

Review Article



# Advancing Renewable Energy: The Prospects of Hydrothermal Liquefaction (HTL) for Biomass into Bio-oil Conversion

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**Abstract:** Hydrothermal liquefaction (HTL) offers a promising approach to convert biomass into bio-oil, contributing to sustainable energy solutions and reducing dependence on fossil fuels. HTL mimics natural geological processes by decomposing biomass at high temperatures (200–350°C) and pressures (10–25 MPa) in a water-based environment, producing bio-oil that can be refined for various energy applications. Despite its potential, several technical challenges limit the efficiency and scalability of HTL. The high energy requirements for maintaining these conditions also pose economic challenges, making HTL less competitive against traditional energy sources. HTL is the complex composition of bio-oil, which contains a mix of organic compounds that make refining and upgrading challenging. This complexity also affects bio-oil's stability, requiring advanced purification techniques to ensure quality and usability. Solid residue formation during HTL reduces bio-oil yields and increases processing costs. Recent advances aim to address these limitations. New catalysts, such as metal oxides, improve bio-oil yield and reduce oxygen content, enhancing fuel quality. Innovations in reactor design, including continuous flow and microwave-assisted reactors, improve heat transfer and operational stability. Integrating HTL with other biomass conversion technologies, like anaerobic digestion, also offers pathways to increase efficiency and energy recovery. Advances in analytical techniques, like gas chromatography and mass spectrometry, are also improving bio-oil characterization, informing more effective upgrading strategies. While challenges remain, ongoing research in catalyst development, reactor optimization, and process integration strengthens HTL's potential as a sustainable energy solution, supporting its role in advancing bio-oil production for a cleaner, renewable future.

**Keywords:** Biofuel Production; Environmental Sustainability; Green Technology; Hydrothermal Processing; Renewable Fuel Sources.

## 1. Introduction

Global energy demand is increasing, concurrent with worldwide promises to diminish greenhouse gas emissions and pursue renewable energy sources, which are essential global concerns [1]–[3]. Sustainable energy sources are crucial for fostering economic growth and alleviating the environmental consequences of fossil fuel usage [4]. Biomass has emerged as one of this initiative's most potential renewable energy sources. Research demonstrates that biomass, organic material from living organisms or their by-products, possesses significant potential owing to its widespread availability in many ecosystems and carbon-neutral properties [5].

The carbon emitted by the combustion or processing of biomass is almost equal to the carbon sequestered throughout its life cycle, hence exerting a negligible impact on atmospheric CO<sub>2</sub> concentrations. This characteristic renders biomass an eco-friendly energy alternative, diminishing dependence on fossil fuels, which are significant sources of CO<sub>2</sub> emissions [6]. Moreover, advancing biomass as a renewable energy source facilitates effective resource management, particularly in tackling agricultural, forestry, and urban waste issues [7].

Bio-oil is a valuable product derived from biomass, a liquid fuel compatible with existing energy infrastructure. Bio-oil has the potential to replace fossil fuels in sectors with high energy demands, such as transportation and industry [8], [9]. As a liquid fuel, bio-oil offers greater

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flexibility than solid biomass, making it easier to store, transport, and use in power systems that require liquid fuels. Furthermore, bio-oil derived from biomass has lower potential emissions than fossil fuels, providing a more environmentally friendly energy alternative [10], [11]. Converting biomass to bio-oil also enables sustainable waste management, particularly for agricultural and urban biomass waste that might otherwise go unused [12], [13]. Using biomass waste for bio-oil production can address energy supply challenges and waste disposal issues, supporting a more circular and sustainable energy system.

Besides its ecological benefits, bio-oil enhances national energy security, especially in nations that depend significantly on imported oil [14]. Generating bio-oil from native biomass enables countries to diminish reliance on energy imports and utilize locally accessible resources. Both biomass and bio-oil are essential in mitigating environmental damage and enhancing global energy resilience [15]. Employing this energy source provides a cleaner, more sustainable, and renewable future in the face of the pressing difficulties posed by global climate change [16], [17].

## 2. Basics of Hydrothermal Liquefaction

### 2.1. Fundamental Principles

Hydrothermal Liquefaction (HTL) is a thermochemical method that transforms wet biomass into bio-oil by applying high temperatures and pressures in a water-based environment [18], [19]. This process simulates the natural geological formation of fossil fuels but operates on significantly shorter timescales. HTL is especially beneficial for processing wet biomass, including algae, sewage sludge, and agricultural residues, as it eliminates the need for energy-intensive drying processes often required by other thermochemical conversion methods, such as pyrolysis or gasification [20], [21].

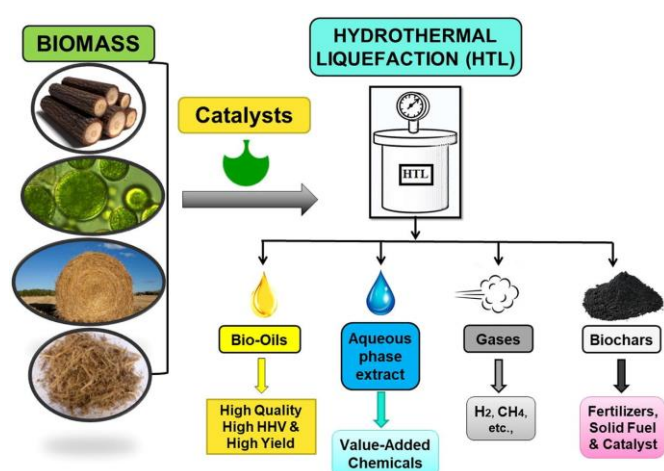


Figure 1. Process Chart for Hydrothermal Liquefaction [22].

The fundamental principle behind HTL lies in the unique properties of water at elevated temperatures and pressures, where it acts both as a solvent and a reactant. At these conditions—typically between 250°C and 450°C and pressures ranging from 100 to 350 bar—water can facilitate the breakdown of complex organic polymers such as lignin and cellulose into smaller molecules [23], [24]. The transformation results in bio-oil production, biochar, gases, and an aqueous phase containing soluble organics [25].

### 2.2. Water's Role in HTL

Under the high-temperature, high-pressure conditions of HTL, water exhibits properties crucial for the efficient conversion of biomass. In its supercritical state, where the temperature exceeds 374°C and pressure surpasses 221 bars, water's dielectric constant drops significantly, enhancing its ability to dissolve non-polar organic molecules. Water's ionic product also increases in the subcritical range, promoting ionic reactions that favor bio-oil formation rather than solid residues [26].

At subcritical conditions, water's high ionic product facilitates hydrolysis reactions, where large polymeric molecules in the biomass are broken down into more minor, soluble organic compounds. These soluble intermediates undergo further reactions, such as dehydration and decarboxylation, to produce smaller organic molecules like alcohols, acids, and phenols—standard in lignocellulosic feedstocks [27]. The supercritical state of water also plays a crucial role in deoxygenating bio-oil, improving its energy content, and making it more suitable for upgrading into fuels [28].

### 2.3. Reaction Mechanism in HTL

The HTL process consists of several interconnected reaction stages. The first step, hydrolysis, involves the breakdown of biomass into water-soluble organic compounds. This is followed by depolymerization reactions, which convert these compounds into smaller fragments through dehydration and decarboxylation. These reactions release gases such as CO<sub>2</sub> and form intermediates either soluble in water or insoluble [29].

The final stage involves re-polymerization, where some smaller molecules recombine to form bio-oil and biochar. Condensation reactions and other complex polymerization mechanisms influence this stage. Bio-oil formation, in particular, depends highly on the feedstock composition, reaction conditions, and the presence of catalysts or pH modifiers [30].

The by-products of HTL include gases dominated by CO<sub>2</sub>, though varying amounts of H<sub>2</sub>, CH<sub>4</sub>, and CO can also be produced depending on the type of biomass and specific reaction conditions [31]. Additionally, an aqueous

phase rich in soluble organics—such as alcohols, acids, and phenols—remains, which can be processed further for bio-based chemical production [32].

#### 2.4. Factors Influencing HTL Efficiency

Several factors influence the efficiency of the HTL process, including temperature, pressure, feedstock composition, and the use of catalysts. The reaction temperature and pressure, in particular, are critical parameters that determine the phase behavior of water and the products formed. Most studies suggest that temperatures above 350°C and pressures of up to 250 bars are ideal for bio-oil production, as they promote ionic reactions conducive to liquefaction while avoiding the formation of solids or gases (Kruse, 2009).

The role of pressure in HTL, particularly at near- and supercritical conditions, has been somewhat overlooked in past studies, which primarily emphasized temperature as the dominant factor [33]. Recent research, however, shows that pressure significantly impacts the reaction pathways. For instance, at supercritical conditions, water can maintain a high ionic product at elevated pressures, enabling the continuation of liquefaction processes even at temperatures as high as 400°C. These conditions also allow for more complete deoxygenation of bio-oil, leading to a higher-quality end product [34]–[36].

The composition of the biomass feedstock also plays a crucial role in determining the reaction pathways and product yields. Lignocellulosic biomass, rich in cellulose and lignin, undergoes different reaction mechanisms than protein- or lipid-rich feedstocks such as algae or sewage sludge. This variability necessitates tailored approaches to HTL for different feedstock types, as different materials may require adjustments in reaction conditions to optimize bio-oil yield and quality [25], [37].

Catalysts and pH modifiers are often employed to enhance HTL efficiency. Alkali catalysts, such as sodium hydroxide, are commonly used to accelerate depolymerization reactions and improve bio-oil yields [38]. Catalysts can also reduce the formation of unwanted by-products, such as coke or gases, by promoting specific reaction pathways that favor bio-oil production [23].

#### 2.5. Supercritical Conditions in HTL

Supercritical water conditions, where temperature and pressure exceed critical points, significantly advance HTL technology. Supercritical water behaves differently from water in its liquid or gaseous states. Its low compressibility and specific heat capacity make it energy-efficient, while its enhanced solubility for organic compounds enables faster reaction kinetics [26].

One of the most critical findings in recent HTL research is that pressure, particularly at supercritical conditions, can dramatically influence the outcome of the process. For example, at 400°C and 350 bar, the ionic product of water is nearly equivalent to that at 350°C and 250 bar—conditions commonly cited as optimal in the literature [20]. These high-pressure, high-temperature environments allow for greater reaction completeness, facilitating the production of deoxygenated bio-oil that requires minimal further processing.

Furthermore, the energy cost associated with reaching and maintaining supercritical conditions is relatively low due to the low compressibility of water in these states. This finding has been one of the most significant developments in HTL over the past decade, as it has enabled more efficient bio-oil production at industrial scales without prohibitive energy inputs [39].

### 3. Key Parameters in HTL

HTL is an innovative technology for converting wet biomass into bio-oil by applying specific temperature, pressure, reaction time, and catalyst presence conditions. These parameters play a crucial role in influencing both the yield and quality of the bio-oil, and they are typically optimized according to the type of feedstock used and the desired characteristics of the final product.

#### 3.1. Temperature

HTL processes typically operate within a temperature range of 200 to 350 °C, with the optimal temperature varying depending on the feedstock and target product composition. The temperature is critical as it influences the breakdown of complex organic compounds in biomass. Higher temperatures enhance reaction kinetics, leading to greater bio-oil yields while reducing the formation of solid residues like char. Higher temperatures promote the cleavage of C–C and C–O bonds in biomass polymers, facilitating the conversion of lignocellulosic components (cellulose, hemicellulose, and lignin) into smaller, energy-dense molecules [40].

However, excessively high temperatures may also promote undesirable side reactions, such as polymerization and re-polymerization of bio-oil components, which can reduce the quality of the bio-oil by increasing the formation of tars and char. Studies indicate an optimal temperature range is critical to balancing bio-oil yield with quality. Temperatures above 350 °C have been associated with increased gas formation at the expense of bio-oil yield, impacting the efficiency of the process [23].

### 3.2. Pressure

The pressure in HTL processes is generally maintained between 10 to 25 MPa to keep water in its subcritical state and prevent the vaporization of the reaction mixture. This high-pressure environment enables water to act as a solvent and reactant, essential for facilitating biomass breakdown [20]. Under subcritical conditions, water exhibits unique properties such as higher ion product and lower dielectric constant, enhancing its ability to dissolve organic compounds and increase reaction efficiency.

Higher pressure improves the solubility of non-polar compounds in water, which aids in the homogeneous distribution of organic reactants, leading to a more uniform reaction environment and potentially higher bio-oil yields. Additionally, maintaining water in a liquid state at high pressure promotes hydrolysis reactions and enhances the overall reactivity of the system [41]. However, using very high pressures can also raise operational costs and may contribute to wear and tear on equipment, necessitating a balance between reaction efficiency and economic considerations.

### 3.3. Reaction Time

The reaction time in HTL is another crucial factor influencing bio-oil's yield and quality. The ideal reaction time depends on the specific feedstock and reaction conditions; however, reaction times typically range from a few minutes to several hours. Shorter reaction times may not allow for complete biomass conversion, potentially resulting in lower yields and an incomplete breakdown of high-molecular-weight compounds [42], [43].

Conversely, prolonged reaction times can increase the likelihood of secondary reactions, such as condensation and polymerization, which lead to solid by-products like char. This decreases the bio-oil yield and affects its quality, as extended exposure to high temperatures can lead to thermal degradation of desired compounds [44]. Therefore, optimizing reaction time is essential for maximizing bio-oil yield while minimizing the formation of undesired by-products.

### 3.4. Catalysts

Using catalysts in HTL can significantly enhance bio-oil yield and quality by promoting specific reactions that reduce undesirable elements like oxygen, nitrogen, and sulfur in the final product. Catalysts, particularly transition metals such as nickel (Ni), cobalt (Co), and iron (Fe), play a crucial role in deoxygenation and hydrogenation reactions, helping to produce bio-oil with lower oxygen content, higher stability, and greater energy density [45].

Catalysts can also decrease char formation by promoting targeted reactions that favor bio-oil production. The effectiveness of a catalyst depends on several factors, including its type, loading, and distribution within the reaction mixture. Ni-based catalysts are known for their high hydrogenation activity, which can help lower the acidity and improve the chemical stability of bio-oil [46]. The choice of catalyst should be optimized according to the feedstock composition and desired product characteristics to enhance the HTL process [47].

### 3.5. Composition and Quality Challenges of Bio-Oil

Bio-oil derived from hydrothermal liquefaction (HTL) is a complex blend of organic compounds, including phenols, ketones, aldehydes, and fatty acids. While bio-oil offers promising potential as a renewable fuel, several inherent characteristics limit its immediate usability and create a need for further upgrading. One key challenge is the high oxygen content present in bio-oil due to its biomass origin. This oxygen exists in various organic compounds that diminish the energy density and stability of the bio-oil, making it less efficient as a fuel. High oxygen levels also lead to poor combustion properties and cause the bio-oil to be acidic and unstable over time. Reducing the oxygen content, often achieved through catalytic deoxygenation, is crucial for improving bio-oil quality; a lower oxygen content corresponds to higher calorific value and better fuel properties, as outlined [48], [49].

Another major issue with bio-oil is its thermal stability. Due to unstable oxygenated compounds, bio-oil is susceptible to thermal degradation during storage and handling, leading to polymerization over time. This process can cause phase separation and form solid residues, reducing the energy yield and making bio-oil challenging to manage and use effectively. According to Bridgwater [50], further processing, such as hydrotreatment or catalytic upgrading, is often required to remove or stabilize these reactive components, thus improving the thermal stability of the bio-oil.

Bio-oil is frequently characterized by high viscosity, complicating its handling, pumping, and atomization in combustion systems. The oil's high water and polar compound content can also lead to phase separation, further complicating storage and usage. Gollakota et al. [51] highlight that post-processing to reduce water and oxygen content can help address these issues, making bio-oil more viable for fuel applications. Upgrading methods that target these limitations—such as viscosity reduction and phase stability improvement—are essential to transform bio-oil into a more practical and efficient renewable energy source.



## 4. Applications of HTL

To fully harness the potential of biomass conversion via hydrothermal liquefaction (HTL), it is critical to develop effective strategies for valorizing HTL products. The HTL process produces five main streams: biochar, heavy bio-oil/chemicals, light bio-oil/chemicals, an aqueous phase, and gaseous products. Efficient and economically viable separation methods for these products are crucial to optimize resource recovery and minimize environmental risks associated with unprocessed releases. Implementing these methods ensures that HTL can contribute

meaningfully to sustainable biomass utilization, enhancing both environmental and economic outcomes.

Biochar, a solid residue from hydrothermal liquefaction (HTL), is a sustainable resource for producing advanced carbon materials with tailored surface properties. Researchers and manufacturers utilize biochar to create materials such as porous carbon, heteroatom-doped biochar, carbon nanotubes, graphene, and carbon quantum dots. These innovations demonstrate outstanding potential for applications in various industries, including semiconductors, supercapacitors, and high-performance construction materials.

Table 1. Application of HTL

Steps	Purposes	Specific Uses	Sources
Gas	Renewable Energy Production, Biogas and Hydrogen Generation, and Chemical Manufacturing	Biofuel, Fermentation, Algal Cultivation, Hydrogen Source, HTL Recirculation	[52]–[60]
Solid	Soil Enhancement, Carbon Capture, Waste Disposal, Adsorbent Materials, and Energy Production.	Wastewater Treatment, Soil Enhancement, Graphene Production, Fertilizer Creation, Bioenergy, Catalyst Production, Energy Generation, and HTL Recycling	[61]–[73]
Liquid (hydrophobic & hydrophilic)	Renewable Energy, Fuels for Transportation, Chemical Raw Materials, Power Generation, Heating Solutions, Energy Storage	Gasoline, Aviation Fuel, Diesel, Microbial Fuel Cells (MFC), Anaerobic Digestion, Microbial Electrolysis Cells (MEC), Biobatteries, Algal Cultivation, Fertilizer Production, HTL Recycling	[50], [61], [74]–[85]

Biochar and hydrochar are also commonly utilized as catalysts, fertilizers, and bioremediation in wastewater treatment, and contaminated soil recovery produced from HTL also presents significant opportunities, especially as nutrient-rich fertilizers. This phase often contains around one-third of the feedstock's organic carbon and a substantial portion of nitrogen compounds, which accumulate due to the deamination of amino acids, yielding water-soluble ammonia. The aqueous phase (AP) holds considerable amounts of oxygen and phosphorus. Recirculating AP in hydrothermal processes is increasingly attractive, as it boosts bio-crude yields and reduces wastewater disposal costs. Studies have demonstrated that AP recirculation positively influences biocrude and hydrochar production and supports microbial growth.

## 5. Biomass Conversion to Bio-Oil

One of the primary methods to utilize biomass is converting it into bio-oil. This liquid fuel can be upgraded into high-quality fuels compatible with existing fuel infrastructure [86]. Bio-oil presents several advantages over solid and gaseous biofuels: it is easier to transport and store, compatible with conventional fuel engines, and

suitable for refining into transportation fuels. Bio-oil can be produced through multiple conversion technologies, including pyrolysis, gasification, and hydrothermal liquefaction (HTL), each with distinct characteristics and challenges.

Pyrolysis involves the thermal decomposition of biomass in the absence of oxygen, typically at 400–600°C [87]. Pyrolysis produces bio-oil, biochar, and gases but requires dry feedstock, meaning biomass with high moisture content must undergo energy-intensive drying beforehand [50]. This limits its application to certain biomass types and increases energy costs.

Gasification operates at higher temperatures (700–1200°C) and partially oxidizes biomass to generate synthesis gas (syngas), a mixture of hydrogen and carbon monoxide [88]. Syngas can be converted into liquid fuels through processes like Fischer-Tropsch synthesis, though this pathway is complex and involves high-energy inputs [89]–[91].

Hydrothermal Liquefaction (HTL) offers distinct advantages, especially for wet biomass. It operates under subcritical water conditions, requiring temperatures of 200–350°C and 10–25 MPa pressures, where water acts as a solvent and reactant [31]. This high-moisture compatibility makes HTL particularly efficient for biomass

such as algae, sewage sludge, and other wet organic residues that would require substantial drying if processed through pyrolysis or gasification.

HTL stands out as an energy-efficient approach, especially for high-moisture biomass, due to its ability to bypass drying, thereby conserving the energy that would otherwise be spent on pre-treatment [32]. During HTL, water's unique properties at high temperatures and pressures promote the breakdown of complex organic structures like lignin and cellulose into smaller molecules that can re-polymerize into liquid hydrocarbons, yielding a bio-oil with a higher energy density and reduced oxygen content compared to pyrolysis-derived oils [92].

## 6. Catalytic Processes

Transforming biomass into bio-oil through catalytic processes marks a significant breakthrough in renewable energy production, positioning bio-oil as a viable substitute for fossil fuels [86]. Biomass, a renewable source of organic materials like agricultural residues, forestry

waste, and energy crops, can be thermochemically converted into liquid fuels. One of the most common techniques employed in this conversion is pyrolysis, a process where biomass is subjected to high temperatures (400–600°C) in an oxygen-free environment. During pyrolysis, the complex lignocellulosic components of biomass (cellulose, hemicellulose, and lignin) are thermally decomposed into bio-oil, biochar, and syngas [93].

Catalysts play a pivotal role in enhancing the efficiency and selectivity of the biomass-to-bio-oil conversion process. Catalytic pyrolysis, in particular, is recognized for its ability to optimize bio-oil yield while improving its quality by reducing its oxygen content, acidity, and viscosity [94]. The primary role of a catalyst in this context is to modify reaction pathways, facilitating the deoxygenation, cracking, and aromatization reactions that transform biomass components into hydrocarbons similar to conventional fuels. By promoting these targeted reactions, catalysts help produce bio-oils with greater energy density and stability, which are essential for practical fuel applications [95].

**Table 2.** Research on the Catalytic HTL of Biomass

Raw Material	Catalyst	Temp. (°C)	Time (min.)	Effects on Bio-Oil	Sources
<i>Nannochloropsis sp.</i>	Pd/C	350	60	20%	[96]
<i>Dunaliella Tertiolecta</i>	5% Na <sub>2</sub> CO <sub>3</sub>	360	50	25.8%	[97]
<i>Spirulina Platensis</i>	Na <sub>2</sub> CO <sub>3</sub>	350	60	11.7%	[98]
<i>Chlorella Pyrenoidosa</i>	Ce/HZSM-5	300	20	33%	[99]
<i>Microcystic Viridic</i>	Na <sub>2</sub> CO <sub>3</sub>	300-340	30-60	33%	[100]
Corn Stalk	1 wt.% Na <sub>2</sub> CO <sub>3</sub>	300	30	13.8%	[101]
Wood Biomass	0.94 M K <sub>2</sub> CO <sub>3</sub>	280	15	25.2%	[102]
Pretreated Sorghum Bagasse	K <sub>2</sub> CO <sub>3</sub>	300	60	39%	[83]
<i>Cladophora glomerata</i>	Graphene Oxide/Polyurethane Composite	320	20	54%	[103]
<i>Prosopis Juliflora</i>	Nb/Al <sub>2</sub> O <sub>3</sub>	420	60	22.6	[104]

### 5.1. Zeolite-Based Catalysts

Zeolites, crystalline aluminosilicate minerals with a well-defined microporous structure, are among the most effective and widely used catalysts for biomass conversion, particularly in catalytic pyrolysis. Their unique framework of interconnected pores and channels allows them to selectively facilitate various reactions while providing high thermal stability, an essential characteristic given the high temperatures involved in pyrolysis (typically 400–600 °C) [105].

Zeolites contain acidic sites within their structure, which are instrumental in catalyzing deoxygenation, cracking, and aromatization reactions. In catalytic pyrolysis,

these acidic sites help break down large, oxygen-rich biomass molecules into smaller hydrocarbons, converting them into bio-oil with lower oxygen content and water production. This leads to a more stable bio-oil product with higher energy density. ZSM-5, a widely used zeolite catalyst, is particularly effective in promoting aromatization reactions, generating hydrocarbons with aromatic structures that enhance the stability of the bio-oil [106]. This improves the bio-oil's chemical composition and brings it closer to a conventional fuel profile.

Zeolites like ZSM-5, H-Y, and H-Beta each have distinct pore structures and acidity levels, allowing them to target specific reaction pathways in biomass pyrolysis. For example, ZSM-5's narrow channels favor the production of

smaller, aromatic hydrocarbons. At the same time, with its larger pores, H-Beta is more suited for cracking larger biomass molecules, which can help enhance liquid yields in the pyrolysis process [107], [108].

## 5.2. Metal Oxide Catalysts

Metal oxides, including titanium dioxide ( $\text{TiO}_2$ ), cerium oxide ( $\text{CeO}_2$ ), and magnesium oxide ( $\text{MgO}$ ), are effective in promoting deoxygenation and other reactions that help in reducing the oxygen content of bio-oil. These catalysts are often used in mixed forms or with supports like alumina to enhance their catalytic activity and minimize coke formation, which can otherwise deactivate the catalyst over time [109].

Metal oxides work primarily by facilitating decarboxylation and decarbonylation reactions, which remove oxygen in the form of  $\text{CO}_2$  and  $\text{CO}$ , respectively. For example,  $\text{TiO}_2$  promotes selective deoxygenation by supporting dehydration and decarboxylation, resulting in a bio-oil product with a more hydrocarbon-rich composition. With its primary sites,  $\text{MgO}$  can neutralize some acidic by-products, enhancing the bio-oils stability and reducing corrosiveness [110].

Mixed metal oxides, such as  $\text{Ni/MgO}$  and  $\text{Co/Al}_2\text{O}_3$ , are particularly noteworthy. Adding metals like nickel ( $\text{Ni}$ ) or cobalt ( $\text{Co}$ ) improves the efficiency of deoxygenation and hydrogenation reactions, producing bio-oils with lower oxygen content and higher energy density.  $\text{Ni}$ -based catalysts, for instance, are known for their hydrogenation capability, which can reduce bio-oil acidity and lead to a composition closer to traditional diesel fuels [111].

## 5.3. Modified Clay Catalysts

Modified clay catalysts, particularly montmorillonite clays treated with acids or metal ions, offer a cost-effective alternative to more expensive zeolites and metal oxides. Clays have a layered structure that provides active sites for catalytic reactions, and their modification with acidic or metallic components enhances their catalytic performance by introducing additional active sites or altering pore structures to facilitate the breakdown of biomass molecules [112].

Acid-treated montmorillonite, for example, has effectively catalyzed cracking reactions, producing smaller hydrocarbons that improve the flow properties of bio-oil. The acid modification increases the density and strength of the acidic sites within the clay, promoting deoxygenation and cracking reactions essential for converting biomass into high-quality bio-oil with lower viscosity and reduced oxygen content. Modified clays also reduce coke formation compared to other catalysts,

extending their lifespan and reducing operational costs [113].

Metal-modified clays, where metals like  $\text{Fe}$ ,  $\text{Ni}$ , or  $\text{Zn}$  are introduced into the clay matrix, enhance cracking and deoxygenation capabilities. These metal ions can also facilitate the formation of specific hydrocarbon structures, tailoring the bio-oil properties to suit different fuel applications [114]. Additionally, clays have shown promise in reducing acidity in bio-oil, a beneficial property for minimizing corrosion in storage and transport systems.

In catalytic pyrolysis, the catalyst is mixed with the biomass feedstock or used in situ within the reactor, where it alters the reaction environment to favor the production of desirable compounds. As biomass decomposes, the catalyst aids in breaking down the larger oxygenated molecules into smaller hydrocarbons through dehydration, decarboxylation, and decarbonylation. The resulting bio-oil has a reduced oxygen content and an increased proportion of hydrocarbons, making it closer in composition to conventional fuels [51].

## 7. Prospects of HTL Technology

Hydrothermal liquefaction (HTL) technology shows significant promise for converting biomass into bio-oil, yet various technical challenges still limit its wider adoption and efficiency. One of the significant challenges is corrosion within HTL reactors. The high temperatures and pressures required for HTL, especially in aqueous environments rich in organic acids formed during biomass conversion, can lead to severe corrosion of reactor materials. According to Ramirez et al. [115], this corrosion can shorten the reactor's lifespan, increase maintenance costs, and even create safety risks. To mitigate these issues, selecting corrosion-resistant materials or applying protective coatings is essential for ensuring the reactor's long-term operational stability.

Another significant technical barrier is the high energy requirement of the HTL process. This process demands substantial energy input to maintain constant high temperatures and pressures. Without efficient heating methods, these energy demands can make HTL economically challenging. Research by Brown et al. [116] highlights that recent HTL studies focus on integrating renewable energy sources and improving thermal efficiency within HTL systems. These efforts aim to reduce energy costs and enhance the overall economic viability of HTL processes.

The composition of the bio-oil produced through HTL also adds complexity to the process. Bio-oil from HTL is a complex mixture of organic compounds, such as phenols, ketones, acids, and water, which complicates further refining and upgrading for use as fuel. This intricate

composition also poses challenges in storage and handling, as certain unwanted compounds can degrade bio-oil quality over time. Jazrawi et al. [117] note that advanced purification techniques are necessary to separate and refine these components, thus enhancing bio-oil's stability and usability as a sustainable fuel source.

Solid residue formation, or char, during the HTL process presents additional challenges. This solid residue can limit the overall yield of bio-oil and often requires additional processing for removal or reuse, adding to HTL's operational complexity and costs. Weir et al. [118] point out that while char can contain valuable minerals for potential utilization, proper systems for separation and processing are essential to capitalize on this potential.

In response to these challenges, recent advancements in HTL technology focus on optimizing processes and improving the quality of bio-oil produced. One area of progress is the development of novel catalysts. Researchers have introduced heterogeneous catalysts, such as metal oxides and supported metal catalysts, which enhance reaction selectivity and increase bio-oil yield. These catalysts also facilitate reactions like deoxygenation and hydrodeoxygenation, which reduce oxygen content in the bio-oil, improving its overall quality. According to López Barreiro et al. [79], using catalysts can reduce the formation of unwanted compounds, resulting in a more stable and higher-quality bio-oil.

Reactor design innovations also hold promise for the HTL process. Advanced reactor designs, such as continuous flow and microwave-assisted HTL reactors, have been developed to improve heat and mass transfer. These designs enhance reaction efficiency, reduce processing time, minimize fouling risks, and improve operational stability. Research by Arpia et al. [119] shows that such designs allow for more uniform heating and better control over reaction conditions, leading to a more stable and efficient HTL process.

Optimization of HTL processes has also become a critical focus area. Researchers are adjusting parameters such as temperature, pressure, and residence time through computational modeling and experimental approaches to maximize bio-oil yield and quality across different feedstocks. Xu and Savage [120] found that this research enables the development of more tailored HTL processes suited to specific feedstock characteristics, resulting in more energy-efficient production.

Exploring the integration of HTL with other biomass conversion technologies, such as anaerobic digestion and gasification, has shown potential for improving energy efficiency and resource recovery. Combining multiple technologies makes it possible to process a wider variety of biomass feedstocks, minimize waste, and enhance the sustainability of biofuel production. Kumar et al. [105]

emphasize that such integration can reduce dependency on fossil fuels and maximize resource use within the HTL process.

Finally, advances in analytical techniques have greatly improved the characterization of bio-oil, providing valuable insights into its chemical composition. Techniques such as mass spectrometry, gas chromatography, and nuclear magnetic resonance (NMR) spectroscopy have proven essential in analyzing bio-oil's chemical makeup, guiding the development of more effective upgrading methods. Elliott et al. [20] highlight that these characterization techniques provide data crucial for developing high-quality bio-oil suitable for commercial and transport applications.

Although HTL technology faces considerable challenges, ongoing research in catalyst development, reactor design, process optimization, and characterization is paving the way for more efficient and economically viable biomass conversion. Continued innovation in these areas is essential for overcoming existing barriers and advancing HTL as a sustainable energy solution.

## 8. Conclusion

The conclusion highlights the potential and challenges of hydrothermal liquefaction (HTL) for converting biomass into bio-oil, a sustainable energy source. HTL technology promises to reduce fossil fuel reliance by producing bio-oil compatible with current energy infrastructures. However, significant challenges remain, including reactor corrosion, high energy requirements, and the complex composition of bio-oil. These obstacles impact the scalability and economic feasibility of HTL.

Recent advancements aim to address these issues through catalyst innovation, optimized reactor designs, and improved analytical techniques for bio-oil characterization. Continuous research focuses on integrating HTL with other biomass conversion methods, which could increase energy efficiency and make the process more sustainable. If these technical and economic barriers are overcome, HTL could play a significant role in sustainable energy production, supporting a cleaner and renewable future.

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