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Catalytic Pyrolysis of Biomass

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<http://dx.doi.org/10.5772/67569>

Abstract

Biomass pyrolysis has been a popular research topic due to versatility in products: char, bio-oil, and syngas. What makes the biomass pyrolysis so important is that it provides product options such as fuels or green chemicals. In the case of biomass pyrolysis, lignocellulosic materials undergo thermal degradation in the absence of oxidative environment at atmospheric pressure during a definite residence time, which produces solid char, bio-oil, and syngas. If the bio-oil is going to be used as a fuel source or to be processed for producing chemicals, it requires an upgrading. Catalytic pyrolysis is the most promising method to improve the quality of bio-oil. The present study presents an updated review on catalytic pyrolysis of biomass for the production of upgraded bio-oil. In this context, this review considers recent advances in catalysts and catalytic pyrolysis process.

Keywords: pyrolysis, catalysts, bio-oil upgrading

1. Introduction

The continuous growth in economies over the world requires demand for energy at a high rate. For meeting the energy demand, high energy production via fossil fuels leads to an increase in CO₂ emissions. In addition, considering the issue in terms of the effects of global climate change and environmental responsibility, the need for renewable energy resources has become inevitable. Also, diminishing reserves of fossil fuels and the necessity of reducing CO₂ emissions that is emitted by fossil fuel burning processes force us to seek environmentally and economically beneficial ways to produce energy from renewable energy resources [1–5].

Biomass is a general term for nonfossilized and biodegradable organic material originating from plants, animals, and microorganisms. Given the fact that biomass is abundant, and it accounts for 38–43% of primary energy consumption in developing countries, the use of waste-based biomass sources and feedstock is of utmost importance for research in terms of clean energy generation via thermochemical or biochemical conversion processes [6–8]. Agricultural, aquaculture and forestry products (also by-products, residues, and wastes), dedicated energy crops, biodegradable organic fraction of industrial wastes, biodegradable organic fraction of municipal solid waste, and food processing wastes can be included in primary biomass resources [8–12].

Pyrolysis is a thermochemical conversion process in the absence of an oxidizing agent and can be regarded as the initial stage of gasification and combustion. Solid char, liquid pyrolysis oil, and gas are the main products of biomass pyrolysis. The amount of products and their fractions are influenced by many factors such as heating rate, pyrolysis temperature, biomass composition, and catalyst effect [8, 13, 14]. Since biomass pyrolysis is feedstock composition-dependent process, finding suitable catalysts to regulate pyrolysis processes is an alternative way to reduce overall energy consumption [15]. Also, catalytic pyrolysis of biomass provides, with optimum catalyst/biomass ratio, chemically more homogenous fractions of pyrolysis products. In recent years, different biomass feedstock or biomass originated waste materials have been studied using several catalysts in order to understand the effects of catalyst to pyrolysis process [16–22].

Bio-oil possesses many undesirable components, such as high content of volatile acids, water, and highly oxygenated compounds, which in turn lowers the heating value. In order to use bio-oil in fuel applications, upgrading of bio-oil is necessary. Catalytic pyrolysis is a promising way to improve bio-oil quality by removing of oxygenated compounds, increasing calorific value, lowering viscosity, and increasing stability. Of the various catalysts studied for biomass catalytic pyrolysis, zeolites have been shown to be effective for reducing oxygenated compounds of pyrolysis oil. One of the most common zeolites have been studied is ZSM-5, which can be synthesized with different Si/Al ratios, thus having different acidity characteristics [23]. Studies have shown that using ZSM-5 as catalyst in biomass pyrolysis increased aromatic hydrocarbons content and decreased oxygenated aromatic compounds content in bio-oil [1, 19, 23–25].

2. Fundamentals of biomass pyrolysis

Pyrolysis is the heating of the feedstock in the absence of oxygen at a specified heating rate to a definite temperature and holding it there for a certain time. During pyrolysis, large hydrocarbon molecules are broken into relatively smaller ones via reactions such as depolymerization, dehydration, decarbonylation, decarboxylation, deoxygenation, oligomerization, and aromatization [23, 26]. The amount and the ratio of these fractions are influenced by many factors such as heating rate, pyrolysis temperature, biomass composition, and catalyst effect, which can be seen in **Table 1** [8, 13, 14].

Reactor type	T (°C)	Sweeping gas flow rate	Residence time (s)	Catalyst type	Catalyst to biomass ratio	Bio-oil (wt.%)		Total (aqueous + organic)	Gas (wt.%)	Char (wt.%)	Ref.
						Aqueous	Organic				
Fixed bed	600	30 cm ³ min ⁻¹	10	La/HZSM-5	3	14.4	7.7	22.4	34.2	39.9	[27]
Fluidized bed	450	3.75 l min ⁻¹	*	H-Beta	0.4	13.1	15.8	28.9	49.4	21.7	[28]
Auger reactor	500	120 l h ⁻¹	2	ZSM-5	5	*	*	50.3	26.2	13.6	[29]
Fixed bed	500	30 cm ³ min ⁻¹	4.5	Al-MCM-41	0.46	37.5	10.91	48.41	7.49	37.43	[30]
Fixed bed	500	50 cm ³ min ⁻¹	0.03	CoO	0.46	22.37	34.10	56.47	21.29	22.24	[31]
Fixed bed	500	50 cm ³ min ⁻¹	0.03	Co ₃ O ₄	0.46	26.30	29.18	55.48	33.78	22.55	[31]
Fixed bed	500	50 cm ³ min ⁻¹	0.03	NiO	0.46	24.81	22.65	47.46	27.73	24.84	[31]
Fixed bed	550	150 ml min ⁻¹	*	ZnO	0.05	*	*	47.02	21.38	31.6	[17]
Fixed bed	490-540	50 cm ³ min ⁻¹	*	ZSM-5	0.01	*	*	38.29	19.45	42.27	[32]
Fixed bed	490-540	50 cm ³ min ⁻¹	*	Al-MCM-41	0.01	*	*	39.98	18.80	43.15	[32]
Fixed bed	490-540	50 cm ³ min ⁻¹	*	Al-MSU-F	0.01	*	*	39.59	19.18	43.31	[32]
Fluidized bed	425-450	*	3	HZSM-5	*	20.9	11.9	32.8	46.8	20.3	[33]
Fluidized bed	400	27 l min ⁻¹	*	ZnO	*	*	*	57	20	12	[34]
Fixed bed	450	50 ml min ⁻¹	*	α-Al ₂ O ₃	0.5	19.1	42.4	61.5	10.5	17.6	[20]
Fixed bed	500	100 cm ³ /min ⁻¹	*	ZnO	0.15	*	*	45.22	30.46	24.32	[35]
Fixed bed	550	100 cm ³ /min ⁻¹	*	Al ₂ O ₃	0.1	*	*	40.95	37.69	21.36	[35]
Fixed bed	500	70 ml min ⁻¹	4	Na ₂ CO ₃ /γ-Al ₂ O ₃	0.5	28	9	37	23	19	[36]

* Data is not available

Table 1. Pyrolysis conditions and pyrolysis products of several research studies.

2.1. Pyrolysis operating parameters

2.1.1. Temperature

The effect of reaction temperature on amount of each pyrolysis product is regarded as one of the most important and significant parameters. Studies have shown that increasing pyrolysis temperature causes a reduction in char yields, suggesting that secondary reactions of the liquid fraction and further char decomposition reactions are promoted with increase in temperature, resulting in enhanced gas yields at temperatures over 600°C [17, 27, 37, 38]. Previous studies have confirmed that the maximum liquid yield is obtained at temperatures in the range of 500–550°C [17, 37–39]. In a study of Pütün [37], bio-oil yields of 41, 46, and 43% were obtained at temperatures 400, 550, and 700°C, respectively. At temperatures between 350 and 400°C, char yields were close to maximum within the range of 29–38.48% (wt.) for most cases, suggesting that biomass could not be decomposed completely [17, 37, 39]. Similarly, solid char formation is favored at low temperatures (<350°C) mainly due to reason of cross-linking reaction of cellulose and lignin. However, volatiles are released at temperatures higher than 350°C as a result of depolymerization reactions [40].

2.1.2. Particle size

Biomass, being poor conductor of heat, often possesses heat transfer difficulties during pyrolysis. The size of particle has a direct effect on heat transfer, which in turn influences the yield and properties of bio-oil. Understanding the effect of particle size distribution on pyrolysis product yields also help to optimize residence times of the pyrolysis reactions. It is a known fact that the particle size of the feed influences the heat and mass transfer rate and release rate of volatile matter during pyrolysis process [35]. Studies have revealed that for larger particles of biomass, the yield of gaseous fraction was higher than that obtained from smaller particles. This situation can be explained by the fact that larger biomass particles increase the residence time of volatile matter, favoring secondary cracking reactions of tar, thus increasing the gas yield. Enhanced bio-oil yield is obtained using smaller particle size due to the reason that pyrolysis process is kinetically controlled with smaller particle size, whereas it mainly happens on the surface of the biomass in the case of larger particle size. Due to low heat transfer rate, the temperature inside the larger particle is lower than expected, thus causing pyrolysis process to be incomplete; resulting higher char yields and lower bio-oil yields [41, 42]. Also, Asadullah et al. suggested that mass transfer resistance inside the biomass particle was higher in larger particles than smaller ones; resulting increased char yield [40]. Unexpected differences between the product fractions might be due to differences in type of biomasses (for example, oxygen content of the biomass has a known effect on heat transfer mechanism) [40].

2.1.3. Heating rate

As affecting heat transfer, adjusting heating rate to optimum level is of high importance regarding product yields of pyrolysis process. Increasing heating rate has an effect of enhancing liquid yields and decreasing char yields, which suggests that optimum heating rate

prevents secondary reactions resulting maximum liquid yields [39, 40]. Higher heating rate favors rapid formation of volatiles, while lower heating rate causes longer residence time for volatiles, thus enabling the repolymerization reactions forming char [40]. A study on olive residue and sugar cane bagasse pyrolysis has shown that, between the heating rates of 2 and 50 K.min⁻¹, the pyrolysis rate is increased with heating rate. It was suggested that the overlapping differential thermogravimetry (DTG) peaks with high heating rates was a consequence of the fact that some of the constituents of the biomass samples decomposed simultaneously while at low heating rate, those peaks were clear. This can be explained by the fact that the temperature inside the biomass particle increases with an increase in heating rate, and rate of decomposition is higher than the rate of formation and rate of volatile release [4]. This is the reason why optimum heating rate is necessary for an effective pyrolysis process.

As stated above, higher heating rates minimize char formation. In case of lower heating rates, which run for several days, the main product is char. This process is called carbonization. Carbonization enables the conversion of condensable vapor into char and noncondensable gases [26].

2.1.4. Residence time and sweeping gas flow rate

Sweeping gas flow rate is another important parameter, which influences the residence time of volatiles and the yield of gaseous fraction of pyrolysis products. Numerous studies have shown that higher sweeping gas flow rate favors rapid removal of vapors from the reaction medium, thereby reducing secondary reactions such as thermal cracking, repolymerization, recondensation, and char formation. Hence, char yields are decreased, whereas the yields of gaseous products are increased [17, 37, 39]. Additionally, in a study of catalytic and conventional pyrolysis of several biomass types, Huang et al. [27] showed that increasing gas residence time affected the yield of gaseous products of biomass pyrolysis so that secondary cracking reactions are attributable for enhanced gas yield and decreased liquid yield. Moreover, optimum sweeping gas flow is required in order to obtain maximum pyrolysis product yield from the reaction system. A study of Pütün [37] revealed that nitrogen flow rate of 200 mL min⁻¹ was adequate for 48.30% maximum yield of bio-oil for the current system. In fact, flow rate of nitrogen does not have a significant effect on liquid yield of pyrolysis systems as it much more depends on sufficient quenching of pyrolysis vapors and downstream cooling mechanism. The study of Uzun and Sarıoğlu [39] has shown that gas yields reached its maximum value of 30.08% with a nitrogen flow rate of 800 cm³ min⁻¹.

Other than the sweeping gas flow rate, the type of sweeping gas plays an important role in terms of product composition and quality. Melligan et al. revealed that bio-oil obtained by using H₂ as sweeping gas had higher heating value of 24.4 MJ kg⁻¹ relatively higher than that of obtained under N₂ atmosphere with a higher heating value of 17.8 MJ kg⁻¹ [43]. Pütün et al. [18] compared the outcome of biomass pyrolysis using N₂ and steam atmospheres as sweeping gases. The effect of nitrogen as a carrier gas was consistent with other studies in literature [39], while steam lowered the yield of char by diffusing into biomass particles, facilitating desorption, and removing the volatiles.

2.1.5. Biomass composition

Biomass is composed of lignin, hemicellulose, cellulose, extractives, and inorganic elements. The composition and amount of pyrolysis products vary depending on the content of biomass constituents as well as the distribution and percentages of these constituents, which vary with biomass species [44].

Cellulose, being linear-structured polymer, consists of β -1,4 linked glucose units, whereas hemicellulose is a branched-structured polymer composed of sugars such as pentoses and hexoses. Being formed by cross-linked phenylpropane units, lignin is a more complex aromatic compound and more resistant to thermal decomposition than cellulose and hemicellulose [3, 45, 46]. Cellulose is decomposed via two types of reactions: depolymerization and ring scission, which will result in the formation of different compounds. The ring scission reaction mainly results in the formation of hydroxyacetaldehyde, acetol, linear carbonyls, linear alcohols, and esters. However, anhydro oligosaccharides, monomeric anhydrosugars, furans, cyclopentanones, and pyrans are obtained with the depolymerization reactions [43]. Melligan et al. [43] revealed that during conventional pyrolysis of biomass, cellulose decomposition follows depolymerization reaction pathway. Lignin conversion is mainly due to depolymerization reactions and fragmentation reactions, which lead to formation of aromatic compounds of the main precursors of hazardous materials present in tar [46].

During the pyrolysis of biomass, the decomposition of biomass constituents takes place after moisture evaporation. It is a known fact that hemicellulose is the first component to decompose within the temperature range of 160–240°C, and cellulose is generally degraded at temperatures between 240 and 372°C. The decomposition of lignin, however, occurs within wider range of temperature (160–625°C) and at a low rate due to its resistant nature compared to hemicellulose and cellulose [4, 47].

Biomass constituents possess different characteristics and reactivity due to their heterogeneous nature, the effect of main constituents to pyrolysis products is an important parameter to take into consideration. In a study of Haykiri-Acma and Yaman [45], the behavior of sunflower shell and olive refuse was investigated during pyrolysis. It was revealed that sunflower shell with high content of volatile matter (76.0%) favored the formation of gaseous products, whereas high lignin and high ash content in olive refuse samples (34.7 and 13.8%, respectively) provided enhanced yield of solid char. Huang et al. studied various types of biomasses with addition of catalyst at temperature of 600°C and compared them with main biomass components. Cellulose, as one of the main biomass components that gave the highest yield of gaseous products (60.7%), was followed by sugar cane bagasse with yield of 57.0%. It was also found that samples with high lignin content gave more char yield, which can be explained by the presence of stable aromatic compounds present in the lignin matrix. For the major components of biomass, cellulose has the highest olefin yield, whereas lignin has the lowest, which is attributable to the fact that levoglucosan is the main product of cellulose pyrolysis [27, 45]. Collard et al. [46] compared the pyrolysis behavior of beechwood with main biomass constituents. It was noted that cellulose produced highest amount of volatiles followed by the gas and char fractions. Also, beechwood gave high yield

of tar (36.5%) due to its high content of cellulose. However, in a study of Bertero et al. [48], bio-oil obtained from pine sawdust, which had lower cellulose content than that of mesquite sawdust had lower yield.

2.1.6. Catalyst effect

The presence of catalyst in pyrolysis process has also been investigated with different biomass sources [34]. Using catalysts in biomass, pyrolysis influences the decomposition behavior of biomass and composition and quantity of pyrolysis products. ZSM-5 zeolites were found to be effective in improving deoxygenated aromatic content of pyrolysis products while reducing liquid yield [19, 31, 49]. Using silica-alumina with or without deposition of alkali metals favors water formation, increases gas, and char yield, consequently reducing total organic yield comparing to conventional pyrolysis [20].

Catalysts also affect the distribution and the content of chemical compounds of pyrolysis products. Zhou et al. investigated the effect of catalyst to biomass ratio by using zinc oxide as catalyst. With increasing the catalyst amount, approximately 6% (wt.) decrease in bio-oil yield was observed, and the gas yield increased in the range of 21.38–28.74% (wt.) [17]. In a study by Huang et al., HZSM-5 zeolite impregnated with 6% wt. Lanthanum showed that increasing catalyst to biomass ratio improved the chemical composition of pyrolysis liquid in terms of olefin content [27].

2.2. Pyrolysis mechanism

Understanding the pyrolytic behavior of cellulose is crucial due to the fact that it accounts for approximately 50% of biomass [44, 50]. Levoglucosan is the main component of cellulose pyrolysis product [44, 51, 52]. Bai et al. studied the effect of levoglucosan in cellulose pyrolysis. It was suggested that during pyrolysis, cellulose conversion into levoglucosan occurred faster than its vaporization rate [51]. It was suggested that vaporized levoglucosan leaves reaction environment, whereas its polymerized form leads to yield low-molecular-weight volatiles including 5-hydroxymethyl furfural, furan, furfural, H₂O, CO₂, and acetic acid [51].

Stefanidis et al. investigated the pyrolysis of lignocellulosic biomass to see the effect of pyrolysis of each constituent on the overall yield [44]. Similarly, the main product of cellulose pyrolysis was found to be levoglucosan. Also, small amount of phenolic compounds, which were formed as a result of secondary reactions were detected. In this study, formation of acetic acid was considered to be due to dehydration of hydroxyacetaldehyde, resulting formation of ketene, which produces acetic acid via hydration [44].

In order to understand the mechanism of thermal decomposition of hemicellulose and to reveal reaction pathways for the formation of main pyrolysis products, xylan is considered to be a model compound as a replacement of hemicellulose. In a study of Stefanidis et al., the main products of xylan pyrolysis were reported to be phenols and cyclic ketones, which were derived from the cleavage of the ferulic acid ester branch of xylan and cleavage of o-glucosidic bonds followed by removal of hydroxyl groups of xylose rings, respectively [44].

Lignin decomposition mainly leads to the formation of phenolic compounds, which are of more complicated structure than those derived from cellulose and xylan, due to their methoxy and poly-substituted structure [44, 52]. Xin et al. proposed that the primary reaction of lignin pyrolysis was depolymerization and dealkylation due to increased formation of guaiacol at 350°C. As temperature increases to 450 or 550°C, the decomposition of guaiacol leads to formation of phenols and CH₄. Dehydroxylation of phenolic compounds followed by polymerization of ring-containing monomers leads to the formation of Polycyclic Aromatic Hydrocarbons (PAHs) [52].

2.3. Pyrolysis products

2.3.1. Gas

The gaseous fraction of biomass pyrolysis products contains mostly hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene [5, 27, 29, 33, 53]. Pyrolysis gas can be used to provide heat for pyrolysis reactor or for heat and electricity generation in a gas turbine-combined cycle system [38]. Depending on the biomass feedstock and reactor configuration, primary gases of biomass pyrolysis contain 86.7 wt.% of CO₂, 1.2 wt.%, and 6.5 wt.% H₂ [48]. Dependent on the process temperature, the high heating value of gaseous products varies between 6.28 and 14.77 MJ m⁻³ [38].

2.3.2. Char

As solid product of biomass pyrolysis, char, which is comprised of the condensed organic residues and the inorganic phases, with an average high heating value of 28.5–29 MJ kg⁻¹ (depending on the biomass feedstock) can be used as a solid fuel. It is also a well-known material for activated carbon production [38, 45]. Char with >70 wt.% fixed carbon content can be used as a raw material for production.

2.3.3. Pyrolysis oil (bio-oil)

Bio-oil is a dark brown colored liquid mixture, which is composed of an aqueous phase and an organic phase having a large number of different chemical compounds derived from depolymerization and fragmentation reactions of biomass main components: cellulose, hemicellulose, and lignin [17, 20, 30, 32, 48, 54]. Aqueous phase of bio-oil contains a wide variety of oxygenated organic compounds such as acetic acid, methanol, and acetone. Organic phase of bio-oil contains single-ring aromatic hydrocarbons such as benzene, toluene, indene, alkylated derivatives, and polycyclic aromatic hydrocarbons including naphthalene, fluorene, phenanthrene, and oxygenated organic compounds such as aliphatic alcohols, carbonyls, acids, phenols, cresols, benzenediols, and guaiacol [17, 30, 32, 48]. Due to its relatively higher organic compound content, organic phase of bio-oil has higher carbon concentration and higher calorific value than aqueous phase [21, 48].

The chemical composition of bio-oil varies depending on biomass feedstock characteristics, mainly the percentages of main biomass constituents. The decomposition of cellulose leads to formation of levoglucosan and furfural which are considered valuable organic com-

pounds in terms of fuel quality of bio-oil [32]. Phenolic compounds are the products of lignin depolymerization and cracking reactions. Among the phenolic compounds present in bio-oil, guaiacol and its alkylated compounds are the most important ones due to being thermally unstable and being able to transform through secondary reactions to alkylated phenols and aromatic compounds, which are desirable for bio-oil quality [54]. Acetic acid, generally the main compound in the group of acids in bio-oils, is formed by the deacetylation of hemicellulose [54].

2.3.3.1. *Bio-oil characteristics*

Due to heterogeneous structure of biomass, bio-oil contains different types of acidic compounds as well as high amount of water and highly oxygenated hydrocarbons, which lead to poor combustion properties, instability, lower calorific value, and higher viscosity compared to fossil fuels [24, 55].

Water in bio-oil is primarily formed as a result of dehydration reactions and depolymerization reactions of hemicellulose, cellulose, and lignin [48]. The presence of water in bio-oil is a drawback in terms of utilization of bio-oil, because it lowers the heating value and delays the ignition [17]. However, high water content also leads to low viscosity so that the fluidity of bio-oil is enhanced, which is a good indicator of bio-oil quality for utilization in combustion engines [32, 48]. The water yield in bio-oil varies depending upon the biomass composition and process conditions, such as 15.0 wt.% for hybrid poplar [33], 15.32 wt.% for rice husk [17], 44.3 wt.% for chañar fruit [54], 16.0 wt.% for rice straw, and 18.0 wt.% for sawdust [56].

Traditionally obtained bio-oil shows high viscosity due to presence of large molecules. Levoglucosan, as a heavily oxygenated compound produced from cellulose pyrolysis, significantly affects the viscosity of bio-oil by causing crystallization in time at room temperature [20, 33, 43]. Also, high level of heavy phenols, which are derived from lignin depolymerization reactions, increases the viscosity of bio-oil [43]. Due to the fact that chemical reactions at higher temperatures between reactive components such as ketones and aldehydes resulting heavier compounds increase viscosity and cause instability [31, 43], the storage of bio-oil becomes a major issue [20, 57]. In a study of Duman et al., it was reported that addition of methanol improved the stability of bio-oil such that the viscosity of bio-oil increased at 29.82% in 168 h period instead of 46.63% [57]. Bio-oils with lower content of carbonyl compounds are considered thermally more stable [20].

High oxygen content (generally 35–40 wt.%), which means low H/O ratio, lowers the energy density of bio-oil. High oxygen content is also the reason of the immiscibility with petroleum products [20]. Oxygenated aromatic hydrocarbons decrease the heating value of bio-oil and stability but increase the viscosity due to their high molecular weight [17, 31, 54].

Bio-oil is considered highly acidic compared to conventional fuels and need to be upgraded before utilized commercially [17, 31]. Chemical composition, especially the amount of acidic compounds, determines the acidity of bio-oil. Acid content in bio-oil leads to corrosive characteristics towards metals such as copper and iron, which makes transportation, utilization, and storage of bio-oil a major issue [43]. Biomass pyrolysis oils typically contain 3–6 wt.%

volatile acids, with the main compounds being acetic and formic acids [58]. Carboxylic acids, mainly acetic acid, are formed from the cleavage of acetyl groups in the hemicellulose components of biomass [20, 58] and from ring scission of cellulose [43]. For noncatalytic bio-oil, acidity accounts for its pH in the range of 2.0–3.0 [32, 33, 54].

2.3.3.2. Utilization of bio-oil

Bio-oils can be used in many applications. It can be used as a substitute in chemical industry as food flavorings, fertilizers, emission control agents [39], and as an energy carrier in stationary applications for heat and electricity generation in boilers, furnaces, engines, and turbines [16, 39].

Furans are valuable chemical compounds present in bio-oil because they can be used for organic solvent production and for substituting fossil fuels [43]. Aromatic hydrocarbons in bio-oils with lower molecular weight are more favorable than the ones with higher molecular weight, in terms of utilization as fuel additives because they have lower boiling points [16]. Oxygenated compounds decrease the stability and energy density [54] and thus the quality of bio-oil [43]. However, low levels of oxygenated molecules such as (alkyl)-furans compounds are favorable due to the reason that high octane number of these compounds enhances energy density of bio-oil, thereby facilitating the utilization of bio-oil as fuel additive [20]. Phenolic compounds in bio-oil (particularly phenolic ethers such as vanillin, guaiacol, and syringol) are the precursors for the synthesis of pharmaceutical and polymeric compounds or adhesives [54].

Using the bio-oil as a fuel without upgrading results in several significant problems such as poor volatility, high viscosity, high water content, low polymerization temperature ($<100^{\circ}\text{C}$), and corrosiveness for engine equipment [59]. Emulsification and blending are among the most preferred methods to upgrade the bio-oil when substituting conventional diesel [59–61]. Van de Beld et al. investigated the performance of bio-oil derived from pine wood in a modified diesel engine connected to a generator to convert mechanical power to electricity. It was noted that, at air inlet temperatures in the range of $100\text{--}120^{\circ}\text{C}$ and at an engine compression ratio of 17.6, bio-oil/ethanol blends were found to reduce CO emissions and increase NO_x emissions. Adding up to 30 wt.% of ethanol to the bio-oil improved combustion performance due to better atomization of the fuel, resulting in lower CO emissions [59]. Similar results were obtained by Yang et al. [62]. In a study of wood pyrolysis oil, it was revealed that using pure bio-oil in diesel engines leads to the widening of spray channels, thus damaging the injector. The results of this study showed that at 200°C tip temperature, the needle of nozzle was stuck in a short period of operation time [63]. Sugarcane bio-oil was blended with gasoline in the range of 5–14 vol.%. The results showed that blending up to 10 vol.% of bio-oil with gasoline did not affect the operation of Otto engine of 4 kW capacity connected to a 2-kWe generator suggesting that power and fuel consumption were similar with that of gasoline-operated engine [64]. However, specific modifications of diesel engines are necessary for using the bio-oil or bio-oil-derived fuels in diesel engine systems. Dedicated fuel feeding system parallel to diesel feeding line, a pilot diesel fuel injection, use of cleaning fuels such as methanol and corrosive resistant or stainless steel fuel pump, and injector design are among the modifications

adapted by researchers [60, 62, 63]. Furthermore, in order to reduce viscosity of the fuel, short preheating at temperatures $<90^{\circ}\text{C}$ is needed, and direct heating is not recommended [65].

Boucher et al. investigated softwood bark pyrolysis oil with the addition of methanol as a possible liquid fuel for gas turbines. The results of this study showed that the viscosity of bio-oil was close to the gas turbine requirements with the value of 5.3 cSt at 90°C , and the net heating value of 32 MJ kg^{-1} was recorded as relatively high. However, due to the fact that the ash and solid content present in the bio-oil will eventually cause degradation in gas turbines, filtering and upgrading of bio-oil are required [66]. Lopez Juste and Salva Monfort [67] conducted a preliminary study on combustion performance of a gas turbine operated with bio-oil/ethanol (80/20, wt.%) mixture. At high air flow rate, considerable increase in CO emission was observed suggesting that using bio-oil/ethanol mixture leads to inefficient operation of the combustor. In order to utilize bio-oil for gas turbine applications, fuel preheating at temperatures $70\text{--}90^{\circ}\text{C}$ is necessary to keep viscosity lower than that of 10 cSt. Resistant materials to acidity of bio-oil should be selected in order to prevent wear corrosion damage [65]. Modifications must also include nozzle adaptations for bio-oil-specific properties because using standard nozzles does not allow for full load (thus causing power decrease). It is of high importance that start-ups and shut-downs must be done using standard fossil fuels in order to warm up combustion chamber facilitating bio-oil ignition [65].

3. Utilization of catalysts in biomass pyrolysis

Depending on the biomass type used, the low calorific value, high water content, high viscosity (due to large molecules), high oxygen content (due to oxygenated hydrocarbon content) as well as instability, immiscibility with other fossil fuels make bio-oil difficult to use directly as a fuel without upgrading [24, 55]. In order to upgrade bio-oil to use in fuel applications, two different methods have been utilized: hydrodeoxygenation and catalytic cracking. In hydrodeoxygenation, bio-oil compounds react with hydrogen under high pressure and moderate temperature to produce hydrocarbon compounds and water. Catalytic cracking is used to upgrade bio-oil through a catalytic medium, removing oxygen from bio-oil compounds in the form of H_2O and CO_2 , involving the chemical reactions of rupturing the C–C bonds via dehydration, decarboxylation, and decarbonylation [1, 16, 24, 55]. Catalytic cracking has several advantages over hydrodeoxygenation including operating at atmospheric pressure and in an environment with no need of extra hydrogen supply [1].

3.1. System configurations for catalysts used in biomass pyrolysis

There are two methods for catalytic pyrolysis in use: catalytic bed and catalyst mixing. In catalytic bed method, which is also referred to as “*in-situ*” upgrading or ex-bed method, pyrolytic vapors coming from the first reactor pass through a catalytic reactor which is called catalytic bed, resulting bio-oil, char, and gaseous products. In catalyst mixing (in-bed) method, however, biomass and catalyst samples are mixed physically before being inserted in pyrolysis reactor [1, 30, 37].

3.1.1. Catalyst bed method (*in situ*)

Catalyst bed method, also called *in-situ* pyrolysis, involves catalytic upgrading subsequent to thermal conversion of biomass resulting pyrolysis vapors [1]. In general, *in-situ* catalytic pyrolysis of biomass can be performed using different reactor configurations: single stage and two stage reactor configurations. Single stage pyrolysis involves catalytic pyrolysis of biomass in the same reactor with catalyst, whereas two-stage configuration involves fixed bed/fluidized bed reactor followed by a fixed bed catalytic reactor. The former produces more coke than the latter [33]. A study by Mante and Agblevor [33] using two stage reactor configuration for catalytic pyrolysis of hybrid poplar wood with HZSM-5 reported low yield of coke with 3.8% of value which was relative to the weight of biomass. Advantage is that catalytic pyrolysis of evolved vapors from biomass can be operated at a different temperature than that of the main pyrolysis reactor in case of two stage reactor configuration is employed [18]. However, compared to catalyst mixing, the catalyst bed method also leads to high amount of char resulting clogging of catalyst pores, which prevents the diffusion of vapors through the pores [1].

In a study of Thangalazhy-Gopakumar et al., it was noted that some noncatalytic bio-oil compounds were detected when using catalyst bed method, suggesting that primary tar compounds were converted into secondary and tertiary tar compounds before reaching the catalyst bed to be cracking into aromatics [1]. Uzun and Sarioğlu reported that using catalyst bed method with several types of catalysts decreased the liquid yield compared to catalyst mixing method [39]. Iliopoulou et al. studied catalytic pyrolysis of lignocellulosic biomass and explained the *in-situ* effect of metal modified ZSM-5 with various percentages. It was suggested that transition metals favored the formation of hydrogen, which leads to hydrocarbon reactions on the zeolite acid sites via catalyst bed mode [31].

3.1.2. Catalyst mixing method (*in-bed*)

Catalyst mixing method can be done by either addition of catalyst to biomass with defined amounts or by wet impregnation of biomass. Due to better physical surface contact between biomass and catalyst in pyrolysis reactor, mixing allows immediate interaction of evolved pyrolysis vapors with the catalyst suggesting that evolved vapors can be adsorbed on the catalyst surface to be diffused into the pores for catalytic cracking [1, 39]. Disadvantage is that the catalytic conditions are irreversible so that biomass and catalyst should be operated under the same conditions [18].

Aromatic content of bio-oil is of utmost importance, and utilizing catalysts is one alternative way to increase aromatization reactions (thus enhance bio-oil quality). Studies have shown that catalytic mixing method provides better mass transfer for cracking of bio-oil compounds in terms of aromatization and deoxygenation [1, 39].

Thangalazhy-Gopakumar et al. investigated the catalytic effect of ZSM-5 zeolite in pyrolysis of pine wood chips under helium environment. It was revealed that using catalyst mixing method with 1:9 biomass to catalyst ratio gave 41.5% of aromatic yield compared to that of 9.8% using catalyst bed method with 1:5 biomass to catalyst ratio. In this study, the absence of guaiacol compounds in bio-oil shows that catalyst mixing is an effective method for cracking

of lignin-derived compounds to aromatics [1]. Pütün et al. studied pyrolysis of cotton seed with the addition of MgO with defined proportions to the biomass samples. Compared to conventional pyrolysis results, aromatic and aliphatic content was enhanced to the values of 35 and 23%, and the oxygen content was reduced from 9.56 to 4.90% [37]. The results of rice husk pyrolysis with ZnO studied by Zhou et al. showed that catalyst mixing with various amounts significantly improved bio-oil quality in terms of hydrogen content, H/C ratio, higher heating value, and reducing carboxylic acid content of bio-oil [17]. Thus, in order to design large-scale pyrolysis plants, effective and homogenous mixing systems are necessary.

3.2. Metal oxide catalysts

Metal oxide catalysts have been extensively studied in literature, using miscellaneous biomass species, with regard to their effect on the quality and quantity of pyrolysis products. It is a known fact that metal oxides, as any catalysts, influence the decomposition temperature. Accordingly, in a thermogravimetric study conducted by Chattopadhyay et al. using Cu/Al₂O₃ as a catalyst, it was noted that transition metal supported alumina had a strong effect on decreasing the devolatilization temperature of volatiles [15]. Zabeti et al. applied amorphous silica alumina (ASA) supported with alkali or alkaline earth metals in pyrolysis of pinewood. Maximum bio-oil was obtained with nonsupported amorphous silica alumina with the value of 42.4 wt.%. However, the fraction with Cs/ASA showed the best performance in terms of oxygen elimination in aromatic hydrocarbons thus increasing the heating value of bio-oil [20]. Wang et al. [68] investigated the catalytic effect on pyrolysis of lignocellulosic biomass using catalysts including NiMo/Al₂O₃, CoMo/Al₂O₃, CoMo-S/Al₂O₃, activated alumina, and porous silica. In order to enhance the production of pyrolysis intermediates (benzene, toluene, xylene, naphthalene), it was suggested that CoMo-S/Al₂O₃ was most favorable among all. However, NiMo/Al₂O₃ gave highest yield of CH₄ with the value of 51.82%. Shadangi and Mohanty [69] studied CaO and Al₂O₃ in pyrolysis of *Hyoscyamus niger L.* and confirmed that, consistent with other studies mentioned above, adding catalysts to pyrolysis process considerably decreased the bio-oil yield, however, eliminated the oxygenated groups present in bio-oil thus improving its fuel quality. Aysu and Küçük investigated the pyrolysis of eastern giant fennel (*Ferula orientalis L.*) comparing the effect of ZnO and Al₂O₃ catalysts [35]. Al₂O₃, with the value of 79.94%, was found to be more effective than ZnO in terms of conversion of biomass. However, the effect of the catalyst on the bio-oil yield was different from each other. ZnO increased the bio-oil yield with increasing catalyst to biomass ratio, whereas bio-oil yield decreased with increasing Al₂O₃ addition. This indicated that Al₂O₃ promoted gas formation. In a study of Yorgun and Şimşek, activated alumina was used in pyrolysis of *Miscanthus × giganteus*, and it was noted that at high heating rates, 60 wt.% of catalyst loading to biomass is effective for maximum liquid production with the value of 51 wt.%. The oxygen content of bio-oil was found to be higher than that of noncatalytic bio-oil [70]. Nguyen et al. investigated the pyrolysis vapors of pine wood chips over 20 wt.% Na₂CO₃/γ-Al₂O₃. It was reported that liquid yield was lowered but decarboxylation of carboxylic acids was favored with the catalyst, resulting a pH value of 6.5 suggesting that the sodium-based alumina catalyst is effective on improving acidity of bio-oil. Hydrocarbon concentration was increased from 0.5 to 17.5% indicating a higher energy density of bio-oil [36]. Chen et al. presented the gaseous product distribution of biomass (rice

straw and saw dust) pyrolysis, at a temperature of 800°C, utilizing different metal oxides such as Cr_2O_3 , MnO , FeO , Al_2O_3 , CaO , and CuO . It was noted that except for CuO and Al_2O_3 , all the catalysts noticeably improved gas production [56]. Zhou et al. [17] studied the pyrolysis of rice husk with the addition of ZnO . The results of this study indicated that ZnO showed a trend to decrease bio-oil yield with increasing biomass to catalyst ratio. However, ZnO improved the bio-oil compositional quality in terms of low-molecular-weight compounds including alkanes, alkenes, styrene, and alkyl phenols (thus increasing bio-oil stability). Nokkosmaki et al. also studied the same catalyst for the conversion of pyrolysis vapors of pine sawdust and the viscosity of catalytic bio-oil was shown to be reduced by 40% compared to noncatalytic pyrolysis results [34]. Pütün et al. [37] revealed that utilizing MgO as a catalyst in cotton seed pyrolysis in a fixed bed reactor improved the bio-oil quality by removing oxygenated compounds, enhancing higher heating value, and increasing aromatic content of bio-oil.

3.3. Zeolite catalysts

Zeolites, having a tetrahedral structure and acidic nature, are three-dimensional aluminosilicates linked through oxygen atoms and supported with channels and cavities, resulting porous structure of exceptional catalytic activity. Each type of these tetrahedral zeolites with overall charge balance of minus one have Si or Al at the center and oxygen atoms at the corners of the structure [71].

Zeolites possess following characteristics: (1) cracking of deoxygenated compounds via shape selectivity, (2) high surface area, (3) varied dimensions of channels and pores, and (4) high adsorption capacity [22, 72]. The physical properties of zeolites depend on the synthesis conditions including temperature, gel precursors, structure-directing agent [73]. The pore size and framework of zeolites tend to affect the product composition via several reactions restricting formation of hydrocarbons larger than that of pore size of zeolites. This is called shape selectivity and is one of the most important factors differentiating zeolites from other type of catalysts. Selectivity is based on whether the aromatics derived from pyrolysis vapors can enter, form in, and diffuse out of the pores of the zeolite [22, 23]. Shape selectivity of zeolites is elaborately discussed in Section 3.3.1.1 demonstrating ZSM-5 as a zeolite type.

The main reason why zeolites are commonly used in biomass pyrolysis is that their varied acidity and shape-selectivity provide advantage over silica-alumina catalysts of amorphous structure, in terms of aromatization reactions. Acidity depends on the Si/Al ratio of zeolite structure and can be caused by Brønsted and Lewis acid sites [22]. Acidity affects the catalytic reactions by providing enhanced cracking activity with decreasing Si/Al ratio [23]. Hence, the distribution of acid sites in the pores of zeolites is of high importance in terms of preventing coke-forming reactions in internal pores of zeolite. Low of Si/Al ratio causes higher amounts of acid sites with close proximity. Due to this reason, coke-forming reactions, which convert aromatic hydrocarbons into coke compounds, will increase. Therefore, an optimum acidity is required for zeolites if it is used in biomass pyrolysis [19].

Aside from the distribution of acid sites, the pore structure of the individual zeolite plays an important role for selectivity of products and in terms of aromatic content of bio-oil. The pores

of zeolites are characterized by the size of the ring defining the pore, that is, the n-number of the ring, which is referred to as the number of Si or Al atoms in the ring [74]. Hydrocarbon chain length of pyrolysis products, thus the size distribution of aromatic compounds, depends on the zeolite pore size and internal pore surface area. In general, larger pores and surface area lead to long chain-structured hydrocarbons. Microporous surface area of the catalyst determines the yield of gaseous products of pyrolysis, whereas macroporous area determines the liquid yield [24, 37]. A range of zeolites with different pore sizes has been studied in literature [39, 75, 76]. Y zeolite (faujasite), having a cubic structure with a pore system composed of 12-membered circular ring channels, has the largest average pore size (7.4 Å) and internal pore space (11.24 Å) [22, 23]. Such relatively large pore size affects the catalyzed reactions resulting less contact between pore surface and pyrolysis vapors, thereby leading to less cracking of biomass-derived oxygenates. Also, straight channels with larger pore size do not provide shape selectivity compared to other zeolites, which have smaller and sinusoidal channels that enable shape selectivity [23]. Despite having large pore size [73], beta zeolite is of tetragonal crystal structure and has 12-membered straight channels crossed with 10-membered ring channels, which makes it more effective for production of aromatic hydrocarbons than Y-zeolites [23]. Ferrierite, as a medium pore size zeolite, has orthorhombic structure with 8 and 10 membered channels with internal pore space 6.31 Å [23, 73].

Due to having two parallel channels connected with 12-membered rings and 8-membered rings, Mordenite is classified as a large pore-sized zeolite and have orthorhombic structure [22, 23, 73]. ZSM-5, consisting of an MFI orthorhombic structure, is composed of 10-membered straight channels connected by 10-membered sinusoidal channels [71]. General physicochemical properties of zeolites are presented in **Table 2**.

Zeolites with medium and large pore size facilitate faster reactant diffusion compared to zeolites with smaller pore size, thus yielding more aromatics in liquid fraction of pyrolysis product. However, large-pore size zeolites produce less aromatic than medium-pore size zeolites because large pores promote coke formation [22]. Accordingly, a recent study confirmed that ZSM-5 of medium pore size and medium internal pore surface area favors higher aromatics production and lower coke yield [19].

Catalyst	ZSM-5	Mordenite	Beta zeolite	Y zeolite	Ferrierite
IZA code	MFI	MOR	BEA	FAU	FER
Pore dimension	3	2	3	3	2
Channel system	10–10	12–8	12–12	12–12	8–10
Pore size (Å)	5.1 × 5.5	7.0 × 6.5	7.6 × 6.4	7.4 × 7.4	4.2 × 5.4
	5.3 × 5.6	5.7 × 2.6	5.6 × 5.6		3.5 × 4.8
Internal pore space (Å)	5.2–5.5	4.2–6.7	6.1–6.68	11.24	6.31
BET surface area (m ² /g)	395.5	558.7	643.1	809.1	*

*Information not available.

Table 2. Physicochemical properties of zeolites most commonly used [22, 72, 76, 77].

3.3.1. ZSM-5 zeolite

ZSM-5, as one of the most common used zeolites in biomass pyrolysis [23], consists of pentasil units and has orthorhombic structure [74]. Being composed of 10-membered straight channels connected by 10-membered sinusoidal channels enables ZSM-5 to have significantly more cracking activity than the other zeolites [23, 27]. ZSM-5 has been widely used as catalyst in petroleum industry due to its shape selectivity, exceptional pore size with steric hindrance, thermal stability, and solid acidity [78].

Compared to other zeolites, medium-scaled pore size of ZSM-5 makes it difficult for larger aromatic coke precursors to form inside the pores [79]. Studies have shown that, regardless of feedstock, utilizing ZSM-5 in biomass pyrolysis reduces the oxygenated compound content in bio-oil and simultaneously increases aromatic species [80–84]. Deoxygenation of oxygenated organic compounds occurs inside the ZSM-5 zeolite pores via reactions such as dehydration, decarboxylation, and decarbonylation [27, 31, 32]. At lower temperatures, oxygen is found to be removed in the form of H_2O , whereas in case of higher temperatures, CO and CO_2 are the main products of oxygen removal [31]. Oxygen removal, primarily in the form of CO and CO_2 , is more preferable as it leads to less carbon deposition on the zeolite and more hydrogen formation and consequently less water content in bio-oil [31].

3.3.1.1. Shape selectivity of ZSM-5

The phenomenon of shape selectivity can be explained by the combined effect of molecular sieve and catalytic reaction that occurs at the external and internal acidic sites of zeolites [85]. ZSM-5, having porous structure, can be used for shape-selective catalysis providing that not only the pore size but also dimensions of reacting and diffusing molecules are similar to zeolite pores [19]. Thus, the effect of pore size and steric hindrance of ZSM-5 on the catalytic reactions must be investigated if zeolites with better performance are to be designed for biomass conversion [73].

The formation of pyrolysis products with shape selective catalysis depends on two types of selectivity: (1) reactant and product selectivity and (2) transition state selectivity, which are described with their mass transfer effects and intrinsic chemical effects, respectively [22, 73, 85]. The main idea behind reactant and product selectivity lies behind the fact of hindered diffusion of reactants and products inside zeolite pores. Specific pore size of ZSM-5 affects the diffusion of reactants inside the pores excluding the ones with dimensions larger than the pore openings of ZSM-5, thereby preventing them from reaching the catalytic active sites and consequently allowing catalytic decomposition only at the external active sites [73, 85]. Due to pore geometry of ZSM-5, formation of certain products is restricted affecting the chemical reaction and thus causing selectively homogenization of pyrolysis products [85].

Selectivity of ZSM-5 has been extensively studied, and it is more commonly found to cause selectivity over aromatic compounds [49]. Mihalcik et al. [23] studied different zeolites for the conversion of several types of biomass and biomass components. According the results of this study, ZSM-5 was found to promote the formation of *p*-xylene in abundance for every case of biomass pyrolysis. In a study of Foster et al. [19], HZSM-5 for furan conversion showed

a tendency for aromatic selectivity giving higher yield of aromatics as naphthalene having the highest percentage of 30.4% of overall aromatic species. Fogassy et al. [86], investigating the shape selectivity of zeolites for lignin fragments, revealed that majority of the phenolic compounds derived from lignin decomposition are too large to enter through zeolite pores, therefore, the conversion of these compounds occurs at the external active sites. As Yu et al. [22] suggested, however, at higher temperatures effective pore size of ZSM-5 increases, enabling bigger molecules than that of ZSM-5 pore size to reach the internal catalytic active sites. Jae et al. investigated the role of pore size of several types of zeolites in glucose pyrolysis (using kinetic diameters for products and reactants as affecting parameters) to determine whether the catalytic reaction occurs inside the pores or at the external surface [73]. Kinetic diameter was estimated from the properties at the critical point. It was revealed that ZSM-5 allowed pyrolysis intermediates and products (such as benzene, toluene, indene, ethylbenzene, *p*-xylenes) to diffuse into pores due to their significantly small kinetic diameters than that of ZSM-5 pore size.

As temperature increases to 600°C, due to thermal distortion, compounds like naphthalene which gave the highest yield in aromatics are likely to be formed inside the pores as well as on the surface. According to this study, it was concluded that, in addition to pore size, internal pore space of ZSM-5 affects the catalytic reaction. This suggests that biomass conversion with ZSM-5 is affected from mass transfer limitations as well as transition state effects [73].

3.3.1.2. Acidity of ZSM-5

Aside from the shape selectivity, the acidity of ZSM-5 plays an important role for the conversion of oxygenates into aromatics. It is generally accepted that Brønsted acid sites are the active sites that converts oxygenated compounds into aromatics rather than Lewis acid sites. Cracking of large oxygenated occurs at the acid sites of external surface of ZSM-5, whereas conversion of smaller ones into aromatics takes place at the acid sites inside the pores [22, 87]. Therefore, the abundance of both external and internal acid sites must be investigated in order to design a better process for aromatics formation. As explained by Van Santen, Brønsted acid sites are generated as a result of replacement of silica, which has a valency of four, by a metal atom, most commonly aluminum with a valency of three [88]. Thus, this makes Brønsted acid sites proton donors. Si and Al are connected with a proton-attached oxygen atom, which leads to a chemically more stable structure [88, 89]. On the other hand, Lewis acid sites are electron pair acceptors, and the nature of these sites is related to aluminum atoms positioned in the framework [89, 90].

In addition to nature of the acid sites, the molar ratio between SiO₂ and Al₂O₃ in zeolite framework also influences the reactivity and performance of ZSM-5. Optimum Si/Al ratio is necessary to provide high availability of Brønsted acid sites for adequate acidity and to maintain the distance between acid sites in order to limit coke-forming reactions [19]. As Si/Al ratio decreases (increase the acidity of ZSM-5), the acid sites will be in close proximity to each other, resulting in secondary reactions for conversion of aromatic compounds to coke species [19]. Foster et al. [19] investigated the effect of ZSM-5 with varying Si/Al ratio on pyrolysis of glucose. This study showed that decreasing Si/Al ratio contributed formation of the

additional acid sites for ZSM-5 with increasing coke yields. In a study of Carlson et al. [79], ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 15$) promoted coke formation mostly on the catalyst surface giving the highest yield of 33% for coke (where the catalyst to biomass ratio was 19). It was also indicated that coke formation on the external pores of ZSM-5 did not significantly decrease the yield of aromatics but affected the selectivity toward light hydrocarbons, resulting lower yields for benzene and toluene, higher yields for naphthalene and indane.

3.4. General effects of catalysts on bio-oil

It is a known fact that catalysts have strong influence on pyrolysis in terms of product distribution, chemically homogenization, and enhancing fractional product yield, upgrading the pyrolysis products to better quality. Among catalysts, zeolites and metal oxides have been mainly investigated for biomass conversion and found to be effective in changing the composition of bio-oil by reducing the oxygenated compounds via deoxygenation reactions and enhancing the aromatic yield, thus producing a more homogeneous and stable organic fraction that can be upgraded to diesel grade fuels [30, 39]. To consider pyrolysis products, particularly bio-oil, for stationary fuel applications or heat/electricity generation, properties including acidity, viscosity, stability, and aromatic content of bio-oil should be evaluated [20]. Therefore, the effects of catalysts to bio-oil must be addressed, as elaborately discussed below, in order for better understanding of biomass conversion.

3.4.1. Aromatic yield of bio-oil

Aromatic content of bio-oil is of high importance in terms of producing diesel grade fuels from biomass feedstock and biomass-originated waste materials. Among aromatics, the amount of benzene, toluene, ethyl-benzene, and xylenes (BTEX components) are the most significant feedstock materials to take into consideration for petroleum chemical industry [68, 87].

Utilizing catalysts has been shown to increase the yield of bio-oil as well as the content of aromatics in bio-oil, which is a good indicator fuel quality. Kim et al. [87] studied catalytic pyrolysis of mandarin residues with high lignin content and found that using HZSM-5 of 23 and 80 acidity increased yield of monoaromatics from 3.4 to 36.0 and 41.0%, respectively. From the study of Zheng et al. [76], changing crystal size of ZSM-5 affected the aromatic yield and BTX selectivity so that smaller crystal size gave maximum aromatic yield and lowest BTX selectivity with the values of 38.4 and 36.3%, respectively. However, larger crystal size exhibited lowest aromatic yield and highest BTX selectivity with the values of 31.1 and 42.6%, respectively. Thus, smaller crystal size (200 nm) was found to be optimum for high aromatic yield.

Zhang et al. [83] compared the behavior of pyrolysis of aspen lignin under the effect of H-Y and HZSM-5 catalyst. At catalyst to feed ratio of 3:1, production of aromatics exhibited a maximum value of 23% using HZSM-5 as catalyst, where the oxygen content of the aromatics decreased to about 4% and the HHV of the fraction was estimated to be approximately 46 MJ/kg, which is closer to that of gasoline and diesel. It was indicated that HZSM-5 was more effective than H-Y in converting phenolic compounds to aromatic hydrocarbons [83] due to

its higher acidity and smaller pore size compared to HY [83]. Similarly, Pattiya et al. [75] studied ZSM-5 and two mesoporous materials including Al-MCM-41 and Al-MSU-F to investigate the fast pyrolysis of cassava rhizome. It was revealed that, of all the catalysts tested in the study, ZSM-5 gave the highest yield of aromatic hydrocarbons in order of toluene > benzene > 4,7-dimethylindane > *p*-ethyl-styrene > 5-methylindane > xylenes.

Aside from zeolites, the effect of metal oxides toward aromatization has been studied by researchers [7, 49, 91, 92]. From the results of the study of Ateş and Işıkdağ [91], using alumina as catalyst on corn cob pyrolysis exhibited a trend to promote the formation of 1,1,3,3-tetramethylindane, benzene, and 1-methyl-4-(penylmethyl) being most significant monoaromatic compounds. The formation of naphthalene, 1-(2-propenyl)-, a PAH compound, was found to be increased at moderate temperature using catalyst. Smets et al. [93] compared various catalysts including HZSM-5, γ -Al₂O₃, and Na₂CO₃. Sodium carbonate was the most effective catalyst to increase the yield of aromatics following HZSM-5. Wang et al. [92] also conducted a comparative study for catalytic conversion of herb residues over alumina, ZSM-5 and Al-SBA-15, where alumina was found to give the highest bio-oil yield. Thus, the researchers of this study investigated the effect of alumina to the aromatic yield in terms of toluene, ethylbenzene, and *p*-xylene compounds and revealed that the percentage of aromatic fractions increased from 8.02 to 10.93%.

3.4.2. Acidity of bio-oil

The acidity of bio-oil is due to volatile acids, mainly carboxylic acids, that is, formic acid and acetic acid [58]. Phenolic compounds also contribute the acidity of bio-oil [20]. Determination of acidity in bio-oil is performed either by measuring pH value or total acid number. pH value is an indicator for evaluating the corrosiveness of bio-oil, whereas total acid number is used as a quality indicator for bio-oil utilization in co-processing of petroleum-refining facilities, and it relates to the level of acidic components in the oil [58].

Studies have clearly shown that organic acids are reduced by catalysts [36], thereby, facilitating the utilization of bio-oil in fuel applications. The main question is to find the most suitable catalyst-biomass match, taking the process conditions into account for pyrolysis systems, in order to replace bio-oil with fossil fuel equivalents (such as diesel and gasoline).

Zabeti et al. [20] studied amorphous silica alumina modified with alkali or alkali earth metals such as Na, K, Cs, Mg, and Ca. It was concluded that among all the catalysts tested in the study, K/ASA was the most effective catalyst to reduce the carboxylic acids and carbonyl substituted-phenols content in bio-oil. Zhou et al. [17] investigated the effect of ZnO to physicochemical properties of rice husk bio-oil. pH value of catalytic bio-oil was recorded as 4.35, whereas noncatalytic bio-oil had 4.15 of pH value. Thus, this indicated the effect of ZnO catalyst toward reduction of acidic compounds in bio-oil. Abu Bakar and Titiloye [32] studied rice husk pyrolysis over various catalysts including ZSM-5, Al-MCM-41, Al-MSU-F, and (Brunei rice husk ash) BRHA. Catalysts have been shown to reduce the acid number from 55 mg/KOH to 39–47 mg/KOH, with ZSM-5 and BRHA having the lowest value. Also, pH value of the catalytic rice husk bio-oil was recorded in the range of 2.7–3.0. Majority of acidic compounds

were carboxylic acids, as acetic acid having the highest percentage. Mante and Agblevor [33] studied HZSM-5 as deoxygenating catalyst to convert hybrid poplar wood to biosyncrude oil. As indicated in the study, the pH value of light biosyncrude oil containing mainly aromatic hydrocarbons was increased from 2.60 to 4.05 due to HZSM-5.

3.4.3. Viscosity of bio-oil

High viscosity of bio-oil, compared to conventional fuels, is one of the drawbacks for its utilization in fuel applications. Most importantly, in case of bio-oil using combustion engines, high viscosity increases the droplet size from the injector spray thereby affecting the ignition of droplets [94]. Therefore, decreasing viscosity of bio-oil to improve fuel properties is essential. Studies revealed that use of catalysts improved fuel properties of bio-oil by decreasing viscosity [53, 95].

Azargohar et al. conducted noncatalytic pyrolysis experiments for several biomass waste materials, and it was observed that the viscosity of bio-oil, ranging between 63 and 418 cP, was much more higher than that of crude petroleum oil (~23 cP), requiring a further upgrading process. It was also revealed that the reason of high viscosity was mainly due to lignin-derived hydrocarbons of large molecular weight [96]. However, in a study of Fan et al. on rape straw pyrolysis over nanocrystalline HZSM-5, the dynamic viscosity was reported to be $5.12 \text{ mm}^2 \text{ s}^{-1}$ which was between the accepted limits for diesel fuel as indicated in the study [95]. Mante et al. investigated the hybrid poplar wood pyrolysis with the additive effect of Y-zeolite-based FCC catalyst to ZSM-5. FCC/ZSM-5 catalyst was found to be more effective than pure ZSM-5 in decreasing viscosity of bio-oil samples, indicating synergistic effect of hybrid catalyst, also suggesting that lower weight hydrocarbons was attributed to be formed by the presence of catalyst [53]. Mante and Agblevor [33] studied hybrid poplar wood pyrolysis with the addition of ZSM-5. They classified the liquid fraction of pyrolysis product as LBS (low biosyncrude) oil containing mainly aromatic hydrocarbons and HBS (high biosyncrude) oil which consists of mainly phenols, methyl-substituted phenols, naphthalenes, benzenediols, and naphthalenol. The viscosity of LBS oil, which was significantly lower than that of non-catalytic bio-oil (285 cSt), was reported to be 4.90 cSt. It was suggested that lower viscosity was attributed to the catalytic cracking of levoglucosan and depolymerization of lignin-derived products [33]. Shadangy and Mohanty conducted several studies using various biomass species over CaO, kaolin, and Al_2O_3 [69, 97, 98]. Regardless of the biomass type, CaO was found to produce bio-oil of lower viscosity than that of noncatalytic bio-oil compared to other catalysts used for their studies. The viscosities of bio-oil obtained by using CaO were 0.019629 Pas [98] and 9.007 cP [69], indicating that utilizing catalyst favored a decrease in viscosity about 62 and 74.5%, respectively. Abu Bakar and Titiloye studied ZSM-5, Al-MCM-41, Al-MSU-F, and BRHA (Brunei rice husk ash) for the conversion of rice husk to bio-oil, and the viscosities of bio-oils were, as indicated, 1.55, 1.65, 1.49, and 1.57 cSt, respectively. All the catalysts used in the study decreased viscosity about 1.7–11.3% and slightly increased water content, which indicates that the catalysts favored dehydration reaction [32].

3.4.4. Stability of bio-oil

Bio-oil is not as chemically or thermally stable as fossil fuels due to its high content of oxygenated compounds [94]. At temperatures above 40°C or during long-term storage situations, the

viscosity of bio-oil is reported to increase due to chemical reactions between components such as ketones and aldehydes, leading to formation of compounds of heavy molecular weight [20]. Thus, it is expected that bio-oil with lower content of carbonyl groups would be more stable. Utilizing catalysts, in order to facilitate transportation and storage of bio-oil, leads to enhanced cracking reactions of heavy molecules as well as removal of oxygenated compounds, thus leading to production of bio-oil with high stability [99]. There is no standard method for determination of stability of bio-oil; however, several methods have been developed by researchers [100–102].

In a study of Zabeti et al., where Cs/ASA was found to be most effective catalyst to eliminate oxygenated compounds and increase aromatic yield compared all the catalysts tested in the study. The results of size exclusion chromatography (SEC) showed that bio-oil molecular weight shifted to higher weight regions after aging [20]. Mante and Agblevor conducted a stability test for the catalytic bio-oils (low and high biosyncrude oil) produced from hybrid poplar wood. The stability and aging tests were performed in a gravity oven at 90°C for 24 hours. Also, the viscosities of the bio-oil samples stored at 40°C for over 10 months were also measured, and the change in viscosity was found to be 5% for low biosyncrude oil and 27.9% for high bio syncrude oil. It was concluded that catalytic bio-oils were thermally stable and could be stored in room temperature for over 10 months without any significant increase in viscosity [33]. Nokkosmaki et al. studied pine sawdust pyrolysis with the addition of ZnO as catalyst. The stability test was performed at 80°C for 24 h and showed that viscosity was changed with the use of ZnO. The change in viscosity was 55%, which was significantly lower than that of noncatalytic bio-oil (129%) [34]. Duman et al. investigated the effect of methanol addition to the stability of bio-oil produced from safflower oil cake using FCC as catalyst. Addition of methanol reduced the viscosity. The viscosity was much lower at higher temperatures, thus indicating a more stable bio-oil. After aging test at 40°C for 168 h, the viscosity increased by 46.63 and 21.08% in case of raw bio-oil and methanol amended bio-oil, respectively [57].

4. Deactivation and regeneration of catalysts

Catalyst deactivation, the loss of catalytic activity and selectivity over time, is one of the major problems concerning industrial application of catalyst in pyrolysis process [25, 53].

The causes of deactivation are mainly due to chemical, mechanical, and thermal mechanisms of catalyst delay [103], but in this section only physical deactivation is addressed. Physical deactivation is done either by coke deposition on the catalyst pores or by covering active catalytic sites preventing pyrolysis vapors to enter through the pores for catalytic reactions such as aromatization, depolymerization, and isomerization [53, 103, 104]. As suggested by Forzatti and Lietti [104], catalyst deactivation reactions proceeding via carbonium ion intermediates involve series of chemical reactions, which vary by the variety of components of reaction mixture, catalyst type, reactions conditions.

Coke is deposited on catalyst pores, in the form of carbon oxides via oxidation. In case of deactivation, if irreversible, regeneration of catalysts under more severe conditions than

that of main process is necessary to remove coke [105]. Mante et al. compared the catalytic activity of different zeolites in terms of coke deposition and reported that Y-zeolite was more prone to produce coke than ZSM-5 because of its faujasite structure, larger pore size, and acidity [53]. In a study of Lisa et al., ZSM-5 zeolite was regenerated via oxidation and after five regeneration cycles; no reduction in catalytic activity was recorded [25]. Nokkosmaki et al. [34] observed catalyst deactivation at 400°C. The catalyst affected the degradation of polysaccharides, so that between the first and the fifth pyrolysis cycles, the ratio of levoglucosan was raised from 1.0 to 2.0%. Zabeti et al. studied regeneration of Cs/ASA catalyst by calcinating under air atmosphere at 600°C for 5 h operation [20]. The regenerability of catalyst was evaluated measuring the BET surface area and bio-oil yield obtained after regeneration. It was reported that BET surface area of regenerated catalyst decreased by 10.6%, whereas bio-oil yield remained the same with 45.0 wt.%, suggesting that Cs/ASA catalyst is regenerable. Similar results were obtained by Aho et al. investigating the effect of regenerated catalyst to pyrolysis of biomass with H-Beta zeolite with Si/Al ratio of 25. After regeneration, surface area of catalysts decreased, though, the bio-oil yield increased [28].

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