and disposal difficult. However, from an optimistic viewpoint, these residues represent an opportunity to be transformed into energy and valuable products through HTP, especially HTL and HTC, where research has yielded promising results [20,21].



Biomass Source		Advantages	Disadvantages
Woody	Wood residues Forest biomass, Wood-processing waste	Abundant High yields (17- 68 wt%) No food competing	Yield often lowerthan algae limited conversion efficiency
Wastes	Agricultural, Industrial (food/non-food), sewage and Municipal wastes	Plentiful Good conversion in BC	Diverse (heterogeneity) nitrogen-containing compounds complicate upgrading
Microalgae	Several species of microalgae	Fast growth, High yields (25 to 64 wt%.) No competing with agricultural land	Challenges remain in the efficient separation and upgrading of algal biocrude

Fig. 2. Flexibility of the feedstock in hydrothermal processes.

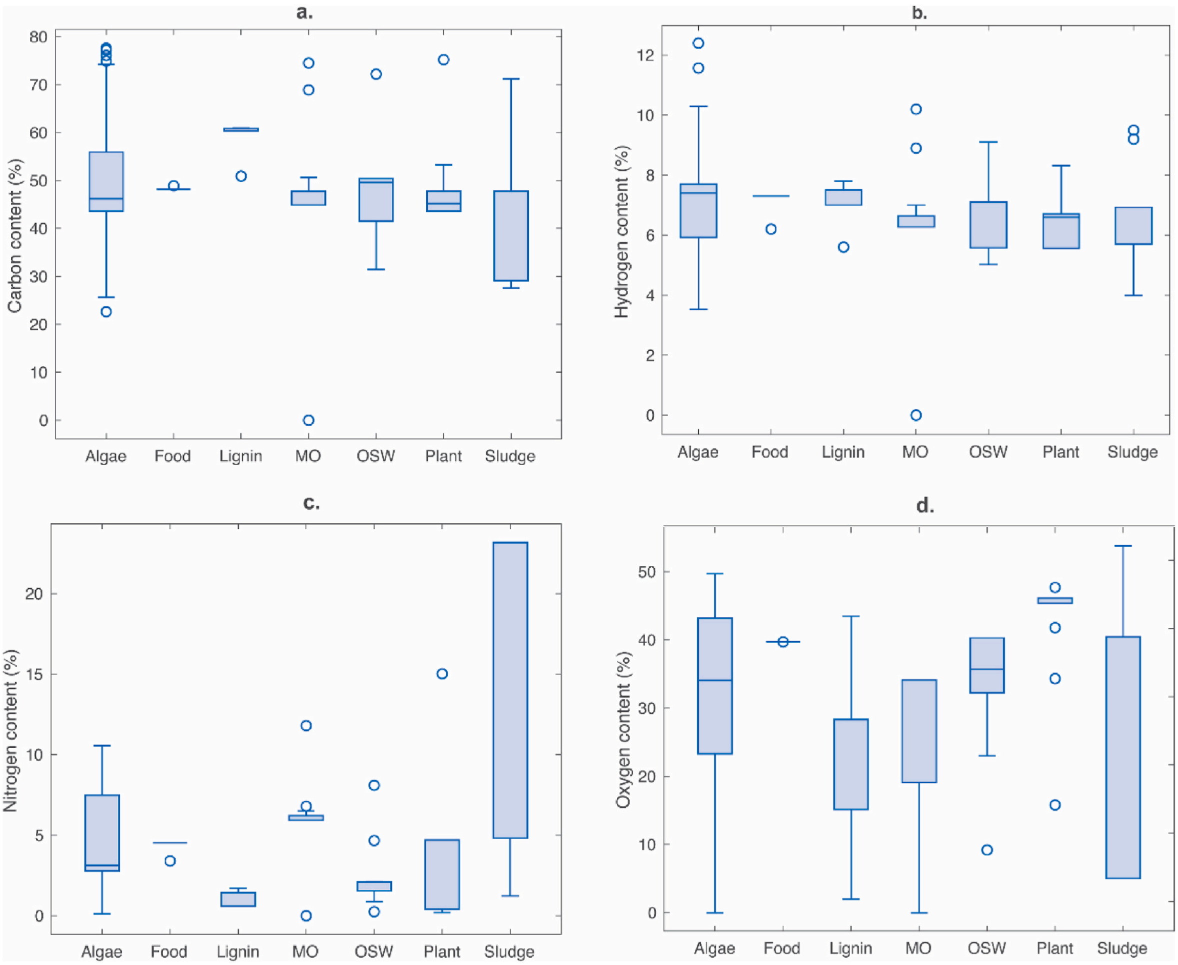


Fig. 3. Distribution of Carbon (**a**), Hydrogen (**b**), Nitrogen (**c**), and Oxygen (**d**) in the biomass types used in the hydrothermal process.

Table 1
Summary of dry biomass feedstocks.

Feedstocks	Components (wt.% dry basis)			Elemental compositions (wt.%)					Reference
	Cellulose	Hemicellulose	Lignin	C	H	N	S	O	
Sugarcane bagasse	43.6	33	21.8	46.6	5.9	0.1	0.1	43.5	[22]
Coffee husk	19–26	24–45	18–30	46.8	4.9	0.6	0.6	47.1	[23]
Spent coffee grounds	61.5		28	54.9	7.9	3.5	–	33.7	[24]
Rice husk	48.0	32.0	25.0	45.8	6.0	0.3	–	47.9	[25]
Cocoa bean shells	24–35	9–11	14.5–26.5	50.3	5.7	3.5	–	40.6	[26]
Cocoa pod	18–23	15	32.5	43.87	5.84	0.17	0.17	37.2	[27]
Corn stover	37.72	20.62	30.50	43.57	5.84	0.56	0.05	49.98	[28]
Poplar wood	52	16	23	47.04	5.60	0.91	–	43.20	[29]
Aspen wood	47.14	19.64	22.11	50.39	6.19	0.19	–	43.23	[30]
Pine	39.54	20.61	30.15	49.52	6.49	0.05	0.05	43.89	[30]
Beech wood	45.05	31.50	22.25	44.68	6.08	–	–	49.24	[30]
Oakwood	38.10	23.00	32.00	45.60	4.30	–	–	50.1	[30]
Food waste	**Protein**	**Carbohydrate**	**Lipid**	48.9	6.2	3.4	1.5	39.7	[20]
	21.4	52.8	20.5						
Food waste	9.1	40.17	3.60	54.74	7.32	1.66	0.12	36.16	[31]
Food waste	16.4	46.5	15.8	48.0	7.2	2.8	0.3	37.7	[32]
Food waste	26.46	52.54	2.0	51.26	7.65	4.46	0.41	36.22	[33]
Algae *Nannochloropsis salina*	27	13.5	19.7	55.9	7.8	2.8	2.8	23.3	[34]
Algae *Derbesia* sp	21.6	10.4	26.90	73.0	7.5	6.5	0.7	10.6	[35]
MSW	–	–	–	52.5	6.78	1.2	0.14	39.38	[36]
MSW	–	–	–	33.50	4.60	1.2	0.12	–	[37]

(-)data not provided, Protein, carbohydrate, and Lipid are in the same units as other Components (wt.% dry basis).

The primary characterization of several example feedstocks is detailed in Table 1.

Residual biomass is a significant environmental pollutant, particularly in developing countries, where a considerable amount is either deposited in landfills, burned, or dispersed in rural areas without proper measures or treatments [38]. Globally, there is an annual residual biomass supply of 100 billion metric tons, with MSW contributing 1300 million metric tons yearly [39] (Table 2).

MSW is an attractive raw material for HTL due to its organic fraction, mainly containing food waste with high humidity and heterogeneity. At the same time, it presents many difficulties for its application in other thermochemical processes requiring prior drying and perhaps densification. For this reason, this work emphasizes MSW. This fraction includes household food waste (until 52 % wt. see Table 2), pruning from gardens and parks, and waste generated in primary markets or supermarkets. The world generates 2.01 billion tons of MSW annually and it is expected to grow to 3.40 billion tons by 2050. Currently, the contribution of high-income countries to the generation of MSW is approximately 33.4 %. The leading producers are East Asia and the Pacific with 23 %, Europe and Central Asia with 20 %, South Asia with 17 %, North America with 14 %, Latin America and the Caribbean with 11 %, and Africa with 15 % [40]. Among countries, waste generation is led by the USA, China, and Germany with 265.2, 215.2, and 53.7 billion tons/year, respectively, while Latin America and the Caribbean (LATAM) countries such as Colombia, Chile, and Costa Rica report 12.1, 8.2, and 1.6 billion tons/year, respectively [41].

The composition of MSW can vary significantly in each region depending on its economic development, culture, and geographical characteristics (Table 2). It is divided into different fractions: food, garden, glass, paper and cardboard, plastics, wood, textiles, rubber and leather, metals, and others. Upper-middle-income countries generally have the highest percentage of waste in landfills, at 54 %. This rate decreases in high-income countries down to 39 %, with 35 % of waste diverted to recycling and composting and 22 % to incineration [40].

The composition of the MSW in the USA is largely paper and cardboard with 23.05 %, and food fractions with 21.59 %. A significant fraction in the United Kingdom and Brazil is food, with 41.5 and 52 %, respectively. LATAM generates from 52 to 75 % of the organic fraction depending on the highest to lowest income countries; e.g., Colombia, an upper-middle income country, generated approximately 14 million tons of MSW in 2018 (rate of 0.77 kg/person/day), with up to 59 % of organic wed wastes [42]. These figures are evidence of the potential in these regions for energy recovery by feasible techniques like HTP.

By analyzing differences in feedstock suitability—ranging from dry lignocellulosic materials like wood chips and agricultural residues in DTL to wet organic materials such as algae and sewage sludge in HTL—Table 3 shows how each process could be optimized for different biomasses. The analysis also delves into the varying operating conditions, such as temperature, pressure, and moisture content, and their impact on the quantity and quality of the BC produced, thus providing insights into the advantages and limitations of each method for specific biomass types.

Table 2
MSW composition: Global [40], USA [43], London [38], Brazil [44], LATAM, and Colombia [42].

Fraction	Composition [% wt.]					
	Global	USA	UK	Brazil	LATAM	Colombia
Food	44	21.59	41.5	52	52–75	59
Garden (green)		–	12.7			
Glass	5	4.19	4.1	–	2–5	2
Paper and cardboard	17	23.05	10.4	10	5–16	9
Plastics	12	12.20	8.9	16	7–12	13
Wood	2	6.19	0.6	5	–	–
Textiles, rubber, and leather	2	8.96	1.2		–	–
Metals	4	8.76	0.9	17	2–8	1
Others	14	15.06	19.7		12–16	16

(-)data not provided.

3. Thermochemical conversion processes

There are four main categories of processes (mechanical, biochemical, chemical, and thermochemical) to transform organic materials into biofuels and bioproducts. However, certain limitations must be noted. Mechanical methods usually provide pretreatment, such as milling and grinding, are energy-intensive, and often lead to high operational costs. Additionally, these processes can produce undesirable by-products or cause structural damage to feedstocks, thus reducing their effectiveness in subsequent conversion steps [51]. Emerging combined mechanical plus microwave methods offer improved efficiency but require advanced infrastructure that may not be accessible in all regions [52]. Biochemical methods, such as fermentation and enzymatic hydrolysis, are constrained by the high cost of enzymes [53], inefficiency in degrading recalcitrant biomass due to their slow conversion rates [54], and their efficiency is highly dependent on the type of biomass, with significant variability in yield [55]. Chemical processes, such as acid hydrolysis and transesterification, are effective in breaking down biomass but present notable challenges as the use of strong acids or bases generates hazardous waste, requiring careful handling and disposal [56], catalysts are expensive, and they can degrade over time [57,58], thus requiring frequent replacement or regeneration. The chemical composition of different biomass sources affects reaction efficiency and product quality [59].

Unlike previous methods, thermochemical processes—which encompass several types that will be detailed later—can efficiently handle a wide range of feedstocks, including wet and lignocellulosic biomass, without requiring extensive pretreatment. These processes do not depend on expensive enzymes or microorganisms, and their high operating temperatures and/or pressures enable rapid conversion, significantly reducing processing time [60,61]. Furthermore, thermochemical processes produce a variety of valuable outputs, such as biofuels, syngas, and biochar, offering multiple pathways for energy and material recovery. Despite these advantages, challenges remain, particularly in achieving efficient scale-up, product separation, and economic feasibility, which are areas of ongoing scientific research.

Moreover, moisture content affects the degree of contact between water and biomass during the reaction, thereby affecting the reaction rate and product yield of biomass. Water provides a favorable environment (low dielectric constant, high ion product) for organic chemical reactions. The moisture content of biomass is a crucial factor influencing reaction rate, product distribution, and energy efficiency. One of the key advantages of HTP over other thermochemical conversion processes, such as pyrolysis, is its capability to process wet biomass feedstocks directly without extensive drying. This feature significantly reduces energy and costs associated with preprocessing steps required by other conversion technologies.

Thermochemical conversion processes have regained attention, driven by the need to meet rising global energy demands and address environmental concerns associated with conventional fossil fuel production and use (Fig. 4).

The primary thermochemical conversion methods include torrefaction, gasification, and combustion. Fast pyrolysis and HTPs are considered advanced technologies. The main objective of these is to produce liquid intermediates, often called BC or bio-oil (BO), to feed downstream processes in the biorefinery that produces finished fuels and chemicals [62].

3.1. Fast pyrolysis

Fast Pyrolysis operates at high temperatures (typically 500–650 °C) and high heating rates (up to 1000 °C/s), with very short residence times

Table 3
Comparison of products from various feedstocks processed by HTP.

Feedstock	Process and Conditions	Catalyst	BC Yield (%)	Gas Yield (%)	Aqueous Phase (%)	Hydrochar (%)	HHV (MJ/kg)	References
Microalgae Xw: 80 %	**DTL** T: 350 °C Pi: 2 MPa Pf: 20.6 Mpa HR: ~3.3 °C min^{-1} time: 60 min	–	40.7	19.2	31.9	6.7	34.21	[45]
Kraft Lignin	**HTL** T: 280 °C time: 30 min IPA-water co-solvent	10Ni–3Ti/γ-Al2O3	65–74.8	17–20	–	~8	27.2–31.1	[46]
Alkali Lignin	**HTL** T: 280 °C time: 30 min 400 rpm	syn-10Cu-5Zn/γ-Al2O3	74.7	3.5–5.5	–	19.7	~36.4	[47]
Black Liquor	**HTL** T: 250–400 °C P: 7.5–21 Mpa time: 15–60 min	NaOH, KOH	52.6–57.7	~13	20–30	29.1–34.1	–	[48]
Diatom Biomass	**HTL** T: 300 °C P: 40 bar time: 30 min	K2CO3 (10 % w/w)	22	–	–	–		[49]
Fecal Sludge (FS) and Organic Solid Waste (OSW)	**HTL** T: 320 °C P:10–12 MPa time: 60 min Water-Ethanol (1:1)	–	32.7–44.6	28–32.5	–	25.8–39.3	37.5	[50]

*Xw: moisture, Pi: initial pressure, Pf: final pressure, T: temperature, HR: heating rate of the heater, Gas: Non-condensable gases. (-)data not provided.

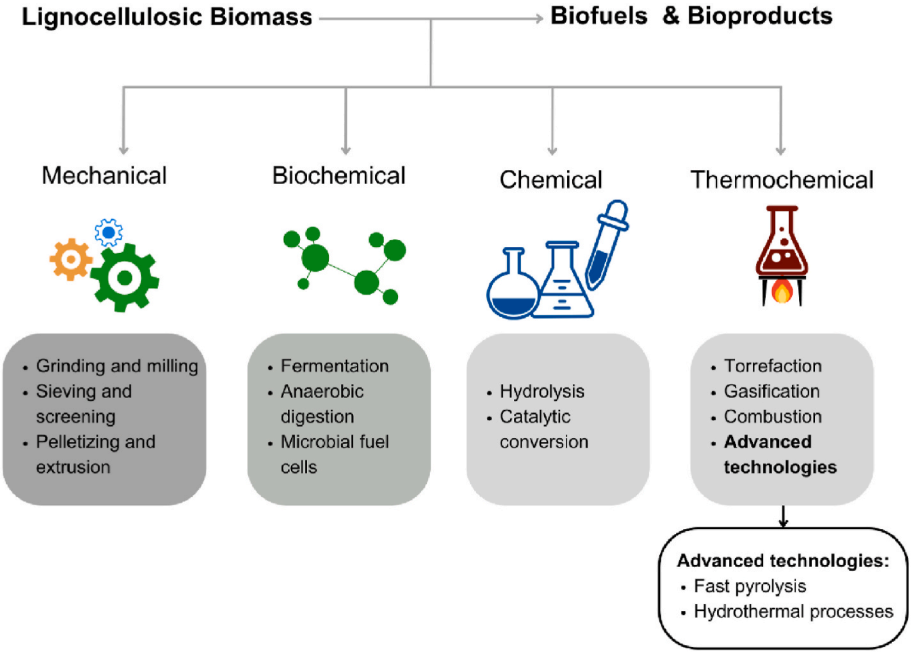


Fig. 4. Scheme of biomass conversion processes into energy and bioproducts.

of less than 2 s [63,64]. This rapid process causes the organic matter to decompose quickly, producing mostly vapors and aerosols and maximizing the yield of liquid BO. Smaller quantities of biochar and syngas are generated [64], and the BO can be used directly as a renewable fuel for certain applications or upgraded to higher-value chemicals and/or transportation fuels.

3.2. Hydrothermal processes (HTP)

HTPs are advanced thermochemical conversion techniques that use water's unique properties at elevated temperatures and pressures to convert biomass and other organic materials into liquids, solids, and gas products. Unlike conventional thermal processes like pyrolysis or gasification, HTPs utilize water as both solvent and reaction medium [65]. This makes them particularly effective for wet biomass feedstocks, eliminating energy-intensive drying steps.

Water's properties under hydrothermal conditions—such as density, dielectric constant, and ionic product—change significantly, enabling it to act as a powerful solvent and catalyst [66]. For instance, water's ionic product increases by several orders of magnitude, facilitating acid- or base-catalyzed reactions without adding catalysts [67]. These altered properties allow water to hydrolyze, depolymerize, and solubilize complex organic molecules, resulting in the efficient conversion of feedstocks into target products such as BC, hydrochar, and gases.

4. Principles of hydrothermal processes

HTPs are thermochemical conversion techniques at high temperatures and pressure exceeding saturation. At these conditions, the physicochemical properties of water, such as density, dielectric constant, and ionic product are altered, and this reactivity can induce feedstock reactions to result in the production of liquids, solids, and gasses [65] (Fig. 5). These processes are subdivided according to the operating conditions of pressure and temperature as well as the desired product yields in HTC, HTL, Hydrothermal Gasification (HTG), and Supercritical Liquefaction (SL) [65].

4.1. HTP classification

4.1.1. Hydrothermal carbonization (HTC)

HTC converts biomass in the presence of water into solid biofuel, liquid, and gaseous products. It is a low-energy alternative for transforming waste of different origins compared to pyrolysis processes because it has a relatively low operating temperature moderate pressure (Fig. 7), and residence time. However, separating solid and liquid products and drying the solid phase for further use is a disadvantage [68].

HTC is relatively new and turns water-soluble and water-insoluble carbon fractions into insoluble carbonaceous solids (biochar) over hours at temperatures between 150 and 200 °C. Under supercritical upgrading, heavy oils are changed into lighter oils in minutes between 300 °C and 500 °C [69]. This process requires lower energy expense than conventional carbonization and allows for a higher product yield in less time [70]. Fig. 6 illustrates the HTL process, highlighting the production of liquids (aqueous extract and BC), solids (hydrochar), and gaseous by-products.

4.1.2. Hydrothermal liquefaction (HTL)

HTL is similar to solvent liquefaction, but water is used instead of the organic solvent and transforms feedstocks into a more energy-dense BC than the one typically obtained by biomass pyrolysis. This process occurs in a closed reactor, devoid of oxygen, through pressurization with inert gases like N_2 or He or reducing gases such as H_2 or CO (the reactor pressure must meet or exceed the saturated pressure) [71]. Usually, the reaction pressure is not controlled in the process and is autogenic, with the saturation vapor pressure of water (subcritical water) corresponding to the reaction temperature. Typically, water is used as a solvent and reaction medium under conditions close to critical, although an organic solvent like ethanol can also be utilized. The resulting products of this process consist of two liquid phases: BC (organic phase), aqueous extract (AP), and hydrochar (solid), and gasses (gas phase) [72], using moderate temperatures (200–400 °C) and elevated pressures (10–25 MPa) under inert gases like nitrogen (N_2) or helium (He) [73,74]. A shared characteristic among the three processes is the forming of aqueous products due to water's involvement in all pathways [71]. HTL is a promising thermochemical method to generate intermediates for advanced biofuels, especially from biomasses with high moisture content, such as sewage sludge, MSW, and waste from the food or agricultural industry, with minimal treatments. A distinct advantage of HTL is avoiding the drying requirement for wet feedstock demanded by other processes.

HTL offers advantages over other thermochemical processes due to its higher rate of conversion reactions, elimination of mass transfer limitations, better heat transfer characteristics, and reduction in solid residue yield [75]. By using solvents under conditions close to their critical point, their viscosity and density decrease; therefore, diffusion increases and facilitates mass transfer. The performance of the process depends on both the parameters and the characteristics of the raw material, as well as the state of the reactor. Major components such as lipids, proteins, and carbohydrates significantly affect the reaction mechanisms and kinetics, and eventually, some modifications in reactor design may be required [75].

4.1.3. Hydrothermal gasification (HTG)

HTG operates in the supercritical water region, as shown in Fig. 7, where water acts as a unique solvent, catalyst, and reactant, enhancing biomass breakdown into syngas [65,76]. Syngas is the main product, primarily composed of carbon monoxide, methane and hydrogen [65,77]. This technology is also flexible with several feedstocks, e.g., HTG of algae, at 460 °C and 27 Mpa, catalyzed with the hydrochar to maximize the H_2 production (9.63 mmol/g) [78], and co-hydrothermal gasification (co–HTG) at 650 °C and 30 Mpa to promote H_2, CH_4 formation [79].

4.1.4. Supercritical Liquefaction (SL)

SL converts biomass into liquid biofuels using solvents at conditions above critical point (see Fig. 7) as a subset of solvent liquefaction. The solvents used are typically water, ethanol, or methanol. E.g., supercritical water (scH_2O) operates at 374 °C and 22.39 MPa [80], while

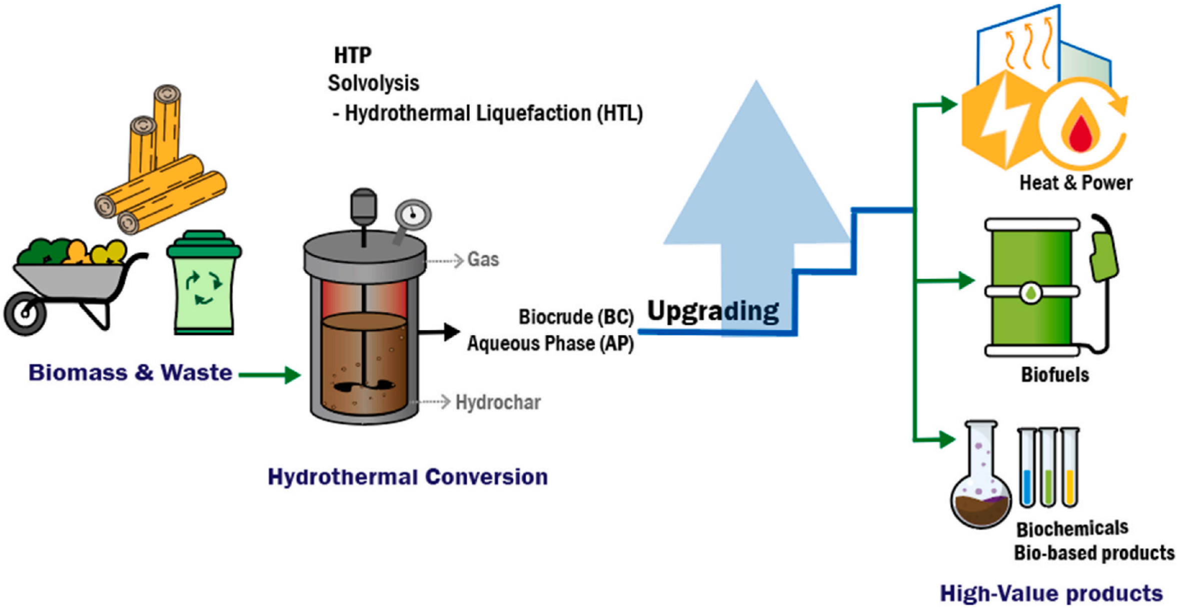


Fig. 5. Products from the hydrothermal processes.

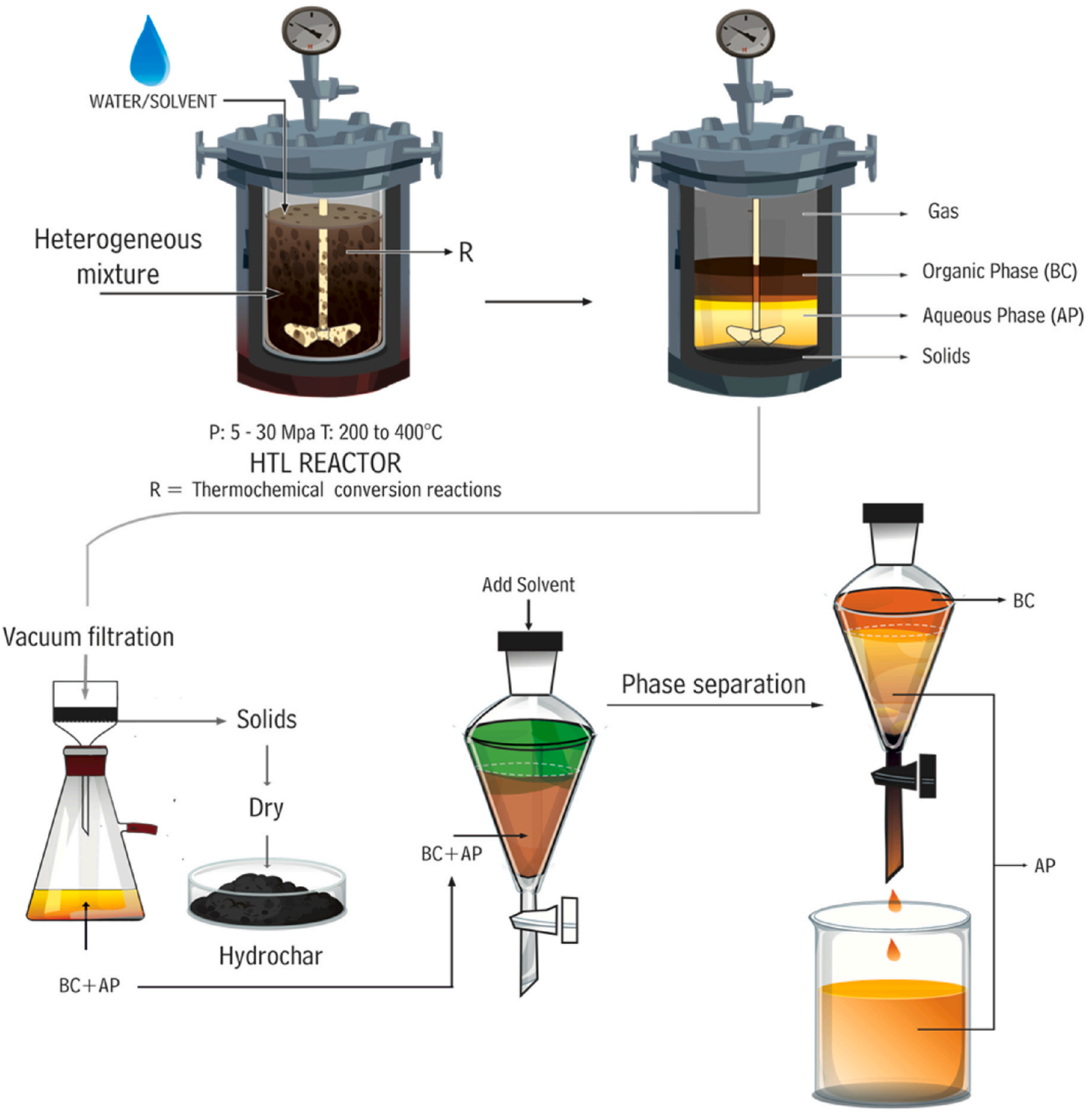


Fig. 6. Illustrative diagram of the HTL process.

supercritical ethanol (scEtOH) operates at 240 °C and 6.3 MPa [81]. Under these conditions, the solvent exhibits unique properties, such as increased solvation power and enhanced reactivity, where distinct liquid and gas phases no longer exist. This enhances mass and heat transfer, leading to faster reaction rates. This technology offers flexibility for various biomass or plastic feedstocks and product targets [82], the potential for high product yields, the ability to process wet biomass, and reduced char formation. However, due to the extreme process conditions, high energy consumption is required and can cause corrosion issues in reactor systems.

The above HTL, SL, and HTG processes are achieved using supercritical or near supercritical water temperatures and pressures as the phase diagram of water (Fig. 7), which displays its triple point and critical point. HTL is usually practiced in a small window slightly above the vapor-liquid co-existence curve or at pressures somewhat higher than the critical pressure of water (221 bar). The environment is generally more reactive as temperature rises and pressures above water vapor pressure are applied. With an increase in the severity of the reaction, different types of HTP are possible, as shown in Fig. 7. The HTL process parameters initiate reactions of the feed material, which will be extensively discussed in the next section. Process parameters that affect the outcome include total solids content (TS), holding temperature, heating rate (β), retention time (RT), pressure, and the utilization of reducing gases and catalysts (25).

Considering the variability of feedstocks that can be processed in HTL and their characteristics, it is essential to highlight the long-term permeability of a suspension with a high concentration of suspended solids as one of the main obstacles to HTL in continuous reactors [84, 85]. Many studies have been carried out on microalgae, and there is a need to optimize conditions for the practical viability of the liquefaction process. Prestigiacomo et al. [86] investigated the transfer of HTL from digested sewage sludge from batch reactors to continuous reactors, characterized by suspensions with solid particles that obstruct pumping systems, which limits its industrial application. Thus, xanthan gum, HCOOH, and KOH were used as homogenizers to prevent the precipitation of particles, resulting in improvements in performance, BC quality, and the reduction of solid waste. HTL also offers the possibility of deriving valuable organic chemicals from Kraft black liquor, a challenging waste to manage. However, it has been shown that the influence of sulfides in the black liquor (sulfur and sulfide) must be considered for

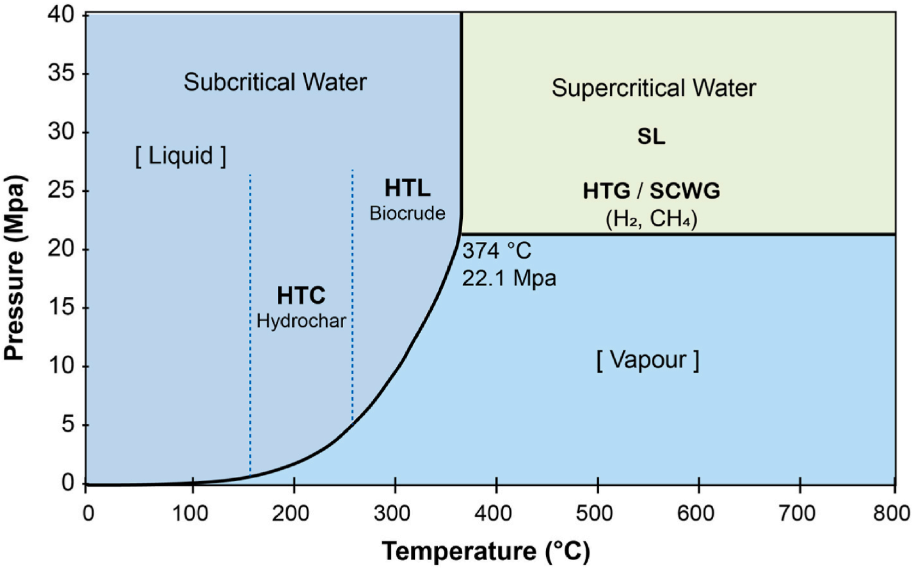


Fig. 7. P-T diagram of water to identify the different types of hydropyrolysis. Adapted from Ref.[83]

HTL treatment and subsequent processes. This is because sulfur bound to inorganic molecules actively participates in reaction pathways and is partially converted into organic sulfur compounds. An acceleration effect on lignin depolymerization caused by sulfur and sulfide has also been observed [87].

Economic and environmental analysis are necessary to accelerate the deployment of HTL and identify research and development opportunities for enhancement. Li et al. [88] addressed stochastic techno-economic analysis to evaluate the economic feasibility and risks of the wet waste HTL process in a continuous flow process. Quantification results show that the mean value of biocrude selectivity, thermal efficiency, carbon efficiency, Total Capital Investment, and minimum biocrude selling price are 42 wt %, 60 %, 57 %, 52 MM$, and $3.69/gasoline gallon equivalent (gge), respectively. In addition, feed moisture, HTL reactor model, and capital investment are the main contributors to the economic uncertainty of the HTL process. A recent analysis of sewage sludge HTL process suggests an estimated biocrude yield from 42.2 to 52.4 %, an estimated fuel yield from 34.7 to 42.7 %, an estimated minimum fuel selling price from $2.28/gge to $3.45/gge, and an estimate reduction in supply chain greenhouse gas emissions greater than 70 % relative to petroleum-derived diesel [89]. Another study by PNNL [90] evaluated four aqueous-phase product treatment and monetization options based on experimental data. These options can cut minimum fuel selling prices by up to 13 % compared to water recovery process after the hydrothermal liquefaction reactor.

An environmental analysis for hydrothermal conversion of sewage sludge (>95 % by weight moisture) showed that incineration, gasification, and pyrolysis had net global warming potentials of 129–800, 50–3183, 181–385, and 80–364 kg CO_2 equivalent per ton of total solid sewage sludge (CO_2eq/t SSdry), respectively [91–94]. In contrast, HTL presented a comparatively lower carbon footprint, with a maximum of 172 kg CO_2eq/t SSdry [95]. HTL has been demonstrated to be beneficial for producing high-energy density fuel (HHV of 25–40 MJ/kg) from wet biomass, such as sewage sludge [96], showcasing significant advantages over other thermochemical processes. For example, Jena and Das [97] evaluated HTL and pyrolysis for algal biomass. The bio-oil yield from HTL was higher (~41 %) than from pyrolysis (23–29 %).

Commercialization of HTL will require advancing from laboratory-scale batch research systems to larger continuous flow reactor systems and eventually integrating HTL into comprehensive biorefinery facilities. However, challenges such as substantial equipment costs, high operational energy consumption, and technical complexities associated with complex raw materials and products have limited the scale-up of continuous flow reactors for HTL [98].

4.2. Reactors

Reactors used in the HTP must have high-pressure and high-temperature capabilities; the reactor material must be compatible and resistant to corrosion and degradation by water, biomass feedstock, and its products at these conditions; hence, stainless steel and high-grade alloys are common choices [99]. Uniform heat distribution and efficient mixing ensure consistent reaction conditions and improve conversion efficiency. Scalability is essential to transition from lab or pilot-scale to full-scale operations; safety features like pressure relief valves and proper insulation are also critical to prevent accidents [100]. The reactor should allow for easy sampling, monitoring, maintenance, and cleaning to avoid clogging and the buildup of residues. Reactor geometry should suit the specific process requirements, including the type of feedstock and desired output [101].

Reactors used for HTP can be batch and continuous flow systems. Batch reactors are often employed in laboratory-scale studies due to their simplicity and ability to handle small sample volumes, making them ideal for process optimization and feedstock evaluation. This reactor is a stirred tank with a fixed volume and no input and output streams during the operation. Batch reactants can be stirred using different methods, such as mechanical agitators and spargers. Fig. 8 a shows a typical batch reactor. In turn, continuous flow reactors are more suited for large-scale operations, as they have a constant charge of reactants and discharge of chemicals, leading to higher throughput and more consistent product yields. The two types commonly used in literature are shown in Fig. 8 b and *c*: continuous stirred tank reactor (CSTR) and plug flow reactor (PFR).

CSTR has a continuous charge of reactants and discharge of chemicals; reactants are well mixed as in a batch reactor via mechanical impellers [102]. Impeller design and number depend on tank size and mixed material properties. PFR is a flow reactor that moves along in the direction of the flow, and all the reaction mixtures move along at the same speed; there is no mixing or backflow. The reaction mixture is well mixed, just like in a batch reactor, within each plug or on the cross-section plane of the PFR. A back pressure regulator is generally used to pressurize the system.

Additionally, if catalysts are used, the reactor design should accommodate and facilitate them, ensuring proper mixing and contact

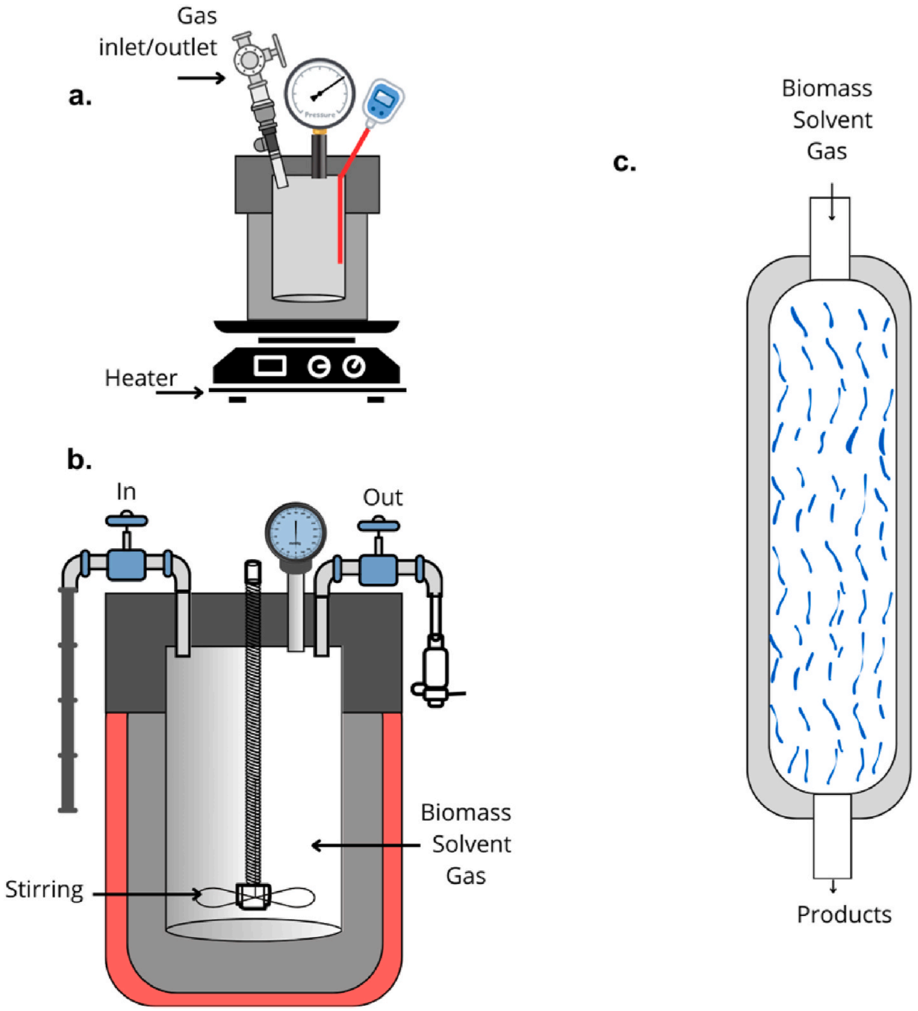


Fig. 8. The most common reactors used in HTL are a) STR, b) CSTR, and c) PFR reactors.

with the biomass feedstock. A trickle bed reactor is a gas-liquid-solid contacting vessel that can be used in these cases. Microwave and solar reactors are innovative devices used in recent years [103]. Continuous flow reactors are more suited for large-scale operations, as they enable the constant processing of biomass, leading to higher throughput and more consistent product yields (see Fig. 8). Additionally, if catalysts are used, the reactor design should accommodate and facilitate their use, ensuring proper mixing and contact with the biomass feedstock. These characteristics collectively maximize efficiency, safety, and product quality in HTP.

In Stirred-Tank Reactors (STRs), several studies have explored HTL processes for various biomass feedstocks. Zhu et al. [104] found that using isopropanol as a solvent significantly improved bio-oil yield due to its hydrogen-donating properties. Cu and Zn-loaded γ-Al_2O_3 catalysts outperformed commercial Cu/γ-Al_2O_3 catalysts in bio-oil production. Zhang et al. [105] discovered that a mixture of ethanol and water (75:25 v/v) was more effective than solvent alone. Jain et al. [106] demonstrated that HTL of high moisture content feedstock like microalgae, with potassium carbonate (K_2CO_3) as a catalyst, enhanced conversion efficiency and product quality, and produced BC rich in valuable compounds such as alcohols, long-chain saturated hydrocarbons, and esters. Cheikhwafa et al. [107] reported that various catalysts produced BC with a higher heating value (HHV) greater than 30 MJ/kg and increased biochar yield. Liu et al. [108] studied $FeCl_3$-catalyzed HTL of coffee husk, finding optimal conditions at 280 °C, 75 min retention time, and a 0.5 mol/L Fe_3+ catalyst concentration, with solvent choice significantly impacting bio-oil properties.

Although less common, continuous-flow reactors showed promising results for high-moisture feedstocks and suggested commercial viability, but they require design improvements. In most cases, continuous tube reactors are used, and CSTR are rarely applied. Emphasis will now be placed on the types and main characteristics of the reactors used in HTP applied to various raw materials, conditions, and performances (see Table 4). Barreiro et al. did experiments with microalgae [109], and Forcheim et al. [110] compared batch reactor experiments with measurements in a CSTR reactor and modeled the lignin degradation in the solvent ethanol. Silva Thomsen et al. (2024) demonstrated effective continuous wet air oxidation of the HTL aqueous phase in a tube reactor, significantly reducing organonitrogen compounds and producing volatile fatty acids. However, auto-thermal operation was not achieved [111]. L.B. Silva Thomsen et al. highlighted that heat recovery could be integrated into these processes if there is wet oxidation (WO) due to the advantage of additional heat release, which could facilitate auto thermal operation of continuous WO treatment when operating the reactors at temperatures higher than 350 °C [112]. Patel & Hellgardt (2015) highlighted that continuous plug flow reactors effectively perform HTL of microalgae with constant biocrude yields but noted challenges in pumping algae slurry and the effectiveness of co-solvents like cyclohexane in preventing char formation. Further reactor design and conditions improvements are recommended to enhance BC yield and quality [113].

STR reactors offer uniform reaction conditions, ease of operation,

Table 4
Comparison of reactor types and conditions.

Reactor	Feedstock	Conditions	Comments	Reference
STR – 100 ml Parr reactor	3 g Kraft lignin, solvents: IPA, water, water-IPA	Stirring 400 rpm, IPA for 30 min at 280 °C	Incorporating oxophilic metal ions (Mo, Zr, Ti) into Ni/γ-Al_2O_3 catalysts significantly improved catalytic activity, yielding a maximum BC production of 72 wt% with a conversion rate of 91.5 % using 3 % 10Ni–3Ti/Al.	[104]
STR – 100 ml Parr reactor	Alkali lignin, solvents: ethanol, water, water-ethanol	Stirring velocity at 400 rpm	The optimal catalyst (syn-10Cu-5Zn/Al) achieved a BC yield of 74.7 wt%, substantially increasing from the 40 wt% yield of non-catalytic reactions and 47.7 wt% yield with commercial catalysts.	[105]
STR – 1 L Parr reactor	Wet diatom biomass (80 % moisture content) microalgae	Temperature 300 °C, pressure 40 bar, duration 30 min	Catalyst K2CO3 (10 % w/w). The BC yields 22 %. Bio-silica structures products yield 56 %, and AP the remaining value.	[106]
STR – 1 L batch-type autoclave (Parker Autoclave Engineers)	Raw sewage sludge	Stirring velocity 140–160 rpm. 350 °C and 5 bar at the end 180 bar.	The tested elements (except for Cd) in the BC were identified. The highest BC yield (21.9 %) was achieved using Ni/NiO with MSS2, while the lowest yield (15.8 %) was observed for MSS1 with FeS2.	[114]
Batch reactor – 25 mL	Fecal sludge sample from septic tank located in Khulna University of Engineering and Technology Campus in Bangladesh	Temperature 320C with a corresponding pressure range of 10–12 MPa	The BC yield was 55.7 % (co-liquefaction of fecal sludge and organic solid waste with water-ethanol co-solvent). The BC has a heating value of 37.5 MJ/kg, indicating the potential to replace petrocrude.	[50]
STR – 1 L autoclave	Municipal wastewater treatment plant of Reus in Tarragona, Spain	300 °C and 86.9 bar for 30 min and agitation rate of 100 rpm.	The highest BC yield was achieved using CuSO4 (10 %), resulting in a 42.20 % yield, while TiO_2 (20 %) also significantly improved the yield to 41.90 %.	[107]
STR	Dried coffee husk	Temperature between 190 and 300 °C,	Coffee husk conversion rate of 68.47 %, with a light BC yield of 11.51 % with 34.81 MJ/kg and a heavy BC yield of 35.99 % with (40.56 MJ/kg). Overall energy recovery exceeded 60 % using n-hexane extraction	[108]
CSTR	microalgae	350 °C, 15 min Low feed (LF): 9.1 wt% High feed (HF): 18.2 wt%	Yield BC: *S almeriensis* 42.6 wt % (LF) and 51.0 wt% (HF) N. gaditana 50.8 wt% (LF) and 54.8 wt% (HF)	[115]
Laboratory-scale continuous – PFR	Microalgae, specifically Nannochloropsis sp.	Temperatures range from 300 to 380 °C with residence times of 0.5–4 min. Cyclohexane is a co-solvent that enhances extraction and prevents char formation.	The highest BC yield of 38 wt% was achieved at 380 °C and a residence time of 30 s. The BC produced had a Higher Heating Value (HHV) ranging from 36.64 to 39.27 MJ/kg, comparable to crude oil (40–50 MJ/kg).	[113]
Continuous reactor – 400 ml	The aqueous phase of the HTL liquefaction of sewage sludge	300, 325, and 35 °*C* with different residence times (3.4 and 24.8) and pressure 180, 170 and 190 bar	The WAO process removed up to 95.3 % of the chemical oxygen demand and 91.8 % of the total organic carbon, generating volatile fatty acids, acetic acid, CO2, and H2O.	[111]

IPA: isopropanol.

and flexibility, which make them suitable for various biomass feedstocks and experimental conditions. They are easier to scale up due to well-understood fluid dynamics but typically have lower throughput and higher energy consumption due to continuous stirring. In turn, constant-flow reactors provide higher throughput, better thermal efficiency, and consistent product quality, making them ideal for industrial-scale operations. However, they require precise control of overflow rates, temperature, and pressure, complicating operation and maintenance. Continuous flow reactors, especially tube ones, are more energy-efficient and scalable but prone to clogging with high solid content feedstocks and have higher initial setup costs. In terms of clogging, CSTR reactors are advantageous. The choice between these reactors depends on specific process requirements, desired product yield and quality, and economic considerations.

4.3. Products

4.3.1. Biocrude oil (BC)

HTL of biomass typically yields BC oil in the range of 35 %–60 % of the dry biomass weight. This yield can vary depending on the type of biomass and the specific conditions during the HTL process. For instance, a study by Biller et al. found that HTL of sewage sludge in batch reactors produced BC yields of around 35.4 %. In comparison, continuous flow systems yielded up to approximately 37 % with heating values between 26.6 MJ/kg and 36.6 MJ/kg [116].

Different types of biomass significantly influence bio-oil yield due to variations in their chemical composition and physical properties. e.g., lignocellulosic biomass, which has a high lignin and cellulose content, generally produces lower BC yields compared to wet biomasses like algae. As shown in Fig. S3, lignocellulosic biomasses were grouped as “plant”. Lignocellulosic materials require higher energy input to break down their rigid structures that can reduce efficiency [117]. Conversely, algal biomass, with its high lipid and protein content, typically yields between 25 % and 60 %, depending on the species and process conditions, and has a heating value of 33.1 MJ/kg, depending on the specific algal species and process parameters [118]. Furthermore, feedstocks like food waste, rich in carbohydrates and fats, tend to produce higher BC yields, sometimes exceeding 60 %, due to their hydrolysable nature [20, 119].

Additionally, BC yields from HTL of algal biomass have been shown to range between 25 % and 60 %, with a heating value of 33.1 MJ/kg, depending on the specific algal species and process parameters [118]. At mild temperatures, strain-specific parameters, such as resistant cell walls, seemed to affect conversion to BC, but the severe conditions concurring at 375 °C take apart those structures [109].

BC oil generally has a lower oxygen content (10–20 wt%) than raw biomass, enhancing its thermal stability and reducing the extent of upgrading needed [120]. However, it often contains higher levels of heteroatoms, such as nitrogen and sulfur, thus requiring further refining to meet transportation fuel standards. Despite its benefits, this BC typically requires upgrading through hydrodeoxygenation and catalytic cracking to reduce the oxygen, nitrogen, and sulfur contents and improve properties such as viscosity and heating value. These upgrades are crucial to producing fuel that meets current diesel, gasoline, or jet fuel standards [120,121].

4.3.2. Aqueous phase (AP)

In HTL, the aqueous phase also represents a useful product, with the challenge of extracting its valuable components. Pola et al. [122] used various hydrophobic eutectic solvents as extracting agents for valorizing and detoxifying the aqueous phase from the hydrothermal liquefaction of Kraft black liquor. Eutectic solvents demonstrated high selectivity for phenolic compounds and ethanol, low selectivity for volatile fatty acids and methanol, and no selectivity for fructose and non-volatile hydroxy acids. It has also been shown that advanced oxidation using persulfate as a pretreatment for this aqueous phase reduces its content of phenolic compounds and alcohols. At higher oxidant concentrations, these intermediates were oxidized to acetic acid. When Fe (II) was added as a catalyst, low concentrations (<9 mM) enhanced degradation. However, higher doses of Fe (II) led to the sequestration of sulfate radicals, thereby decreasing the oxidation yield and generating unwanted parallel reactions [123].

4.3.3. Hydrochar

Hydrochar is another valuable product obtained through HTL. Literature suggests various alternative applications of hydrochar, such as solid fuel in boilers, as activated carbon, in obtaining carbon nanotubes, and as a nutrient storage medium source after catalytic pretreatment [124]. Hydrochar has a surface area of up to 874 m^2/g [125], with high porosity, high pH value, and cation exchange capacity. These properties have sparked interest in their use as adsorbents to remove organic contaminants and heavy metals from the aqueous phase and as a soil remediation agent to improve fertility, carbon sequestration, and immobilize heavy metals [126]. Recently, it has become an effective method to selectively synthesize necessary chemicals and functional materials, as shown in Fig. 9.

The first efforts aimed at understanding the physicochemical properties of hydrochar. Then, studies were addressed to change its properties to get functional hydrochar with unique characteristics, such as heavy metal adsorption. Right now, hydrochar is a very relevant topic of study worldwide.

In this context [128], found that hydrochar produced from HTL of sewage sludge has a high phosphorus content (61,750 mg/kg), significant amounts of magnesium (58,170 mg/kg) and potassium (9873 mg/kg), and notable levels of heavy metals like zinc, copper, nickel, and chromium. However, hydrochar showed low toxicity to *Aliivibrio fischeri* and low concentrations of PAHs and PFAS. The extraction of phosphorus from hydrochar using inorganic acids has been evaluated; a maximum extraction (94 %) was achieved using 0.7 M H_2SO_4 and 6.5 h as extraction time. These results suggest that hydrochar could be a sustainable phosphorus resource for agriculture, potentially replacing mineral phosphorus fertilizers.

Compared with pyrolysis, ionic reactions are favored in aqueous medium, and cellulose, hemicellulose, and lignin depolymerization occur at relatively low temperatures under hydrothermal conditions. Specifically, most of the hemicelluloses can be extracted from the lignocellulosic materials at a hydrothermal temperature below 180 °C, and the degradation of cellulose becomes evident as the hydrothermal temperature reaches 230 °C. Additionally, unlike char from pyrolysis processes, hydrochar obtained from hydrothermal carbonation contains abundant functional groups, such as hydroxyl and carboxyl groups, suggesting that hydrochar is formed through a different pathway [129]. A possible hydrochar formation pathway is illustrated in Fig. 10.

During HTC, cellulose and hemicelluloses are hydrolyzed into oligosaccharides and monosaccharides through the cleavage of their glycosidic bonds in hot compressed water. These water-soluble oligosaccharides and monosaccharides are further degraded into small molecule compounds, such as 5-hydroxymethyl furfural, furfural, acetic acid, etc., at relatively mild conditions or decomposed into syngas at more severe conditions. Meanwhile, the ether linkages of lignin (mainly *β-O-4* and *α-O-4* linkages) are also unstable under hydrothermal conditions, and a large amount of lignin is converted into various water-soluble phenolic compounds when the lignocellulosic material is hydrothermally treated at 240 °C [130]. However, most carbon-carbon bonds in lignin (mainly *β-β*, *β-5*, *β-1*, and *5-5* linkages) are relatively stable, and they are left as the initial skeleton of "aggregated hydrochar" [131,132]. These furan compounds, derived from hemicelluloses and cellulose, subsequently react with the soluble phenolic compounds derived from lignin, forming "dispersed hydrochar" through polymerization. The reactive oxygen-containing groups on the surface of the "dispersed hydrochar" further react with the "aggregated hydrochar" and cover the surface of the "aggregated hydrochar," resulting in a hydrochar with relatively low specific surface area and poor porosity.

5. Modeling HTP

5.1. Kinetics models

Despite numerous investigations into the HTL process, its mechanism and kinetics still need to be better understood [75]. This is attributed to the complexity of chemical reactions and the generation of various compounds in the BC and AP. HTL reaction pathways can be highly intricate and contingent on the utilized feedstock's initial chemical composition. These reaction schemes still require further research for a comprehensive understanding. Zhichao Wang et al. [133] used single-model-compounds (egg albumin, microcrystalline cellulose, xylose, D-glucose, and butter) and mixed model compounds (protein/cellulose, protein/lipid, proteins/xylose, protein/glucose, and

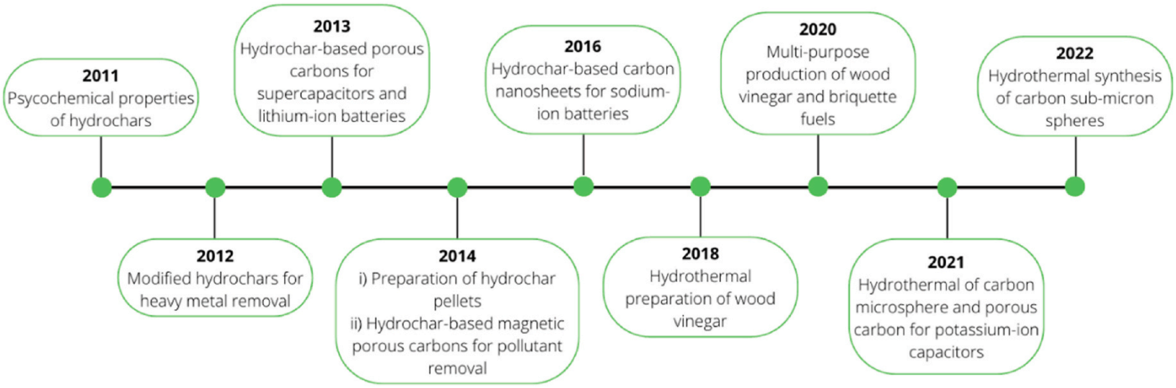


Fig. 9. Timeline of the development of high-value-added bioproducts through hydrothermal treatment. Adapted from Ref. [127].

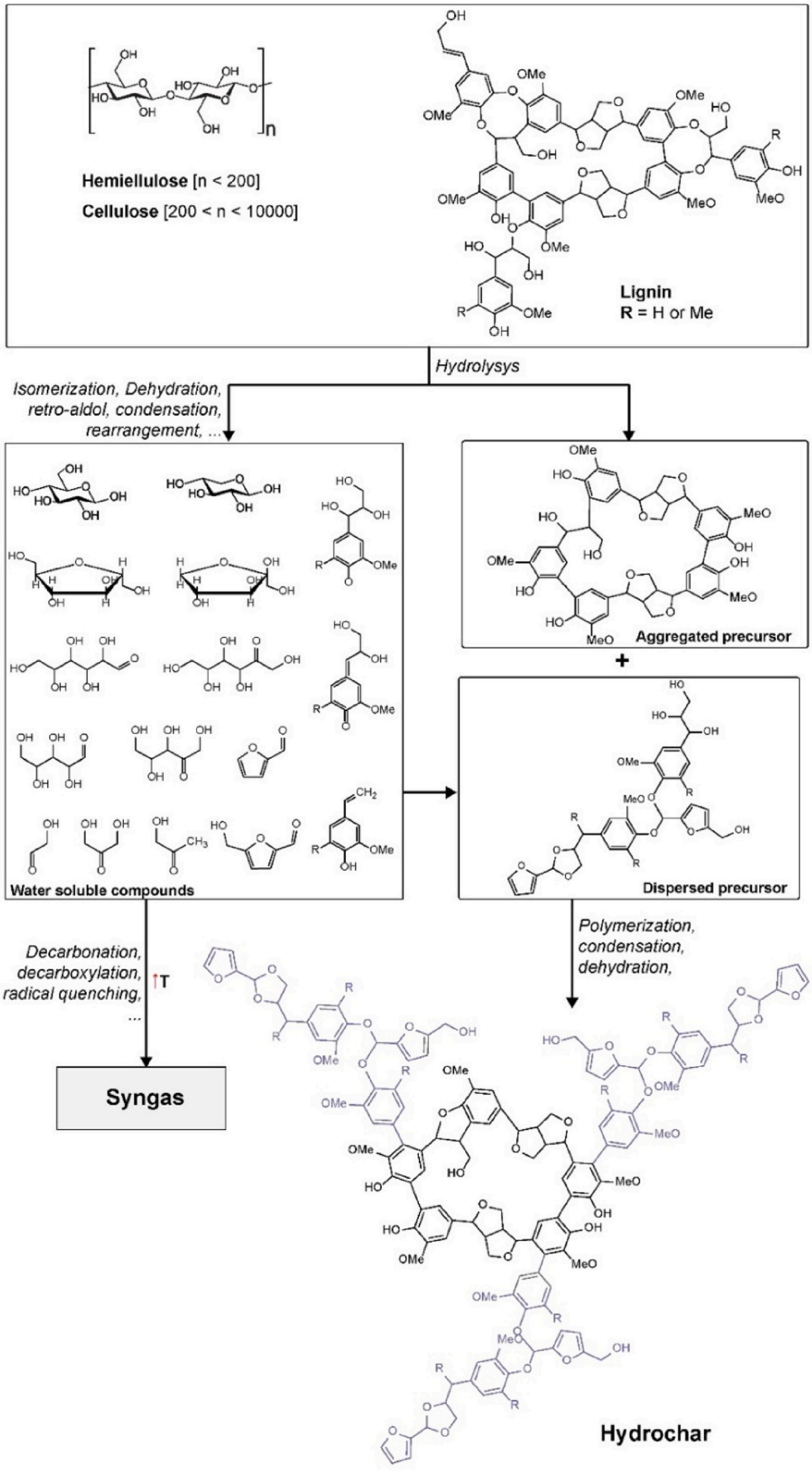
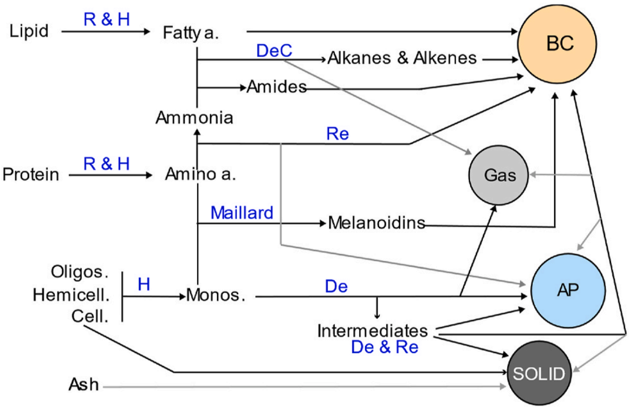
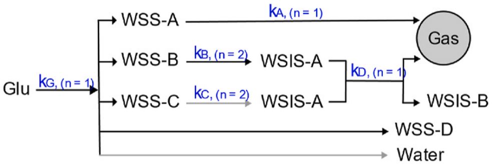
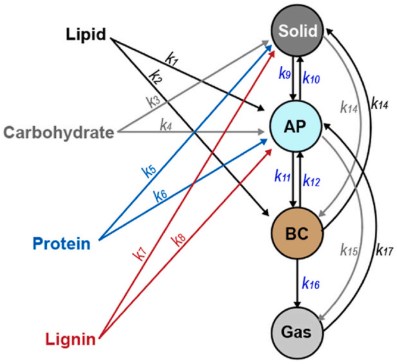
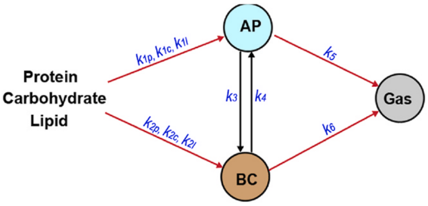
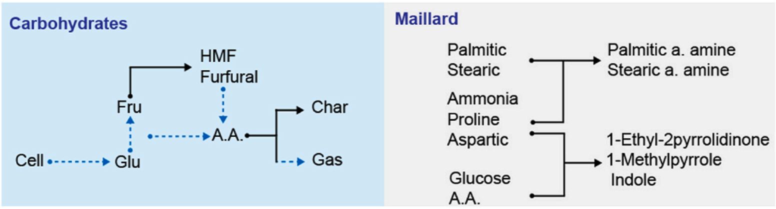


Fig. 10. A possible formation pathway of hydrochar. Adapted from Ref. [129].

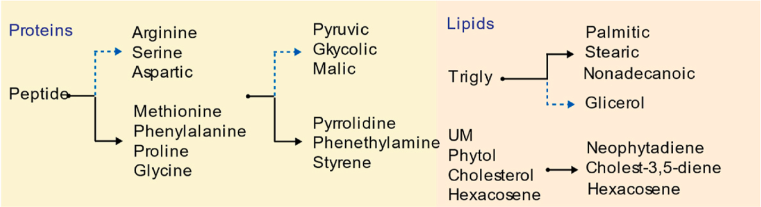
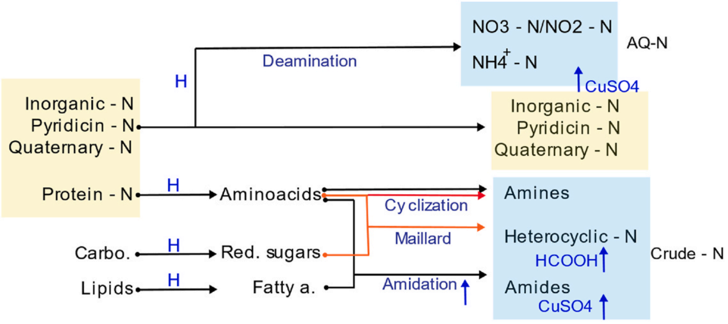
lipid/cellulose) to represent the feedstock and tracking the yield of the products (Schee 1 in Table 5). It was observed that binary mixtures reacted independently at relatively mild temperatures (300 °C, 20 min). However, under more severe conditions (350 °C, 60 min), the mixture's overall yield increased by approximately 10 %, indicating an interaction between the two model components [133]. Following Schee 2 [134], glucose decomposition in hot compressed water adhered to first-order kinetics with an activation energy of 114 kJ/mol. The reaction rate

Table 5
Mechanisms aimed at analyzing the HTL process.

No	[Reactor/Sample] Conditions	Reaction Scheme	Measured Products	Reference
1	2L/800 g T: 300–350 °C initial P of 0.65 MP t: 20–60min		BC AP Gas Solid	[133]
2	Batch quartz capillary reactors T: 250–350 °C P: non defined t: 1–14400min	 **Subgroups: A-D*	Water Carbon WSS WSIS Gas	[134]
3	11 mL/5.5g T: 250–350 °C) P: 200 bar t: 0–60 min		BC AP Gas Solid	[135, 138]
4	4.1 mL/2.3–3.7 g T: 250–400 °C P: >4 Mpa t: 10–90 min		BC AP Gas Solid	[139]
5	CSTR reactor of 1.11 m^3 with a residence time of 58.7 min. Optimized at 250 bar and 378.9 °C		Specific compounds and intermediates as presented in the scheme	[142]

(*continued on next page*)

Table 5 (*continued*)

No	[Reactor/Sample] Conditions	Reaction Scheme	Measured Products	Reference
		 *(Dashed line: aqueous, solid line: biocrude, dot-dashed line: gas)*		
6	Bath micro-autoclaves T: up to 350 °C P: up to 40 MPa (Initially pressurized to 2 MPa using nitrogen gas before heating)	 *(up arrow means increase)*	N-containing compounds	[147]

AP: Aqueous phase, BC: biocrude, H: hydrolysis, R: release, De: decomposition, DeC: Decarboxylation, WSS: water-solvent soluble, WSIS: water-solvent insoluble fractions, Oligos: oligosaccharides, Monos: monosaccharides, Hemicell: Hemicellulose, Cell: cellulose, Glu: glucose, Carbo: carbohydrates.

increased with temperature. The main products formed were aqueous phase, char, and gases primarily composed of CO_2. Char formation was associated with polymerization reactions of the primary decay products, while the gas phase was mainly formed from water-soluble decay products.

Obeid et al. [135] used model compounds representing lipids, carbohydrates, proteins, and lignin to simulate the diverse organic fractions present in biomass, according to Schee 3, which includes multiple reaction pathways and interactions between different organic components. BC yield and composition varied significantly depending on the reaction conditions and specific model compounds. This work demonstrated both synergistic and antagonistic effects in binary and quaternary mixtures. For instance, adding lignin generally reduced BC yields in binary mixtures, while certain combinations, such as carbohydrates and proteins, increased the BC yield under specific conditions. It is known that interactions between amino acids and carbohydrates increase BC yields while char formation is decreased [136,137]. Reactive intermediates from carbohydrate degradation, which cause char formation like furan and HMF, are involved in Maillard reactions and form N-containing compounds while cyclization and dimerization of amino acids are suppressed.

The kinetic model of Obeid et al. [138] evaluated the effect of biomass composition. The highest crude yield was obtained from microalgae (up to 30 %), followed by sludge (up to 25 %) and pine wood (up to 10 %). The optimal temperature for maximum crude oil yield was 300 or 350 °C, with minimal variation in BC yield after 5 min of reaction time. The model demonstrated that different types of biomasses require different kinetic parameters due to the high variability in product fractions depending on their composition. The model achieved up to 15 % accuracy in predicting product performance, showing that it still requires improvements.

Valdez et al. [139] developed a general kinetic model for different algae species (Schee 4). The rate constants showed that lipids and proteins are the major contributors to biocrude (BC). Incorporating biochemical content (protein, lipid, carbohydrate, and ash) into the reaction network and kinetic model extended its applicability to various microalgae species regardless of their growth conditions. Hao B. et al. [140] grouped several schemes for microalgae, proteins, and paunch waste, which differ in some steps or products, distinguishing, in some cases, light BC from heavy BC, primary and secondary gases, and ashes. Similar schemes have also been used in simulations with Aspen Plus and MATLAB to predict the yields of HTL products and calculate the activation energies starting from these biocomponents [141].

Shia & Yu [142] developed a detailed reaction network, considering carbohydrates, lipids, proteins, and Maillard reactants (Schee 5). This network comprises 55 components and 41 individual reactions (micro kinetics) to predict the composition changes under various conditions of algae's HTL. Also, Arrhenius's kinetic parameters were optimized to predict HTL product yields from diverse algae species. Considering the reaction routes in entry 5, these kinetic models were also used for economic analysis based on experimental results from the literature.

Catalysts play a crucial role in HTL by altering reaction pathways, thereby enhancing the efficiency and selectivity of the conversion process. In HTL, catalysts are employed to lower the activation energy required for breaking down complex organic molecules in biomass, leading to improved yields of BC oil with desirable characteristics, such as higher energy density and reduced oxygen content. By influencing the reaction mechanisms, catalysts can promote specific reactions that optimize the quality of the final products.

A catalyst is essential to stabilize the unsaturated and reactive molecules and to avoid repolymerization, e.g., redox-active catalyst stabilizes the lignin fragments and promotes the depolymerization into monophenolic compounds [143,144], the cleavage of less accessible ß-O-4-bonds, and enables the extraction of small phenolic fragments [145]. Catalysts ease the use of methanol or carbohydrates instead of pure hydrogen for dissolving the liquid product during solvolysis. It can act as a hydrogen donor [144,146]. The chemical properties of phenolic monomers differ depending on the selected catalyst [143].

Yujie Fan et al. [147], demonstrated that $CuSO_4$ is a highly effective transition metal catalyst for HTL, enhancing biocrude (BC) yields and improving its elemental composition (Schee 6). It promotes deoxygenation by reducing oxygen content and slightly lowering nitrogen levels.

$CuSO_4$ facilitates Maillard reactions between carbohydrates and amino acids, transforming nitrogen from organic to inorganic forms. It also accelerates fatty acid conversion to hydrocarbons and reduces nitrogen heterocycles through cyclization, preventing extensive polymerization into solid residues and improving biocrude quality. Although $CuSO_4$ is not a direct hydrogen donor, it indirectly supports hydrogenation by altering the reaction environment and enabling hydrogen incorporation from *in-situ* sources like fatty acids. This catalyst effectively reduces nitrogen content by promoting deamination and forming non-polar compounds while limiting nitrogen-rich heterocycles.

The heterogeneous catalyst $CuNi/SiO_2$ exhibits minimal activity in improving biocrude yields, likely due to deactivation from sulfur poisoning, standard in sewage sludge. While it slightly enhances hydrocarbon formation via deoxygenation, its performance is hindered by surface blocking from nitrogen-containing heterocycles and unsaturated fatty acids, leading to coke formation and reduced efficiency. In contrast, HCOOH acts as an acidic catalyst and hydrogen donor, promoting decarboxylation and dehydration. It boosts biocrude yields at lower temperatures but loses effectiveness at higher temperatures due to forming oxygenated intermediates like furans, which interact with amino acids to form nitrogen-containing heterocycles. While HCOOH increases yields, it also raises nitrogen content through intensified Maillard reactions, presenting benefits and limitations for HTL processes [147].

Thus, numerous reaction networks at both global and microkinetic levels explain the conversion of significant components present in various feedstocks through HTL, with a particular emphasis on algae. Consequently, all the necessary parameters for modeling are detailed in the supplementary information. This aims to provide scientists with tools to facilitate their work and better understand this technology's nature.

Biomass varies in chemical composition and structure, influencing conversion pathways, product distribution, and properties under hydrothermal conditions. It can be categorized into (**i**) lipid-rich biomass (animal fats, vegetable oils, waxes); (**ii**) carbohydrate-rich biomass (sugars, starches); and (**iii**) lignocellulosic biomass (wood residues, agricultural byproducts, energy crops, and starchy vegetables like potatoes) [148]. These components, primarily lignin, cellulose, and hemicellulose, significantly impact biocrude yield, with the trend: lipid > protein > carbohydrate [149,150].

Lipids play a dominant role in BC production due to their hydrophobic fatty acid molecules. In contrast, proteins and carbohydrates generate hydrophilic compounds, such as amino acids and sugars, that predominantly mix with the aqueous phase [151,152]. Experimental studies using model lipid compounds, such as sunflower and castor oils, have shown BC yields exceeding 90 %, significantly outperforming proteins (30–35 %) and carbohydrates (10–15 %), thus underscoring the effectiveness of lipid-rich feedstocks in BC production [150]. Carbohydrates and proteins contribute substantially to the AP, producing organic acids, phenolics, and other hydrophilic compounds, further demonstrating the challenges of converting these components into BC [153]. In addition, according to Castellano et al. [154], Miscanthus, a lignocellulosic biomass, is high in cellulose, hemicellulose, and lignin, producing BCs dominated by oxygenated compounds such as phenolic derivatives (e.g., guaiacols and syringols) and furans from carbohydrate decomposition. These BCs are characterized by heavier fractions due to lignin-derived compounds. In contrast, microalga Spirulina, rich in proteins and lipids, yields BC with a high proportion of nitrogen-containing compounds (e.g., pyrroles, pyridines) and long-chain hydrocarbons from lipid degradation, featuring lower oxygen content and easier upgrading. Sewage sludge, composed of lipids, proteins, and minor carbohydrates, generates biocrude dominated by straight-chain hydrocarbons and fatty acids, producing a lighter fraction closely resembling diesel-range fuels. Lipid-rich feedstocks (e.g., Spirulina, sewage sludge) favor lighter BC with fewer oxygenates, while lignocellulosic feedstocks like Miscanthus produce heavier, oxygen-rich BC dominated by aromatic compounds. Nitrogen content from protein-rich feedstocks complicates BC upgrading due to stable nitrogenous heterocycles, while oxygenated compounds from lignocellulosic biomass require additional processing to meet fuel-grade specifications.

5.2. *Atomistic and molecular modeling*

Understanding the fundamental mechanisms of synergistic reactions involved during liquefaction would considerably advance using molecular and atomistic modeling techniques. Complex reaction mechanisms are complicated to examine using typical experimental methods. Reactions occur at a picosecond time scale (10− 12 s), and specific behaviors of organic molecules can only be tracked and captured at an Angstrom scale (10− 10 m). Hence, theoretical calculations using molecular dynamics (MD) and density functional theory (DFT) have been widely adopted as indispensable research tools to assess reactions, interactions, and interfaces [155]. Currently, MD and DFT are regarded as "computational" tests that assist the design and improvement of typical experiment programs. To the best of our knowledge, only some studies have explored the details of the process involved in HTP at this level. Table 6 shows an overview of the publications on Molecular Dynamics.

Regarding DFT studies, Barreiro et al. [160] present the first molecular model for BC derived from HTL of microalgae in a continuous reactor at 350 °C. Based on the experimental characterization and literature, they proposed a set of molecules representative of each class of compounds to create the first molecular model of biocrude oil. They characterize the reactivity of the model molecules through DFT reactivity descriptors, such as chemical hardness and Fukui function. The proposed aliphatic molecules such as 3, 7, 11, 15 – Tetramethyl-2-hexadecene, hexadecenoic acid, 1-docosene, 1-heptadecene, heptadecane, 9Z-octadecenoic acid, 9Z-octadecenamide, hexadecamenitrile, 9Z-octadecenenitrale for light fraction and algaenam monomer, algaenam dimer, and diacylglyceride for the heavy fraction. The proposed aromatic molecules are shown in Fig. 11.

These models present some insights into HTP at atomistic and molecular scales; however, despite the potential of these techniques, significant challenges limit the accuracy and applicability of these models for biomass hydrothermal processes.

5.3. *Phenomenological models*

Due to the complexity of thermochemical conversion in HTL processes, attempts have been made to predict product yields and elemental distribution through different approaches: (**i**) multicomponent additive approach and (**ii**) kinetic model based on molecule clustering using biomass absolute or model compounds [75]. In the first case, a linear component additive approach has been used to calculate the overall biocrude (BC) yield. The simplest model (Eq. (1)) is handled as the sum of returns of individual components [161]. Then, a model (Eq. (2)) is based on different linear combinations of biochemical components and their mixture [162]. The groundbreaking study by Leow et al. [163] improved the model to predict biocrude oil yield from microalgae, but these models only predict CBO yield [164] A novel Multiphase Component Additivity (MCA) model was introduced, offering a significant advancement in predicting the outcomes of HTL processes. This model intricately links the yields and elemental compositions of HTL products to the biochemical and elemental composition of the feedstock, incorporating considerations for ash content (A) in Eq. (3). Validated against microalgae and residual biosolids, the MCA model's yield predictions were particularly notable for their ability to closely align with experimental results, as evidenced by the high R^2 values ranging from 0.646 for biochar to 0.765 for gas products. This level of predictability showcases the model's efficacy in capturing the complex interactions within HTL processes and providing a reliable framework for anticipating the yields and compositions of HTL products based on feedstock properties.

Table 6
Main studies related to HTP through molecular dynamics.

Process	Model compounds	Simulation parameters	Main results	Reference
Hydrothermal co-liquefaction	Synthetic aliphatic and aromatic polymer wastes	MD calculations based on the ReaxFF used canonical NVT and NPT ensemble in OVITO.	Insight into the synergistic reactions involved in hydrothermal Liquefaction. The synergistic radical-related reactions included 1) the ring opening of PHAs and 2) the recombination of PHA branches and short-chain aliphatic.	[156]
Degradation by supercritical water	Methyl hydrazine	MD simulations using ReaxFF using an isothermal-isobaric NPT ensemble to relax the system and a canonical NVT ensemble to simulate the oxidative degradation under different temperatures.	The principle of supercritical water oxidation is that OH radicals are fragments, thus speeding up the decomposition—proposal of two main pathways at low temperature and low oxygen content.	[157]
Depolymerization by supercritical water	Scrap tires (natural, butadiene, styrene-butadiene rubber)	MD calculations based on the ReaxFF used canonical NVT and NPT ensemble in LAMMPS. Reaction energy barriers were calculated through DFT in Material Studio using a GGA with BLYP functional and double numerical plus polarization.	Detail sulfur migration mechanism during scrap tire depolymerization with supercritical water technology.	[158]
Hydrothermal coliquefaction	Biomass model compounds and plastics	ReaxFF used a canonical NVT and NPT ensemble.	Optimal range of feedstock blended ratios and temperatures for the co-liquefaction of biomass-plastic mixtures.	[159]

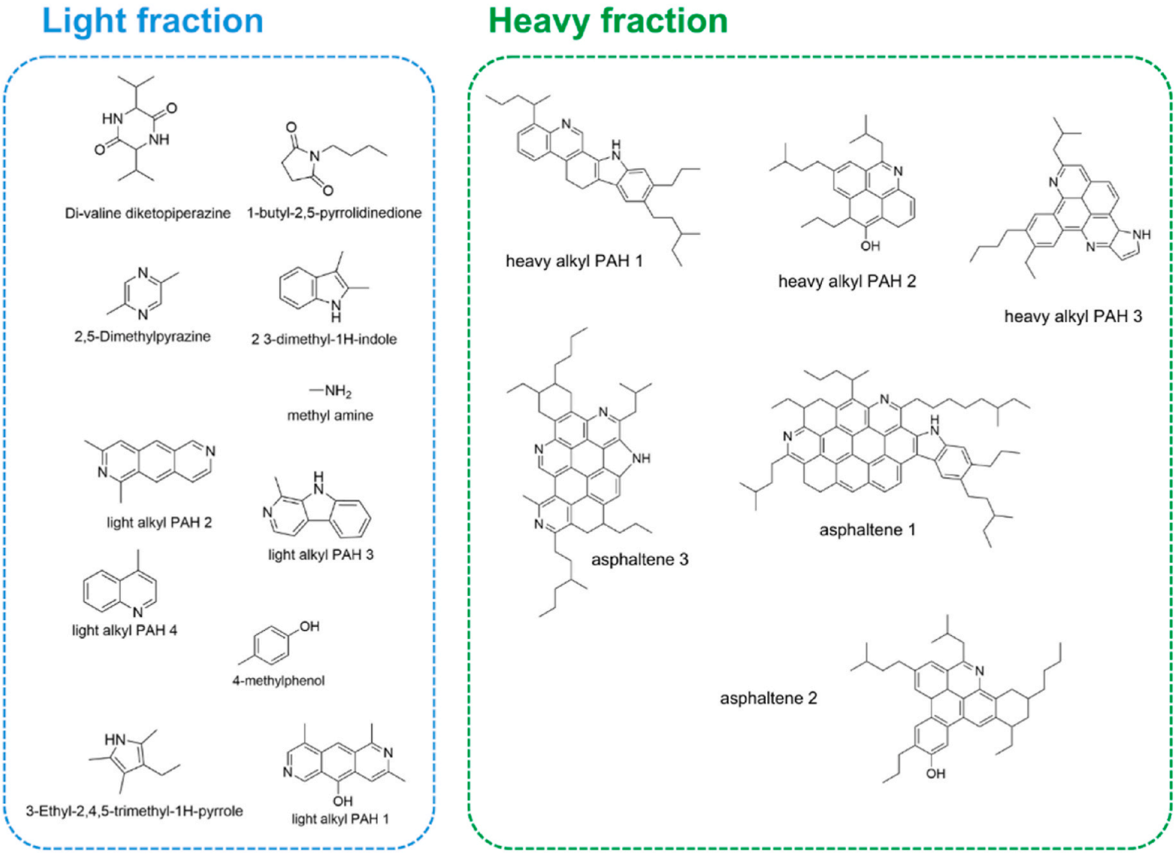


Fig. 11. Set of proposed model compounds for the light and the heavy fraction of BC derived from HTL microalgae. Adapted from Ref. [160].

$$BC_{yield}(wr\%) = k_{iL}xL + k_{iP}xP + k_{iC}xC \tag{1}$$

$$BC_{yield}(wr\%) = axL + bxP + cxC + dX_PX_C + eX_PX_L + fX_CX_L \tag{2}$$

where ***L, P, and C*** represent the lipids, proteins, and carbohydrates weight percentage. The term ***k ij*** represents the coefficient of the HTL products model. $\mathbf{X_i}$ represents the mass fraction of lipids, carbohydrates, and proteins in the mixture, and ***a, b, c, d, e,*** and ***f*** are the parameters. The first three terms represent the biocrude oil yield from each model compound individually, while the last three represent the potential interaction between components.

$$Y_i = \sum Y_{ij} = \sum k_{ij}xj = k_{iL}x\,L + k_{iP}\,x\,P + K_{iC}\,x\,C + k_{iA}x\,A \tag{3}$$

For this model, it is assumed that a fixed fraction ($\mathbf{k_{ij}}$) of each biomass component ***j*** is converted into a particular product ***i***, with the total yield of that product ($\mathbf{Y_i}$) being a linear sum of the yields of individual components ($\mathbf{Y_{ij}}$) (see Fig. 12). The elemental composition (carbon, hydrogen, and nitrogen) of the HTL product is defined as Eq. (4).

$$M_i = a\,x\,J + b \tag{4}$$

Yang et al. [165] focus on developing advanced prediction models of HTL for product yields and exploring reaction pathways, including

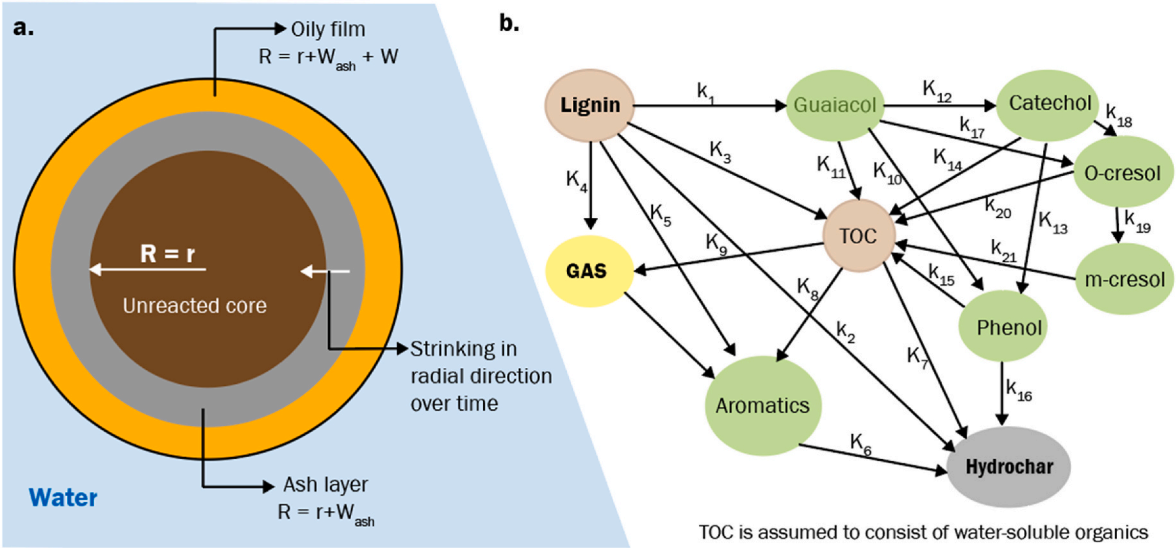


Fig. 12. a) Shrinking core model assumed for the hydrolysis of the lignin/wood particle of model components submerged in water, and b) kinetics reaction network for particle conversion. Adapted from Jayathilake et al. [176]/Hydrothermal liquefaction of wood using a modified multistage shrinking-core model (2021).

Maillard reactions. A mixture design with five model components (xylan, crystalline cellulose, alkaline lignin, soy protein, and soybean oil) was used to predict biocrude and solid residue yields. Significant findings include synergistic and antagonistic interactions between model components, which influence the yield and quality of HTL products, as shown in ternary diagrams. The model proposed by Ref. [166] in their study on microalgae HTL is notable for its rigorous and generalized approach, addressing critical aspects such as the development of reaction networks, kinetic models, and the integration of physical properties for process design and optimization. Their model is distinguished by its predictive capabilities, accurately forecasting 117 out of 160 published biocrude yields within a ±10 wt% range and 28 out of 39 published HHVs within ±5 MJ/kg. The model's multi-objective optimization identified optimal trade-offs between biocrude yield (37.2–60.0 wt%) and HHV (27.5–33.5 MJ/kg). The previous work could be helpful for preliminary process design and economic analysis, offering a solid foundation for further HTL research. The authors call for additional research to clarify reaction pathways and suggest incorporating more experimental data to refine model parameters. However, it is crucial to note that despite its advancements, this model primarily remains additive and does not incorporate phenomenological laws, which could further enrich its predictive accuracy and scope. Similarly, a global kinetic model for HTL of various algae species was proposed by Borazjani et al. [141], focused on optimizing kinetic parameters across different algae types and including an economic analysis, leveraging global kinetic modeling to assess HTL's commercial viability. This study marks a pivotal step toward understanding HTL's kinetics and its financial implications, providing a solid foundation for future research and application in biofuel production [141].

Table 7 summarizes the models and coefficients in the literature, like those explained above. They differ mainly in the coefficient values that depend on the feedstocks they applied. These models focus on calculating product yields, especially biocrude and energy values.

Rakesh [75] highlights critical areas that require further research and development, such as the need for models to account for various operating parameters more comprehensively and integrating kinetic models with advanced process simulation tools like Aspen and CFD simulations. Additionally, it points out the operational challenges faced during continuous HTL reactor operation, emphasizing the need for improved reactor design and the development of process technologies to overcome issues like choking, plugging, and corrosion during scaling-up. This summary effectively encapsulates the main findings

Table 7
Predictive models used in the HTL process for diverse feedstocks.

No	Model	Feedstock	Reference
1	BC = 0.18[a]XP + 0.06[a]XC + 0.8[a]XL	Albumin, soy protein, asparagine, glutamine	[161].
2	BC = 33.4[a]XP + 5.8[a]XC + 95.1[a]XL − 1.9[a]XPXC +27.1[a]XPXL −1.6[a]XCXL BC = 33.7[a]XP + 12.2[a]XC + 93.8[a]XL + 40.2[a]XPXC −20.5[a]XPXL −0.3[a]XCXL		[150]
3	BC = 31.6[a]XP + 6.1[a]XC + 94.9[a]XL + 3.8[a]XPXC + 35.9[a]XPXL − 21.2[a]XCXL BC = 34.0[a]XP + 11.9[a]XC + 85.2[a]XL + 33.6[a]XPXC − 2.4[a]XPXL + 10.2[a]XCXL	Albumin	
4	BC = 0.42[a]XP + 0.17[a]XC + 0.97[a]XL	Nannochloropsis oculate carbohydrate	[148]
5	BC = 0.45[a]XP + 0.22[a]XC + 0.85[a]XL SR = 0.41[a]XC + 0.18[a]XA	Microalgae	[167]
6	BC = 0.385[a]XP + 0.025[a]XC + 0.9[a]XL + 0.052[a] XLXP/1XL-XPl + 0.093[a]XLXC/1XL-XCl + 0.003[a]XPXC/1XP-XCl	Model compounds + Nanochloropsis	[168]
7	BC = 10.7 + 575[a]XSat − 4130[a]X2Mon + 65[a]X2Pro + 51.2[a]X2Car + 223[a]XSatXMon − 928[a]XSatXCar + 316[a]XMonXCar − 514[a]XPolXPro + 547[a]XPolXCab	Multiple algae specie	[169]
8	HHV = 0.3491Xc + 1.1783XH+ 0.1005Xs- 0.1034XO- 0.0151XN- 0.211Xash ΔHsf, solid = (HHV)(MW) + a (ΔHsf, CO) + b (ΔHsf, H_2O) + c (ΔHsf, SO_2) + d (ΔHsf, NO) $C_{PS} = C_1 + C_2T + C_3T^2 + \frac{C_4}{T} + \frac{C_5}{T^2} + \frac{C_6}{\sqrt{T}}$	Microalgae (Simulation in Aspen Plus)	[142, 170]

[a] BC: Biocrude, SR: Solid residue, HHV: the heating value of BC (MJ/kg), Cp: heat capacity, ΔHsf, solid was calculated in units of kJ/mol, where ΔHsf, CO = − 393.14 (kJ/mol), ΔHsf, H_2O = − 286.64 (kJ/mol), ΔHsf, SO_2 = − 294.286 (kJ/mol), and ΔHsf, NO = − 89.75 (kJ/mol), Y_{LBO} represents the yield of light BC, Y_{HBO} refers to the yield of heavy BC and C_{CS} is the percent conversion of CS feedstocks. HHV_{BC} is the HHV of BC, Y_{BC} is the yield of BC, and HHV_{CS} represents the HHV of raw CS.

regarding HTL modeling limitations and suggests future research directions to enhance the process's predictive accuracy, efficiency, and scalability.

Riju De [171] proposed an equation for optimizing a batch hydrothermal liquefaction of two microalgal species] optimized strategies of batch HTL of microalgal species through a phenomenological model in MATLAB software. The maximization of BC yield is determined according to the model equations in Eq. (5).

$$max_{THTL\ (t)} = \frac{x_{biocrude}\left(t_f = 60\right)}{x_{biomass}(t = 0)} x100\% \tag{5}$$

The first reactor configuration obtained an 11 % and 6.18 % increment for optimal BC yields and reduced batch times, respectively.

A different path is applying a thermodynamic approach to modeling, which offers advantages over the additive and kinetic models described above. Thermodynamic equilibrium modeling allows for the prediction of helpful information about feedstocks and process conditions that have not been tried before. Although the performance of a kinetic model or a component additivity model may be superior to the thermodynamic one, this is true only for a narrow range of feedstock and process conditions, i.e., those used to build such models; therefore, it is necessary to be carefull when using them to predict new systems. Cascioli and Baratieri [172] made a first attempt at a predictive model using high-pressure thermodynamic analysis, with a model based on the Gibbs free energy minimization method extended to multi-component and multiphase systems by considering the excess Gibbs free energy (G) to account for the different behavior of mixtures under high-pressure conditions. To solve the system, it was necessary to consider the fugacity calculated using the SRK EoS and the activity coefficient determined by the UNIFAC contribution method.

The SRK *(Soave-Redlich-Kwong)* equation of state *(EoS)* is used to model vapor-liquid equilibria, particularly in high-pressure systems. It extends the van der Waals equation by introducing an attractive term to account for intermolecular forces, thus improving predictions of non-ideal gas behavior. The SRK EoS is represented as:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \tag{6}$$

where a and b are parameters derived from critical temperature (T_c) and critical pressure (P_c) of the species. The SRK equation also calculates the fugacity coefficient (ϕ) to account for deviations from ideal gas behavior, which is crucial in phase equilibrium modeling.

The **UNIFAC** *(Universal Quasi-Chemical Functional-Group Activity Coefficients)* model [173] is a group-contribution method used to calculate activity coefficients in liquid-phase systems. It predicts the non-ideal behavior of mixtures by dividing molecules into functional groups and estimating their interactions. The activity coefficient (γ) is split into two parts: the combinatorial term, which accounts for the size and shape of molecules, and the residual term, which accounts for specific interactions between groups. This approach is particularly useful for modeling multicomponent systems without requiring extensive experimental data, as it allows for predicting activity coefficients under various conditions. Variants, such as the Modified UNIFAC Dortmund model [174], improve accuracy by incorporating temperature-dependent interaction parameters and additional corrections for specific molecular interactions.

Together, the UNIFAC model and SRK equation provide a robust framework for thermodynamic modeling by enabling accurate predictions of phase behavior in multicomponent and multiphase systems. This integration is essential for designing and optimizing processes such as biomass conversion under high-pressure conditions.

Furthermore, X is considered a solid particle in the multi-component system, so it was extended to a number of phases, 'k' (NP), with a number of chemical species; 'I' (NS), with constant temperature (T) and pressure (P), as in Eq. (7):

$$G = \sum_{i=1}^{NS} \sum_{k=1}^{NP} n_i^k . \ \mu_i^k \tag{7}$$

μ_i^k *and* μ_i^k are the number of moles and the chemical potential of species i in phase k. G is divided into the ideal part and the excess of G as in Eq. (7) where f_i^k represents the fugacities of the i$^{\text{-th}}$ species in the k$^{\text{-th}}$ phase as in Eqs (9) and (10).

$$\mu_i^k(P,T) = \mu_i^0(P) + RT \ln \frac{f_i^k}{f_i^0} \tag{8}$$

$$f_i^g = \phi_i^g \ . \ x_i^g . \ P \tag{9}$$

$$f_i^l = \gamma_i^l \ . \ x_i^l . \ f_i^{0,l} \tag{10}$$

Being fugacity coefficient (Φi), the activity coefficient (γil), the molar fraction of the gaseous phase (x_i^g), and the molar fraction of the liquid phase (x_i^l). The fugacity of the liquid phase at standard conditions is represented by $f_i^{0,l}$.

This gas-liquid equilibrium model was implemented by using the UNIFAC model, and the SRK equation of state [175] was able to predict BC yield with an error of 23 % (17.60 wt% predicted vs. experimental yield of 14.23 wt%) using model systems. More details of the model and considerations are described in Ref. [172].

Furthermore, Jayathilake et al. [176] proposed a mathematical model for biomass using a shrinking core approach to model lignin particle hydrolysis and a similar model for wood particles. The model focuses on the radial decomposition of the particle, the formation of an oily film, and an ash layer around the particle during the liquefaction process. It also includes a kinetic model to describe further decomposition and polymerization reactions and a layer model to study the processes inside the particle. This model considers mass and energy transfer, as well as variations in temperature and concentration of chemical species, providing a detailed insight into lignin liquefaction under hydrothermal conditions. Another model for hydrothermal lignin depolymerization was made by Forchheim et al. [177] by lumping main reaction products and determining formal kinetic rate coefficients.

This model's predictions showed good agreement with experimental data, especially at longer residence times, supporting the model's reliability. However, the formation and behavior of the oil film and ash layer around the lignin particles were not experimentally validated. Additionally, the behavior of particles within the process, such as mass and energy transfer and variations in temperature and concentration, was not validated either [176]. Therefore, significant work to improve the model and develop strategies to validate specialized models like this one is still needed, which are promising for understanding biomass particle conversion by HTL.

5.4. Phase equilibria models

Phase equilibria are of fundamental importance to understanding and designing HTP. While it is generally assumed that there is a single, homogeneous liquid phase present at reaction conditions, one initial study suggests that there might be two liquid phases [178]. Additionally, vapor-liquid equilibria play a role, and given the high partial pressures achieved during operation, dissolved gases must be modeled adequately. Another aspect to consider is the presence of a solid phase given by the hydrochar particles generated in the reactor. These aspects are directly related to reaction kinetics modeling since different phases and their relative concentrations directly affect reactions taking place. It is therefore of fundamental importance to connect phase equilibria with reaction models to better understand phenomena taking place inside the reactor.

Another important aspect of phase equilibria has to do with the problem of product recovery, which is discussed in more detail below (section 6.3). The method of product recovery from the two product phases, biocrude and aqueous phase, decides the yield and quality of the main biocrude product. Understanding extraction is key to design efficient and economically viable processes and helps understanding differences between laboratory studies that apply different solvents for product recovery [179].

Even though there are phase equilibria models, how they could be applied to HTL is mainly unknown. While it is pretty straightforward to assume that an equation of state needs to be applied to cover reaction conditions, it is also possible to apply gE-models for product recovery because typically (near) ambient conditions are applied in that case. The main challenge associated with modeling biocrude is the interplay of its complex composition, unknown oligomers, missing thermophysical properties of most of the biocrude's compounds, and parameters to feed the chosen phase equilibrium model [180]. A framework to model liquid-liquid equilibria of fast pyrolysis derived bio-oil has been proposed, but it remains unknown how that applies to the specific characteristics of biocrude [181]. The specific nature of compounds derived from thermochemical decomposition of biomass needs to be addressed because many of the compounds used to develop current models are based on fossil derived data, i.e., consider chemical compounds of less relevance to this new application [182]. It was shown that optimizing parameters, e.g. for UNIFAC, as an interesting gE-model leads to an improvement in predictive capability [183].

A correct representation of the chemical composition of the present phases is key when using phase equilibrium models to understand what phenomena are occurring in the reactor of hydrothermal processes. As a strategy, mixtures of surrogate compounds could be used to represent the chemical structures of still unknown oligomers using theoretical structures from the literature. This has achieved promising results for levoglucosan extraction systems from fast pyrolysis bio-oil [181,184] and could significantly help understanding the nature of hydrothermal processes. However, it is advisable to combine efforts to elucidate the unknowns fraction using combined analytical techniques and computational tools, which could model the processes more efficiently.

6. Challenges

6.1. Modeling challenges

One of the most challenging topics, yet one that offers significant opportunities for future research, is the mathematical modeling of hydrothermal processes. As highlighted in this review, the hydrothermal process involves multiple simultaneous and sequential reactions, such as hydrolysis, depolymerization, decarboxylation, and hydrogenation [185], which are challenging to model accurately due to the lack of comprehensive kinetic data. Furthermore, biomass is highly heterogeneous, consisting of various organic components like cellulose, hemicellulose, lignin, proteins, and lipids, each reacting differently under hydrothermal conditions [101]. In addition to chemical heterogeneity, there is heterogeneity in phases within the reactor under high pressure and temperature conditions, with at least two immiscible liquid phases (polar and apolar) present at the same time, a gaseous phase dissolved in the liquids by the effect of high pressure, and a solid phase corresponding to the hydrocarbon particles. These heterogeneities complicate the definition of input parameters for kinetic models and represent an enormous challenge in defining strategies for their experimental measurement over time.

In addition, developing reactor-scale models that account for chemical kinetics and transport phenomena is a significant challenge. As previously mentioned, the current scientific literature includes several mathematical models that incorporate particle-scale transport phenomena [186–189], primarily based on the well-known Shrinking Core Model (SCM). Although these models account for particle-scale transport phenomena, they are insufficient for making reactor-scale predictions. Thus, significant advances are needed in several areas, as outlined below.

At the particle scale, current particle models based on the SCM are strictly valid for non-porous particles, where reactions occur exclusively on the external surface of the particle. However, this assumption does not hold true for all materials because HTL technology can also be applied to porous materials with internal microstructures. In those materials, reactions may occur throughout the particle's volume rather than being confined to their external surface; in such cases, reaction models like the Changing Grain Size Model (CGSM) [190] or the Random Pore Model (RPM) with diffusional constraints [191] are more appropriate. These models explicitly account for the porous nature of materials by representing the structure as networks of pores (in the RPM) or ensembles of grains (in the CGSM), offering a more accurate depiction of the process compared to traditional SCM-based models. Additionally, the current SCM-based models are not suited for predicting product yields from a general multicomponent biomass feedstock in HTL [192], and several challenges remain for future research. One of them is predicting the structural evolution of the biomass particle, such as variations in porosity, specific surface area, and shrinkage or swelling phenomena—factors already modeled in other thermochemical processes like pyrolysis [193] and gasification [191]. Finally, aspects such as particle shape and anisotropic transport properties should also be addressed, as has been explored in biomass pyrolysis studies [194].

Another aspect that future HTL mathematical models should address is particle non-uniformity. While some particle-scale modeling approaches have been discussed, these models typically describe the behavior of a single-sized particle, whereas the particles entering the reactor exhibit a size distribution. Therefore, a potential area of future research in HTL modeling could focus on using methods such as population balance models [195] to describe the behavior of the entire particle size distribution.

Finally, to fully capture reactor-scale phenomena, it is essential to model extraparticular processes occurring at reactor scale. This can be achieved through methods such as finite volume (FVM) or finite element methods (FEM), which allow for the simulation of the momentum equation at the reactor scale, considering the complexity of fluids under subcritical conditions, potential extraparticular reactions and phase equilibrium phenomena.

This review proposes the following strategy to advance HTL process modeling.

i. We suggest focusing research efforts initially on developing detailed particle models for general multicomponent biomass feedstock, including intraparticle mass and energy transport.
ii. Subsequently, strategies such as population balance models should be explored to account for the non-uniformity of particle size distribution.
iii. Defining strategies to evaluate phase equilibrium models (liquid-liquid equilibrium, vapor-liquid equilibrium, and solid-liquid or solid-vapor equilibrium) that enable understanding interactions and mass transfer between them.
iv. Finally, a Computational Fluid Dynamics (CFD) model would be appropriate, which, in addition to solving the momentum equation to determine velocity profiles within the HTL reactor, also considers extraparticular reactions.

It is also challenging to model the complexity of the process at the molecular scale using techniques related to DFT and MD to elucidate production routes, dilution capacity, and the respective thermodynamic properties in multiphase and multicomponent systems. The complexity of biomass composition, high-temperature and high-pressure conditions, reaction mechanism complexity, water's role as a reaction medium, lack of experimental data for validation, computational resources and time scales, modeling catalyst-biomass interactions, multiphase systems, and model transferability and scalability. Some future directions could be advanced force fields that can capture the behavior of complex biomass structures and water under extreme conditions and improved experimental techniques to develop better ones for probing biomass processes, providing more data for model validation.

High-pressure and high-temperature conditions further complicate modeling efforts, resulting in the non-ideal behavior of solvents and reactants. The process operates in a liquid or quasi-liquid medium where biomass interacts with added solvents or water, along with solids and gases released by thermochemical conversion reactions within a closed reactor. The effects of different solvents, especially water in supercritical or near-supercritical states, significantly influence reaction pathways and phase behavior, thus requiring detailed understanding and data. Catalysts also play a crucial role in altering reaction kinetics and pathways, thus requiring detailed kinetic and mechanistic information for accurate modeling. Predicting the yield and composition of the diverse products—BC, hydrochar, AP, and gases—is another major challenge made up by complex interactions and transformations.

Efficient heat and mass transfer are crucial for HTL, yet modeling these aspects in a rapidly changing reaction environment is challenging. Scaling-up from laboratory to industry involves addressing differences in reactor design, flow dynamics, and operational conditions, all impacting the HTL process. Finally, integrating all these factors into a comprehensive phenomenological model results in high computational complexity that demands significant computational resources and advanced numerical techniques.

6.2. Technical and environmental challenges

The technical and environmental challenges of hydrothermal Liquefaction (HTL) include handling a wide range of biomass feedstocks with varying compositions, which can affect the efficiency and output of the process. HTL operates under high temperatures and pressure and requires robust and corrosion-resistant equipment. Environmentally, while HTL reduces greenhouse gas emissions by converting biomass into renewable energy, it also generates wastewater containing organic compounds and nutrients, which requires effective treatment before discharge to prevent pollution. Optimizing energy use and minimizing by-product formation are crucial for improving HTL's sustainability and commercial viability.

HTL is regarded as an alternative offering significant advantages over other thermochemical process-based technologies, such as improved reaction speeds, enhanced heat capacity of bio-oils, and using diverse biomasses with high moisture content without the need for prior drying. However, due to the requirement for managing high pressures and the complexity of feedstocks, specific, high-investment designs may be necessary. This technology can be challenging to implement in developing countries, where feedstocks have more potential, such as the organic fraction of MSW.

6.3. Challenges in liquid products separation

Phase separation of liquid products poses several challenges due to the complex nature of the products generated during the process. One of the main challenges in separation is the formation of Pickering emulsions caused by fine solid particles [196], which complicates the separation of the aqueous (AP) and organic (BC) phases. These emulsions can be stable, sometimes taking days to separate, making gravity-based methods alone insufficient for effective separation [197]. In addition, the presence of solids and ash can cause blockages in the system and fouling of heat exchangers and filtration systems, especially under the high temperature and high-pressure conditions required for the process. These problems require the use of advanced filtration and cleaning techniques to ensure efficient and continuous operation of the process [198]. Solvent extraction is used to improve the efficiency of separating biocrude oil from aqueous and solid phases, which is challenging due to stable interactions between solids and active species at the interface in the aqueous and organic phases. Solvents such as mixtures of toluene and heptane have been proven effective in separating the phases at high temperatures (around 80 °C), favoring rapid sedimentation [199]. Guo B. separated biocrude and solids from the aqueous phase by centrifugation (8000 rpm for 5 min), but the use of DCM as solvent allowed complete phase separation after 2 h and with a higher yield of 9 % of BC, thus demonstrating the usefulness of solvents [200]. In addition to solvent extraction and centrifugation methods, two-phase solvent extraction is often required to isolate BC, using solvents such as toluene and heptane to help separate the phases [201]. In the same way, Mathanker et al. [196] found that solvents such as acetone and THF effectively isolated bio-oil from the aqueous phase while minimizing solid residues. However, in scale-up processes and practical applications, it is necessary to invest in solvent extraction and recovery systems as well as their management.

Currently, eutectic solvents (ES) and deep eutectic solvents (DESs) have gained significant attention as eco-friendly and cost-effective alternatives to conventional solvents for various separation processes due to their unique properties, such as tunable polarity and ease of preparation, making them suitable for a wide range of applications [202]. In this way, Lucía Pola et al. [203] used ES (combinations of menthol or thymol with octanoic, decanoic, or dodecanoic acid) to extract phenolic compounds from the aqueous phase of hydrothermal liquefaction (HTL) of Kraft black liquor. They demonstrated high extraction efficiency with average yields of 66 %–91 % using menthol-based solvents and 34 %–98 % using thymol-based solvents. This process achieves a more biodegradable raffinate that can be used for subsequent catalytic or fermentation processes. Thus, they demonstrated the potential of eutectic solvents to efficiently separate valuable compounds from the aqueous phase while minimizing toxicity and improving sustainability. However, there are still significant challenges in using ES, starting with its recovery and regeneration from waste streams after separation, as it has not yet been studied. This is crucial for the process to be viable on a larger scale. It is compatible with real wastewater because most studies focus on synthetic or model aqueous solutions, leaving questions about real systems unresolved. Finally, although eutectic solvents are considered "sustainable or green" [197], the economic viability of scaling up these processes and the environmental impact of their use on a large scale are still a cause for concern because knowledge on this subject is lacking.

Emerging biorefineries should also consider treatment in the aqueous phase as an important aspect. Kemal Aktas et al. [204] found that granular activated carbon (GAC) was highly effective at removing contaminants, achieving up to 66 % COD removal, 94 % phenolic compound removal, and almost complete removal of pyrazines and pyridines from the aqueous phase. GAC outperformed biochar and hydrochar, which had significantly lower adsorption capacities. GAC also selectively retains valuable volatile fatty acids (VFAs), which can be valorized by anaerobic digestion while removing inhibitory compounds that would otherwise impede biological processes. Also, electrochemical oxidation can reduce 99 % of the chemical oxygen demand of HTL aqueous phase with a significant energy cost [205]. Other treatment methods include direct recycling [206], catalytic hydrothermal gasification (CHG) [207], which converts organics in the aqueous phase into methane and carbon dioxide, achieving near-complete removal of chemical oxygen demand (COD), and anaerobic digestion (AD) [208], which efficiently converts organics into biogas but requires dilution to prevent toxicity from salts and organics. While AD is less costly than CHG, it is more expensive than direct recycling [209].

Although there are significant developments and knowledge, the separation/extraction of liquid products faces ongoing challenges, mainly due to stable Pickering emulsions, which complicate phase separation and require costly, advanced technologies. Scaling up solvent extraction, though effective, adds complexity to solvent recovery and environmental impact, with economic concerns around operational costs. While DESs offer a greener alternative, their recovery and application in real wastewater systems remain under-researched, posing economic risks.

Although efficient, energy-intensive methods like CHG and electrochemical oxidation have high operational costs for AP treatment. GAC is promising for removing contaminants and retaining valuable VFAs, but balancing performance with costs remains an issue, especially in anaerobic digestion. The economic viability of integrating these technologies into biorefineries while managing energy use and material recovery is a key challenge.

6.4. Characterization challenges

The HTC of biomass residuals and waste materials to produce hydrochar is still in its early stage of development. Therefore, many aspects require additional research, thus also product characterization. Hydrochar characterization, such as solid yield and chemical composition of biochar and hydrochar, as well as their morphological characterization, will play a vital role in determining their importance and application in the industry and environment. Therefore, it is essential to analyze the different thermochemical pre-treatments and the different operating conditions in the formation of a final product, which will have different physical and chemical characteristics; e.g., for energy application, it is necessary to have a hydrochar with high carbon content and low ash content; for applications in agricultural and wastewater treatment industries, it is necessary to have a hydrochar with high surface area and high adsorption capacity.

The analytical challenge in the characterization of HTL products in BC is that most of the formed molecules are too large to be detected via gas chromatography. However, it is often used, and therefore, only a minor part of the formed products is characterized in detail. Only elemental analysis and total organic carbon (TOC) data are generally mentioned to describe the overall composition. High-resolution tandem mass spectrometry (HRMS) allows the observation of the elemental composition and relative abundance of many organic reaction products in BC. The study of Zimmermann et al. [210] uses HRMS to get insight into the characterization of BC from sewage sludge after sequential extraction. The advances in hydrothermal carbonization chemistry of sewage sludge offer huge potential to impact the distribution of the product, its characteristics, and the process energetics. Therefore, advances in these aspects will provide an opportunity to construct a high-efficiency industrial chain for energy and resources recovery from sewage sludge by a controlled hydrothermal process and for considering the critical hydrothermal conditions, their influence on the reaction mechanisms, product characteristics, dewaterability improvement, and process energetics [211,212].

When lignocellulosic biomasses or lignin are depolymerized, organic fractions rich in lignin oligomers are obtained, ranging from monomers to large structures. Characterization has been achieved for small structures that can be analyzed by GC-MS (mostly monomers). However, the larger structures are still unknown, which represents a challenge to fully elucidate them despite the existence of robust spectrophotometric (FT-ICR MS, GALDI-MS and MALDI-FT-ICR MS, H-ESI-FT-Orbitrap MS, NMR 1D and 2D) and chromatographic (SEC/GPC, Gas and liquid chromatography and its derivatives) analytical techniques. However, the problem lies in several aspects, among which the following stand out: the impossibility of analyzing large structures in GC-MS, thermal instability of the structures that, instead of volatilizing when subjected to high temperatures, decompose and lose their nature, and lack of commercial analytical standards to identify and quantify these compounds by chromatographic techniques such as HPLC and UPLC. There are also no databases to compare the results, which makes their elucidation and understanding even more difficult. However, some alternatives could be a start using advanced techniques with columns (resistant to high temperatures $\sim 420\ ^{\circ}C$) and special conditions of derivatization and analysis by GCxGC-MS, as Dao Thi et al. [213], who managed to identify 36 phenolic dimers, and 21 trimers obtained from lignin fractions. The use of analytical techniques combined with robust sample fractionation and cleanup and compositional tools could be an excellent start to elucidate the mysteries of these up-and-coming liquid products.

6.5. Economic challenges

In comparison to other thermochemical conversion technologies, HTL has both significant advantages and disadvantages with respect to economic viability and barriers to entry. As noted above, a major advantage to HTL is that it does not require a drying step to accept wet feedstocks such as MSW, sewage sludge and food waste, which are usually significantly less valuable than dry feedstocks such as woody biomass and agricultural residues. These dry feedstocks, although in abundance, often do have other uses and therefore are a cost to the biorefinery. Moreover, they often have a cost of disposal or a gate fee, that largely offsets the costs of transporting waste to the HTL plant [214,215]. Another consideration is that HTL BC is often less oxygenated than the corresponding pyrolysis bio-oil and that can lead to cost savings during the upgrading and refining steps, for example consuming less hydrogen or needing less frequent catalyst replacements [216]. Jing et al. reported a minimum fuel selling price (MFSP) for fuels derived from HTL and hydrotreating upgrading of the BC at $2.28–3.45 gge. Rhaman et al. [216] compared the cost to produce jet fuel from MSW via HTL or pyrolysis followed by BC upgrading and found that the cost was $2.72/gallon for HTL and $3.21/gallon for pyrolysis. Conversely, for wood (a dry feedstock), Moreira et al. [217,218] found that BC from HTL as a direct replacement for fuel oil would require a price of $1.75-$2.97 per kg for a 5-year payback in Brazil, whereas pyrolysis would only require a price of $0.87 for bio-oil.

Despite the advantages HTL poses for wet feedstocks, there is still a high barrier to entry. Due to the requirements for high pressure processing, capital expenditures for HTL are generally higher than for pyrolysis. For example, in the above-mentioned wood-bio-oil production study, Moreira et al. [217,218] found that the capital costs were 3–5 times higher for HTL than for pyrolysis. Similarly, for MSW in a 2000 ton per day plant, Rhaman et al. [216] reported a $78.1 million cost for the HTL plant, and a $65.1 million cost for the pyrolysis plant.

7. Conclusions

This study explores the potential of hydrothermal conversion processes as promising options for converting wet biomass resources into valuable liquid intermediates that can be upgraded into renewable chemicals biofuels in integrated biorefineries. Several challenges need to be overcome to make these biorefinery concepts economically and environmentally sustainable.

- The hydrothermal process demonstrates remarkable versatility for converting diverse biomass types, including lignocellulosic residues, microalgae, municipal solid wastes, and sewage sludge, which positions these technologies as viable options for advanced biorefineries. However, variability in the composition and structure of these feedstocks presents significant challenges regarding consistent performance. For instance, BC yields from HTL can vary considerably, ranging from 35 % to 60 % of the biomass dry weight depending on biomass type and process conditions. This underscores the need for adaptive models that optimize conversion efficiency and ensure operational stability.
- Feedstocks are plentiful and inexpensive (or cost-negative) but also heterogeneous; the range of biomasses used in HTL and HTC, and their physicochemical characteristics is highly diverse. This study analyzes a broad selection, highlighting lignin's notable performance in biocrude BC yield and organic co-solvents (EtOH, IPA) and water, contributing to an enhanced calorific value. While other biomass characteristics did not exhibit clear trends, these insights could be refined by collecting and analyzing a larger dataset. As the data set grows, it will be better able to predict results for different potential

HTL feedstocks, including MSW, food wastes, algae, animal manures, and other emerging waste streams.

- Advances in modeling are essential to improve simulation accuracy for hydrothermal processes, which often operate under extreme conditions of up to 350 °C and 20 MPa. Current models based on population balance equations and high-resolution simulations allow for more accurate predictions of reaction dynamics and optimization of product yields. Recent studies have shown that BC derived from fecal sludge and organic solid waste in batch reactors achieved yields of up to 55.7 % using a water-ethanol co-solvent system, with a heating value of 37.5 MJ/kg, comparable to that of petroleum crude. Additionally, in continuous reactors, BC produced from microalgae reported yields ranging from 42.6 % to 54.8 %, depending on feed concentration, highlighting the importance of precise control over operational parameters.
- Properly representing the composition of the phases involved in the process is a challenge for science, especially with the fraction of unknown oligomers, which represents one of the most significant gaps in understanding the process. Strategies such as using surrogate mixtures that may include theoretical chemical structures may be viable to enable the use of phase equilibrium models.
- Scaling up the processes to industrial levels presents significant challenges. While continuous systems increase throughput, they encounter operational issues such as clogging when processing high-solids feedstocks. Energy recovery in hydrothermal liquefaction processes can exceed 60 % when cosolvents like n-hexane are used for extraction; however, economic viability depends on optimizing solvent recovery and minimizing energy costs.
- Sealing existing knowledge gaps requires a rigorous integration of theoretical and experimental approaches. The proposed roadmap in this review emphasizes the importance of combining kinetic and phenomenological models with experimental data to improve predictive accuracy. Recent studies have achieved high predictive precision for BC yields (with R^2 values of up to 0.765 and heating values from 36.64 to 39.27 MJ/kg for microalgae-based BC, providing a robust foundation for optimizing reactor design and developing operational strategies. These advances aim to position HTL as a viable technology for sustainable biomass conversion at industrial scale.
- Finally, more research is also needed to valorize BC. While biocrude from HTL process is nominally of higher quality than biomass pyrolysis oil, for instance lower O/C, higher H/C, there is less work available on the separations and upgrading of HTL BCs. Again, modeling that can predict the compositions of the BC will be helpful to optimize the upgrading. Integrated biorefineries need to be dynamic and responsive to market needs in order to be sustainable, and a clearer predictive understanding of the possible product compositions in response to inputs and conditions can help drive product flexibility.

CRediT authorship contribution statement

Myriam Rojas: Salas, Writing – review & editing, Writing – original draft, Visualization, Formal analysis, Data curation, Conceptualization. **Raiza Manrique:** Writing – review & editing, Writing – original draft, Visualization, Data curation, Conceptualization. **Ursel Hornung:** Writing – review & editing, Writing – original draft, Validation. **Axel Funke:** Writing – review & editing, Validation, Supervision. **Charles A. Mullen:** Writing – review & editing, Formal analysis, Conceptualization. **Farid Chejne:** Writing – review & editing, Writing – original draft, Formal analysis, Conceptualization. **Juan C. Maya:** Writing – review & editing, Writing – original draft, Validation, Formal analysis.

Data Availability Statement

The Supplementary Information consists of i) a list of feedstocks, characteristics, and yields of products obtained in HTL and ii) figures about findings on biomass.

Conflict of interest

The authors declare no conflict of interest.

Ethics approval was not required for this research.

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Glossary

HTP	Hydrothermal Processes
HTL	Hydrothermal Liquefaction
PNNL	Pacific Northwest National Laboratory
HTC	Hydrothermal Carbonization
HTG	Hydrothermal Gasification
MSW	Municipal Solid Waste
OSW	Organic Solid Waste
RMSD	Root Mean Square Deviation
gge	gasoline gallon equivalent
BC	Biocrude Oil
AP	Aqueous Phase
HHV	Higher Heating Value
DTL	Direct Thermochemical Liquefaction
STR	Stirred-Tank Reactor
CSTR	Continuous Stirred Tank Reactor
PFR	Plug Flow Reactor
IPA	Isopropanol
co-HTG	Co-hydrothermal gasification
scH_2O	Supercritical Water
scEtOH	Supercritical Ethanol
TS	total solids content
WSS	Water-Solvent Soluble
WSIS	Water-Solvent Insoluble
HMF	Hydroxymethylfurfural
RMSD	Root Mean Square Deviation
FAO	Food and Agriculture Organization of the United Nations
LATAM	Latin America and the Caribbean
GHG	Greenhouse Gas
TS	Total Solids
Pi	Initial Pressure
Pf	Final Pressure
HR	Heating Rate
RT	Retention Time
scH_2O	Supercritical Water
WAO	Wet Air Oxidation
WO	Wet Oxidation
MD	Molecular Dynamics
DFT	Density Functional Theory
MCA	Multiphase Component Additivity
SRK	Soave-Redlich-Kwong
EoS	Equation of state
UNIFAC	Universal Quasi-Chemical Functional-Group Activity Coefficients
SCM	Shrinking Core Model
CGSM	Changing Grain Size Model
RPM	Random Pore Model
FVM	Finite Volume Method
FEM	Finite Element Method
CFD	Computational Fluid Dynamics
ES	Eutectic solvents

DES	Deep Eutectic Solvents
GAC	Granular Activated Carbon
CHG	Catalytic Hydrothermal Gasification
COD	Chemical Oxygen Demand
AD	Anaerobic digestion
HRMS	High-Resolution tandem mass spectrometry
GC/MS	Gas Chromatography/Mass Spectrometry
FT-ICR MS	Fourier Transform Ion Cyclotronic Mass Spectrometry
NMR	Nuclear Magnetic Resonance
HPLC	High Performance Liquid Chromatography
UPLC	Ultra Performance Liquid Chromatography
MFSP	Minimum Fuel Selling Price
H	Hydrogen
C	Carbon
O	Oxygen
N	Nitrogen
S	Sulfur
AC	Activated Carbon
$FeCl_3$	Iron(III) Chloride

Appendix A. Supplementary data

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References

[1] A. Niranjan, 'Era of global boiling has arrived,' says UN chief as July set to be hottest month on record, Guardian (2023). https://www.theguardian.com/science/2023/jul/27/scientists-july-world-hottest-month-record-climate-temperatures (accessed August 1, 2023).
[2] IEA, Net Zero by 2050 A Roadmap for the Global Energy Sector, 2021, p. 222. www.iea.org/t&c/no.
[3] Climate Watch data, Historical GHG emissions. https://www.climatewatchdata.org/ghg-emissions?end_year=2021&start_year=1990, 2023. (Accessed 18 May 2023).
[4] F. Cherubini, The biorefinery concept: using biomass instead of oil for producing energy and chemicals, Energy Convers. Manag. 51 (2010) 1412–1421, https://doi.org/10.1016/J.ENCONMAN.2010.01.015.
[5] R. van Ree, E. de Jong, K. Kwant, Leader of Task42 Co-leader of Task42 Operating Agent Task42, IEA, 2012. www.iea-bioenergy.task42-biorefineries.comwww.ieabioenergy.com. (Accessed 21 July 2024).
[6] N. Jan van Eck, L. Waltman, VOS: A New Method for Visualizing Similarities between Objects, n.d.
[7] A.S.A. Hamed, M.S. Yahya, N.A.A. Latiff, N.I.F.M. Yusof, N.F. Munajat, Thermochemical conversion of oil palm biomass and its applications: a bibliometric exploration of global trends over two decades, J. Anal. Appl. Pyrolysis 181 (2024), https://doi.org/10.1016/j.jaap.2024.106568.
[8] E. Ocampo, V.V. Beltrán, E.A. Gómez, L.A. Ríos, D. Ocampo, Hydrothermal liquefaction process: review and trends, Current Research in Green and Sustainable Chemistry 7 (2023), https://doi.org/10.1016/j.crgsc.2023.100382.
[9] European Commission: Directorate-General for Research and Innovation, M. Georgiadou, T. Goumas, D. Chiaramonti, Development of Outlook for the Necessary Means to Build Industrial Capacity for Drop-In Advanced Biofuels – Final Report, 2024.
[10] Licella. https://www.licella.com/. (Accessed 11 January 2025).
[11] Steeper Energy, Transforming biomass waste into low carbon intensity fuels. https://steeperenergy.com/. (Accessed 11 January 2025).
[12] Genifuel - Welcome. https://genifuel.com/. (Accessed 11 January 2025).
[13] Sludge2Fuel - the first full-scale demonstration for producing biofuel from sewage sludge - WaterCycle Denmark. https://watercycledenmark.com/sludge2fuel-the-first-full-scale-demonstration-for-producing-biofuel-from-sewage-sludge/. (Accessed 11 January 2025).
[14] European Comission, Completion of key 'Fit for 55'' legislation. https://ec.europa.eu/commission/presscorner/detail/en/ip_23_4754, 2023. (Accessed 11 January 2025).
[15] M. Usman, S. Cheng, S. Boonyubol, J.S. Cross, From biomass to biocrude: Innovations in hydrothermal liquefaction and upgrading, Energy Convers. Manag. 302 (2024) 118093, https://doi.org/10.1016/J.ENCONMAN.2024.118093.
[16] R. Bao, S. Wang, J. Feng, Y. Duan, K. Liu, J. Zhao, H. Liu, J. Yang, A review of hydrothermal biomass liquefaction: operating parameters, reaction mechanism, and bio-oil yields and compositions, Energy Fuel. 38 (2024) 8437–8459, https://doi.org/10.1021/ACS.ENERGYFUELS.4C00240/ASSET/IMAGES/MEDIUM/EF4C00240_0012.GIF.
[17] P.M. Guirguis, M.S. Seshasayee, B. Motavaf, P.E. Savage, Review and assessment of models for predicting biocrude yields from hydrothermal liquefaction of biomass, RSC Sustainability 2 (2024) 736–756, https://doi.org/10.1039/D3SU00458A.
[18] A. Dimitriadis, S. Bezergianni, Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: a state of the art review, Renew. Sustain. Energy Rev. 68 (2017) 113–125, https://doi.org/10.1016/j.rser.2016.09.120.
[19] Hamish Forbes, Eloise Peacock, Nettie Abbot, Michael Jones, Think Eat Save tracking progress to Halve global food waste, United Nations Environment Programme (2024). https://www.unep.org/resources/publication/food-waste-index-report-2024.
[20] H. Bayat, M. Dehghanizadeh, J.M. Jarvis, C.E. Brewer, U. Jena, Hydrothermal liquefaction of food waste: effect of process parameters on product yields and chemistry, Front. Sustain. Food Syst. 5 (2021), https://doi.org/10.3389/fsufs.2021.658592.
[21] S. Wu, Q. Wang, M. Fang, D. Wu, D. Cui, S. Pan, J. Bai, F. Xu, Z. Wang, Hydrothermal carbonization of food waste for sustainable biofuel production: advancements, challenges, and future prospects, Sci. Total Environ. 897 (2023), https://doi.org/10.1016/j.scitotenv.2023.165327.
[22] J. Montoya, B. Pecha, D. Roman, F.C. Janna, M. Garcia-Perez, Effect of temperature and heating rate on product distribution from the pyrolysis of sugarcane bagasse in a hot plate reactor, J. Anal. Appl. Pyrolysis 123 (2017) 347–363, https://doi.org/10.1016/j.jaap.2016.11.008.
[23] J.F. Vélez, F. Chejne, C.F. Valdés, E.J. Emery, C.A. Londoño, Co-gasification of Colombian coal and biomass in fluidized bed: an experimental study, Fuel 88 (2009) 424–430, https://doi.org/10.1016/j.fuel.2008.10.018.
[24] L. Limousy, M. Jeguirim, P. Dutournié, N. Kraiem, M. Lajili, R. Said, Gaseous products and particulate matter emissions of biomass residential boiler fired with spent coffee grounds pellets, Fuel 107 (2013) 323–329, https://doi.org/10.1016/j.fuel.2012.10.019.
[25] J.F. Vélez, F. Chejne, C.F. Valdés, E.J. Emery, C.A. Londoño, Co-gasification of Colombian coal and biomass in fluidized bed: an experimental study, Fuel 88 (2009) 424–430, https://doi.org/10.1016/j.fuel.2008.10.018.
[26] G. Grillo, L. Boffa, A. Binello, S. Mantegna, G. Cravotto, F. Chemat, T. Dizhbite, L. Lauberte, G. Telysheva, Cocoa bean shell waste valorisation; extraction from lab to pilot-scale cavitational reactors, Food Res. Int. 115 (2019) 200–208, https://doi.org/10.1016/j.foodres.2018.08.057.
[27] C.A. a b Forero-Nuñez, J. c d Jochum, F.E.S. e f g Vargas, Effect of particle size and addition of cocoa pod husk on the properties of sawdust and coal pellets [Efecto del tamaño de partícula y la adición de cáscara de cacao en las propiedades de los pellets de aserrín y carbón], Ing. Invest. 35 (2015) 17–23, https://doi.org/10.15446/ing.investig.v35n1.46157.
[28] M.B. Mensah, H. Jumpah, N.O. Boadi, J.A.M. Awudza, Assessment of quantities and composition of corn stover in Ghana and their conversion into bioethanol, Sci Afr 12 (2021), https://doi.org/10.1016/j.sciaf.2021.e00731.
[29] F. Rego, A.P. Soares Dias, M. Casquilho, F.C. Rosa, A. Rodrigues, Fast determination of lignocellulosic composition of poplar biomass by thermogravimetry, Biomass Bioenergy 122 (2019) 375–380, https://doi.org/10.1016/j.biombioe.2019.01.037.
[30] P. Tirumareddy, B.R. Patra, V.B. Borugadda, A.K. Dalai, Co-hydrothermal liquefaction of waste biomass: comparison of various feedstocks and process optimization, Bioresour. Technol. Rep. 27 (2024), https://doi.org/10.1016/j.biteb.2024.101898.
[31] B. Biswas, T. Rahman, S. Adhikari, Mono-and bi-metal catalytic hydrothermal liquefaction of food waste: Screening the process parameter on product yield and characterizations, J. Clean. Prod. 471 (2024), https://doi.org/10.1016/j.jclepro.2024.143398.
[32] T.A. Moonsamy, G. Rajauria, A. Priyadarshini, M.A.K. Jansen, Food waste: analysis of the complex and variable composition of a promising feedstock for valorisation, Food Bioprod. Process. 148 (2024) 31–42, https://doi.org/10.1016/j.fbp.2024.08.012.
[33] A.R. Maag, A.D. Paulsen, T.J. Amundsen, P.E. Yelvington, G.A. Tompsett, M.T. Timko, Catalytic hydrothermal liquefaction of food waste using cezrox, Energies 11 (2018), https://doi.org/10.3390/en11030564.
[34] F. Cheng, Z. Cui, L. Chen, J. Jarvis, N. Paz, T. Schaub, N. Nirmalakhandan, C.E. Brewer, Hydrothermal liquefaction of high- and low-lipid algae: bio-crude oil chemistry, Appl. Energy 206 (2017), https://doi.org/10.1016/j.apenergy.2017.08.105.
[35] R. Kaur, P. Gera, M.K. Jha, T. Bhaskar, Reaction parameters effect on hydrothermal liquefaction of castor (Ricinus Communis)residue for energy and valuable hydrocarbons recovery, Renew. Energy 141 (2019), https://doi.org/10.1016/j.renene.2019.04.064.
[36] A.R. Saleh, B. Sudarmanta, H. Fansuri, O. Muraza, Syngas production from municipal solid waste with a reduced tar yield by three-stages of air inlet to a downdraft gasifier, Fuel 263 (2020), https://doi.org/10.1016/j.fuel.2019.116509.
[37] A. Saravanakumar, W.H. Chen, K.D. Arunachalam, Y.K. Park, H. Chyuan Ong, Pilot-scale study on downdraft gasification of municipal solid waste with mass and energy balance analysis, Fuel 315 (2022), https://doi.org/10.1016/j.fuel.2022.123287.
[38] L. Grande, I. Pedroarena, S.A. Korili, A. Gil, Hydrothermal liquefaction of biomass as one of the most promising alternatives for the synthesis of advanced liquid biofuels: a review, Materials 14 (2021), https://doi.org/10.3390/MA14185286.
[39] Global TerraGreen, Waste — Solvable problem as a renewable energy resource | by TerraGreen, Medium (2019). https://medium.com/@support_61820/global-waste-solvable-problem-as-a-renewable-energy-resource-5d8f05cc1a7d (accessed January 7, 2024).

[40] S. Kaza, L.C. Yao, P. Bhada-Tata, F. Van Woerden, What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050, what a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050, 2018, https://doi.org/10.1596/978-1-4648-1329-0.

[41] Statista, Municipal Waste Generation by Select Country, Statista, 2021. https://www.statista.com/statistics/916749/global-generation-of-municipal-solid-waste-by-country/. (Accessed 9 January 2024).

[42] T.N. Rijkswaterstaat Environment, Colombia: sustainable waste management policies and sustainable waste practises - Rijkswaterstaat Environment. https://rwsenvironment.eu/projects/colombia/colombia/, 2016. (Accessed 11 January 2024).

[43] United States Environmental Protection Agency, National Overview: Facts and Figures on Materials, Wastes and Recycling, 2018.

[44] C. Smith, A.R.F. de Aguiar Martins, F. Pradelle, Modelling, simulation and optimization of a solid residues downdraft gasifier: application to the co-gasification of municipal solid waste and sugarcane bagasse, Energy 210 (2020) 118498, https://doi.org/10.1016/j.energy.2020.118498.

[45] U. Jena, K.C. Das, Comparative Evaluation of Thermochemical Liquefaction and Pyrolysis for Bio-Oil Production from Microalgae, vol. 25, 2011, pp. 5472–5482, https://doi.org/10.1021/ef201373m.

[46] Y. Zhu, Y. Zhao, Q. Li, X. Shi, X. Li, G. Xu, Role of oxophilic metal ions (Mo, Zr, Ti) impregnated Ni/γ-Al2O3 catalysts for hydrothermal liquefaction of kraft lignin, J. Energy Inst. 114 (2024) 101603, https://doi.org/10.1016/J.JOEI.2024.101603.

[47] X. Zhang, Z. Li, F. Zheng, L. Zou, Z. Zhang, B. Fu, G. Xi, Copper and zinc-impregnated mesoporous gamma-alumina catalyst for hydrothermal liquefaction of alkali lignin, J. Energy Inst. 114 (2024) 101548, https://doi.org/10.1016/J.JOEI.2024.101548.

[48] S. Harisankar, R. Vinu, Sustainable Energy & Fuels Platform chemicals from hardwood black liquor via hydrothermal liquefaction: influence of process conditions on product yields and quality †, vol. 7 (n.d.) 4343–4698. https://doi.org/10.1039/d3se00308f.

[49] R. Jain, S. Dhali, A. Malik, R. Satyakam, Sustainable biorefining: hydrothermal liquefaction of diatom biomass for bio-crude and nano-biosilica recovery, Process Saf. Environ. Protect. 187 (2024) 940–949, https://doi.org/10.1016/J.PSEP.2024.05.025.

[50] M. Khalekuzzaman, M.A. Fayshal, H.M.F. Adnan, Production of low phenolic naphtha-rich biocrude through co-hydrothermal liquefaction of fecal sludge and organic solid waste using water-ethanol co-solvent, J. Clean. Prod. 436 (2024), https://doi.org/10.1016/j.jclepro.2024.140593.

[51] A. Díaz-González, M.Y.P. Luna, E.R. Morales, S. Saldaña-Trinidad, L.R. Blanco, S. de la Cruz-Arreola, B.Y. Pérez-Sariñana, J.B. Robles-Ocampo, Assessment of the pretreatments and Bioconversion of lignocellulosic biomass recovered from the husk of the cocoa pod, Energies 15 (2022), https://doi.org/10.3390/en15103544.

[52] A.T. Hoang, S. Nižetić, H.C. Ong, M. Mofijur, S.F. Ahmed, B. Ashok, V.T.V. Bui, M. Q. Chau, Insight into the recent advances of microwave pretreatment technologies for the conversion of lignocellulosic biomass into sustainable biofuel, Chemosphere 281 (2021), https://doi.org/10.1016/j.chemosphere.2021.130878.

[53] I.G. Hakeem, A. Sharma, T. Sharma, A. Sharma, J.B. Joshi, K. Shah, A.S. Ball, A. Surapaneni, Techno-economic analysis of biochemical conversion of biomass to biofuels and platform chemicals, Biofuels, Bioproducts and Biorefining 17 (2023), https://doi.org/10.1002/bbb.2463.

[54] K. Biernat, A. Matuszewska, I. Samson-Bręk, M. Owczuk, Biological methods in biodiesel production and their environmental impact, Appl. Sci. 11 (2021), https://doi.org/10.3390/app112210946.

[55] K. Biernat, A. Matuszewska, I. Samson-Bręk, M. Owczuk, Biological methods in biodiesel production and their environmental impact, Appl. Sci. 11 (2021), https://doi.org/10.3390/app112210946.

[56] M. Hájek, A. Vávra, H. de Paz Carmona, J. Kocík, The catalysed transformation of vegetable oils or animal fats to biofuels and bio-lubricants: a review, Catalysts 11 (2021), https://doi.org/10.3390/catal11091118.

[57] K. Velusamy, J. Devanand, P. Senthil Kumar, K. Soundarajan, V. Sivasubramanian, J. Sindhu, D.V.N. Vo, A review on nano-catalysts and biochar-based catalysts for biofuel production, Fuel 306 (2021), https://doi.org/10.1016/j.fuel.2021.121632.

[58] L. Lin, X. Han, B. Han, S. Yang, Emerging heterogeneous catalysts for biomass conversion: studies of the reaction mechanism, Chem. Soc. Rev. 50 (2021), https://doi.org/10.1039/d1cs00039j.

[59] S. Meenakshisundaram, A. Fayeulle, E. Léonard, C. Ceballos, X. Liu, A. Pauss, Combined biological and chemical/physicochemical pretreatment methods of lignocellulosic biomass for bioethanol and Biomethane energy production—a review, Appl. Microbiol. 2 (2022), https://doi.org/10.3390/applmicrobiol2040055.

[60] A.T. Hoang, H.C. Ong, I.M.R. Fattah, C.T. Chong, C.K. Cheng, R. Sakthivel, Y. S. Ok, Progress on the lignocellulosic biomass pyrolysis for biofuel production toward environmental sustainability, Fuel Process. Technol. 223 (2021), https://doi.org/10.1016/j.fuproc.2021.106997.

[61] Farid Chejne, Myriam Rojas, Juan C. Maya, David Granados, Robert J. Macías, Carlos Valdés, Javier Ordoñez, Manuel García-Pérez, Experimental and Theoretical Research of Thermochemical Processes, first ed., Editorial Universidad Nacional de Colombia, Bogotá D. C., 2023.

[62] Axel Funke, Nicolaus Dahmen, Direct Thermochemical Liquefaction of Biomass – Characteristics, Processes and Technologies, IEA Bioenergy, 2020, p. 1, in: https://www.ieabioenergy.com/blog/publications/new-publication-direct-thermochemical-liquefaction-of-biomass-characteristics-processes-and-technologies/. (Accessed 19 May 2023).

[63] R.H. Venderbosch, W. Prins, Fast pyrolysis technology development, Biofuels, Bioproducts and Biorefining 4 (2010) 178–208, https://doi.org/10.1002/bbb.205.

[64] A. Al-Rumaihi, M. Shahbaz, G. Mckay, H. Mackey, T. Al-Ansari, A review of pyrolysis technologies and feedstock: a blending approach for plastic and biomass towards optimum biochar yield, Renew. Sustain. Energy Rev. 167 (2022) 112715, https://doi.org/10.1016/J.RSER.2022.112715.

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

[66] I. Pavlovič, Ž. Knez, M. Škerget, Hydrothermal reactions of agricultural and food processing wastes in sub- and supercritical water: a review of fundamentals, mechanisms, and state of research, J. Agric. Food Chem. 61 (2013), https://doi.org/10.1021/jf401008a.

[67] G. Brunner, Reactions in hydrothermal and supercritical water, in: Supercritical Fluid Science and Technology, Elsevier B.V., 2014, pp. 265–322, https://doi.org/10.1016/B978-0-444-59413-6.00005-4.

[68] K. Czerwińska, M. Śliz, M. Wilk, Hydrothermal carbonization process: fundamentals, main parameter characteristics and possible applications including an effective method of SARS-CoV-2 mitigation in sewage sludge, A review, Renewable and Sustainable Energy Reviews 154 (2022), https://doi.org/10.1016/j.rser.2021.111873.

[69] A. Matayeva, F. Basile, F. Cavani, D. Bianchi, S. Chiaberge, Development of upgraded bio-oil via liquefaction and pyrolysis, in: Stud Surf Sci Catal, Elsevier Inc., 2019, pp. 231–256, https://doi.org/10.1016/B978-0-444-64127-4.00012-4.

[70] K. Tekin, S. Karagöz, S. Bektaş, A review of hydrothermal biomass processing, Renew. Sustain. Energy Rev. 40 (2014) 673–687, https://doi.org/10.1016/j.rser.2014.07.216.

[71] C. Tian, Z. Liu, Y. Zhang, Hydrothermal liquefaction (HTL): a promising pathway for biorefinery of algae, Algal Biofuels: Recent Advances and Future Prospects (2017) 361–392, https://doi.org/10.1007/978-3-319-51010-1_18/FIGURES/11.

[72] P.J. Valdez, M.C. Nelson, H.Y. Wang, X.N. Lin, P.E. Savage, Hydrothermal liquefaction of Nannochloropsis sp.: Systematic study of process variables and analysis of the product fractions, Biomass Bioenergy 46 (2012) 317–331, https://doi.org/10.1016/J.BIOMBIOE.2012.08.009.

[73] Y. Zhang, W.T. Chen, Hydrothermal Liquefaction of Protein-Containing Feedstocks, Direct Thermochemical Liquefaction for Energy Applications, 2018, pp. 127–168, https://doi.org/10.1016/B978-0-08-101029-7.00004-7.

[74] C. Tian, Z. Liu, Y. Zhang, Hydrothermal liquefaction (HTL): a promising pathway for biorefinery of algae, Algal Biofuels: Recent Advances and Future Prospects (2017) 361–392, https://doi.org/10.1007/978-3-319-51010-1_18/FIGURES/11.

[75] R. Kumar, A review on the modelling of hydrothermal liquefaction of biomass and waste feedstocks, Energy Nexus 5 (2022) 100042, https://doi.org/10.1016/J.NEXUS.2022.100042.

[76] E. Damergi, H. Madi, S. Sharma, N. Boukis, F. Marechal, J. Van Herle, C. Ludwig, A combined hydrothermal gasification - solid oxide fuel cell system for sustainable production of algal biomass and energy, Algal Res. 41 (2019) 101552, https://doi.org/10.1016/J.ALGAL.2019.101552.

[77] A. Kruse, Hydrothermal biomass gasification, J. Supercrit. Fluids 47 (2009) 391–399, https://doi.org/10.1016/J.SUPFLU.2008.10.009.

[78] F. Safari, O. Norouzi, A. Tavasoli, Hydrothermal gasification of Cladophora glomerata macroalgae over its hydrochar as a catalyst for hydrogen-rich gas production, Bioresour. Technol. 222 (2016), https://doi.org/10.1016/j.biortech.2016.09.082.

[79] G. Sztancs, L. Juhasz, B.J. Nagy, A. Nemeth, A. Selim, A. Andre, A.J. Toth, P. Mizsey, D. Fozer, Co-Hydrothermal gasification of Chlorella vulgaris and hydrochar: the effects of waste-to-solid biofuel production and blending concentration on biogas generation, Bioresour. Technol. 302 (2020), https://doi.org/10.1016/j.biortech.2020.122793.

[80] P. Zhao, Z. Yuan, J. Zhang, X. Song, C. Wang, Q. Guo, A.J. Ragauskas, Supercritical water co-liquefaction of LLDPE and PP into oil: properties and synergy, Sustain. Energy Fuels 5 (2021) 575–583, https://doi.org/10.1039/D0SE01486A.

[81] S. Brand, R.F. Susanti, S.K. Kim, H. shik Lee, J. Kim, B.I. Sang, Supercritical ethanol as an enhanced medium for lignocellulosic biomass liquefaction: influence of physical process parameters, Energy 59 (2013) 173–182, https://doi.org/10.1016/J.ENERGY.2013.06.049.

[82] M.J. Boel, H. Wang, A. AL Farra, L. Megido, J.M. González-LaFuente, N.R. Shiju, Hydrothermal liquefaction of plastics: a survey of the effect of reaction conditions on the reaction efficiency, React. Chem. Eng. 9 (2024) 1014–1031, https://doi.org/10.1039/D2RE00510G.

[83] H.S. Kambo, A. Dutta, A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications, Renew. Sustain. Energy Rev. 45 (2015) 359–378, https://doi.org/10.1016/J.RSER.2015.01.050.

[84] C. Prestigiacomo, Y. Fan, U. Hornung, N. Dahmen, O. Scialdone, A. Galia, Hydrothermal liquefaction of sewage sludge: use of HCOOH and KOH to improve the slurry pumpability in a continuously operated plant, Heliyon 10 (2024) e26287, https://doi.org/10.1016/J.HELIYON.2024.E26287.

[85] Y. Fan, U. Hornung, N. Dahmen, Hydrothermal liquefaction of sewage sludge for biofuel application: a review on fundamentals, current challenges and strategies, Biomass Bioenergy 165 (2022) 106570, https://doi.org/10.1016/J.BIOMBIOE.2022.106570.

[86] C. Prestigiacomo, Y. Fan, U. Hornung, N. Dahmen, O. Scialdone, A. Galia, Hydrothermal liquefaction of sewage sludge: use of HCOOH and KOH to improve the slurry pumpability in a continuously operated plant, Helyon 10 (2024), https://doi.org/10.1016/j.heliyon.2024.e26287.

[87] M. Wörner, L. Werner, U. Hornung, N.I. Canabarro, D. Baudouin, N. Dahmen, The impact of sulfur-containing inorganic compounds during the depolymerization of lignin by hydrothermal liquefaction of black liquor, Energy & Fuels 38 (2024) 6036–6047, https://doi.org/10.1021/ACS.ENERGYFUELS.3C04737.

[88] S. Li, Y. Jiang, L.J. Snowden-Swan, J.A. Askander, A.J. Schmidt, J.M. Billing, Techno-economic uncertainty analysis of wet waste-to-biocrude via hydrothermal liquefaction, Appl. Energy 283 (2021), https://doi.org/10.1016/j.apenergy.2020.116340.

[89] Y. Jiang, C. Mevawala, S. Li, A. Schmidt, J. Billing, M. Thorson, L. Snowden-Swan, Uncertainty analysis for techno-economic and life-cycle assessment of wet waste hydrothermal liquefaction with centralized upgrading to produce fuel blendstocks, J. Environ. Chem. Eng. 11 (2023), https://doi.org/10.1016/j.jece.2023.109706.

[90] Y. Jiang, L. Ou, L. Snowden-Swan, H. Cai, S. Li, K. Ramasamy, A. Schmidt, H. Wang, D.M. Santosa, M.V. Olarte, M. Guo, M.R. Thorson, Aqueous-phase product treatment and monetization options of wet waste hydrothermal liquefaction: comprehensive techno-economic and life-cycle GHG emission assessment unveiling research opportunities, Bioresour. Technol. 397 (2024), https://doi.org/10.1016/j.biortech.2024.130504.

[91] F. Gievers, A. Loewen, M. Nelles, Life cycle assessment of sewage sludge pyrolysis: environmental impacts of biochar as carbon sequestrator and nutrient recycler, Detritus 16 (2021) 94, https://doi.org/10.31025/2611-4135/2021.15111, 2020.

[92] J. Havukainen, A. Saud, T.F. Astrup, P. Peltola, M. Horttanainen, Environmental performance of dewatered sewage sludge digestate utilization based on life cycle assessment, Waste Management 137 (2022) 210–221, https://doi.org/10.1016/J.WASMAN.2021.11.005.

[93] C. Huang, B.A. Mohamed, L.Y. Li, Comparative life-cycle assessment of pyrolysis processes for producing bio-oil, biochar, and activated carbon from sewage sludge, Resour. Conserv. Recycl. 181 (2022) 106273, https://doi.org/10.1016/J.RESCONREC.2022.106273.

[94] X. Zhou, J. Li, X. Zhao, J. Yang, H. Sun, S.S. Yang, S. Bai, Resource recovery in life cycle assessment of sludge treatment: contribution, sensitivity, and uncertainty, Sci. Total Environ. 806 (2022) 150409, https://doi.org/10.1016/J.SCITOTENV.2021.150409.

[95] S. Neha, L. Vergeynst, P. Biller, Evaluating hydrothermal liquefaction hydrochar from sewage sludge as a phosphorus resource through struvite production, J. Environ. Chem. Eng. 12 (2024), https://doi.org/10.1016/j.jece.2024.113014.

[96] X.Y. Duan, Y. Cao, T.Z. Liu, L. Li, B. Wang, X.D. Wang, Nutrient stability and sorption of sewage sludge biochar prepared from co-pyrolysis of sewage sludge and stalks/mineral materials, Environmental Pollutants and Bioavailability 32 (2020) 12–18, https://doi.org/10.1080/26395940.2019.1710259.

[97] U. Jena, B.E. Eboibi, K.C. Das, Co-solvent assisted hydrothermal liquefaction of algal biomass and biocrude upgrading, Fuels 3 (2022) 326–341, https://doi.org/10.3390/fuels3020020.

[98] F. Cheng, C.E. Brewer, Best practices for bio-crude oil production at pilot scale using continuous flow reactors, 3rd Generation Biofuels: Disruptive Technologies to Enable Commercial Production (2022) 1061–1119, https://doi.org/10.1016/B978-0-323-90971-6.00003-6.

[99] M. Liu, Y. Zeng, Key processing factors in hydrothermal liquefaction and their impacts on corrosion of reactor alloys, Sustainability 15 (2023) 9317, https://doi.org/10.3390/SU15129317, 2023.

[100] F. Cheng, T. Le Doux, B. Treftz, S. Woolf, J. Yu, J. Miller, U. Jena, C.E. Brewer, Modification of a pilot-scale continuous flow reactor for hydrothermal liquefaction of wet biomass, MethodsX 6 (2019) 2793–2806, https://doi.org/10.1016/J.MEX.2019.11.019.

[101] D. Castello, T.H. Pedersen, L.A. Rosendahl, Continuous hydrothermal liquefaction of biomass: a critical review, Energies 11 (2018) 3165, https://doi.org/10.3390/EN11113165, 2018.

[102] S. Liu, Ideal flow reactors, in: Bioprocess Engineering, Elsevier, 2017, pp. 179–257, https://doi.org/10.1016/b978-0-444-63783-3.00005-8.

[103] M. Elhassan, R. Abdullah, M.R.R. Kooh, Y.F. Chou Chau, Hydrothermal liquefaction: a technological review on reactor design and operating parameters, Bioresour. Technol. Rep. 21 (2023), https://doi.org/10.1016/j.biteb.2022.101314.

[104] Y. Zhu, Y. Zhao, Q. Li, X. Shi, X. Li, G. Xu, Role of oxophilic metal ions (Mo, Zr, Ti) impregnated Ni/γ-Al2O3 catalysts for hydrothermal liquefaction of kraft lignin, J. Energy Inst. 114 (2024), https://doi.org/10.1016/j.joei.2024.101603.

[105] X. Zhang, Z. Li, F. Zheng, L. Zou, Z. Zhang, B. Fu, G. Xi, Copper and zinc-impregnated mesoporous gamma-alumina catalyst for hydrothermal liquefaction of alkali lignin, J. Energy Inst. 114 (2024), https://doi.org/10.1016/j.joei.2024.101548.

[106] R. Jain, S. Dhali, A. Malik, R. Satyakam, Sustainable biorefining: hydrothermal liquefaction of diatom biomass for bio-crude and nano-biosilica recovery, Process Saf. Environ. Protect. 187 (2024) 940–949, https://doi.org/10.1016/j.psep.2024.05.025.

[107] J. Cheikhwafa, E. Torrens, C. Bengoa, Influence of catalysts on the hydrothermal liquefaction of municipal primary sludge: upgrading to a higher quality biocrude, Fuel 369 (2024), https://doi.org/10.1016/j.fuel.2024.131715.

[108] G. Liu, F. Chen, K. Cao, B. Jin, L. Rao, X. Jin, F. He, Q. Huang, Fe-catalyzed low-temperature hydrothermal liquefaction of coffee shells: influence of operating parameters on bio-oil yield, distribution of bio-oil products, J. Energy Inst. 113 (2024), https://doi.org/10.1016/j.joei.2024.101525.

[109] D. López Barreiro, C. Zamalloa, N. Boon, W. Vyverman, F. Ronsse, W. Brilman, W. Prins, Influence of strain-specific parameters on hydrothermal liquefaction of microalgae, Bioresour. Technol. 146 (2013) 463–471, https://doi.org/10.1016/j.biortech.2013.07.123.

[110] D. Forchheim, J.R. Gasson, U. Hornung, A. Kruse, T. Barth, Modeling the lignin degradation kinetics in a ethanol/formic acid solvolysis approach. part 2. validation and transfer to variable conditions, Ind. Eng. Chem. Res. 51 (2012) 15053–15063, https://doi.org/10.1021/ie3026407.

[111] L.B. Silva Thomsen, J. de C. Carregosa, A. Wisniewski, K. Anastasakis, P. Biller, Continuous wet air oxidation of aqueous phase from hydrothermal liquefaction of sewage sludge, J. Environ. Chem. Eng. 12 (2024), https://doi.org/10.1016/j.jece.2024.112672.

[112] L.B. Silva Thomsen, K. Anastasakis, P. Biller, Wet oxidation of aqueous phase from hydrothermal liquefaction of sewage sludge, Water Res. 209 (2022), https://doi.org/10.1016/j.watres.2021.117863.

[113] B. Patel, K. Hellgardt, Hydrothermal upgrading of algae paste in a continuous flow reactor, Bioresour. Technol. 191 (2015) 460–468, https://doi.org/10.1016/J.BIORTECH.2015.04.012.

[114] A. Strugała-Wilczek, W. Basa, M. Pankiewicz-Sperka, D. Xu, P. Duan, B. Hao, Y. Wang, L. Leng, L. Yang, L. Fan, K. Kapusta, Distribution characteristics and migration pathways of metals during hydrothermal liquefaction of municipal sewage sludge in the presence of various catalysts, Sci. Total Environ. 920 (2024), https://doi.org/10.1016/j.scitotenv.2024.171023.

[115] D.L. Barreiro, B.R. Gómez, U. Hornung, A. Kruse, W. Prins, Hydrothermal liquefaction of microalgae in a continuous stirred-tank reactor, Energy Fuel. 29 (2015) 6422–6432, https://doi.org/10.1021/acs.energyfuels.5b02099.

[116] K. Anastasakis, P. Biller, R.B. Madsen, M. Glasius, I. Johannsen, Continuous hydrothermal liquefaction of biomass in a novel pilot plant with heat recovery and Hydraulic Oscillation, Energies 11 (2018) 2695, https://doi.org/10.3390/EN11102695, 2018.

[117] Y.H. Xu, M.F. Li, Hydrothermal liquefaction of lignocellulose for value-added products: mechanism, parameter and production application, Bioresour. Technol. 342 (2021), https://doi.org/10.1016/j.biortech.2021.126035.

[118] B.B. Makut, G. Goswami, D. Das, Evaluation of bio-crude oil through hydrothermal liquefaction of microalgae-bacteria consortium grown in open pond using wastewater, Biomass Convers Biorefin 12 (2022) 2567–2581, https://doi.org/10.1007/S13399-020-00795-X/TABLES/8.

[119] B. Motavaf, R.A. Dean, J. Nicolas, P.E. Savage, Hydrothermal carbonization of simulated food waste for recovery of fatty acids and nutrients, Bioresour. Technol. 341 (2021), https://doi.org/10.1016/j.biortech.2021.125872.

[120] J.A. Ramirez, R.J. Brown, T.J. Rainey, A review of hydrothermal liquefaction bio-crude properties and prospects for upgrading to transportation fuels, Energies 8 (2015) 6765–6794, https://doi.org/10.3390/EN8076765, 2015.

[121] S. Sohail Toor, L. Aistrup Rosendahl, J. Hoffmann, T. Helmer Pedersen, R. Pankratz Nielsen, E. Gydesen Søgaard, S.S. Toor, Á.L. A Rosendahl Á J Hoffmann Á T H Pedersen, R.P. Nielsen, Á.E.G. Søgaard, Hydrothermal Liquefaction of Biomass, 2014, pp. 189–217, https://doi.org/10.1007/978-3-642-54458-3_9.

[122] L. Pola, S. Collado, M. Wörner, U. Hornung, M. Díaz, Eutectic solvents for the valorisation of the aqueous phase from hydrothermally liquefied black liquor, J. Environ. Chem. Eng. 11 (2023) 111040, https://doi.org/10.1016/J.JECE.2023.111040.

[123] L. Pola, S. Collado, M. Wörner, U. Hornung, M. Díaz, Valorisation of the residual aqueous phase from hydrothermally liquefied black liquor by persulphate-based advanced oxidation, Chemosphere 339 (2023) 139737, https://doi.org/10.1016/J.CHEMOSPHERE.2023.139737.

[124] S. Neha, N. Remya, Raw and processed data set for optimization of bio-oil production from microwave co-pyrolysis of food waste and low-density polyethylene with response surface methodology, Data Brief 42 (2022) 108093, https://doi.org/10.1016/J.DIB.2022.108093.

[125] H. Liu, I.A. Basar, A. Nzihou, C. Eskicioglu, Hydrochar derived from municipal sludge through hydrothermal processing: a critical review on its formation, characterization, and valorization, Water Res. 199 (2021) 117186, https://doi.org/10.1016/J.WATRES.2021.117186.

[126] S. Neha, P. Rajput, N. Remya, Biochar from microwave co-pyrolysis of food waste and polyethylene using different microwave susceptors - production, modification and application for metformin removal, Environ. Res. 210 (2022), https://doi.org/10.1016/J.ENVRES.2022.112922.

[127] C. Wang, W. Zhang, X. Qiu, C. Xu, Hydrothermal treatment of lignocellulosic biomass towards low-carbon development: production of high-value-added bioproducts, EnergyChem 6 (2024), https://doi.org/10.1016/j.enchem.2024.100133.

[128] S. Neha, L. Vergeynst, P. Biller, Evaluating hydrothermal liquefaction hydrochar from sewage sludge as a phosphorus resource through struvite production, J. Environ. Chem. Eng. 12 (2024) 113014, https://doi.org/10.1016/J.JECE.2024.113014.

[129] X. Cao, S.S. Ab, R. Sun, Application of biochar-based catalysts in biomass upgrading, a review (2017), https://doi.org/10.1039/c7ra09307a.

[130] M. Jalilian, R. Bissessur, M. Ahmed, A. Hsiao, Q.S. He, Y. Hu, A review: hydrochar as potential adsorbents for wastewater treatment and CO2 adsorption, Sci. Total Environ. 914 (2024), https://doi.org/10.1016/j.scitotenv.2023.169823.

[131] X. Cao, S. Sun, R. Sun, Application of biochar-based catalysts in biomass upgrading: a review, RSC Adv. 7 (2017) 48793–48805, https://doi.org/10.1039/c7ra09307a.

[132] S. Kang, X. Li, J. Fan, J. Chang, Characterization of hydrochars produced by hydrothermal carbonization of lignin, cellulose, d-xylose, and wood meal, in: Ind Eng Chem Res, 2012, pp. 9023–9031, https://doi.org/10.1021/ie300565d.

[133] Zhichao Wang, Reaction Mechanisms of Hydrothermal Liquefaction of Model Compounds and Biowaste Feedstocks, University of Illinois at Urbana-Champaign, 2011. https://hdl.handle.net/2142/26090. (Accessed 15 January 2024).

[134] D. Knežević, W.P.M. Van Swaaij, S.R.A. Kersten, Hydrothermal conversion of biomass: I, glucose conversion in hot compressed water, Ind. Eng. Chem. Res. 48 (2009) 4731–4743, https://doi.org/10.1021/IE801387V/ASSET/IMAGES/LARGE/IE-2008-01387V_0008. JPEG.

[135] R. Obeid, D.M. Lewis, N. Smith, T. Hall, P. Van Eyk, Reaction kinetics and characterization of species in renewable crude from hydrothermal liquefaction of mixtures of polymer compounds to represent organic fractions of biomass feedstocks, Energy Fuel. 34 (2020) 419–429, https://doi.org/10.1021/ACS.ENERGYFUELS.9B02936/ASSET/IMAGES/LARGE/EF9B02936_0005.JPEG.

[136] Y. Fan, U. Hornung, N. Dahmen, A. Kruse, Hydrothermal liquefaction of protein-containing biomass: study of model compounds for Maillard reactions, Biomass Convers Biorefin 8 (2018) 909–923, https://doi.org/10.1007/s13399-018-0340-8.

[137] Y. Fan, U. Hornung, N. Dahmen, Hydrothermal liquefaction of sewage sludge for biofuel application: a review on fundamentals, current challenges and strategies, Biomass Bioenergy 165 (2022), https://doi.org/10.1016/j.biombioe.2022.106570.

[138] R. Obeid, N. Smith, D.M. Lewis, T. Hall, P. van Eyk, A kinetic model for the hydrothermal liquefaction of microalgae, sewage sludge and pine wood with product characterisation of renewable crude, Chem. Eng. J. 428 (2022) 131228, https://doi.org/10.1016/J.CEJ.2021.131228.

[139] P.J. Valdez, V.J. Tocco, P.E. Savage, A general kinetic model for the hydrothermal liquefaction of microalgae, Bioresour. Technol. 163 (2014) 123–127, https://doi.org/10.1016/J.BIORTECH.2014.04.013.

[140] B. Hao, D. Xu, Y. Wei, Y. Diao, L. Yang, L. Fan, Y. Guo, Mathematical models application in optimization of hydrothermal liquefaction of biomass, Fuel Process. Technol. 243 (2023) 107673, https://doi.org/10.1016/J.FUPROC.2023.107673.

[141] Z. Borazjani, R. Azin, S. Osfouri, Kinetics studies and performance analysis of algae hydrothermal liquefaction process, Biomass Convers Biorefin 1 (2023) 1–28, https://doi.org/10.1007/S13399-023-04067-2/FIGURES/2.

[142] Y.P. Shia, B.Y. Yu, Development of a rigorous and generalized model on the hydrothermal liquefaction (HTL) process for bio-oil production, Process Saf. Environ. Protect. 171 (2023) 541–554, https://doi.org/10.1016/J.PSEP.2023.01.046.

[143] W. Schutyser, S. Van Den Bosch, T. Renders, T. De Boe, S.F. Koelewijn, A. Dewaele, T. Ennaert, O. Verkinderen, B. Goderis, C.M. Courtin, B.F. Sels, Influence of bio-based solvents on the catalytic reductive fractionation of birch wood, Green Chem. 17 (2015), https://doi.org/10.1039/c5gc01442e.

[144] T. Renders, G. Van den Bossche, T. Vangeel, K. Van Aelst, B. Sels, Reductive catalytic fractionation: state of the art of the lignin-first biorefinery, Curr. Opin. Biotechnol. 56 (2019), https://doi.org/10.1016/j.copbio.2018.12.005.

[145] I. Kumaniaev, E. Subbotina, J. Sävmarker, M. Larhed, M.V. Galkin, J.S.M. Samec, Lignin depolymerization to monophenolic compounds in a flow-through system, Green Chem. 19 (2017), https://doi.org/10.1039/c7gc02731a.

[146] S. Van Den Bosch, T. Renders, S. Kennis, S.F. Koelewijn, G. Van Den Bossche, T. Vangeel, A. Deneyer, D. Depuydt, C.M. Courtin, J.M. Thevelein, W. Schutyser, B.F. Sels, Integrating lignin valorization and bio-ethanol production: on the role of Ni-Al2O3 catalyst pellets during lignin-first fractionation, Green Chem. 19 (2017), https://doi.org/10.1039/c7gc01324h.

[147] Y. Fan, L. Meyer, M. Gong, B. Krause, U. Hornung, N. Dahmen, Understanding the fate of nitrogen during catalytic hydrothermal liquefaction of sewage sludge, Fuel 339 (2023) 126948, https://doi.org/10.1016/J.FUEL.2022.126948.

[148] S. Leow, J.R. Witter, D.R. Vardon, B.K. Sharma, J.S. Guest, T.J. Strathmann, Prediction of microalgae hydrothermal liquefaction products from feedstock biochemical composition, Green Chem. 17 (2015) 3584–3599, https://doi.org/10.1039/C5GC00574D.

[149] R. Bao, S. Wang, J. Feng, Y. Duan, K. Liu, J. Zhao, H. Liu, J. Yang, A review of hydrothermal biomass liquefaction: operating parameters, reaction mechanism, and bio-oil yields and compositions, Energy Fuel. 38 (2024) 8437–8459, https://doi.org/10.1021/acs.energyfuels.4c00240.

[150] G. Teri, L. Luo, P.E. Savage, Hydrothermal treatment of protein, polysaccharide, and lipids alone and in mixtures, Energy Fuel. 28 (2014) 7501–7509, https://doi.org/10.1021/EF501760D/ASSET/IMAGES/EF-2014-01760D_M001.GIF.

[151] W. Yang, Z. Wang, J. Han, S. Song, Y. Zhang, W. Gong, The role of polysaccharides and proteins in bio-oil production during the hydrothermal liquefaction of algae species, RSC Adv. 9 (2019), https://doi.org/10.1039/c9ra07150d.

[152] P.M. Guirguis, M.S. Seshasayee, B. Motavaf, P.E. Savage, Review and assessment of models for predicting biocrude yields from hydrothermal liquefaction of biomass, RSC Sustainability 2 (2024), https://doi.org/10.1039/d3su00458a.

[153] R.B. Madsen, P. Biller, M.M. Jensen, J. Becker, B.B. Iversen, M. Glasius, Predicting the chemical composition of aqueous phase from hydrothermal liquefaction of model compounds and biomasses, Energy Fuel. 30 (2016), https://doi.org/10.1021/acs.energyfuels.6b02007.

[154] D. Castello, M.S. Haider, L.A. Rosendahl, Catalytic upgrading of hydrothermal liquefaction biocrudes: different challenges for different feedstocks, Renew. Energy 141 (2019), https://doi.org/10.1016/j.renene.2019.04.003.

[155] H. Shahbeik, H. Kazemi Shariat Panahi, M. Dehhaghi, G.J. Guillemin, A. Fallahi, H. Hosseinzadeh-Bandbafha, H. Amiri, M. Rehan, D. Raikwar, H. Latine, B. Pandalone, B. Khoshnevisan, C. Sonne, L. Vaccaro, A.S. Nizami, V.K. Gupta, S. S. Lam, J. Pan, R. Luque, B. Sels, W. Peng, M. Tabatabaei, M. Aghbashlo, Biomass to biofuels using hydrothermal liquefaction: a comprehensive review, Renew. Sustain. Energy Rev. 189 (2024), https://doi.org/10.1016/j.rser.2023.113976.

[156] S. Yan, D. Xia, N.C. Lai, B. Jiang, X. Liu, New insight into the synergistic reactions involved in the hydrothermal co-liquefaction of synthetic polymer wastes by molecular dynamics and DFT methods, J. Hazard Mater. 449 (2023), https://doi.org/10.1016/j.jhazmat.2023.131032.

[157] J. Jiang, Y. Zhao, F.Q. Zhao, S.Y. Xu, X.H. Ju, The mechanism of methyl hydrazine degradation by supercritical water oxidation using ReaxFF simulation, J. Hazard Mater. 440 (2022), https://doi.org/10.1016/j.jhazmat.2022.129832.

[158] S. Yan, D. Xia, X. Liu, Beneficial migration of sulfur element during scrap tire depolymerization with supercritical water: a molecular dynamics and DFT study, Sci. Total Environ. 776 (2021), https://doi.org/10.1016/j.scitotenv.2021.145835.

[159] S. Yan, D. Xia, T. Zhang, X. Liu, Enhancing oil production via radical reactions during hydrothermal coliquefaction of biomass model compounds and plastics: a molecular dynamic simulation study, Waste Management 189 (2024) 166–176, https://doi.org/10.1016/j.wasman.2024.08.019.

[160] D. López Barreiro, F.J. Martin-Martinez, C. Torri, W. Prins, M.J. Buehler, Molecular characterization and atomistic model of biocrude oils from hydrothermal liquefaction of microalgae, Algal Res. 35 (2018) 262–273, https://doi.org/10.1016/j.algal.2018.08.034.

[161] P. Biller, A.B. Ross, Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content, Bioresour. Technol. 102 (2011) 215–225, https://doi.org/10.1016/J.BIORTECH.2010.06.028.

[162] Z. Wang, Reaction Mechanisms of Hydrothermal Liquefaction of Model Compounds and Biowaste Feedstocks - ProQuest, University of Illinois at Urbana-Champaign, 2011. https://www.proquest.com/openview/d842cd261088ba4efd1dc3fecb6d809d/1?cbl=18750&pq-origsite=gscholar&parentSessionId=LhKhe%2B14mEPVnPLRNZQ7ylFaRepYxBqrgFt0YgdVUqw%3D. (Accessed 28 January 2024).

[163] S. Leow, J.R. Witter, D.R. Vardon, B.K. Sharma, J.S. Guest, T.J. Strathmann, Prediction of microalgae hydrothermal liquefaction products from feedstock biochemical composition, Green Chem. 17 (2015) 3584, https://doi.org/10.1039/c5gc00574d.

[164] Y. Li, S. Leow, A.C. Fedders, B.K. Sharma, J.S. Guest, T.J. Strathmann, Quantitative Multiphase Model for Hydrothermal Liquefaction of Algal Biomass, vol. 19, 2017, p. 1163, https://doi.org/10.1039/c6gc03294j.

[165] J. Yang, Q. Sophia He, H. Niu, K. Corscadden, T. Astatkie, Hydrothermal liquefaction of biomass model components for product yield prediction and reaction pathways exploration, Appl. Energy 228 (2018) 1618–1628, https://doi.org/10.1016/J.APENERGY.2018.06.142.

[166] Y.P. Shia, B.Y. Yu, Development of a rigorous and generalized model on the hydrothermal liquefaction (HTL) process for bio-oil production, Process Saf. Environ. Protect. 171 (2023) 541–554, https://doi.org/10.1016/J.PSEP.2023.01.046.

[167] Y. Li, S. Leow, A.C. Fedders, B.K. Sharma, J.S. Guest, T.J. Strathmann, Quantitative multiphase model for hydrothermal liquefaction of algal biomass, Green Chem. 19 (2017) 1163–1174, https://doi.org/10.1039/C6GC03294J.

[168] L. Sheng, X. Wang, X. Yang, Prediction model of biocrude yield and nitrogen heterocyclic compounds analysis by hydrothermal liquefaction of microalgae with model compounds, Bioresour. Technol. 247 (2018) 14–20, https://doi.org/10.1016/J.BIORTECH.2017.08.011.

[169] D.C. Hietala, C.K. Koss, A. Narwani, A.R. Lashaway, C.M. Godwin, B.J. Cardinale, P.E. Savage, Influence of biodiversity, biochemical composition, and species identity on the quality of biomass and biocrude oil produced via hydrothermal liquefaction, Algal Res. 26 (2017) 203–214, https://doi.org/10.1016/J.ALGAL.2017.07.020.

[170] S.A. Channiwala, P.P. Parikh, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, Fuel 81 (2002) 1051–1063, https://doi.org/10.1016/S0016-2361(01)00131-4.

[171] R. De, Comparative dynamic optimization study of batch hydrothermal liquefaction of two microalgal strains for economic bio-oil production, Bioresour. Technol. 398 (2024) 130523, https://doi.org/10.1016/J.BIORTECH.2024.130523.

[172] A. Cascioli, M. Baratieri, Enhanced thermodynamic modelling for hydrothermal liquefaction, Fuel 298 (2021) 120796, https://doi.org/10.1016/J.FUEL.2021.120796.

[173] A. Fredenslund, R.L. Jones, J.M. Prausnitz, Group-contribution estimation of activity coefficients in nonideal liquid mixtures, AIChE J. 21 (1975), https://doi.org/10.1002/aic.690210607.

[174] E. Muzenda, From UNIQUAC to modified UNIFAC Dortmund : a discussion. 3rd International Conference on Medical Sciences and Chemical Engineering (ICMSCE'2013), 2013.

[175] J.G. Van Bennekom, J.G.M. Winkelman, R.H. Venderbosch, S.D.G.B. Nieland, H. J. Heeres, Modeling and experimental studies on phase and chemical equilibria in high-pressure methanol synthesis, Ind. Eng. Chem. Res. 51 (2012) 12233–12243, https://doi.org/10.1021/IE3017362.

[176] M. Jayathilake, S. Rudra, L.A. Rosendahl, Numerical modeling and validation of hydrothermal liquefaction of a lignin particle for biocrude production, Fuel 305 (2021) 121498, https://doi.org/10.1016/J.FUEL.2021.121498.

[177] D. Forchheim, U. Hornung, A. Kruse, T. Sutter, Kinetic modelling of hydrothermal lignin Depolymerisation, Waste Biomass Valorization 5 (2014) 985–994, https://doi.org/10.1007/s12649-014-9307-6.

[178] W. Feng, H.J. van der Kooi, J. de Swaan Arons, Phase equilibria for biomass conversion processes in subcritical and supercritical water, Chem. Eng. J. 98 (2004), https://doi.org/10.1016/S1385-8947(03)00209-2.
[179] D. Castello, F. Collard, D. Cronin, M. Thorson, A. Funke, Mass Balances for DTL Processes - Considerations and Best Practice IEA Bioenergy: Task 34, IEA Bioenergy, 2022.
[180] F. G Fonseca, A. Funke, Modeling of liquid-vapor phase equilibria of pyrolysis bio-oils: a review, Ind. Eng. Chem. Res. (2024), https://doi.org/10.1021/acs.iecr.4c00775.
[181] M. Rojas Salas, F. Fonseca, A. Araujo, M. Garcia-Perez, A. Funke, Liquid-liquid equilibrium prediction in fast pyrolysis bio-oil systems: a framework for incorporating bio-oil complexity, Energy & Fuels (2024).
[182] A. Jalalinejad, J.Y. Seyf, A. Funke, N. Dahmen, Phase equilibrium calculation of bio-oil-related molecules using predictive thermodynamic models, Energy & Fuels (2024), https://doi.org/10.1021/acs.energyfuels.3c04395.
[183] A. Jalalinejad, J.Y. Seyf, A. Funke, N. Dahmen, Solvent Screening for separation of lignin-derived molecules using the NIST-UNIFAC model, ACS Sustain Chem Eng 11 (2023) 7863–7873, https://doi.org/10.1021/ACSSUSCHEMENG.3C00906/SUPPL_FILE/SC3C00906_SI_008.XLSX.
[184] K.Parku George, R.P. Santos, Funke, Axel, D. Nicolaus, Phase equilibria Aided optimization of levoglucosan extraction during Condensation of fast pyrolysis bio-oils, Energy & Fuels 38 (2024), https://doi.org/10.1021/acs.energyfuels.4c01097.
[185] I.A. Basar, H. Liu, H. Carrere, E. Trably, C. Eskicioglu, A review on key design and operational parameters to optimize and develop hydrothermal liquefaction of biomass for biorefinery applications, Green Chem. 23 (2021) 1404–1446, https://doi.org/10.1039/D0GC04092D.
[186] M. Jayathilake, S. Rudra, L.A. Rosendahl, Hydrothermal liquefaction of wood using a modified multistage shrinking-core model, Fuel 280 (2020) 118616, https://doi.org/10.1016/J.FUEL.2020.118616.
[187] M. Jayathilake, S. Rudra, L.A. Rosendahl, Numerical modeling and validation of hydrothermal liquefaction of a lignin particle for biocrude production, Fuel 305 (2021) 121498, https://doi.org/10.1016/J.FUEL.2021.121498.
[188] D. Iryani, S. Kumagai, M. Nonaka, K. Sasaki, T. Hirajima, Hydrothermal carbonization kinetics of sugarcane bagasse treated by hot compressed water under variabel temperature conditions, J. Eng. Appl. Sci. 11 (2016) 4833–4839.
[189] E. Kamio, H. Sato, S. Takahashi, H. Noda, C. Fukuhara, T. Okamura, Liquefaction kinetics of cellulose treated by hot compressed water under variable temperature conditions, J. Mater. Sci. 43 (2008) 2179–2188, https://doi.org/10.1007/S10853-007-2043-6/METRICS.
[190] C. Georgakis, C.W. Chang, J. Szekely, A changing grain size model for gas-solid reactions, Chem. Eng. Sci. 34 (1979) 1072–1075. http://www.sciencedirect.com/science/article/pii/0009250979800123.
[191] S.K. Bhatia, D.D. Perlmutter, A random pore model for fluid-solid reactions: II. Diffusion and transport effects, AIChE J. 27 (1981) 247–254, https://doi.org/10.1002/aic.690270211.
[192] P.M. Guirguis, M.S. Seshasayee, B. Motavaf, P.E. Savage, Review and assessment of models for predicting biocrude yields from hydrothermal liquefaction of biomass, RSC Sustainability 2 (2024) 736–756, https://doi.org/10.1039/D3SU00458A.
[193] M. Sánchez, J.C. Maya, B. Pecha, F. Chejne, A. Quinchía, Effect of particle characteristics, kinetics and transport phenomena on the prediction of particle mass loss and products yields during biomass fast pyrolysis, J. Anal. Appl. Pyrolysis 168 (2022) 105786, https://doi.org/10.1016/J.JAAP.2022.105786.
[194] M.A. Sánchez, J.C. Maya, F. Chejne, B. Pecha, A.M. Quinchía-Figueroa, Mathematical modeling of multi-phenomena anisotropic systems: Ejection of primary aerosols during the fast pyrolysis of biomass, Mathematics 12 (2024), https://doi.org/10.3390/math12060925.
[195] D. Ramkrishna, Population Balances Theory and Applications to Particulate Systems in Engineering, Academic Press, San Diego, 2000.
[196] A. Mathanker, S. Das, D. Pudasainee, M. Khan, A. Kumar, R. Gupta, A review of hydrothermal liquefaction of biomass for biofuels production with a special focus on the effect of process parameters, co-solvents and extraction solvents, Energies 14 (2021), https://doi.org/10.3390/en14164916.
[197] M.A.R. Martins, E.A. Crespo, P.V.A. Pontes, L.P. Silva, M. Bülow, G.J. Maximo, E. A.C. Batista, C. Held, S.P. Pinho, J.A.P. Coutinho, Tunable hydrophobic eutectic solvents based on Terpenes and Monocarboxylic acids, ACS Sustain Chem Eng 6 (2018) 8836–8846, https://doi.org/10.1021/acssuschemeng.8b01203.
[198] R. Ghadge, N. Nagwani, N. Saxena, S. Dasgupta, A. Sapre, Design and scale-up challenges in hydrothermal liquefaction process for biocrude production and its upgradation, Energy Convers. Manag. X 14 (2022), https://doi.org/10.1016/j.ecmx.2022.100223.
[199] U. Kilgore, E. Diaz, B. Spry, Y. Jiang, S. Li, A. Schmidt, M.R. Thorson, Solvent processing for improved separation of hydrothermal liquefaction products, Sustain. Energy Fuels 8 (2024) 3279–3289, https://doi.org/10.1039/d4se00516c.
[200] B. Guo, B. Yang, P. Weil, S. Zhang, U. Hornung, N. Dahmen, The effect of Dichloromethane on product separation during continuous hydrothermal liquefaction of Chlorella vulgaris and aqueous product recycling for algae Cultivation, Energy Fuel. 36 (2022) 922–931, https://doi.org/10.1021/acs.energyfuels.1c02523.
[201] U. Kilgore, E. Diaz, B. Spry, Y. Jiang, S. Li, A. Schmidt, M.R. Thorson, Solvent processing for improved separation of hydrothermal liquefaction products, Sustain. Energy Fuels 8 (2024) 3279–3289, https://doi.org/10.1039/d4se00516c.
[202] A. Bjelic, B. Hočevar, M. Grilc, U. Novak, B. Likozar, A review of sustainable lignocellulose biorefining applying (natural) deep eutectic solvents (DESs) for separations, catalysis and enzymatic biotransformation processes, Rev. Chem. Eng. 38 (2022) 243–272, https://doi.org/10.1515/REVCE-2019-0077/ASSET/GRAPHIC/J_REVCE-2019-0077_CV_005.JPG.
[203] L. Pola, S. Collado, M. Wörner, U. Hornung, M. Díaz, Eutectic solvents for the valorisation of the aqueous phase from hydrothermally liquefied black liquor, J. Environ. Chem. Eng. 11 (2023), https://doi.org/10.1016/j.jece.2023.111040.
[204] K. Aktas, H. Liu, C. Eskicioglu, Treatment of aqueous phase from hydrothermal liquefaction of municipal sludge by adsorption: comparison of biochar, hydrochar, and granular activated carbon, J Environ Manage 356 (2024), https://doi.org/10.1016/j.jenvman.2024.120619.
[205] A. Matayeva, P. Biller, Hydrothermal liquefaction aqueous phase treatment and hydrogen production using electro-oxidation, Energy Convers. Manag. 244 (2021), https://doi.org/10.1016/j.enconman.2021.114462.
[206] A. Taghipour, U. Hornung, J.A. Ramirez, R.J. Brown, T.J. Rainey, Aqueous phase recycling in catalytic hydrothermal liquefaction for algal biomass and the effect on elemental accumulation and energy efficiency, J. Clean. Prod. 289 (2021), https://doi.org/10.1016/j.jclepro.2020.125582.
[207] P. Karka, I. Johannsen, S. Papadokonstantakis, Hydrothermal liquefaction integrated with wastewater treatment plants - life cycle assessment and technoeconomic analysis of process system options, Sustain. Energy Fuels 8 (2024) 3438–3451, https://doi.org/10.1039/d3se01211e.
[208] B. Egerland Bueno, L. Américo Soares, D. Quispe-Arpasi, I. Kimiko Sakamoto, Y. Zhang, M.B. Amancio Varesche, R. Ribeiro, G. Tommaso, Anaerobic digestion of aqueous phase from hydrothermal liquefaction of Spirulina using biostimulated sludge, Bioresour. Technol. 312 (2020), https://doi.org/10.1016/j.biortech.2020.123552.
[209] Y. Zhu, S.B. Jones, A.J. Schmidt, K.O. Albrecht, S.J. Edmundson, D.B. Anderson, Techno-economic analysis of alternative aqueous phase treatment methods for microalgae hydrothermal liquefaction and biocrude upgrading system, Algal Res. 39 (2019), https://doi.org/10.1016/j.algal.2019.101467.
[210] J. Zimmermann, S. Chiaberge, S.B. Iversen, K. Raffelt, N. Dahmen, Sequential extraction and characterization of nitrogen compounds after hydrothermal liquefaction of sewage sludge, Energy Fuel. 36 (2022) 14292–14303, https://doi.org/10.1021/acs.energyfuels.2c02622.
[211] C. Wang, S. Zhang, S. Huang, Z. Cao, J. Xu, J. Lyu, Effect of hydrothermal treatment on biomass structure with evaluation of post-pyrolysis process for wood vinegar preparation, Fuel 305 (2021), https://doi.org/10.1016/j.fuel.2021.121513.
[212] L. Wang, Y. Chang, A. Li, Hydrothermal carbonization for energy-efficient processing of sewage sludge: a review, Renew. Sustain. Energy Rev. 108 (2019) 423–440, https://doi.org/10.1016/j.rser.2019.04.011.
[213] H. Dao Thi, K. Van Aelst, S. Van den Bosch, R. Katahira, G.T. Beckham, B.F. Sels, K.M. Van Geem, Identification and quantification of lignin monomers and oligomers from reductive catalytic fractionation of pine wood with GC × GC – FID/MS, Green Chem. 24 (2022) 191–206, https://doi.org/10.1039/D1GC03822B.
[214] Y. Jiang, C. Mevawala, S. Li, A. Schmidt, J. Billing, M. Thorson, L. Snowden-Swan, Uncertainty analysis for techno-economic and life-cycle assessment of wet waste hydrothermal liquefaction with centralized upgrading to produce fuel blendstocks, J. Environ. Chem. Eng. 11 (2023), https://doi.org/10.1016/j.jece.2023.109706.
[215] E. Medina-Martos, P. Miranda-Rey, J.L. Gálvez-Martos, J. Dufour, Techno-economic assessment of a hydrothermal liquefaction process for energy recovery from food waste, in: Computer Aided Chemical Engineering, Elsevier B.V., 2020, pp. 1729–1734, https://doi.org/10.1016/B978-0-12-823377-1.50289-5.
[216] W.U. Rahman, M. Patel, V. Kurian, A. Kumar, A comparative techno-economic assessment of fast pyrolysis, hydrothermal liquefaction, and intermediate pyrolysis of municipal solid waste for liquid transportation fuels production, Energy Convers. Manag. 267 (2022), https://doi.org/10.1016/j.enconman.2022.115877.
[217] G.D.O. Moreira, G.F. Costa, R.M. Cavalcante, A.F. Young, Process simulation and economic evaluation of pyrolysis and hydrothermal liquefaction as alternatives for the valorization of wood waste from the pulp and paper industry, Energy Convers. Manag. 325 (2025), https://doi.org/10.1016/j.enconman.2024.119387.
[218] G.D.O. Moreira, G.F. Costa, R.M. Cavalcante, A.F. Young, Supplementary Material for “Process Simulation and Economic Evaluation of Pyrolysis and Hydrothermal Liquefaction as Alternatives for the Valorization of Wood Waste from the Pulp and Paper Industry,” n.d.