catalysts

Review

An Approach towards the Conversion of Biomass Feedstocks into Biofuel Using a Zeolite Socony Mobil-5-Based Catalysts via the Hydrothermal Liquefaction Process: A Review

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Abstract: The conversion of biomass to biofuels as a renewable energy source is continuously gaining momentum due to the environmental concerns associated with using fossil fuels. Biomass is a cost-effective, long-term natural resource that may be converted to biofuels such as biodiesel, biogas, bio-oil, and biohydrogen using a variety of chemical, thermal, and biological methods. Thermochemical processes are one of the most advanced biomass conversion methods, with much potential and room for improvement. Among various thermochemical processes, hydrothermal liquefaction (HTL) is a promising technology that can convert higher water-content feedstocks into biofuel with significantly lower oxygen content and higher calorific value without requiring the biomass to be dried first. In HTL, temperature, pressure, residence time, catalyst, and solvent all play a vital role in bio-oil quality. This study provides a comprehensive review of the research and development on the effects of catalysts and the need to optimise existing catalysts for optimum biomass conversion into high-value bio-oil and other products. The catalyst of interest is ZSM-5, a heterogenous catalyst that has been seen to increase the hydrocarbon content and decrease oxygenated compounds and other unwanted by-products. The use and modification of this catalyst will play a vital role in generating renewable and carbon-neutral fuels.

Keywords: renewable energy; biomass conversion; thermochemical conversion; hydrothermal liquefaction; zeolite catalysts

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1. Introduction

As the global economy continues to grow and with increasing population, the demand for the earth's energy resources is rising. These resources, such as fossil fuels, may be difficult to obtain, expensive, or risky to the environment [1]. Traditional energy sources like coal, petroleum, and natural gas meet primary energy needs. These sources are in danger of becoming extinct. Energy extraction from these sources pollutes the atmosphere, contributing to issues like global warming, acid rain, etc. A switch to non-conventional sources like wind, sunlight, water, biomass, etc., is inevitable, given the rise in energy demands and consideration of pollution [2]. Fossil fuels are regarded as non-renewable resources due to their lengthy formation cycle, and their combustion has resulted in environmental pollution issues, such as the emissions of toxic gases leading to air pollution and irreversible climate change [3].

Production of renewable and CO_2-emission-free fuels is essential for sustainability and meeting current energy demands [4]. Among numerous alternatives, biomass has drawn significant interest as a renewable energy resource to replace traditional fossil fuels because of its capacity to provide a constant energy supply and its nature of being environmentally friendly [5]. In this context, agricultural biomass wastes are potential sources of renewable energy for manufacturing biofuels [6].

Energy from biomass can be derived in various forms; the form of determination suggests the conversion process and depends on the availability, type, and quantity of the biomass. The conversion of biomass to biofuels involves the use of various treatment technologies classified as biochemical, physical, and thermochemical. Biochemical conversion involves the use of both anaerobic digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation (production of ethanol) [7]. The biochemical conversion process generally takes a long time and can only employ biomass's cellulose and hemicellulose parts.

Physical conversion is a mechanical extraction used to produce liquid biofuels from organic matter containing oils and/or fats such as rapeseeds, oil palm fruits, sunflower seeds, etc. [8]. Despite the fact that it is an environmentally friendly and clean transformation technology with great future energy security, it is still in its infancy and is notably constrained by the high cost of raw materials [3].

Thermochemical conversion involves heating biomass to high temperatures in either an oxygenic or anoxygenic environment to induce structural breakdown [3]. Thermochemical conversion techniques have drawn the attention of researchers because they can be effectively applied to almost any biomass feedstock, not limited by the use of enzymes to break down a limited range of feedstock. There is a relatively higher production of desired products such as oil due to the chemical nature of the reaction, and mostly, the biomass is completely utilised [9]. There are four main thermo-chemical routes to produce fuels, i.e., direct combustion, gasification, pyrolysis, and hydrothermal liquefaction, each differing in the temperature, heating rate, and oxygen level present during the treatment [3]. The three most important process parameters for all thermochemical conversions are temperature, heating rate, and residence time, as they are known to affect the thermochemical processes are illustrated in both Figures 1 and 2, respectively. Figure 1 shows the temperature ranges for thermochemical processes, and Figure 2 shows typical ranges of the heating rate and residence time for pyrolysis. Figure 1 shows that the higher the temperature of your conversion reaction, the more gaseous the products will be.

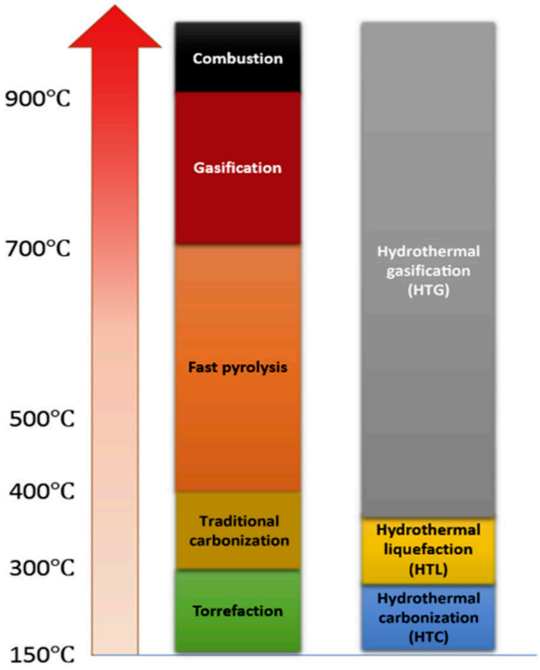

Figure 1. Standard temperature ranges for different thermochemical conversion techniques [9].

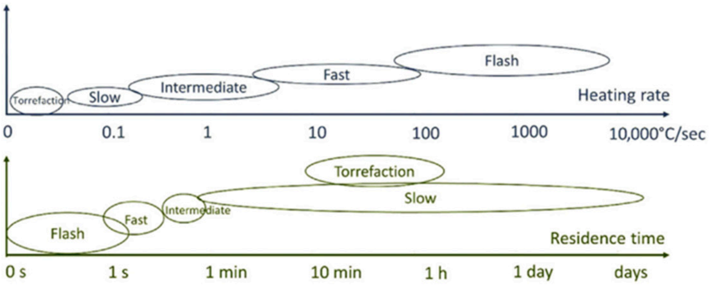

Figure 2. Heating rate and residence time for biomass using different thermochemical techniques. Slow: slow pyrolysis; fast: fast pyrolysis; intermediate: intermediate pyrolysis; flash: flash pyrolysis [9].

Generally, hydrothermal liquefaction (HTL) is the most promising process over direct combustion, gasification, and pyrolysis because it is a potential method for turning raw materials into liquid biofuels due to its various benefits, such as transforming wet feedstocks directly into bio-oil or crude bio-oil to save energy on drying or pre-treatment. As a consequence, results in higher energy recovery efficiency and decreased energy usage during biofuel production [10].

The use of a catalyst during thermochemical processes reduces the required reaction temperature by improving reaction kinetics and, consequently, the yield of the desired products; it also increases process efficiency by lowering the formation of tar and char and by removing heteroatoms like oxygen, nitrogen, and sulphur [11].

In thermochemical processes, catalysts can be used to increase yield, decrease solid waste production, and minimise reaction pressure and temperature [12]. Both homogeneous and heterogeneous catalysts can facilitate the conversion of biomass to biofuels via thermochemical processes. Various classes of catalysts have been studied to efficiently convert biomass into biofuels. The conventional homogenous catalysts have been used over the years, but they pose a problem with separation as it is difficult to separate them from the product, making the process more energy-intensive and more costly [13]. The use of homogenous catalysts results in wastewater generation, difficulty in catalyst separation, and non-recyclable. However, the limitations of the homogeneous catalysis process can be solved using heterogeneous catalysts. Heterogeneous catalysts are more environmentally friendly than homogenous catalysts, and they are more efficient and easier to separate from products [14]. Compared to homogeneous catalysts, heterogeneous catalysts are more desirable than homogenous catalysts to produce fuels from biomass. Additional advantages of heterogeneous catalysts include easy recyclability, non-toxic, not naturally corrode, economically viable, and not producing soap [12,15].

The unique function of different heterogeneous catalysts can change product yields and process selectivity, which in turn affects the composition of the bio-oil and its physical and chemical properties [16]. Several heterogeneous catalysts have been studied by researchers for biomass conversion via suitable thermochemical processes. Alkali and alkaline earth metals (AAEMs) and nickel-based catalysts are some of the catalysts that have been used in biomass conversion. These catalysts have been studied, and AAEMs have been found to have promising results in terms of biochar formation and non-condensable gases. Na, K, Mg, and Ca's effects were investigated. Compared to K, Na, and Ca, Mg was relatively inert. The carbon yield of aromatics and olefins was decreased as a result of AAEM catalysts, while the rate at which biochar was formed thermally increased [17].

Studies on the feasibility of employing commercial steam-reforming Ni catalysts in biomass gasification were conducted by Aznar et al. [18] and Caballero et al. [19]. The syngas composition (CO and H_2) was improved, and CH_4 and CO_2 concentrations were decreased as a result of the catalysts' success in lowering tar content. Conventional heterogeneous catalyst types such as zeolites have been studied as catalysts for biomass conversion or for the upgrading of bio-oil. Zeolite catalysts are extremely acidic; ZSM-5's small/medium pore size and two-dimensional channel-like pore system also make it very shape-selective. Due to their distinct characteristics, zeolites are a form of heterogeneous catalyst that is interesting for biomass conversion. Zeolites can operate as molecular sieves by selectively trapping some molecules while letting others pass through due to their porous structure. They can therefore be used to catalyse reactions involving big molecules, such as those in biomass. Because the pores of a given zeolite are a defined size and shape, zeolite catalysts can act only on specific compounds. This is crucial for biomass conversion since the reactants and products may contain intricate molecule mixtures [20]. Zeolites are extremely active in a wide range of catalytic processes because of their adjustable acidity. This is crucial for the conversion of biomass since the reactants and products can both be quite acidic or basic [21]. Zeolites can survive high temperatures without degrading since they are thermally stable. This is crucial for biomass conversion since complicated compounds are frequently broken down at high temperatures. Zeolites are economical and environmentally friendly because they may be reused. This is crucial for biomass conversion because it frequently calls for significant quantities of catalysts [22].

H-ZSM-5 causes several processes during petroleum oil cracking or pyrolysis, including protolytic cracking or β-scission, alkylation, isomerisation, cyclisation, oligomerisation, and aromatisation. The same reactions can occur during biomass conversion, such as HTL; however, before these hydrocarbon-based reactions, the holocellulose and lignin fragments are deoxygenated via dehydration and decarbonylation or decarboxylation reactions [23,24]. Among zeolites, ZSM-5 has primarily been studied as a catalyst for biomass conversion and has been found to significantly alter the composition of the bio-oils by simultaneously increasing the aromatic species and decreasing the amounts of oxygenated compounds via deoxygenation reactions, resulting in an organic fraction (bio-oil) that can be upgraded to gasoline and diesel type fuels [25].

Moreover, the molecular weight of the bio-oil is reduced. According to reports, using a ZSM-5 catalyst reduced the oxygen content in bio-oil from 33 to 13%. Oxygen removal occurs in the form of H_2O at lower temperatures and as CO and CO_2 at higher temperatures [26]. Due to H-ZSM-5's strong acidity and increased inclination to dehydrate, oxygen is primarily removed in the form of water, thus reducing the water content of the bio-oil [27]. Therefore, this review paper is aimed at extensively examining the current research development on the application of zeolite ZSM-5 catalysts in hydrothermal liquefaction of biomass to enhance simultaneously the bio-oil yield and quality.

In this review article, the authors aim to contribute to the understanding and advancement of biomass conversion into biofuels, with a specific focus on the hydrothermal liquefaction (HTL) process using the ZSM-5 catalyst. The novel aspect lies in exploring the potential of ZSM-5, a heterogeneous catalyst, to enhance the efficiency of the HTL process. The authors highlight the significance of ZSM-5 in influencing the hydrocarbon content while reducing oxygenated compounds and unwanted by-products in the resulting bio-oil. By emphasising the role of temperature, pressure, residence time, catalyst, and solvent in HTL, the review aims to provide insights into optimising these parameters for achieving high-value bio-oil production. The study not only reviews the existing research but also emphasises the need to further develop and optimise ZSM-5 as a catalyst, positioning it as a key element in the generation of renewable and carbon-neutral fuels. Overall, the authors aim to present a comprehensive overview and new perspectives on the use of ZSM-5 in HTL for biomass-to-biofuel conversion, contributing to the ongoing efforts in the field of sustainable energy.

2. Thermochemical Processes

2.1. Direct Combustion

In direct combustion, biomass is directly burnt in the presence of oxygen from the surrounding air to convert the energy stored in biomass into heat, mechanical power, electricity, etc. [2]. The combustion process consists of an exothermic chemical reaction. Chemical energy is released when biomass is burned in the presence of air. Combustion takes place inside combustion chambers at temperatures between 800 and 1000 °C. It is important to point out that the biomass burned to produce biofuels by combustion must have a humidity level lower than 50% [28]. The combustion of biomass has several advantages, such as volume reduction, controlled emissions, use of heat for power generation, and it can be silent and odourless; however, there are even more disadvantages of using combustion as a form of biomass conversion. The disadvantages of combustion include the possibility of producing health-harmful products (dioxins, furans, and heavy metals), potential conflicts with initiatives to cut waste production, and more energy enquired to handle waste with high humidity and high costs to prevent pollution by emissions [28].

2.2. Gasification

In gasification, biomass is oxidised at high temperatures with gasification media such as oxygen to produce a combustible gaseous mixture [3]. Air, pure oxygen, steam, carbon dioxide, or mixes are all suitable gasifying agents. Air is the most affordable and popular agent, but it contains a significant amount of nitrogen, which slows down the heating rate of the synthesis gas obtained. Higher heating rates are produced using pure oxygen; however, the method is less economically profitable due to the cost of producing oxygen [29]. There are discrete types of catalysts, such as AAEMs (alkali and alkaline earth metals) and Ni-based catalysts, which have been subjected to the gasification process and have reported positive results. The reaction time and temperature required to produce useful gases can be significantly decreased using these distinct catalyst types [11]. Gasifiers are divided into three categories based on configuration: fixed bed, fluidised bed, and entrained flow [30]. Fixed-bed gasifiers are perfect for using biomass on a small scale. Biomass and fuel derived from waste (FDW) are treated using fluidised bed gasifiers. These fluidised bed gasifiers are further separated into bubbling and circulating types. While bubbling-type beds are utilised to treat FDW, circulating-type beds are more frequently employed for biomass. Finally, entrained flow gasifiers are used to treat coal and, in certain situations, biomass. They require raw materials with a micrometric order of magnitude [31]. Some advantages of gasification include the formation of a synthesis gas with a range of applications (production of electricity, fuel, and the production of chemicals). It also prevents the production of harmful nitrogenous, halogenated and sulphur compounds. On the other hand, biomass gasification has limited large-scale use. It also requires a lot of energy if waste with high humidity percentages is handled [28].

2.3. Pyrolysis

Biomass pyrolysis is a thermochemical decomposition process that converts organic material/biomass in the absence of oxygen with possible products of liquid (bio-oil), solid (biochar) and gases [32]. Pyrolysis is made up of numerous spontaneous reactions whose efficiency is affected by a number of variables, including temperature, heating rate, residence time, particle size, pressure, type of biomass, moisture content, and the pre-treatment process of the biomass [28]. The pyrolysis conditions have the biggest impact on product yields. For instance, when the reaction temperature is below 450 °C, the main product is biochar, and when the reaction temperature is between 450 and 800 °C, the main product is bio-oil. At temperatures greater than 800 °C, gases are then formed [33]. Pyrolysis can be divided into three types: slow, fast and flash pyrolysis and the division is based on experimental conditions such as temperature, residence time, heating rate, and particle size [34].

When compared to alternative methods, the pyrolysis process has a number of advantages. It may yield a variety of useful products from solid waste streams (such as liquid fuels, fertilisers, activated carbon, and H_2, CH_4, and CO); it can be incorporated into microturbine, fuel cell, and thermophotovoltaic (TPV) systems for power generation. The product stream is more complicated for pyrolysis processing than for many alternative treatments, which is its main drawback [35].

2.4. Hydrothermal Liquefaction

Liquefaction is a thermochemical process that converts biomass into liquid fuels by breaking down the polymer structure into liquid components in a high-temperature pressured environment [11]. The process is usually carried out at pressures of 1 to 25 Mpa and temperatures of 250 to 450 °C [36]. Liquefaction improves the quality of bio-oil, such as HHV, bio-oil yield, and oxygen and nitrogen contents. Compared to pyrolysis, which generates a highly oxygenated bio-oil, liquefaction produces a bio-oil with a lower oxygen content [35].

The liquefaction process has several advantages over pyrolysis, including higher energy efficiency, lower operating temperature, and reduced coke formation than fast pyrolysis. Furthermore, the bio-crude produced from HTL conversion has higher quality and energy density, as well as excellent thermal and storage stability [37]. Studies have shown that temperature, residence time, heating rate, feedstock particle size, and type of solvent media all affect the HTL process, and temperature, pressure, and solvent media are crucial parameters [31]. Hydrothermal liquefaction is one of the most promising thermochemical liquefaction techniques (HTL) as it is a method that can effectively treat both wet and dry biomass from lignocellulosic to organic waste without limiting the amount of lipid present. The product produced in this process is known as bio-crude, a renewable alternative to oil since it is an energy-dense intermediate that can be converted into various liquid fuels [28]. The flow diagram in Figure 3 shows the reaction process for dry lignocellulose biomass. Dry biomass usually needs pre-treatment, especially woody biomass, to reduce particle size, remove contaminants and alkaline treatment to obtain a stable slurry for easy pumping [38].

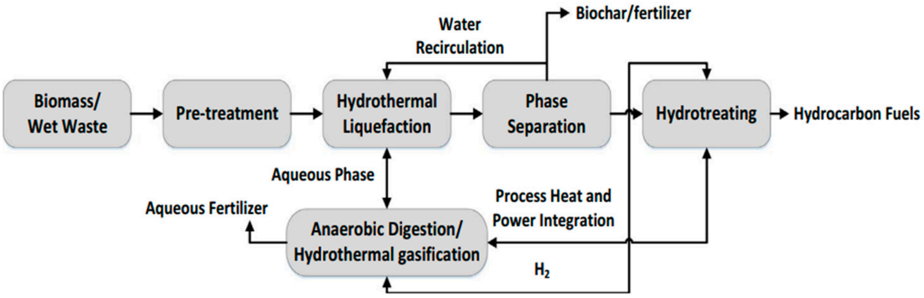

Figure 3. Process flow diagram of HTL process of lignocellulose biomass [38].

Table 1 below outlines the primary distinctions among all four thermochemical processes. These distinctions effectively function as both the advantages and disadvantages of each process in comparison to the others.

Table 1. The differences between four thermochemical processes, namely combustion, gasification, pyrolysis, and hydrothermal liquefaction.

Property	Combustion	Gasification	Pyrolysis	Hydrothermal Liquefaction
Process type	Oxidative reaction with oxygen	Partial oxidation without complete combustion	Thermochemical decomposition in the absence of oxygen	Liquefaction in the presence of water under high pressure and temperature
Products	CO_2, H_2O, heat, and ash	Syngas (CO, H_2), ash	Biochar, bio-oil, syngas, and gases	Biocrude oil, gaseous products, and solid residues
Temperature range	Above 700 °C	500 °C–1000 °C	350 °C–800 °C	250 °C–450 °C
Oxygen availability	Oxygen-rich environment	Controlled oxygen supply	Oxygen-limited	Oxygen present in the form of water

Table 1. *Cont.*

Property	Combustion	Gasification	Pyrolysis	Hydrothermal Liquefaction
Energy efficiency	High	Moderate to high	Moderate	Moderate
Feedstock sustainability	Broad range of organic materials	Biomass, coal, and waste materials	Biomass and waste materials	Biomass, algae, and organic waste
Syngas composition	CO_2, CO, H_2, and water vapour	CO, H_2, CH_4, tar, and ash	H_2, CO, CH_4, and other hydrocarbons	CO_2, CO, H_2, and other hydrocarbons
End-Products Use	Heat generation, electricity, or direct heat use	Syngas for electricity, heat, or biofuels	Biochar for soil improvement, bio-oil for bioenergy	Biocrude for biofuels, gaseous fuel, and by-products
Residue/Char quality	Ash residue	High-quality biochar	Solid biochar	Solid residues with potential applications
Environmental impact	CO_2 emissions, air pollutants	Lower CO_2 emissions compared to combustion	Moderate emissions, biochar sequestration potential	Lower CO_2 emissions, potential carbon capture
Application focus	Traditional power generation, heat	Bioenergy synthetic fuels	Bioenergy, soil improvement	Biofuels, wastewater treatment, biomass conversion

Zeolite Catalysts in HTL Conversion of Biomass

Zeolites, encompassing varieties such as ZSM-5, are integral catalysts in the hydrothermal liquefaction (HTL) process, exerting significant influence via their acidity, confinement effects, and morphology. The tuneable acidity of zeolites, including both Brønsted and Lewis acid sites, is pivotal in promoting the breakdown of complex biomass molecules during HTL [39]. This catalytic activity enhances the production of valuable hydrocarbons while minimising undesired by-products. The unique microporous structure of zeolites contributes to a confinement effect, influencing reaction pathways and product selectivity in HTL. This effect stabilises reactive intermediates, potentially improving catalytic efficiency and controlling molecular interactions within zeolite channels [21]. The morphology of zeolites, including particle size and shape, is a critical factor influencing catalytic performance. Smaller particles with higher surface areas may enhance accessibility to active sites and impact reaction kinetics. Moreover, the stability of zeolites under harsh HTL conditions is crucial for sustained catalytic activity [40]. Researchers often modify zeolites using strategies like ion exchange or metal impregnation to tailor their properties, further enhancing acidity, selectivity, and stability. In summary, zeolites, as catalysts in HTL, offer a versatile platform for efficient and selective biomass conversion into biofuels, with their unique acidity, confinement effects, and morphology playing key roles in optimising catalytic performance [41].

Catalysts play a significant role in the reaction by lowering the activation energy, which has various benefits, including increased bio-oil yield and biomass conversion efficiency. The bio-oil yield was reported to have increased by 50 to 60% when a suitable catalyst was used in an HTL process [42]. Catalysts can improve bio-oil flow characteristics while lowering heteroatom content; furthermore, suitable catalysts can improve the higher heating value (HHV) of bio-crude [42]. Numerous studies have been conducted on the utilisation of acidic and alkaline homogeneous catalysts (HCl, H_3PO_4, Na_2CO_3, K_2CO_3, KOH, NaOH, $Ca(OH)_2$, etc). The results revealed that their addition significantly increased the yield and quality of bio-crude, but because these catalysts are homogeneous, expensive separation procedures to remove them at the conclusion of the reaction and corrosion-resistant equipment are needed [43]. Since recovering the catalyst in homogeneous catalysis is difficult and expensive, the catalyst will be discharged with the water phase at the end of the process, and it should request the appropriate neutralising treatments. Recently, heterogeneous catalysts have received a lot of attention due to their high activity and ease of recovery from liquid products. This allows them to be reused, reducing the cost associated with bio-crude production and encouraging large-scale production. Heterogenous catalysts are also not corrosive and have higher thermal stability. It is also known that heterogeneous catalysts enhance bio-oil stability [44].

For instance, the H form of Zeolite Socony Mobil-5 (HZSM-5) increases the bio-oil stability by reducing the organic acid content and by increasing the fraction of alkene, alkane, and ketones. Reusing catalysts is crucial for the cost-effective generation of HTL bio-oil, especially when using expensive metal catalysts [42].

Data from the literature show that ZSM-5 (Zeolite Socony Mobil-5) is one of the most promising catalysts that can be utilised to produce bio-oil from lignocellulosic feedstock. The presence of such a substance facilitates the production of a liquid fraction with a mixture of organic compounds with a lower oxygen content and a greater contribution from aromatics [45]. A number of techniques, including ion exchange, calcination conditions, and the ratio of silica to alumina (Si/Al), are used to regulate the acidity of the zeolite. They can be employed at high temperatures because of their excellent thermal stability, which frequently leads to higher yields and simpler heat recovery [46]. Various synthetic techniques have been proposed to circumvent the limitation imposed by narrow channel entrances of zeolites while maintaining their chemical features. Making hierarchical materials that combine micro and mesoporosity because these materials have mesopores, the acid sites are more easily accessible while maintaining the zeolites' acidity. Because mesopores make active sites more easily accessible, faster diffusion of reactants and products is thought to be the cause of the increase in activity. It is expected that the variations in reaction rates along the individual crystals will be lessened when mesopores are present. Such catalysts can be quite successful at converting biomass because of the wide range of pore sizes found in them [47].

In a study conducted by Cheng et al. (2017), they investigated the effect of heterogeneous Ni/HZSM-5 and homogeneous K_2CO_3 catalysts on bio-crude production from pine sawdust in the batch reactor. The catalytic effect of K_2CO_3 and Ni/HZSM-5 catalysts with different Ni loading ratios on yields and properties of bio-crude and gas were determined. Compared to no catalyst treatment, the introduction of catalysts increased bio-crude and gas yields. The catalysts increased the desirable hydrocarbon contents while decreasing the quantities of undesirable acids, ketones, phenols, esters, and alcohols in bio-crudes. Compared to the parent HZSM-5 catalyst, Ni/HZSM-5 catalysts show better catalytic activity to enhance bio-crude quality. Due to the combined cracking and hydrodeoxygenation reactions, Ni/HZSM-5 was more efficient at converting oxygenated compounds to hydrocarbons. An amount of 6% Ni/HZSM-5 catalyst generated the bio-crude product with the highest hydrocarbon content at 11.02%, compared to HZSM-5 [48]. Table 1 shows the conditions that were employed in catalyst preparation and the conditions of the conversion process.

In another study, Cheng et al. (2018) investigated the catalytic effects of different HZSM-5-supported catalysts on the yields and quality of bio-crude and gas in the liquefaction of pine sawdust in a hydrogen atmosphere generated from zinc hydrolysis. The catalytic liquefaction of pine sawdust was conducted using HZSM-5, Co/ZSM-5, Zn/ZSM-5, and bimetallic Co-Zn/ZSM-5 catalysts. The oxygen content of pine sawdust was 44.87 wt%, which was significantly reduced when compared to the oxygen content of the bio-crude products, which was between 15.29 wt% and 33.99 wt% and the HHV (23.12–34.27 MJ kg1) of these products increased when compared to non-catalytic pine sawdust (19.19 MJ kg1). Compared to no catalyst treatment, the HZSM-5-supported catalysts increased the yields of bio-crude and gas [49].

The bimetallic Co-Zn/HZSM-5 catalyst's activity was enhanced by the synergistic effects of Co and Zn on the HZSM-5 support. This was demonstrated by the bimetallic Co-Zn/HZSM-5 catalyst's improved interaction between Co and HZSM-5, higher stability and activity, and lower coke formation when compared to monometallic Co/HZSM-5 or Zn/HZSM-5 catalyst. The bio-crude yield of the HZSM-5 treatment was 64.31 wt%, while it ranged from 65.02 to 67.38 wt% for the HZSM-5 treatments that were Co or Zn loaded. With a yield of 67.38 wt%, the bimetallic Co-Zn/HZSM-5 catalyst produced the most bio-crude. While increasing the hydrocarbon content of bio-crude products, catalysts lowered the amounts of acids, ketones, phenols, and alcohol in bio-crude products. Due to the synergistic effect of Co and Zn on the HZSM-5 support, bimetallic Co-Zn/HZSM-5 catalysts show higher catalytic performance to increase bio-crude yield and quality compared to monometallic Co/HZSM-5 and Zn/HZSM-5 catalysts. In comparison to the monometallic Co/HZSM-5 catalyst (12.57%) and the Zn/HZSM-5 catalyst (13.18%), the bimetallic Co-Zn/HZSM-5 catalyst produced bio-crude with a greater hydrocarbon concentration (18.59%) [49].

Co and Zn are active centres for the catalytic hydrogenation and deoxygenation processes occurring on the Co-Zn/HZSM-5 catalyst. Three main reasons were given for the bimetallic Co-Zn/HZSM-5 catalyst's enhanced catalytic activity to that displayed by the monometallic Co/HZSM-5 or Zn/HZSM-5 catalysts (synergistic impact of Co and Zn) [49]. Firstly, the interactions between Co and the HZSM-5 support were first improved by loading Zn [50]. Second, compared to monometallic catalysts, bimetallic catalysts have improved stability [51]. Lastly, the addition of a second metal prevented excessive carbon build-up on the metal active sites of the bimetallic catalysts, which prevented coke accumulation in contrast to monometallic catalysts [52]. Therefore, compared to Co/HZSM-5, Zn/HZSM-5, and no catalyst treatment, the content of hydrocarbons in bio-crude produced by Co-Zn/HZSM-5 treatment was higher.

Jacek Grams et al. (2017) found that altering the physicochemical characteristics of the employed zeolites, such as their structure and properties like crystallinity, porosity, acidity, and elemental composition, can control the selectivity of the catalyst and the composition of the obtained bio-oil (including the number of aromatic compounds). Despite its potential to increase the selectivity of the production of aromatics, the larger size of the heavier oxygenates in comparison to the size of the utilised catalyst's pores prevents ZSM-5 from efficiently converting them. The bigger molecules are unable to pass through ZSM-5's internal structure; hence, the reaction yield is decreased [45]. Below is Table 2, which shows different catalysts that were used in HTL for different types of biomasses. Zeolite catalysts have been used, and zeolites modified with metals show a higher oil yield than the unmodified zeolite. When zeolites are used, the optimum conditions seem to be 60 min and a temperature of 300 °C to 340 °C.

Table 2. Catalysts used in the conversion of biomass to bio-oil by hydrothermal liquefaction (HTL) process.

Feedstock	Catalyst	Catalyst Preparation	Reaction Conditions		Yield (wt%)	Reference
			Temperature (°C)	Time (min)		
Pine sawdust	HZSM-5, Ni/HZSM-5, and K_2CO_3	Ni/HZSM-5 catalysts with different Ni loading (6 wt% and 12 wt%) were impregnated with aqueous nickel (II) nitrate hexahydrate solutions. The prepared Ni/HZSM-5 and HZSM-5 catalysts were dried at 120 °C for 4 h, and then calcined at 550 °C for 6 h.	300	60	61–68	[48]
Pine sawdust	Co-Zn modified ZSM-5	Co- or Zn-loaded HZSM-5 catalysts with different Co or Zn mass loading ratios (20 wt% Co/HZSM-5, 10 wt% Co-10 wt% Zn/HZSM-5, and 20 wt% Zn/HZSM-5) were prepared by a wet impregnation method. The catalysts were dried in air at 120 °C for 10 h, and then prepared catalysts were calcined in air at 550 °C for 4 h	300	60	65.02–67.38	[49]
Pomelo peel	Ionic liquid loaded ZSM-5, ZSM-5	ZSM-5 was added to [AMIm]Cl solvent and stirred for 10 h. After stirring, deionised water was added to cool the mixture before extraction. A low-speed centrifuge was used to centrifuge the reaction mixture, and then dried overnight to obtain a solid product.	200–300	60	Ionic liquid loaded ZSM-5: 29.21 (at 200 °C) 20.83 (at 300 °C) ZSM-5: 18.23 (at 200 °C) 17.06 (at 300 °C	[53]

Table 2. *Cont.*

Feedstock	Catalyst	Catalyst Preparation	Reaction Conditions		Yield (wt%)	Reference
			Temperature (°C)	Time (min)		
Spirulina	Pd/HZSM-5@MS, Pd/HZSM-5	$Pd(NO_3)_2$ was added in water, and HZSM-5/HZSM-5@MS were added in a beaker with 10 mL water. The mixture was stirred at room temperature for 24 h, and then dried in the oven for 10 h at 120 °C. The powders were washed with water, filtered, and calcine for 4 h at 400 °C	380	120	Pd/HZSM-5@MS—37.30 Pd/HZSM-5—37.20	[54]
Pine sawdust	HZSM-5, Zn/ZSM-5	Several Zn loadings (5 wt%, 10 wt%, 15 wt%, and 20 wt%) of Zn/HZSM-5 catalysts were prepared by impregnation with aqueous solutions of zinc nitrate hexahydrate. The prepared Zn/HZSM-5 and HZSM-5 catalysts were dried in air for four hours at 120 °C, and then they were calcined for six hours in air at 550 °C.	300	60	15% Zn/ZSM-5—59 wt% Was recorded as the highest yield	[49]
Wood biomass	K_2CO_3	The catalyst was purchased and used as is.	280	15	Run 1—8.6 Run 2—6.4 Run 3—8.5	[55]
Corn stalk	1.0 wt% Na_2CO_3	The catalyst was purchased and used as is.	409.85	15	47.2	[56]
Microalga (Dunaliella tertiolecta)	0 and 5.0 wt% Na_2CO_3	The catalyst was purchased and used as is.	250, 300, 340	5 and 60	31–44	[57]

3. Effects of Operating Parameters

Studies have shown that operating parameters such as temperature, residence time, heating rate, and feedstock composition all affect the HTL process. Any changes made in these parameters significantly impact the HTL process's product output [38].

3.1. Temperature

Temperature has synergistic effects on bio-oil yield since increasing temperatures cause more biomass to fragment. Extensive biomass depolymerisation occurs when the temperature used is high enough to overcome the activation energies for the bond dissociation [58]. Various authors have studied the influence of temperature on the bio-oil yield during hydrothermal liquefaction. The study by Karagoz et al. showed that sawdust liquified at temperatures of 180 °C, 250 °C, and 280 °C. At 15 min of residence time, the total oil yield at these temperatures was 3.7%, 7.6%, and 8.5%, respectively. This shows the synergistic impact of temperature increase on bio-oil yield during hydrothermal liquefaction of sawdust. It may be assumed that a temperature range of 280–350 °C for both subcritical and supercritical circumstances would be an effective range for biomass decomposition. The final temperature of liquefaction differs depending on the type of biomass [59]. The yield of liquefaction products appears to be influenced by temperature in a sequential manner. An initial rise in temperature triggers the yield of bio-oil. An increase in temperature after the oil yield reaches its maximum prevents the liquefaction of biomass. Regarding operational cost and liquid oil yield, producing liquid oils at extremely high temperatures is typically not a good idea [59].

As a function of the reaction temperature, the elemental composition of the biofuel produced via hydrothermal liquefaction varies. While the amount of hydrogen remains constant, the amount of oxygen decreases as the process temperature rises because a higher temperature favours deoxygenation. At higher temperatures, the carbon content is higher, and the bio-crude's H/C and O/C ratios decrease as temperature increases, which is consistent with the Fuel observed increase in calorific value [60]. However, at high temperatures, production falls off, producing less biofuel. As a result, no one temperature is appropriate depending on the needs (quantity or quality) since the best temperature to achieve maximum quality fuel is not the ideal temperature to obtain maximum production [28].

3.2. Residence Time

Residence time is the duration of the reaction, the period during which the temperature for HTL does not account for heating or cooling periods. It is vital to optimise residence time for the efficient conversion of organic compounds in biomass, as there is a critical residence time for a maximum oil yield [61]. During hydrothermal liquefaction of biomass, short residence times are typically anticipated to yield a high amount of bio-oil, but it is not always possible for biomass to react fully in a short period of time. However, long residence times result in the repolymerization of intermediate products, which reduces bio-oil yield [62]. In an investigation conducted by Wang et al., where they converted L. cubeba seed over different residence times of 30–120 min, the bio-oil yield initially increased from 53.5% at 30 min to 56.9% at 60 min. A further increase in residence time had a negative impact on the yield of bio-oil due to the polymerisation and cracking reactions. Moreover, the solid residue yield is insensitive to the residence time, which decreased from 15.3% at 30 min to 13.2% at 60 min. Over longer residence times, the gas yield rises, reaching a maximum of 25.6% at 120 min [57].

3.3. Heating Rates

Higher heating rates during hydrothermal liquefaction support biomass bulk fragmentation while preventing char formation. However, due to improved dissolving and stabilisation of fragmented species in hot compressed water media, the effect of heating rates on the product distributions in hydrothermal liquefaction is very low in comparison to pyrolysis. Char residue typically forms because of secondary reactions during slow heating rates. At extremely high heating rates, secondary processes also dominate, producing high gas yields, similar to during supercritical liquefaction. Additionally, liquid oil yield is not overly sensitive to significant fluctuations in high heating rates [63]. With the appropriate heating rates, there can be significant fragmentation and few secondary reactions. On this logic, moderate heating rates might be sufficient to combat heat [58]. The HTL of Nannochloropsis and Chlorella were studied by Biller et al. at 350 °C for 60 min. Heating rates ranged from 10 °C/min to 25 °C/min. Because of the formation of char residues, bio-oil yields declined from 35.3% and 37.2% to 34.1% and 35.8%, respectively [64].

3.4. Type and Composition of Biomass

The type of biomass used is a crucial factor to consider while performing hydrothermal liquefaction since the biomass can be made up of various components that respond to hydro treatment in different ways. The heterogeneity of the biomass feedstock affects the liquid products and overall yield because the three main biomass components, lignin, hemicelluloses, and cellulose, behave differently during HTL. Bio-oil with high oxygen and moisture content often results from the liquefaction of species of loosely structured biomass, which lowers oil quality and HHV. Such species also have a low viscosity. In general, higher bio-oil yields are produced from biomass with high cellulose and hemicellulose content [65]. The composition of varied biomass can significantly impact the outcomes of a hydrothermal process [63]. Feng et al. investigated the impact of white pine bark, white spruce bark, and white birch back on bio-oil yield in HTL under an initial N_2 pressure of 2.0 MPa at 300 °C for 15 min. The three biomasses produced bio-oil yields of 36%, 58%, and 67%, respectively, during liquefaction, demonstrating the impact of the different biomass types on the bio-oil yield [66].

4. Conclusions and Future Perspectives

Biomass thermochemical conversion is a promising method for generating alternative fuel sources for energy production. This review aims to report the recent development in the use of zeolite heterogeneous catalysts in pyrolysis and liquefaction technologies. The content and quality of the final products are significantly enriched when catalysts are used. The type of zeolite heterogeneous catalyst utilised determines the yield and physicochemical characteristics of the bio-oil. Selective heterogeneous catalysts enhance polymer decomposition, increasing bio-oil yield while decreasing biochar production. The employment of heterogeneous catalysts also results in a higher calorific value and less NOx and SOx emissions by lowering the heteroatom content of bio-oil and increasing the H/C ratio.

The potential for ZSM-5 to become inactive throughout the lignocellulosic biomass conversion process is one of its key drawbacks. The creation of carbon deposits and blockage of the catalyst's pores are linked to the major deactivation mechanism. However, the modification of the ZSM-5 catalyst can further improve the quality of the bio-oil. This modification can be carried out by introducing various kinds of dopants on the catalyst. The development of HTL catalysts with desirable properties, such as high activity (to provide high yield), high stability (to endure HTL working conditions and to provide a longer lifetime), and low cost, should be the focus of future efforts. Future developments in hydrothermal liquefaction catalysts should prioritise key properties to enhance their efficiency and sustainability. Firstly, a catalyst's ability to promote high conversion rates and selectivity in the liquefaction process is crucial for maximising the yield of valuable products. Selectivity towards desired biofuel components and reduced production of undesired by-products are essential objectives. Additionally, catalyst stability under harsh hydrothermal conditions is paramount to ensure a prolonged catalyst lifespan and economic viability. Furthermore, attention should be directed towards catalysts with improved resistance to fouling and deactivation, which commonly occur in the presence of complex biomass feedstocks. The development of catalysts with enhanced activity at moderate temperatures and pressures can contribute to energy efficiency and process sustainability. Ultimately, future catalysts should be designed to facilitate the integration of hydrothermal liquefaction into diverse biomass conversion processes, promoting a more robust and versatile platform for biofuel production.

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