Biomass to Biocrude: A Brief Review of Catalytic Liquefaction

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Biomass energy is the largest source of renewable energy, accounting for approximately 55% of global renewable energy consumption. Therefore, it holds great importance for the efficient utilization of biomass. Hydrothermal liquefaction (HTL) has been demonstrated to convert biomass into liquid biofuels, with physicochemical properties comparable to conventional crude oil. Because moisture content is a key factor in choosing the best conversion method, HTL is especially well-suited for fresh biomass, which usually contains a substantial amount of moisture. This comprehensive review examines the research progress in biomass hydrothermal liquefaction, focusing on biomass types, liquefaction parameters, reactor configurations, and catalyst types, with particular emphasis on a comparative analysis of catalytic mechanisms. This study provides a structured framework for selecting optimal conversion processes by linking biomass types, parameters, reactors, and catalysts. Future research should prioritize the development of cost-efficient bifunctional catalysts and optimization of continuous reaction systems with respect to heat and mass transfer efficiency, and integration design of catalysts, while also aiming to minimize byproduct handling costs.

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INTRODUCTION

Renewable energy sources are currently attracting significant attention worldwide. Biomass consists predominantly of cellulose (40 to 60%), hemicellulose (20 to 40%), and lignin (10 to 25%), forming various feedstocks (woody, herbaceous, or aquatic) (Ji *et al.* 2020; Li *et al.* 2021a; Ren *et al.* 2023; Wang *et al.* 2023; Zhang *et al.* 2024c; Wu *et al.* 2025). Biomass energy type correlates with land use patterns. Most biomass consumption for energy is associated with biomass residues, which prevails in forestland and cropland (Dinesh Mohan *et al.* 2006; Zhang *et al.* 2024b). Biomass can be regenerated within 1 to 10 years, which is much shorter than fossil resources, enabling sustainable utilization. Solid municipal waste including biomass is anticipated to increase from 2.24 billion tons in 2020 to between 3.4 billion and 3.88 billion tons per year by 2050 (Konyannik and Lavie 2025). The waste generated from agriculture and forestry is around 140 billion tons of biomass each year (Tiwari *et al.* 2025). Such a large amount of waste biomass has prompted researchers to urgently develop efficient and low-cost technologies for energy recovery and utilization. In contrast, using biomass energy instead of fossil fuels has the potential to cut net greenhouse gas emissions by 70 to 90% (Cherubini and Strømman 2011). The development of integrated biorefineries combining the co-producing of bioenergy,

biochemicals, and biochar, aligning with circular economy principles, is important (Cai *et al.* 2018).

Biomass has received a lot of support from governments around the world as a renewable energy source. The 14th Five-Year Plan for Bioeconomy Development in China focuses on biomass power generation and biofuel industrialization through financial incentives and technology incubation programs (Zhang *et al.* 2022). In contrast, the Renewable Energy Directive (RED) III in EU has established even more ambitious 2030 targets, including a 14.5% reduction in greenhouse gas emissions intensity and a 29% share of renewables in transport (de Paula Leite *et al.* 2025). The U.S. Inflation Reduction Act (2022) gives more tax breaks to advanced biofuels and biogas projects and a funding of approximately $370 billion for clean energy to reduce carbon emissions by 40% by 2030 (Gu *et al.* 2025). Platforms such as the IEA help with international cooperation, which fosters with the transfer of biomass utilization technology, especially in systems that convert lignocellulosic biomass and algae (Marquez *et al.* 2024).

Significant limitations lie in traditional biomass conversions, such as biochemical (fermentation and anaerobic digestion) (Yu *et al.* 2020; Chen *et al.* 2022; Sun *et al.* 2022b; Du *et al.* 2023; Herrera-Balandrano *et al.* 2023) and physicochemical methods (extraction and transesterification) (He *et al.* 2017; Tang *et al.* 2018). These include extended processing times, rigorous feedstock requirements, and substantial pretreatment procedures, which raise the operational cost and increase energy consumption (Cai *et al.* 2021). In contrast, thermochemical processes such as pyrolysis, gasification, and hydrothermal liquefaction have prominent advantages (Jing *et al.* 2020; Cai *et al.* 2021; Li *et al.* 2021b; Villacrés-Granda *et al.* 2021; Qiu *et al.* 2023; Shao *et al.* 2023). These processes can be completed in shorter reaction times, tolerate diverse feedstocks, and produce high-energy-density outputs such as biocrude, syngas, and biochar (Shen *et al.* 2019; Wang and Wu 2023). Recent advancements highlight the potential of the liquefaction process. For instance, Cutz *et al.* (2025) processed crude olive pomace through hydrothermal liquefaction, achieving biocrude yields exceeding 51 wt% with low oxygen content. As a method that can directly process wet biomass, hydrothermal liquefaction is attracting increased attention.

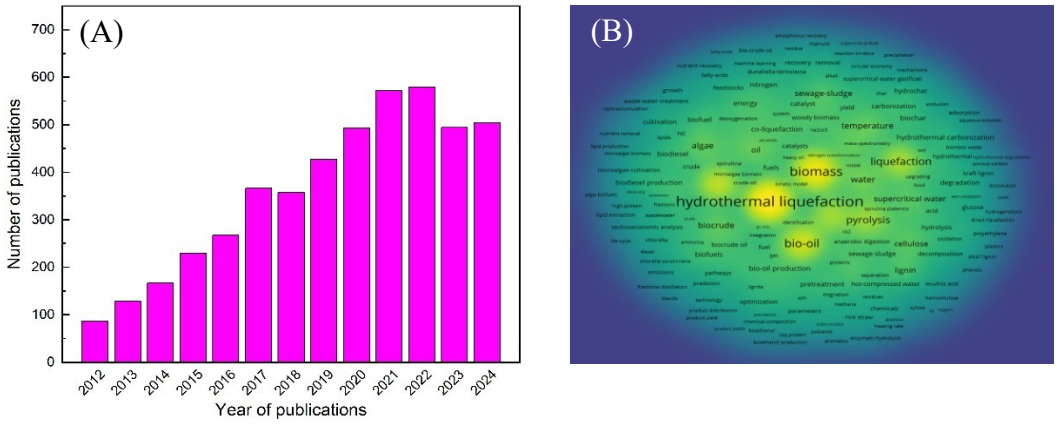

Fig. 1. Publications on hydrothermal liquefaction from 2012 to 2024 (as indexed on the Web of Science database)

Over the past decade, more than 5000 articles have been published on the topic of biomass liquefaction, indicating the importance of this field. Figure 1A represents the

publication tendency of biomass hydrothermal liquefaction based on the Web of Science database since 2012. It shows increased interest in liquefaction of biomass in the past 12 years. The frequency of the keywords was counted and visualized by VOSViewer software based on the content of relevant publications (Fig. 1B). Most existing reviews lack systematic integration of catalytic mechanisms or pay insufficient attention to the quantitative correlation between catalysts and product performance. Thus, this review gives a brief survey of the liquefaction process and discusses the up-to-date liquefaction mechanism towards different catalysts.

HYDROTHERMAL LIQUEFACTION OF BIOMASS

Feedstocks

Based on the biochemical composition, biomass can be conventionally categorized into three primary types: 1) woody biomass (Wu *et al.* 2025), 2) lipid-rich biomass (Ding *et al.* 2020a), and 3) organic waste streams (Sarker *et al.* 2025). The utilization of biomass has evolved over three historical stages: primitive combustion (pre-industrial era), first-generation biofuel production (19th to 20th century), and advanced biorefinery development (21st century onwards) (Demirbas 2008). The conversions of microalgae, algae, and sludge represent prominent research areas contributing to the most publications in the hydrothermal liquefaction research field (Fig. 2).

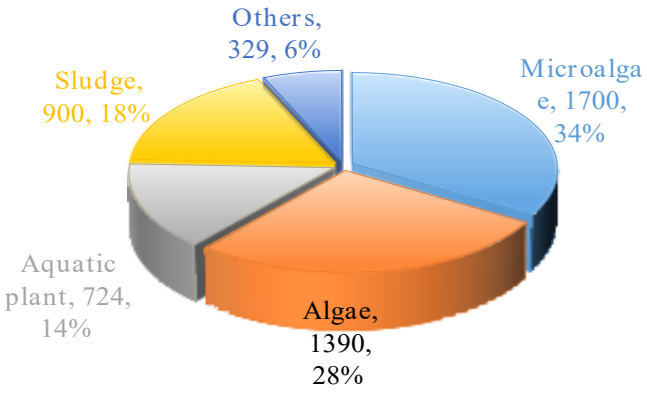

Fig. 2. Distribution of publications based on different feedstocks (as indexed on the Web of Science database from 2012 to 2024)

Microalgae exhibit rapid growth rates, together with high lipid and protein contents, which could enhance biocrude yield during liquefaction (Wang *et al.* 2023; Yin *et al.* 2023; Shah *et al.* 2024). Their low lignin content further reduces the energy requirement for depolymerization, enabling efficient conversion at moderate temperatures (250 to 350 °C). Macroalgae, such as seaweeds, are rich in carbohydrates (Otero *et al.* 2023), which hydrolyze into monosaccharides under subcritical water conditions (Kulikova *et al.* 2022). However, their high ash and low lipid content make them unsuitable for biofuel production by liquefaction (Kulikova *et al.* 2022). Sewage sludge is a byproduct of wastewater treatment containing a large amount of lipids bound within microbial cell walls (Yuan *et al.* 2021), in which the total average of saturated fatty acids reaches 55% (Fan *et al.* 2022). Hydrothermal liquefaction disrupts extracellular polymeric substances at 300 to 350 °C, thereby enhancing biocrude synthesis (Hassan *et al.* 2021; Liu *et al.* 2025; Nazari *et al.*

2025). This process enables concurrent mineralization of heavy metals into stable residues, decreasing disposal costs (Sun *et al.* 2022a). Sludge with over 80 wt% moisture can be directly handled through the liquefaction without extra solvent supply, offering a carbon-negative pathway for sludge treatment (Hu *et al.* 2021).

Liquefaction Process

The HTL has undergone continuous development over several decades. The early liquefaction study started during the oil crisis period (1970s to 1980s). As the 1990s began, the attention changed to model molecules (such cellulose and lignin) to learn more about chemical pathways (Sawayama *et al.* 1999). At that time, Goudriaan and Peferoen (1990) patented the HTU® process for wastewater sludge liquefaction. During the 2000s, the US National Renewable Energy Laboratory highlighted the potential of algal HTL, achieving high biocrude yields (Dutta *et al.* 2016). From the 2010s to the present, research has focused on co-liquefaction, catalysis, and integration of biorefining (Nahar *et al.* 2025; Pathak and Vairakannu 2025).

Hydrothermal liquefaction is a thermochemical conversion process that transforms wet biomass into an aqueous phase (containing biocrude), gas, and solid residue under subcritical conditions (typically 250 to 400 °C, 5 to 25 MPa) (Durak *et al.* 2026). This process circumvents the energy-intensive pre-drying stage, making it an ideal route to convert feedstocks with high moisture content like algae, sewage sludge, and food waste (Gollakota *et al.* 2018; Okoro *et al.* 2025). During liquefaction, water acts as both solvent and reactant (Luo *et al.* 2018; Zhang *et al.* 2018). There are a few important steps in the procedure. Biopolymers, including cellulose, hemicellulose, lignin, proteins, and lipids, break down into monomers including glucose, fatty acids, and amino acids in the first step (Lu *et al.* 2022; Chen *et al.* 2024). Especially, the glycosidic bond in cellulose is broken to form glucose intermediates, while the scission of the β-O-4 bond in lignin releases phenolic compounds (Feng *et al.* 2019; Ji *et al.* 2020; do Couto Fraga *et al.* 2021; Han *et al.* 2021). The second step involves monomer dehydration and decarboxylation, forming relative intermediates (Kruse *et al.* 2013). In the last step, these intermediates recombine through Maillard reactions (proteins + sugars) or Diels-Alder pathways, yielding nitrogenous compounds or polyaromatic hydrocarbons (Zhang *et al.* 2019b; Chen *et al.* 2020; Li *et al.* 2020). Because there are significant differences in the composition of biomass, the mechanisms and involved reactions are consequently complex. To date, the detailed mechanism of hydrothermal liquefaction has not been fully elucidated in the literature.

Comparison of Liquefaction with Pyrolysis

Pyrolysis and liquefaction are the predominant thermochemical processes exhibiting high biofuel conversion efficiency from various feedstocks. Pyrolysis has been widely studied for energy recovery from both dry and moist feedstocks (Li *et al.* 2025; Zhang *et al.* 2025b). Pyrolysis is categorized into three kinds based on the heating rate. Slow pyrolysis involves low heating rates (5 to 30 °C/min) and long residence times (minutes to hours), favoring biochar production (Patra *et al.* 2021; Huang *et al.* 2025). Fast pyrolysis is associated with elevated heating rates (≧ 100 ℃/s) and short residence times (< 2 s), maximizing biocrude production (60 to 75 wt%) (Mohan *et al.* 2006; Rahman *et al.* 2024). Flash pyrolysis means that there is extremely rapid heating (≧ 1000 ℃/s) for enhanced liquid production (Pielsticker *et al.* 2025; Song *et al.* 2025). The oil phase is also the major product of pyrolysis. The typical product distributions from liquefaction and pyrolysis of microalgae, macroalgae, and lignocellulosic biomass are compared in Fig. 3.

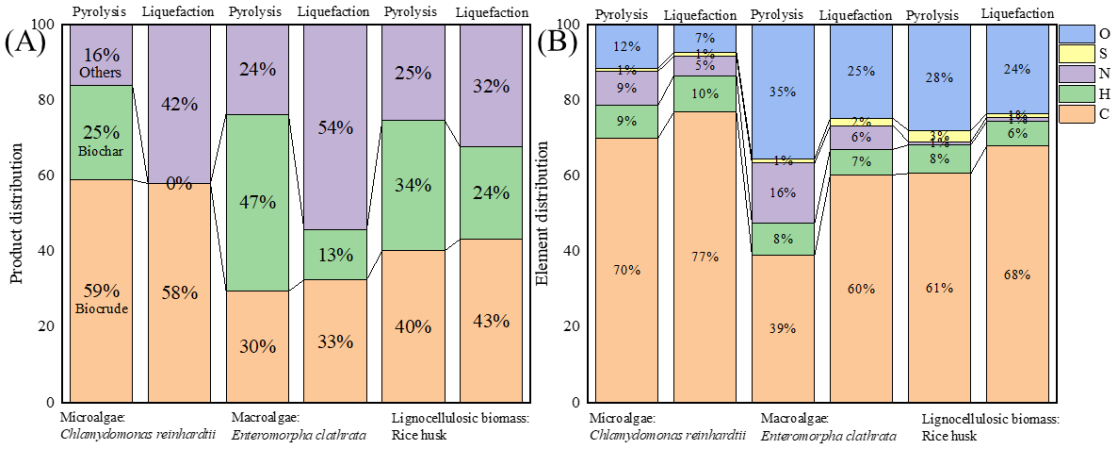

Fig. 3. Product distribution (A) and biocrude oil elemental analysis (B) of hydrothermal liquefaction (300 °C) and pyrolysis (500 °C) with different feedstocks (Hognon *et al.* 2015; Hu *et al.* 2018)

Hognon *et al.* (2015) reported that the biocrude yield from hydrothermal liquefaction of *Chlamydomonas reinhardtii* is comparable with that from the pyrolysis route. The product distribution varies with reaction conditions, resulting from complex reactions within the process. Proteins in microalgae were found to contribute most significantly to pyrolysis oil, while both lipids and proteins are crucial in the production of HTL biocrude. Hu *et al.* (2018) compared the liquefaction and pyrolysis of *Enteromorpha* and rice husk (Hu *et al.* 2018). They reported a higher oil phase yield in the hydrothermal liquefaction of both feedstocks. From the elemental analysis of the oil phase, hydrothermal liquefaction reduced oxygen content while retaining more carbon (Hu *et al.* 2018). Asafu-Adjaye *et al.* conducted a preliminary investigation on hydrothermal liquefaction and pyrolysis of southern yellow pine (Asafu-Adjaye *et al.* 2022). They highlighted the higher oil phase productivity of liquefaction than pyrolysis, and the pyrolysis route did not yield any esterified compounds. Haarlemmer *et al.* investigated the liquefaction and pyrolysis properties of beech wood, which contains higher lignin content compared with southern yellow pine (Haarlemmer *et al.* 2016). They reported low oil phase yield for both routes. In the case of liquefaction, alkaline additives can adjust the system pH, leading to increased biocrude production and reduced oil viscosity. For pyrolysis, increasing the temperature causes more unsaturation and a loss in biocrude yield (Haarlemmer *et al.* 2016). Chernova *et al.* (2022) carried out liquefaction and pyrolysis experiments for *Arthrospira platensis*. They confirmed that the oil phase yield obtained by HTL was significantly higher than that of pyrolysis. At the same time, the biochar yields using both technologies were almost the same.

Liquefaction Reactors

Batch reactors, which have simple structures, are widely used in laboratory-scale liquefaction studies. However, these systems encounter challenges, such as uneven heating, secondary reactions during cooling, and pressure fluctuations during processing (Lak *et al.* 2023; Zhang *et al.* 2025a). Non-uniform heating usually happens in the autoclaves applying outer heating furnaces, resulting in localized overheating and carbide formation, which adversely impacts the overall conversion efficiency and product yield (Ekuase *et al.* 2022). The incorporation of stirring configurations can improve the heat and mass transfer characteristics within the liquefaction system, causing higher conversion efficiency (Zhang

et al. 2019a). Figure 4 shows a schematic diagram of a typical batch reactor used for biomass liquefaction. Batch reactor systems typically consist of a gas supply module, a reactor made of Inconel or stainless steel, a furnace with a temperature controller, a drying unit, and a gas collection or detection module. Batch systems offer enhanced process control (temperature, pressure, and residence time), higher result reproducibility, and compatibility compared with continuous or semi-continuous operations. To achieve higher heating rates and uniform temperature distribution within the reactor, several miniature batch reactors for biomass hydrothermal liquefaction were investigated. Prestigiacomo *et al.* (2020) constructed a mini reactor with 16 mL volume using a Swagelok® VCR male union and caps (316SS). They reported a higher biocrude yield when using the mini reactor compared with the conventional autoclave in the same conditions. A fused-silica capillary reactor system comprising silica capillary tubes with internal diameters of 300 um to 2 mm combined with a microscope and a digital camera was used in biomass liquefaction. Applying this silica system, continuous observation of phase changes during liquefaction is possible (Xie *et al.* 2017; Wang *et al.* 2018).

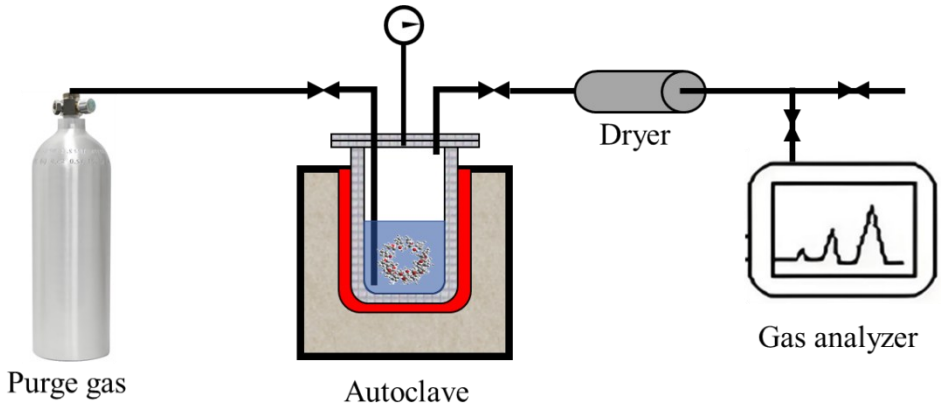

Fig. 4. Schematic diagram of the batch reactor system

Continuous flow systems are essential for scaling up the chemical processes, providing benefits in efficiency, controllability, and scalability compared to batch systems (Ubene *et al.* 2022). The plug flow reactor system displays high heat and mass transfer efficiency profits from the laminar flow (Wodołażski and Smoliński 2025). Because hydrothermal liquefaction conditions are complex, plug flow reactors are more appropriate for continuous flow systems (Tran and Khanh-Quang 2016). Figure 5 shows a schematic diagram of a typical plug flow reactor system used for biomass liquefaction. However, several disadvantages are also reported in the literature, including the risk of clogging from solid residue and intermediates (Cheng *et al.* 2019b), limited feedstock types, and non-uniform mixing of the feedstock with heterogeneous catalysts (Chen *et al.* 2019; Ruiz *et al.* 2020). The solid residue is one of the major products from the liquefaction of biomass, especially the woody feedstock. Thus, the residue combined with heavy oil product increases the plugging risk of the continuous reactor (Lappa *et al.* 2016). Such plugging is more prevalent at turning points with steeper angles within the system. Therefore, in the design of the reactor, it should be alleviated by using an inner wall of the reactor that is as smooth as possible and by reducing sharp elbows with large angles (Cheng *et al.* 2019b). Using an optimized pumping strategy, applying a relatively higher temperature, and using a suitable biomass slurry loading can effectively reduce the risk of reactor plugging (Cheng

et al. 2019a). Cheng *et al.* (2019a) successfully operated a continuous-flow reactor for 4 h at 350 °C and 17 MPa (with a 5 wt% loading) using algal biomass. No blockages occurred during this period. Biocrude with a yield of 28.1 wt% and a calorific value of 38 to 39 MJ/kg was obtained. Furthermore, the quality of light oil compounds produced from the plug-flow reactor was similar to that produced from the batch reactor (Cheng *et al.* 2019a). To further prevent the reactor blockages, Wagner *et al.* (2017) applied an *in-situ* collection module for the solid reaction products by introducing a double-tube design, which enhanced the overall heating rates, leading to extended reaction time. They achieved maximum biocrude yields of 21.9 wt% with 5 wt% algae loading at around 320 °C, which is comparable to that from batch experiments.

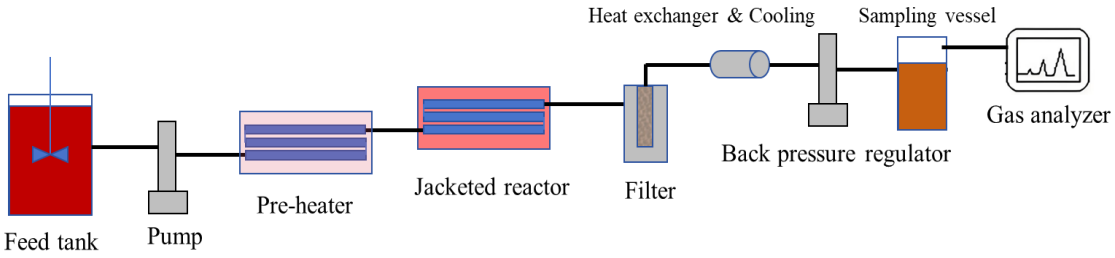

Fig. 5. Schematic diagram of the plug flow reactor system

Advanced reactor systems such as nozzle reactors have garnered significant attention due to enhanced reaction kinetics and product yields through controlled fluid dynamics. Rapid heat and mass transfer makes this reactor suitable for fast biomass hydrothermal liquefaction (Khanh-Quang *et al.* 2017). Intense mixing and shear forces generated by high-velocity fluid jets (Prades *et al.* 2020) significantly reduce reaction time from hours to seconds, while minimizing undesirable secondary char formation (Khanh-Quang 2020). However, material corrosion and structure defects of the mixing reactors cause limitations (Migliorino *et al.* 2022).

Parameter Effects

Among critical operating parameters, reaction temperature has a significant impact on the product distribution and liquefaction pathway (Zhou *et al.* 2017; Tiwari and Mallick 2025). Research indicates that the optimal temperature window for maximizing the yield of biocrude is 280 to 350 °C (Madsen and Glasius 2019; Sudibyo *et al.* 2021). Below 280 °C, lignocellulose components (such as cellulose and hemicellulose) are not completely depolymerized, and large amounts of oxygen-rich compounds are formed (Tang *et al.* 2018). When the reaction temperature exceeds 350 °C, due to the intensification of decarboxylation and dehydration reactions, the organic macromolecules from biocrude will undergo secondary cracking, generating gaseous by-products (CH_4, CO_2) and biochar, which in turn decreases biocrude yield (Rana *et al.* 2019; Bai *et al.* 2023). In the hydrothermal liquefaction process, pressure and temperature collaboratively maintain the solvent in a liquid state, prevent evaporation, and enhance mass transfer (Yu *et al.* 2022). System pressure affects water density, which influences the solubility of organic matter and the reaction kinetics (Toor *et al.* 2025). Increased pressure facilitates the formation of stable reactive intermediates (such as free radicals and glucose derivatives), which promotes repolymerization to form more hydrophobic oil compounds (Wang *et al.* 2019). However, excessively high pressure (> 30 MPa) may hinder the recombination of free

radicals, thereby reducing the biocrude yield (Zhang *et al.* 2007). Reaction time affects the processes of hydrolysis, dehydration, and recombination in the hydrothermal liquefaction of biomass (Barreiro *et al.* 2013). The optimal reaction time depends on reaction temperature. At relatively low temperatures, longer durations are typical to achieve higher conversion rates and biocrude yields (Liu *et al.* 2025). However, when the reaction temperature is high enough, longer duration (about 60 min) would cause further degradation of oil products through Maillard reaction or cracking reactions (Sarker *et al.* 2025). Recent research has identified a time threshold (30 to 45 min) to balance intermediate transitions and stability (Shahbeik *et al.* 2024).

CATALYSTS

Hydrothermal liquefaction biocrude usually exhibits unfavorable characteristics, such as high oxygen and nitrogen content, high acidity, and high viscosity, which limit its direct use as a transportation fuel and requires further refining (Hao *et al.* 2021; Shah *et al.* 2022).

Table 1. Summary of Catalyst Types on Biocrude Production Rate

Author	Feedstock	Catalysts	Conditions	Yields (wt%)
Ahmed Ebrahim *et al.* 2022	Food waste	Fe, $NiMo/Al_2O_3$, Ru/Al_2O_3, Pd/Al_2O_3, Pt/Al_2O_3	350 ºC, 60 min with CO_2 or H_2, 3 to 4.6% catalyst	With CO_2: Fe (39 wt%)>Non>Ru/Al_2O_3With H_2: $NiMo/Al_2O_3$ (58 wt%)>Non> Fe
Alper *et al.* 2019	Wood	KF/Al_2O_3	250 to 350 ºC, 15 to 60 min, 10 to 40% catalyst	KF/Al_2O_3 achieved the highest biocrude yield (14 wt%) at 300 ºC
Cheng *et al.* 2017	Sawdust	Ni/HZSM-5, K_2CO_3, HZSM-5	300 ºC, 60 min	K_2CO_3 (67 wt.%)>HZSM-5>12%Ni/HZSM-5>6%Ni/HZSM-5>Non
Ding *et al.* 2020b	Cellulose	KH_2PO_4, K_2HPO_4, K_3PO_4	280 to 360 ºC, 30 min, 5% catalyst	K_3PO_4 (25 wt.%)>K_2HPO_4>KH_2PO_4>Non (320℃)
Durak *et al.* 2026	*Sinapis arvensis*	Fe/TiO_2, Al/TiO_2, $Fe\text{-}Al/TiO_2$	275 to 325 ºC, 30 min, 10% catalyst	Al/TiO_2 (30.8 wt.%)>Fe/TiO_2>$Fe+Al/TiO_2$>Non (300℃)
Hong *et al.* 2021	Penicillin residue	HCOOH, CH_3COOH, $NaCO_3$, NaOH, MCM-41, MCM-48	280 ºC, 3 h, 1 to 10% catalyst	Organic acids give similar biocrude yield as alkaline catalysts (around 30 wt%). MCM-48 obtained the highest yield of 36.44 wt%.
Zhang *et al.* 2024a	Cotton stalks	H_2SO_4, HCl, HNO_3, NaOH, KOH, Na_2CO_3, K_2CO_3	220 ºC, 4 h, 1 mol/L catalyst	Inorganic acid inhabited the production of biocrude.
Motavaf *et al.*	Food waste	Ni/C, Pt/C, Ru/C, Pd/C	350 ºC, 40 min, 50% catalyst	Non (41 wt%)>Pt/C (27 wt%)>Ru/C>Pd/C

The complexity of biomass composition and the elaborate reaction network occurring under hydrothermal conditions result in unstable yield and quality of the biocrude (Deniel *et al.* 2017). To promote the biomass conversion and biocrude production, the application of catalysts has become an important means. Several types of catalysts have demonstrated negligible effects on either biocrude production rate or the quality (Table 1). Reaction pathways can be optimized through catalyst modification (Shah *et al.* 2022), affecting the relative abundance of different compound categories (phenols, ketones, acids, esters, and hydrocarbons) (Yan *et al.* 2018; Hong *et al.* 2021; Liu *et al.* 2024). Catalysts primarily influence the kinetic rates and selectivity of key reactions, such as deoxidation, denitrification, cracking, and hydrogenation, to adjust the composition, energy density, and combustion performance of biocrude (Hao *et al.* 2021; Shah *et al.* 2022). Reactivity and selectivity under HTL conditions of the catalyst are influenced by parameters such as pH, redox properties, surface area, pore structure, and stability in subcritical water (Robin *et al.* 2015; Zhang *et al.* 2024a). Comprehending the specific functions and mechanisms of the catalysts is crucial for developing efficient and economical HTL processes. This section reviews the roles and characteristics of various types of catalysts in the hydrothermal liquefaction of biomass, with a focus on homogeneous catalysts, noble metal catalysts, and transition metal catalysts.

Homogeneous Catalysts

Homogeneous catalysts are solubilized in the reaction medium facilitating intimate interaction with feedstock and reaction intermediates, potentially leading to high catalytic activity (Shah *et al.* 2022). A range of homogeneous catalysts, such as inorganic acids, bases, and inorganic salts, have been examined in biomass hydrothermal liquefaction. These catalysts predominantly influence the initial hydrolysis and depolymerization stages, along with subsequent cracking and dehydrogenation reactions (Zhang *et al.* 2024a; Yamashita and Suzuki 2025). Alkaline homogeneous catalysts, such as sodium hydroxide, potassium carbonate, sodium carbonate, and potassium hydroxide, have been extensively investigated in biomass hydrothermal liquefaction. For penicillin residues, sodium carbonate was reported to increase the biocrude yield from 26.09 wt% to 31.44 wt% (Hong *et al.* 2021). Sodium hydroxide significantly increased soluble organics in the aqueous phase, while reducing acids and furfural in the biocrude, and hindered the production of solid residues during sugarcane liquefaction (Yan *et al.* 2018). Similarly, sodium hydroxide reported the highest activity in liquefaction of cotton stalk compared with potassium carbonate, sodium carbonate, and potassium hydroxide (Zhang *et al.* 2024a). Alkaline catalysts facilitate the breakdown of biomass macromolecules, particularly lignin and other carbohydrates, thus enhancing the biocrude yield and minimizing solid residues (Yan *et al.* 2018; Zhang *et al.* 2024a). The proposed mechanisms of alkaline catalysis include the cleavage of ester and ether bonds and the disruption of lignin-carbohydrate complex structure by ionic expansion, promoted hydrolysis and cracking reactions (Zhang *et al.* 2024a). However, the impact of homogeneous catalysts on biocrude yield varies with feedstock types. Although these catalysts are active in biomass liquefaction, there are two major drawbacks of homogeneous alkaline catalysts: difficulty in separating them from complex liquid product mixtures and potential corrosion of equipment (Shah *et al.* 2022; Zhang *et al.* 2024a).

Acidic homogeneous catalysts, including inorganic acids, such as hydrochloric acid, sulfuric acid, and nitric acid, along with certain metal salts, have also been investigated in HTL of biomass. Acidic catalysts have been reported to effectively promote

the hydrolysis of polysaccharides into sugars (Xu *et al.* 2025). Research on cotton stalk demonstrates that acidic catalysts affect the yield and composition of biocrude; however, their conversion rate and oil phase productivity improvement is inferior to that of alkaline catalysts (Zhang *et al.* 2024a). Unlike alkaline catalysts, acidic environments typically facilitate the production of furfural and dehydration byproducts (Xu *et al.* 2025). Nonetheless, similar to alkaline catalysts, acidic catalysts also face challenges such as separation issue and potential reactor corrosion (Shah *et al.* 2022). Yamashita *et al.* established that zinc chloride in hydrothermal liquefaction of castor cake increased the yield of biocrude and favored hydrocarbon generation, suggesting that it played a role in promoting cracking and deoxygenation reactions (Yamashita and Suzuki 2025). Potassium phosphate (KH_2PO_4, K_2HPO_4, and K_3PO_4) demonstrated the ability to modify the degradation pathways of biomass model compounds (Ding *et al.* 2020b). Nickel salts were documented to promote the generation of hydrogen and biocrude rich in C1-C3 acids, 5-hydroxymethylfurfural (HMF) and furfural (Shende *et al.* 2015). Despite the homogeneous catalysts that have high activity due to their close contact with reactants, their recovery and reutilization pose significant challenges, resulting in increased process costs and adverse environmental impacts (Shah *et al.* 2022). These limitations encourage vigorous research on heterogeneous catalysts that are readily separable and potentially reusable.

Noble Metals

Noble metal catalysts, including platinum (Pt), ruthenium (Ru), palladium (Pd), and rhodium (Rh), are recognized for their high activity in hydrogenation and deoxygenation reactions, which reduce oxygen and increase hydrogen content, thereby improving the quality of biocrude (Hao *et al.* 2021). Because of their high cost, noble metals are typically dispersed as small metal nanoparticles with minimal loading on high surface area supports. Motavaf *et al.* (2021) investigated the activity of supported catalysts (Pt/C, Ru/C, Pt/Al_2O_3, and Ru/Al_2O_3) in food waste liquefaction and found no increase in biocrude yield for any of those catalysts. This was also confirmed by Ahmed Ebrahim *et al.* (2022), who conducted liquefaction with a Pt-based catalyst but observed minimal impact of the catalyst on biocrude yield. Yang *et al.* (2014) applied a 5 wt% loaded Pt/C catalyst for HTL of microalgae, showing an enhancement in the quality of biocrude compared to experiments that without a catalyst. The biocrude contained large amounts of light compounds and a significant fraction of small molecules. The Pt/C catalyst effectively diminished nitrogen and oxygen levels in the biocrude, highlighting its hydrogenation and de-nitrogenation capabilities. The proposed mechanism involves catalyzing the hydrogenation and hydrolysis reactions of oxygen-containing functional groups (such as hydroxyl, carbonyl, carboxylic acid, and ether) and nitrogen-containing compounds (such as amide, amine, and indole) at active sites, thereby forming hydrocarbons, water, and ammonia (Yang *et al.* 2014; Hao *et al.* 2021).

Ruthenium is another commonly applied noble metal catalyst for biomass liquefaction, which yields relatively high-quality biocrude. Lu *et al.* (2025) synthesized a supported Ru/ZrO_2-SiO_2 catalyst by depositing ruthenium particles onto a mixed oxide support and found a significant positive impact on biocrude composition. An increase in hydrocarbon compound concentration and a decrease in carboxylic acids and esters content, confirming that ruthenium exerts a substantial hydrodeoxygenation impact (Lu *et al.* 2025). The main advantage of noble metal catalysts is their exceptional activity in hydrogenation and deoxygenation, resulting in biocrude with reduced oxygen level and elevated calorific value. However, Zhu *et al.* (2022) showed an increase of less than 5% in biocrude yield

with the addition of Ru/C in the hydrothermal liquefaction of barley straw, significantly lower than the yields obtained with alkaline catalysts, suggesting a limited capacity for enhancing oil phase production. Nguyen *et al.* (2021) even demonstrated an inhibitory effect of commercial Ru/C on biocrude yield during hydrothermal liquefaction of *Cladophora socialis*. Moreover, the high cost and potential failure of noble metals in harsh hydrothermal conditions due to mechanisms, such as leaching, coking, and poisoning, remain significant obstacles to their large-scale application (Robin *et al.* 2015; Shah *et al.* 2022).

Transition Metals

Transition metal catalysts, including various catalysts based on iron (Fe), nickel (Ni), cobalt (Co), copper (Cu), molybdenum (Mo), vanadium (V), manganese (Mn), titanium (Ti), and zinc (Zn), are more economical than noble metals while still offering multiple catalytic activities for HTL (Shah *et al.* 2022; Amarasekara *et al.* 2025). These catalysts manifest in diverse configurations, including unsupported oxides, mixed metal oxides, or loaded on supports such as zeolites, silica, or alumina. Their catalytic activity originates from involvement in redox reactions, providing acidic or basic sites based on the nature of the active component and the support (Robin *et al.* 2015; Bu *et al.* 2018; Zhang *et al.* 2024a).

Supported transition metal catalysts, especially those with zeolites, such as HZSM-5, MCM-41, and MCM-48, have garnered significant interest because of their bifunctional properties. These catalysts integrate the hydrogenation/dehydrogenation activity of the metal with the cracking and isomerization activity of the support to achieve efficient biocrude production (Cheng *et al.* 2017; Liu *et al.* 2024). Compared to unmodified HZSM-5, Ni/HZSM-5 has been found to exhibit higher activity in improving the biocrude quality by diminishing undesired oxygenated components and augmenting hydrocarbon content (Cheng *et al.* 2017). The bifunctionality of Ni/HZSM-5 enables both the cracking of larger molecules through the acidic zeolite and dehydrogenation/hydrogenation reactions through the scattered nickel active sites, thereby generating a superior grade biocrude. Among the evaluated catalysts, 6% Ni/HZSM-5 achieved the highest hydrocarbon content in the biocrude (Cheng *et al.* 2017). Robin *et al.* (2015) deposited Mo, Cu, and Fe onto HZSM-5 and examined their catalytic activity in the hydrothermal liquefaction of microalgae. They reported excellent stability for these catalysts under hydrothermal conditions. Mo-based catalysts increased the formation of aromatic compounds, while Ni- and Cu-based ones demonstrated higher deoxygenation efficiency (Robin *et al.* 2015).

Liu *et al.* performed hydrothermal liquefaction of herbal residue utilizing MCM-41 supported Fe, Ni, and Co single-metal catalysts (Liu *et al.* 2024). The findings showed that biocrude production of single-metal catalysts was significantly higher than that without catalysts, with Co/MCM-41 yielding the greatest oil production (27.05 wt%). Unsupported metal oxides also exhibit superior catalytic performance. Nirmal *et al*. (2025) employed nanostructured magnetic Fe_3O_4 as a catalyst for the hydrothermal liquefaction of microalgae (Nannochloropsis). These economical and reusable catalysts increased the yield (up to 31.4%) and improved the quality of biocrude. The Fe_3O_4 was recycled up to five cycles with minimal reduction in activity, demonstrating its potential in large-scale industrial applications (Nirmala *et al.* 2025). Amarasekara *et al.* (2025) developed transition metal catalysts employing the concept of dual active components ($Fe\text{-}MO_x/SiO_2$, where M = V, Mn, Co, Ni, Cu, Mo) and evaluated their activity under hydrothermal liquefaction conditions. Compared to the single metal oxides, these dual metal oxides

increased the biocrude yield, with Fe-CuO_x/SiO_2 attaining the maximum value of 78.8 wt%. The Fe-CuO_x/SiO_2 catalyst exhibited good performance even after five cycles (Amarasekara *et al.* 2025). Other transition metal oxides, such as TiO_2 and CeO_2, have also been explored. TiO_2 demonstrated significant catalytic activity in the hydrothermal liquefaction of urban sewage sludge, yielding high-quality biocrude and an aqueous phase containing recoverable nutrients (Kumar *et al.* 2022). At a moderate temperature of 220 °C, CeO_2 exhibited considerable activity for cotton stalk liquefaction (Zhang *et al.* 2024a). The combination of Ce^{3+}/Ce^{4+} redox cycling, OH-LCC disruption, and ionic expansion facilitates biomass liquefaction. The total pore volume and average pore width of the oxide have a negative correlation with catalytic efficiency, while the acidic/basic sites on the oxide surface affect the conversion efficiency. A greater concentration of weak bases is associated with an elevated yield of biocrude (Zhang *et al.* 2024a). Furthermore, Alper *et al.* (2019) introduced KF/Al_2O_3 in the pinewood liquefaction process and documented an increased yield of biocrude, with reduced solid residue yield.

FUTURE DIRECTIONS

Based on the current state of research, several key areas require further investigation to advance the field of catalytic biomass HTL: (1) Conduct the comprehensive Lifecycle Assessment (LCA) of catalysts: To minimal the environmental footprints, evaluating the environmental impacts of catalysts throughout their entire lifecycle in crucial, including material acquisition, preparation, application, and disposal. It is also important to optimize the recycling processes for spent catalysts to achieve high sustainability of the system. (2) Consider the Techno-Economic Assessment (TEA) of using catalysts: This includes the development of high-performance transition metal catalysts and non-metal catalysts that can match the activity of noble metals for key reactions is crucial for process cost reduction. The exploration of earth-abundant elements, such as iron, in novel formulations is promising. (3) Integration with Machine Learning for catalyst design: Biomass exhibits significant variation in composition. Designing catalysts specifically tailored to the unique characteristics of different biomass can optimize conversion efficiency and product distribution. Machine learning can predict the performance of catalysts with different physicochemical properties and also the reaction pathways in HTL conditions using regression algorithms or neural networks. This predictive capability guides the rational design of novel catalysts, reducing the experimental costs. (4) Novel catalyst-reactor integration: The optimization of interactions between catalyst properties and reactor design is critical for maximizing catalyst performance and process efficiency. (5) Valorization of aqueous phase: The aqueous phase from HTL is a significant byproduct containing dissolved organics and nutrients. The development of catalysts for the treatment or valorization of this stream is important for improving the overall sustainability and economics of the HTL process.

CONCLUDING REMARKS

Through hydrothermal liquefaction, biomass can be directly converted into liquid fuels. Subcritical liquefaction technology has been extensively studied, with a primary focus on product distribution and related mechanisms. The objective of this review has

been to provide a comprehensive understanding of the liquefaction process by examining the up-to-date research on biocrude generation and emphasizing the challenges and opportunities. This review has presented current knowledge and understanding of the effects of hydrothermal liquefaction driving factors on the yield and quality of biocrude. Various aspects have been discussed, including biomass types, liquefaction reactors, liquefaction parameters, and catalysts. The mechanistic influences of homogeneous and heterogeneous catalysts on the hydrolysis, decomposition, and polymerization of biomolecules during the hydrothermal liquefaction process have been preliminarily elucidated. However, the focus of future attention will mainly regard parameter optimization, novel reactor design, catalysts development with stability, reusability, and long-term availability.

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