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Production of Advanced Biofuels: A Review of Catalytic Hydrothermal Liquefaction of Biomass Using Iron-Based Catalysts

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Abstract

This study explores the catalytic hydrothermal liquefaction of a wide range of biomass feedstock using iron-based catalysts. The utilization of biofuels presents an optimistic answer to the persistent challenges of climate change and the dwindling of finite fuel sources. By deriving these biofuels from renewable biomass sources, we can decrease our dependency on limited resources and strive toward a more sustainable future. In addition to powering our homes and vehicles, biofuels hold great potential as an indispensable raw material for the creation of valuable chemicals. By continuously exploring innovative methods to harness the power of biofuels, we can facilitate the path to a world that is cleaner, greener, and more prosperous for future generations. Using iron-based catalysts in the HTL process provides opportunities to increase biofuel yield, improve its quality, and make it more environmentally sustainable. By reviewing recent literature, this study provides valuable insights into the catalytic mechanisms, process optimization strategies, and product characteristics associated with biofuel production via HTL with iron-based catalysts. The key findings highlight the role of iron-based catalysts in promoting important chemical transformations, such as depolymerization, deoxygenation, and hydrogenation, which lead to improved biofuel properties. Additionally, the review discusses how various biomass feedstocks and catalyst formulations affect biofuel yield and quality.

Keywords

Iron-Based Catalysts, Hydrothermal Liquefaction, Biofuel

1. Introduction

The rapid population growth on the entire earth has led to an increase in global energy demand. Approximately 79% of the world's energy demand is provided by fossil fuels (US Energy Information Administration, 2009). This has increased the consumption of fossil fuels such as coal, and natural gas as the major sources of energy. Currently, the main energy source for the transportation industry is traditional liquid hydrocarbons [1]. The exchange of fossil fuels between supply and demand to fulfill global needs is not balanced due to the depletion of global fuel reserves leading to significant price fluctuations worldwide [2]. Moreover, the increasing global energy demand has prompted significant concerns regarding the rise in atmospheric concentrations of greenhouse gases [3]. The utilization of fossil fuels leads to a continuous rise in greenhouse gas emissions, with carbon dioxide (CO_2) levels escalating from 284 parts per million (ppm) in 1832 [4] to 424.70 as of 24th July 2024 (https://www.co2.earth). Projections indicated that global greenhouse gas emissions were poised to increase and anticipated global average temperatures to ascend by 2.5˚C - 5.4˚C above pre-industrial levels by 2050 if the trajectory persists [5]. The unusual climate change patterns due to greenhouse gas emissions and the swift depletion of fossil resources bring into question the reliability of fossil fuels as the primary energy source.

Considering the escalating energy demands and the concerning pollution levels, a transition to renewable energy sources such as wind, sunlight, water, biomass, etc., has emerged as an essential component of the energy mix, facilitating a restructuring of energy sources, diminishing reliance on fossil fuels, and offering opportunities to mitigate greenhouse gas emissions [1].

Among the renewable energy sources, biomass stands as the primary resource, constituting 47% of total renewable energy consumption and being the largest renewable energy source in use [6]. Biomass sources include wood wastes, energy crops, aquatic plants, crops, and their waste products, and municipal and animal wastes [7]. Different kinds of biomass produce different classes of biofuel. The biofuel produced is classified into first-generation, second-generation, and third-generation biofuels. The first-generation biofuels are produced from edible biomass such as corn, wheat, sugarcane, and grains. Second-generation biofuels are produced from non-edible feedstocks such as wood, agricultural residues, forestry waste, and municipal and industrial wastes [8]. The third-generation biofuels are derived from algae and other aquatic biomass. Aquatic biomass is considered a source of third-generation biofuels due to their perennial and inherent growth, high growth rate, and inability to compete with other crops for arable land [9].

Refining facilities cannot directly utilize biomass. Therefore, biomass-to-biofuel conversion technologies play a pivotal role in converting biomass into high-energy fuel compatible with current infrastructure. Biomass can undergo conversion into biofuels via either biochemical or thermochemical processes. Biochemical methods involve breaking down biomass using enzymes and microorganisms, whereas thermochemical techniques employ heat for biomass degradation [10] [11]. Thermochemical technologies, known for their rapidness compared to biochemical processes [7], are favored for converting diverse biomass inputs into high-energy biofuels. Thermochemical conversion technologies include carbonization (torrefaction), liquefaction, pyrolysis, gasification, and combustion [10]. Nevertheless, liquid biofuels are directly derived from biomass via pyrolysis and hydrothermal liquefaction techniques.

Hydrothermal liquefaction (HTL) emerges as a promising avenue for generating liquid fuel, often referred to as bio-crude because it eliminates the need for costly pre-drying of biomass, operates at lower temperatures, and consequently demands lower energy consumption compared to conventional pyrolysis methods [3]. When producing liquid biofuel through HTL, low conversion efficiency and significant heteroatom presence reduces both yield and quality of biofuel.

Efforts have been extensively dedicated to enhancing the quality and quantity of biofuels, with a promising avenue being the integration of catalysts into the hydrothermal liquefaction process. There are numerous advantages associated with the utilization of catalysts in the hydrothermal liquefaction process, including enhancing both the biofuel yield and biomass conversion rates, improving the flow characteristics of the biofuel, reducing its heteroatom content, and lowering the temperature necessary to achieve higher liquid biofuel yields during hydrothermal liquefaction [12].

Catalysts play a crucial role in enhancing both the yield and quality of biofuel in the hydrothermal liquefaction process, and they can be either homogeneous or heterogeneous. Although homogeneous catalysis by acids, alkalis, or metal salts has been favored in the hydrothermal liquefaction process due to its affordability, its corrosive nature and challenges in recovery have limited its application, shifting focus towards heterogeneous catalysts [13]. Heterogeneous catalysts offer advantages such as straightforward recovery, low corrosion rates, and higher catalytic activity compared to homogeneous counterparts [14]. Four distinct classes of heterogeneous catalysts utilized in HTL have been categorized according to their chemical properties: catalysts comprising alkaline earth metals, transition metals, lanthanides oxides, and zeolites [3]. Among heterogeneous catalysts, iron-based catalysts have been widely used in the hydrothermal liquefaction (HTL) of biomass owing to their non-toxic, abundant, and cost-effective attributes [15]. This review aims to provide an overview of the hydrothermal liquefaction process of biomass using iron-based catalysts and highlight recent advancements and challenges in this field.

Overview of the Hydrothermal Liquefaction Process

Hydrothermal liquefaction (HTL) is a type of thermochemical conversion technology that involves converting biomass feedstocks into a liquid state using water or water-alcohol mixed solvents at relatively low temperatures (usually between 250˚C and 350˚C) and pressures below 15 MPa [16]. Hydrothermal liquefaction stands out as a promising conversion method capable of efficiently managing wet biomass to yield biofuel characterized by a reduced oxygen content. It involves subjecting the biomass to thermal disintegration in hot compressed water, leading to a series of complex reactions due to alterations in key physical properties of water such as density, solubility, and dielectric constant [17]. Utilizing water as a solvent offers numerous benefits: it is inherently present in biomass, environmentally benign, and exhibits tailored characteristics under HTL conditions. Close to its critical point (374˚C and 22.064 MPa), water demonstrates reduced viscosity and dielectric constant, enhancing the solubility of hydrophobic organic compounds, while increasing the ionic product, promoting catalytic activity, and facilitating acid-base reactions [3] [18]. The hydrothermal liquefaction process capitalizes on the advantages of subcritical water, with its crucial characteristics. This enables it to play a pivotal role in the effective conversion of biomass as detailed in **Table 1**.

Table 1. Water properties at ambient and subcritical conditions [19].

	Ambient water	**Sub-critical water**	**Supercritical water**
Temperature (˚C)	25	250 - 350	400
Pressure (MPa)	0.1	5 - 25	25 - 50
Density (g/cm^3)	1	0.8 - 0.6	0.17 - 0.58
Dielectric constant ($F \cdot m^{-1}$)	78.5	27.1 - 14.07	5.9 - 10.5
Ionic product (pKw)	14	11.2 - 12	19.4 - 11.9
Heat capacity ($kJ \cdot kg^{-1} \cdot K^{-1}$)	4.22	4.86 - 10.1	13.0 - 6.8
Dynamic viscosity (mPas)	0.89	0.11 - 0.064	0.03 - 0.07

In such conditions, the heightened auto-dissociation (as described in Equation (1)) results in an increased abundance of ions, thereby promoting various acid and base-catalyzed reactions, including the acceleration of biomass hydrolysis, as noted by Sohail *et al.* [19].

$$2H_2O \rightarrow H_3O^+ \tag{1}$$

This HTL conversion technology favors biomass with high water content, such as municipal sewage sludge, manure, algae, and others, which can be treated in their natural state, bypassing the need for energy-intensive drying processes, which often serve as a significant constraint in utilizing these feedstocks for energy and/or biofuel production [20].

The hydrothermal liquefaction process encompasses a sequence of complex reactions, beginning with biomass hydrolysis and depolymerization into monomers and unit structures. This is followed by the thermal and chemical decomposition/degradation of these monomers into intermediates, subsequent deoxygenation reactions, and the rearrangement of reactive fragments/intermediates through processes such as re-polymerization, condensation, and cyclization to form products. [7] [11] [19]. The basic reaction pathways have been summarized in **Figure 1**.

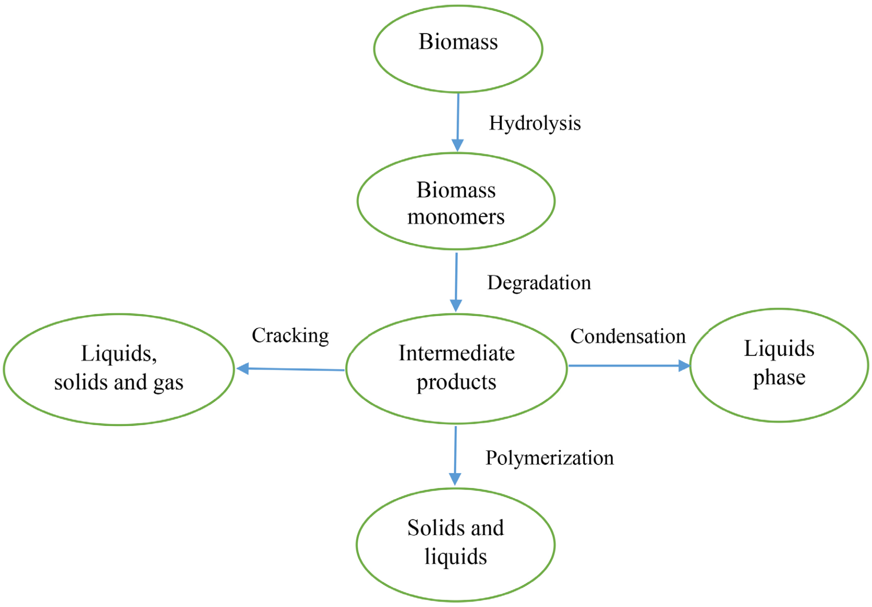

Figure 1. Hydrothermal liquefaction reaction pathway.

In Hydrothermal Liquefaction (HTL), biomass undergoes a comprehensive transformation, yielding bio-crude fuel, water-soluble products (WSP), biochar, and non-condensable gases as primary outputs. The distinct characteristics and quantities of these products depend on HTL's operational parameters. These encompass the nature of the biomass feedstock, the ratio of biomass to water, operational temperature and pressure, residence time within the HTL reactor, the composition of process gases, and the presence or absence of catalysts [21]. Consequently, fine-tuning these parameters plays a pivotal role in optimizing product yields and properties, thereby enhancing the efficiency and viability of HTL as a biomass conversion technology.

The liquid biofuel derived from hydrothermal liquefaction of biomass exhibits promising potential as a fuel source, particularly for diesel and gasoline, owing to its hydrophobic organic composition with decreased oxygen content and elevated energy density [11]. Nonetheless, certain drawbacks persist, including low fuel yield and elevated fuel viscosity, hindering the commercialization of this technology [16]. To enhance both the yield and quality of biofuel, researchers have explored the use of various homogeneous and heterogeneous catalysts in the biomass liquefaction process [22]. Iron-based catalysts are effective in improving biofuel production during hydrothermal liquefaction, while also promoting environmental sustainability. This highlights the potential of iron-based catalysts to lower the costs of biofuel production and to serve as environmentally friendly catalysts. The purpose of this review is to provide insight into the hydrothermal liquefaction of a variety of biomass sources using iron-based catalysts.

2. Iron-Based Catalysts

Iron-based catalysts present an appealing combination of good catalytic performance and cost-effectiveness, making them especially suitable for large-scale hydrothermal liquefaction (HTL) applications. This is particularly relevant in financially sensitive settings, such as developing countries or waste-to-energy projects. In contrast to noble metal catalysts like ruthenium (Ru), platinum (Pt), or palladium (Pd), which are highly efficient but very expensive, iron-based catalysts are much more affordable, abundant, and environmentally friendly [3]. Their relatively low market cost, ease of handling, and non-toxic nature reduce both capital and operational expenses in biofuel production systems. One of the key economic advantages of iron-based catalysts lies in their recyclability, iron can be oxidized in situ by water under HTL conditions, generating hydrogen while converting to magnetite (Fe_3O_4), which retains catalytic activity and can be magnetically separated along with biochar for reuse [20]. This magnetic recoverability not only facilitates catalyst separation without costly filtration or centrifugation steps but also extends the catalyst's operational life, thus enhancing process sustainability [22] [23]. These attributes collectively make iron-based catalysts a cost-effective alternative to more complex or precious metal catalysts, with strong potential for scaling up in commercial HTL platforms.

Iron-based catalysts have found extensive application in hydrothermal liquefaction (HTL) due to their notable effectiveness in enhancing both the yield and quality of biofuel. The specific composition of these catalysts, whether in the form of salts (e.g., $FeSO_4$), oxides (e.g., Fe_2O_3, Fe_3O_4), or supported composites (e.g., Fe-loaded zeolites or biochar composites), plays a decisive role in determining their catalytic behavior. This variation in catalytic efficiency is closely linked to the physicochemical properties of the iron compound, such as oxidation state, solubility, surface area, and interaction with reaction intermediates. For example, in the HTL of lignocellulosic biomass, metallic iron and its oxides have been shown to promote the formation of light oil fractions by suppressing the repolymerization of reactive intermediates and accelerating reactions like retro-aldol condensation of sugars [24]. $FeSO_4$, a common iron salt, has demonstrated a dual role, enhancing oil yield while also reducing water-soluble byproducts, likely due to its capacity to condense lignin-derived intermediates into solid residues [21]. On the other hand, iron-based composite catalysts, such as biochar-supported Fe(0), have been effective in facilitating the depolymerization of biomass macromolecules, thereby promoting the formation of bio-crude-range hydrocarbons [25].

The use of iron-based catalysts in hydrothermal liquefaction (HTL) processes significantly improves both the yield and the chemical quality of the resulting bio-oils. These catalysts facilitate the removal of undesirable heteroatoms, including nitrogen (N), sulfur (S), and oxygen (O). These heteroatoms contribute to the acidity, instability, and corrosiveness of bio-crude, making their reduction essential for producing cleaner, more energy-dense fuels suitable for downstream upgrading and combustion [26]. Iron-based catalysts, including magnetite nanoparticles (MNPs), facilitate key reactions such as hydrodeoxygenation, decarboxylation, and denitrogenation, which effectively strip off oxygen and nitrogen from intermediate compounds during HTL. Egesa *et al.* (2017) demonstrated that the use of iron oxide nanoparticles notably improved the quality of bio-crude by reducing oxygen and nitrogen contents, indicating a strong catalytic role in deoxygenation and denitrogenation [23]. Furthermore, Zhao *et al.* (2021) observed that iron-containing catalysts can efficiently promote hydrodeoxygenation reactions, resulting in a higher hydrocarbon content and lower oxygen levels in bio-oils. These reactions are particularly critical for enhancing the higher heating value (HHV) of the fuel and improving its thermal stability [16]. The catalytic action of iron, therefore, not only aids in biomass depolymerization but also in upgrading the molecular composition of the biofuel to meet more stringent fuel standards.

2.1. Iron as a Catalyst

The use of iron as a catalyst in the HTL process provides numerous advantages due to its abundant availability, low cost, and catalytic versatility. Incorporating iron catalysts in HTL presents a promising approach for producing sustainable biofuels, offering a cost-effective and efficient method to convert various biomass feedstocks into valuable energy resources.

For example, de Caprariis *et al.* conducted a study on the impact of adding iron to oak wood biomass during reductive hydrothermal liquefaction. The study found that biomass decomposition and bio-crude formation began at 150˚C without a catalyst, with peak biofuel yield at 320˚C. Using an iron catalyst at 280˚C significantly increased bio-crude yield and Higher Heating Value (HHV), with optimal iron loading at 10% of biomass weight. Iron addition also enhanced carbon recovery and conversion of the water-soluble organic fraction into liquid products. GC-MS analysis revealed higher concentrations of phenolic and carbonyl compounds in the presence of iron, with a notable absence of aldehydes [20].

Zhao *et al.* (2021) investigated the effect of metallic iron on the hydrothermal liquefaction (HTL) of cornstalk in ethanol-water mixed solvents for crude fuel production. They found that adding iron significantly increased the crude fuel yield, with optimal results achieved at 300˚C for 30 minutes and a 10 wt% iron addition. In pure water and ethanol-water solvents, the yields increased from 28.28 wt% to 43.18 wt% and from 40.91 wt% to 50.46 wt%, respectively [27]. The enhanced yields were due to *in-situ* hydrogen generation and iron's catalytic effect on cellulose and lignin degradation. The bio-crude fuel showed higher carbon content, reduced oxygen content, and increased Higher Heating Value (HHV), with predominant components being phenolics, esters, and hydrocarbons [28].

Okuda *et al.* studied the Fe-assisted hydrothermal liquefaction of lignocellulosic biomass using Empty Fruit Bunches (EFB) from fuel palm trees to produce high-grade biofuel. They found that at 300˚C for 10 minutes, biofuel yield increased from 20% to 29% as the H_2O/EFB ratio rose from 0:1 to 5:1 without Fe, and reached 82% at a 40:1 ratio. With 1.564 g of Fe, the yield jumped from 25% to 79% at a 5:1 ratio and reached 84% at a 40:1 ratio [29]. The increase in biofuel yield was attributed to the inhibition of repolymerization and char formation, with Fe and H_2O facilitating biomass degradation and hydrogen generation, thereby stabilizing EFB degradation products [30].

Caprariis *et al.* investigated the influence of transitional metal catalysts on the hydrothermal liquefaction (HTL) of cellulose, with iron (Fe) showing superior performance. The Fe catalyst (0.1 g) increased the bio-crude yield from 17.4% to 26.5% at 300˚C for 10 minutes, and the higher heating value (HHV) from 27.0 MJ/kg to 29.7 MJ/kg. Additionally, Fe reduced char yield from 17.1% to less than 1%. The reduction in char was attributed to the generation of active hydrogen from the redox reaction between Fe and water, stabilizing reactive intermediates and preventing their recombination. GC/MS analysis revealed a significant reduction in furan derivatives in the bio-crude when Fe was used, due to hydrogenation and catalyzed retro-aldol condensation reactions [31].

Tang *et al.* examined the use of iron catalysts for the fast hydrothermal liquefaction of *Cladophora socialis* macroalgae at 350˚C, 150 bar, for 8 minutes. They found that a 0.2 g Fe catalyst significantly increased crude yield from 31.7% to 36.2% and enhanced carbon recovery from 51% to 62%. The catalyst reduced nitrogen distribution to the biocrude by 6%, minimizing NOx formation and catalyst poisoning. The biocrude produced with Fe had lower oxygen and nitrogen content, with a higher heating value of 37.1 MJ/kg compared to 33.0 MJ/kg without the catalyst. Hydrocarbon formation increased, while carbonyl content and volatile and fatty acid contents decreased. Phenol content increased, improving biocrude stability and reducing corrosiveness through hydride reduction and decarboxylation pathways [32].

In Zhao *et al.* (2021), adding metallic Fe in the HTL of pinewood sawdust significantly improved biofuel yield from 24.81 wt% to 36.82 wt% and increased the higher heating value (HHV) from 27.01 MJ/kg to 29.05 MJ/kg. Improved energy and carbon recovery rates accompanied this enhancement [16]. Similarly, Caprariis *et al.* showed that Fe catalysts increased the bio-crude yield from cellulose from 17.4% to 26.5%, with a corresponding rise in HHV and a reduction in char yield, highlighting Fe's ability to enhance product quality [31].

Tai *et al.* revealed that using a 0.5 g Fe catalyst in HTL of oak wood increased bio-crude yield from 27 wt% to 42.5 wt% and improved HHV to 30.44 MJ/kg. The Fe catalyst also facilitated the hydrogenation of oxidized aromatics into reduced forms, enhancing both yield and quality of the bio-crude [33].

Critically, while iron-based catalysts consistently improve biofuel yields and product quality across various biomass types, the specific outcomes such as increases in HHV, reductions in char, and changes in chemical composition can vary. These variations are influenced by factors such as the type of biomass, HTL conditions, and the specific characteristics of the Fe catalyst used as shown in **Table 2**. Overall, iron-based catalysts play a crucial role in optimizing the HTL process, making it a more efficient and sustainable method for biomass conversion.

Table 2. Effect of iron catalyst in the hydrothermal liquefaction of biomass.

Biomass	Conditions	Yield (wt.%)		HHV(MJ/kg)		Reference
		Blank	With catalyst	Blank	With catalyst	
Oakwood	10 wt% Fe, 280˚C, 15 min	20	40	29.7	32.01	[20]
Cornstalk in water	10 wt% Fe, 300˚C, 30 min	28.28	43.18	26.22	29.54	[27]
Cornstalk in water-ethanol	10 wt%, 300˚C, 30 min	40.91	50.46	29.59	30.86	[27]
Empty Fruit Bunches	1.564 g Fe, 5:1 H_2O/EFB, 300˚C, 10 min	29	79	-	-	[29]
Cellulose	0.1 g Fe, 300˚C, 10 min	17.4	26.5	27.0	29.7	[31]
Cladophora socialis	0.2 g, 350˚C, 150 bar, 8 min	31.7	36.2	33.0	37.1	[32]
Pinewood sawdust	10 wt% Fe, 300˚C, 30 min	24.81	36.82	27.01	29.05	[16]
Oak wood	0.5 g Fe, 330˚C, 10 minutes	27	42.5	28.75	30.44	[33]

2.2. Iron Oxide-Based Catalysts

Iron oxides, such as Fe_2O_3 and Fe_3O_4, have demonstrated substantial potential as catalysts in the hydrothermal liquefaction (HTL) of biomass. These catalysts contribute to the conversion of biomass into higher-quality fuels by improving the selectivity of the products and facilitating reactions that lead to depolymerization, desulfurization, and denitrogenation. Their applications in HTL processes have yielded promising results, indicating their significant role in enhancing biofuel production from various biomass sources.

In their exploration of optimizing reaction conditions for hydrothermal liquefaction (HTL) of microalgae (*Spirulina platensis*) using Fe_3O_4 nanostructures as catalysts, Kandasamy *et al.* made significant strides. The results were remarkable, as with 0.45 g of catalyst, a temperature of 272˚C, and a residence time of 24 minutes, the yield increased from 9% (wt%) to 27.66% (wt%). This increase in yield was accompanied by a reduction in the oxygen content of the biofuel from 25.35% to 10.83%, resulting in a significant increase in the heating value of the biofuel from 23.47 MJ/kg to 30.98 MJ/kg. The Fe_3O_4 catalyst also improved energy recovery, increasing from 35.98% to 47.50%. Gas chromatography-mass spectrometry (GC-MS) analysis of the biofuel showed a significant change in its chemical composition, with increases in hydrocarbons and heterocyclic compounds and decreases in fatty acid derivatives and oxygenated compounds, suggesting enhanced degradation of algal proteins and occurrence of deoxygenation reactions under catalytic HTL conditions [10].

Mukundan *et al.* delved into the hydrothermal liquefaction (HTL) of draff (brewer's spent grains), aiming to harness a highly active and magnetically recoverable heterogeneous catalyst to yield high-quality biofuel. Their findings revealed substantial enhancements across various parameters. The study found that the incorporation of the FeO_x/C (5 wt%) catalyst resulted in a significant increase in biofuel yield, from 41.2% to 49.3%, at 320˚C for 60 minutes. This increase was accompanied by an increase in carbon (81.3%) and hydrogen (8.3%) contents within the biofuel, leading to a higher heating value (HHV) of 37.8 MJ/kg, compared to 30.26 MJ/kg without a catalyst. In addition to improving the yield of biofuel, the use of FeO_x/C catalyst also enhanced its composition, resulting in an excellent energy recovery of 84.4%, compared to 54.28% without a catalyst. The study found that non-catalytic HTL mainly produced heavier biofuels, with compounds predominantly falling within the 400˚C - 600˚C boiling point range. On the other hand, the use of FeOx/C catalyst resulted in a notable increase in the formation of low-boiling compounds, particularly in the gasoline and jet fuel ranges, indicating enhanced cracking and hydrogenation processes facilitated by the catalyst [34].

A study led by Bian *et al.* shown significant advancements in the use of supported Fe_2O_3 nanoparticles for catalytic upgrading of microalgae hydrothermal liquefaction-derived biofuel. The study revealed that Fe_2O_3/MCM-41 catalysts significantly enhanced the quality of biocrude obtained from *Chlorella*. Catalytic liquefaction using Fe_2O_3/MCM-41 (30 mg) led to a higher heating value (HHV) biocrude compared to non-catalytic methods. The conversion of palmitic acid increased from 24.8% without a catalyst to 47.0% with the Fe_2O_3/MCM-41 catalyst at 350˚C, and the conversion of methyl palmitate reached 56.0% within the temperature range of 327˚C - 342˚C with the catalyst. Elemental analysis showed an increase in HHV from 25.57 MJ/kg without a catalyst to 29.68 MJ/kg with the Fe_2O_3/MCM-41 catalyst, along with a rise in the H/C ratio and a decline in the O/C ratio, indicating enhanced energy content and deoxygenation. The catalyst facilitated reactions such as isomerization, reforming, depolymerization, and decomposition, promoting deoxygenation and hydrogenation processes during *Chlorella* HTL and improving biocrude quality [35].

In a study conducted by Egesa *et al.*, it was found that magnetic nanoparticles (MNPs) can efficiently separate microalgae and catalyze hydrothermal liquefaction. The highest bio-crude yield of 30.5% was obtained at 320˚C, 0.12 g/g catalyst to biomass ratio, and 60 minutes in the presence of magnetite (Fe_3O_4), compared to a yield of 22% without MNPs. When Zn and Mg were doped on ferrite MNPs (Zn/Mg/Fe_3O_4), the bio-crude yield increased to 37.1%. The high heating value (HHV) increased from 35.7 MJ/kg to 36.1 MJ/kg with MNPs, while Zn/Mg/Fe_3O_4 decreased the HHV to 35.4 MJ/kg. Gas chromatography-mass spectrometry (GC-MS) revealed the presence of hydrocarbons, aromatic hydrocarbons, nitrogen compounds, phenolic compounds, oxygenated compounds, and organic acids in the bio-crude. The use of Zn/Mg/Fe_3O_4 increased the percentage of hydrocarbons in the bio-crude from 19.9% to 36%, attributed to the decomposition of cellular components. Additionally, uncatalyzed biocrude from Spirulina contained more nitrogen compounds (22.1%) than catalyzed liquefaction with Zn/Mg ferrite (13.4%) [23].

Egesa *et al.*, conducted a study on the hydrothermal liquefaction (HTL) of water hyacinth to determine the effect of process conditions and magnetite nanoparticles (MNPs) on biocrude yield and composition. Results showed that at a temperature of 320˚C, reaction time of 60 minutes, catalyst to biomass ratio of 0.2 g/g, and biomass to water ratio of 0.06 g/g, the biocrude yield increased from 52.3 wt% to 58.3 wt% in the presence of MNPs. Gas chromatography-mass spectrometry (GC-MS) analysis revealed that the use of MNPs in HTL increased the percentage area corresponding to hydrocarbons while reducing the percentage area corresponding to oxygenated, nitrogenated, and sulfur compounds. The elemental analysis also showed an increase in hydrogen and carbon content while reducing nitrogen, oxygen, and sulfur content in the biocrude. Consequently, the higher heating value (HHV) of the biocrude increased from 33.5 MJ/kg without a catalyst to 35.5 MJ/kg in the presence of a catalyst [26].

Aturagaba *et al.* investigated the use of Fe_3O_4/NiO nanocomposite catalysts in catalytic hydrothermal liquefaction (HTL) of water hyacinth, resulting in significant improvements in biofuel yield and composition. The use of this nanocomposite catalyst led to a maximum biofuel yield of 59.4 wt%, compared to 50.7 wt% without the catalyst, under optimal conditions of 320˚C, 1.5 g catalyst dosage, and 60 minutes residence time. Gas chromatography-mass spectrometry (GC-MS) analysis showed an increase in hydrocarbons from 58.3% in uncatalyzed HTL to 88.66% with the catalyst. Elemental analysis revealed enhanced hydrogen and carbon content and reduced nitrogen, oxygen, and sulfur content in the biofuel. The higher heating value (HHV) of the biofuel increased from 33.5 MJ/kg in uncatalyzed HTL to 38.6 MJ/kg with the nanocomposite catalyst, demonstrating the catalyst's effectiveness in improving the energy content and quality of the biofuel [22].

Chen *et al.* investigated the hydrothermal liquefaction of corn straw using a Nano ferrite + inorganic base catalyst system at low temperatures. The researchers found that the yields of heavy biofuel produced by the heterogeneous catalysts $ZnFe_2O_4$, $NiFe_2O_4$, and $CoFe_2O_4$ were lower than that of the homogeneous catalyst NaOH, likely due to the limited contact area between the heterogeneous catalyst and reactants. However, combining the heterogeneous catalyst with the homogeneous catalyst ($ZnFe_2O_4$ + NaOH, $NiFe_2O_4$ + NaOH, and $CoFe_2O_4$ + NaOH) significantly increased the yields of heavy biofuel, producing 31.28 wt%, 24.43 wt%, and 20.49 wt%, respectively. This synergistic interaction is attributed to the homogeneous catalyst's ability to dissolve depolymerization products and prevent repolymerization reactions in the presence of the heterogeneous catalyst, leading to improved conversion efficiency and higher yields of heavy biofuel [36].

Zhao *et al.* delved into the production of biocrude fuel through hydrothermal liquefaction (HTL) of cornstalk using Fe_3O_4 as a catalyst. They used 0.55 g of Fe_3O_4 in pure water at 300˚C for 30 minutes and observed a significant increase in biocrude fuel yield, from 28.28 wt% to 33.29 wt%, with the catalyst. This highlights the catalytic role of Fe_3O_4 in converting cornstalk biomass into valuable biocrude fuel. Further analysis revealed a small but noteworthy increase in the higher heating value (HHV) of the biocrude fuels produced with the catalyst, from 26.22 MJ/kg to 26.51 MJ/kg, demonstrating the catalyst's contribution to improving the energy content of the biocrude fuel [27]. The effect of iron oxide-based catalysts in the hydrothermal liquefaction of different kinds of biomass is summarized in **Table 3**.

Table 3. Effect of iron oxide-based catalysts in the hydrothermal liquefaction of biomass.

Biomass	Conditions	Yield (wt.%)		HHV (MJ/kg)		Reference
		Blank	With catalyst	Blank	With catalyst	
Spirulina platensis	0.45 g of Fe_3O_4, 272˚C 24 min	9	27.66	23.47	30.98	[10]
Brewer's spent grains	5 wt% FeO_x/C, 320˚C, 60 min	41.2	49.3	30.26	37.8	[34]
Chlorella	30 mg Fe_2O_3/MCM-41, 300˚C, 30 min	-	-	25.57	29.68	[35]
Microalgae	0.12 g/g Fe_3O_4, 320˚C, 60 min	22	30.5	35.7	36.1	[23]
Microalgae	0.12 g/g Zn/Mg/Fe_3O_4, 320˚C, 60 min	22	37.1	35.7	35.4	[23]
Water hyacinth	0.2 g/g Fe_3O_4 320˚C, 60 min	52.3	58.3	33.5	35.5	[26]
Water hyacinth	1.5 g Fe_3O_4/NiO 320˚C, 60 min	50.7	59.4	33.5	38.6	[22]
Cornstalk	055 g of Fe_3O_4, 300˚C, 30 min	28.28	33.29	26.22	26.51	[27]

2.3. Salts of Iron

Salts of iron have been widely applied in hydrothermal liquefaction (HTL) processes for biomass conversion due to their promising catalytic properties, including enhancement of bio-crude yield and quality. Their roles include facilitating hydrolysis processes, improving the efficiency of biomass depolymerization, and enhancing the deoxygenation, desulfurization, and denitrogenation of biocrude. These studies demonstrate the significant potential of iron salts as catalysts in enhancing bio-crude yield and quality during hydrothermal liquefaction of various biomass types.

C. Xu & Etcheverry investigated the hydrothermal liquefaction of woody biomass in sub- and super-critical ethanol with iron-based catalysts. Their work demonstrated significant improvements in biofuel yield and biomass conversion rates, providing insights into the role of catalysts in influencing product distribution. At 350˚C for 40 minutes under an initial H_2 pressure of 5.0 MPa, the addition of 5 wt% $FeSO_4$ catalyst led to a remarkable increase in biofuel yield from 44% to 63% and biomass conversion from 72% to 88%. These findings underscore the catalytic effectiveness of iron-based catalysts in promoting biofuel production while reducing the formation of gases, water, and char during biomass hydro-liquefaction. However, it's worth noting that the higher heating value (HHV) slightly decreased from 31.8 MJ/kg without catalyst to 29.3 MJ/kg with 5 wt% $FeSO_4$ [37]. This reduction may be due to changes in the composition of the biofuel induced by the catalytic process, potentially leading to alterations in energy content.

In a study by Zhao *et al.* investigated the combined effects of metallic Fe and various catalysts on the hydrothermal liquefaction of woody biomass. The study revealed that the addition of FeS significantly increased the biofuel yield, from 24.81 wt% to 34.37 wt%, and improved the higher heating value (HHV) of the biofuel from 27.1 MJ/kg to 28.52 MJ/kg.

The study further explored the effects of blending Fe with other catalysts. The results showed that the biofuel yields obtained with mixed additives demonstrated distinct trends, with Fe + Na_2CO_3 exhibiting the highest yield (48.24 wt%) followed by Fe + FeS (46.12 wt%), Fe + NaOH (45.81 wt%), Fe + Ru/C (38.33 wt%), Fe alone (36.82 wt%), Fe + $FeSO_4$ (36.49 wt%), and Fe + MgO (35.25 wt%), surpassing the blank (24.81 wt%). The study also revealed that combinations involving alkaline catalysts (Na_2CO_3 or NaOH), FeS, or Ru/C alongside Fe produced biofuel yields higher than those achieved with individual catalysts or Fe alone, indicating potential synergistic effects. However, $FeSO_4$ and MgO did not exhibit synergistic effects with Fe in promoting biofuel production, as evidenced by slightly lower yields when combined with Fe compared to Fe alone.

Furthermore, blending Fe with other catalysts further improved both the yield and quality of biofuel products, owing to synergistic effects between these catalysts and Fe. The HHV for biofuels obtained from Fe combined with other catalysts followed the order: Fe + Ru/C (30.93 MJ/kg) > Fe + FeS (29.99 MJ/kg) > Fe + Na_2CO_3 (29.62 MJ/kg) > Fe + NaOH (29.11 MJ/kg) > Fe alone (29.05 MJ/kg) [16]. This highlights the importance of selecting appropriate catalysts for enhancing biofuel yield and quality in hydrothermal liquefaction processes.

In Nazari *et al.* investigation into the hydrothermal liquefaction of woody biomass (birchwood sawdust) in hot-compressed water, catalyst screening revealed significant advancements in bio-crude fuel production and quality, particularly with 0.2 g $FeSO_4$ at 300˚C for 30 minutes. $FeSO_4$ was found to condense lignin materials, increasing the yield of solid residues. This led to a significant increase in biofuel yield, from 18.9 wt% without a catalyst to 32.0 wt% with $FeSO_4$. The higher heating value (HHV) of the biocrudes also increased from 29.0 MJ/kg without catalyst to 31.3 MJ/kg with $FeSO_4$. The study also found that the composition of the resulting biofuels differed significantly between non-catalytic and catalyzed liquefaction. In non-catalytic liquefaction, phenols and acids were the dominant compounds, followed by alcohols, ketones, aliphatic, and aromatic compounds. However, including $FeSO_4$ led to a significant reduction in phenolic compounds while elevating the concentration of acids and alcohols in the biofuel. These findings suggest that $FeSO_4$ has the potential to enhance the quality and yield of bio-crude fuel production while mitigating the formation of water-soluble products during the hydrothermal liquefaction of woody biomass [21].

Cirsium yildizianum stalks were subjected to liquefaction in various organic solvents (methanol, ethanol, and acetone) under supercritical conditions, both in the presence and absence of catalysts. The study by Aysu demonstrated that the addition of ferric chloride ($FeCl_3$) significantly enhanced biomass conversion efficiency due to its high acid density, which facilitates the breakdown of complex biomass structures and promotes the formation of hydrocarbon-rich liquid products. Among the tested solvents, acetone produced the highest conversion rates, particularly under catalytic conditions. Specifically, the biomass conversion reached 50.60% in methanol, 55.21% in ethanol, and a peak of 63.88% in acetone at 300˚C with 10% $FeCl_3$. These values were consistently higher than those achieved with NaOH, which served as an alternative catalyst, confirming the superior performance of $FeCl_3$. Additionally, the highest overall product yield (liquid + gaseous) was observed in acetone with 10% $FeCl_3$ at 300 ˚C. The energy content of the resulting bio-oil also improved, with the higher heating value (HHV) increasing from 22.98 MJ/kg without a catalyst to 23.38 MJ/kg with the inclusion of 10% $FeCl_3$. These results underscore the potential of $FeCl_3$ as a highly effective catalyst in supercritical solvent liquefaction of lignocellulosic biomass [38].

Compared to other iron salts, ferric chloride ($FeCl_3$) generally exhibited lower effectiveness in enhancing both biomass conversion and the higher heating value (HHV) of the resulting biofuel. While $FeCl_3$ contributed to some improvement in product yield due to its strong Lewis acidity, studies indicate that its overall catalytic performance in hydrothermal liquefaction is less pronounced than that of $FeSO_4$, which not only improved oil yields but also significantly upgraded the bio-oil quality by promoting lignin condensation and reducing water-soluble by-products [21] [39].

The effect of iron salt-based catalysts in the hydrothermal liquefaction of different types of biomass is summarized in **Table 4**.

Table 4. Effect of iron salt-based catalysts in the hydrothermal liquefaction of biomass.

Biomass	Conditions	Yield (wt.%)		HHV (MJ/kg)		Reference
		Blank	With catalyst	Blank	With catalyst	
Woody biomass	5 wt% $FeSO_4$, 350˚C, 40 min	44	63	31.8	29.3	[37]
Pinewood sawdust	10 wt% FeS, 300˚C, 30 min	24.81	34.37	27.01	28.52	[16]
Pinewood sawdust	10 wt% (Fe + Na_2CO_3), 300˚C, 30 min	24.81	48.24	27.01	29.62	[16]
Pinewood sawdust	10 wt% (Fe + FeS), 300˚C, 30 min	24.81	46.12	27.01	29.99	[16]
Pinewood sawdust	10 wt% (Fe + NaOH), 300˚C, 30 min	24.81	45.81	27.01	29.11	[16]
Pinewood sawdust	10 wt% (Fe + Ru/C), 300˚C, 30 min	24.81	38.33	27.01	30.93	[16]
Pinewood sawdust	10 wt% (Fe + $FeSO_4$), 300˚C, 30 min	24.81	36.49	-	-	[16]
Pinewood sawdust	10 wt% (Fe + MgO), 300˚C, 30 min	24.81	35.25	-	-	[16]
Cirsium yildizianum	10% $FeCl_3$, 300˚C, 75 min	60.05	63.88	22.98	23.38	[38]
Birchwood sawdust	0.2 g $FeSO_4$, 300˚C, 30 min	18.9	32	29.0	31.3	[21]

2.4. Composites of Iron

Iron composites typically refer to materials where iron is combined with other elements or materials to enhance its properties. Iron composites are used as catalysts in biomass conversion and upgrading of biocrude due to their ability to enhance various chemical processes. Composites of iron have been applied in the hydrothermal liquefaction (HTL) of various biomass types and have shown promising results in enhancing bio-crude yield, improving the quality of biofuels, and facilitating various catalytic reactions. These iron composites, often combined with other materials such as oxides or biochar, act as effective catalysts that contribute to the deoxygenation, hydrogenation, and overall upgrading of bio-oil during HTL processes. These applications highlight the significant potential of iron composites as catalysts in enhancing bio-crude yield and quality during the hydrothermal liquefaction of various biomass types.

Liu *et al.* conducted a study to assess the impact of Fe/HZSM-5 catalyst on the distribution of elements and properties of products during hydrothermal liquefaction (HTL) of *Nannochloropsis* sp. The study found that the inclusion of 8 wt % Fe/HZSM-5 catalyst led to a significant increase in the maximum yield of biocrude oil, reaching 38.1% at 365˚C for 60 minutes, which was a substantial 25.33% increase compared to the non-catalytic group. The zeolite catalyst loaded with metals facilitated zeolite-cracking and amplified the Lewis acid sites of the zeolite, enhancing its catalytic efficacy. The results showed significant enhancements in the biocrude oil obtained from catalytic HTL. This phenomenon was attributed to catalytic influences, which led to cracking, dehydroxylation, dehydration, and aromatization reactions, transforming heterocyclic macromolecules into low-molecular-weight compounds such as ketones and hydrocarbons [40].

Li *et al.* research explored the impact of process parameters on biofuel upgradation in the catalytic hydrothermal liquefaction of *Gracilaria corticata* macroalgae. The study utilized a range of nickel-iron-layered double oxides (NiFe-LDO) supported on activated bio-char catalysts during hydrothermal liquefaction (HTL) at 280˚C for 30 minutes.

The results showed that catalytic upgrading significantly improved biofuel yield compared to non-catalytic reactions, due to various reactions such as hydrolysis, hydrogenation, hydrodeoxygenation, and rearrangement during HTL reaction. The biofuel yields displayed a distinct hierarchy, with the highest yield of 56.2 wt% for 5GaNiFe-LDO/AC, followed by 10GaNiFe-LDO/AC (51.3 wt%), NiFe-LDO/AC (46.6 wt%), NiFe-LDO (42.5 wt%), and finally the non-catalytic reaction (blank) at 38.8 wt%.

Moreover, the higher heating value (HHV) of the biofuel followed a similar trend, with 5GaNiFe-LDO/AC exhibiting the highest value of 32.9 MJ/kg, followed by 10GaNiFe-LDO/AC (31.2 MJ/kg), NiFe-LDO/AC (26.8 MJ/kg), NiFe-LDO (25.6 MJ/kg), and the blank (22.4 MJ/kg) [41]. This indicates that catalytic biofuel is of superior quality compared to non-catalytic biofuel, characterized by reduced oxygen content and enhanced carbon element.

In the study conducted by Sharma *et al.*, the researchers investigated the potential of using bauxite residue to create a composite material containing biochar and iron for hydrothermal liquefaction (HTL) of municipal solid waste. The study revealed that the addition of BC-Fe(0) catalyst resulted in a significant increase in bio-crude yield when compared to the HTL process without the catalyst. The highest bio-crude yield obtained was 44 wt% at 300˚C for 30 minutes with 10 wt% BC-Fe(0) loading (containing 2.5 wt% Fe), compared to 38.6 wt% without catalyst.

The catalyst facilitated the degradation of the polymeric chains present in the biomass constituents, leading to the production of bio-crude molecules. Additionally, the catalyst played a crucial role in *in-situ* hydrogenation and deoxygenation of chemical compounds present in the bio-liquid product. As a result, the bio-crude produced with the catalyst had a higher H/C ratio (1.73) and lower oxygen content (9.78 wt%) than the bio-crude obtained without the catalyst. The higher heating value (HHV) also experienced a modest increase from 37.81 MJ/kg without catalyst to 38.20 MJ/kg with the utilization of the catalyst, which highlights the beneficial impact of the catalyst on the energy content of the bio-crude [25]. Overall, the study suggests that the use of bauxite residue composite material containing biochar and iron as a catalyst in the HTL process of municipal solid waste can lead to the production of high-quality bio-crude with improved energy content.

The effect of iron composites in the hydrothermal liquefaction of different kinds of biomass is summarized in **Table 5**.

Table 5. Effect of iron composites in the hydrothermal liquefaction of biomass.

Biomass	Conditions	Yield (wt.%)		HHV (MJ/kg)		Reference
		Blank	With catalyst	Blank	With catalyst	
Gracilaria corticata	5GaNiFe-LDO/AC, 280˚C, 30 min, 15 wt% catalyst	38.8	56.2	22.4	32.9	[41]
Gracilaria corticata	10GaNiFe-LDO/AC, 280˚C, 30 min, 15 wt% catalyst	38.8	51.3	22.4	31.2	[41]
Gracilaria corticata	NiFe-LDO/AC, 280˚C, 30 min, 15 wt% catalyst	38.8	46.6	22.4	26.8	[41]
Gracilaria corticata	NiFe-LDO, 280˚C, 30 min, 15 wt% catalyst	38.8	42.5	22.4	25.6	[41]
Nannochloropsis sp.	8 wt % Fe/HZSM-5, 365˚C, 60 min	12.77	38.1	-	-	[40]
Municipal solid waste	10 wt% BC-Fe(0), 300˚C, 30 min	38.6	44	37.81	38.20	[25]

2.5. Stability and Reusability of Iron-Based Catalysts in Hydrothermal Liquefaction

Iron-based catalysts, particularly those in the form of oxides, are widely recognized for their effectiveness in the hydrothermal liquefaction (HTL) of biomass. However, their long-term stability over multiple reaction cycles is a critical factor in evaluating their suitability for commercial-scale applications. Several studies have examined the performance of these catalysts during repeated use, revealing trends in deactivation.

Tang *et al.* (2021) reported a gradual decline in biocrude yield when an iron-based catalyst was reused over three cycles. The yield decreased from 36.2% with a fresh catalyst to 34.9%, 33.7%, and 33.0% after the first, second, and third reuse, respectively. This decline was also associated with a reduction in catalytic activity related to deoxygenation and denitrogenation (DO/DN). For example, the oxygen content in the bio-crude increased from 10.1% with fresh Fe to 11.0%, 10.7%, and 11.5% after each respective cycle, indicating catalyst deactivation [32].

Similarly, Egesa *et al.* (2017) demonstrated that recycled MNPs could maintain a bio-crude yield of 29%, only slightly lower than the 30.5% yield from fresh MNPs and substantially higher than the 22% yield from uncatalyzed liquefaction. These findings confirm that MNPs remain catalytically active after recycling and can be reused effectively in subsequent HTL processes [23].

Further investigations by Egesa *et al.* (2021) explored the reusability of MNPs over five cycles. The biocrude yield remained high in the first three cycles but started to decline significantly in the fourth and fifth cycles, with the lowest yield recorded at 57.1 wt%. This suggests that MNPs can be magnetically recovered and reused efficiently for at least four cycles before performance degradation becomes substantial. Magnetic separation not only enhances recovery but also contributes to cost-effectiveness and process sustainability [26].

Aturagaba *et al.* (2023) reported similar results using iron oxide/nickel oxide composites. The first recycle yielded 57.1 wt% of bio-oil, which was just 2.3 wt% less than the fresh catalyst run. However, a gradual decline in performance was observed with each subsequent reuse, indicating catalyst wear and deactivation over time [22].

Kandasamy *et al.* (2019) extended the catalyst reuse to eight cycles. In the first recycle, the bio-oil yield dropped to 25.4%, about 8% lower than that of the fresh catalyst. By the fourth cycle, approximately 73% of the initial yield was retained, but the performance plateaued and then dropped to around 18% in later cycles. A notable decrease in carbon content of the bio-oil (from 69.36% to 38.92%) was also observed, indicating a decline in product quality [10].

These studies indicate that iron-based catalysts can be effectively reused for three to four hydrothermal liquefaction (HTL) cycles with only minimal loss in performance. However, after this point, deactivation becomes more significant. This is likely due to morphological changes such as particle agglomeration, sintering, surface fouling, or increased mass-to-volume ratios [10] [22] [42].

3. Conclusion

Given their exceptional potential for sustainable biofuel production and valorization, Iron-based catalysts are increasingly recognized as essential components in the hydrothermal liquefaction (HTL) of biomass. These catalysts act as enablers for crucial chemical transformations, such as depolymerization, deoxygenation, hydrogenation, and carbonization, thereby improving conversion rates and biocrude yields across a wide range of biomass feedstocks. Additionally, these catalysts regulate the composition and characteristics of bio-crude, leading to higher energy content, lower oxygen content, and increased stability. Their adaptability enables customized performance to be achieved for specific biomass types and process conditions, which can be accomplished through adjustments in catalyst composition, particle size, and operation parameters. The integration of iron-based catalysts into the HTL process represents a pivotal approach to unlocking the potential of biomass as a renewable energy source. As a result, ongoing research efforts are directed towards optimizing catalyst performance, scaling up bio-crude production, and driving the sustainability of biofuel technologies forward.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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