

Catalytic Pyrolysis of Biomass to Synthesize Bio-oil and Chemicals: A Review

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Abstract

Increasing of global energy demand and depletion of fossil fuels reserves encourage people to search alternative energy resources. Biomass becomes promising candidate as alternative energy sources since their sustainability. Pyrolysis is one of method to convert biomass into bio-fuel. Almost all of biomass materials can be converted into products by pyrolysis process. However, quality of bio-oil produced by pyrolysis is still considered as low quality, due to their high oxygen content and acidity. This paper provides a critical review of catalytic pyrolysis of biomass to produce bio-oil with better properties. Types of catalysts are discussed in this manuscript, as well as their capability to reduce the oxygen content of product and enhance the properties of bio-oils.

Keywords: *bio-oil, biomass, catalytic pyrolysis, alternative energy*

Introduction

Conversion of biomass into energy sources has been practiced from long time ago. Direct combustion of biomass, historically, has been the primary source of energy throughout the world, particularly for residential activity and small industry in the rural area. Unfortunately, direct burning of loose biomass in conventional grate is always associated with low energy efficiency and contributes adverse impact to the environment, particularly the air quality. Modern technology which offers clean and efficient energy conversion is required to improve the attractiveness of biomass utilization as energy sources. Many techniques have been developed to transform biomass into energy. Hernandez [1] classified the conversion process into two categories biochemical and thermochemical. Biochemical usually consists of two processes: gasification or hydrolysis followed by fermentation to form ethanol. Thermochemical processes required relatively high temperature and sometimes high pressure to decompose biomass into the smaller molecular weight compound that can be converted into hydrocarbons, alcohols or aromatics via the catalytic process.

There are two main pathways in the thermochemical process of biomass conversion: pyrolysis and gasification. Pyrolysis is thermal decomposition of biomass in the absence of oxygen. Main products of pyrolysis are bio-oil or pyrolytic liquid, solid char and gas. Bio-oil produced from biomass contains high oxygenated compounds. This causes problem of the instability of the oil during storage, where viscosity, calorific value, and density all are affected. Therefore, utilization of the oil requires a general decrease in the oxygen content in order to separate the organic product from the water, increase the heating value, and increase the stability [2]. Hydrodeoxygenation, a catalytic reaction between bio-oil and hydrogen becomes the most common bio-oil upgrading process. In this process, oxygen is eliminated from bio-oil as water. Otherwise, the bio-oil can be upgraded by hydrocracking, where the chemical compounds in the bio-oil were cracked into smaller molecules. Feasibility of co-processing of bio-oil upgrading in a Fluid Catalytic Cracking (FCC) facilities of crude oil refinery were also investigated [3]–[5]. Instead of catalytic upgrading of bio-oil, the addition of catalyst during the pyrolysis process was proposed as the alternative pathway to enhance the bio-oil properties. The direct use of catalysts could decrease the pyrolysis temperature, increase the conversion of biomass and the yield of bio-oil, and change the distribution of the pyrolytic liquid products then improve the quality of the bio-oil obtained [5]–[8].

Catalyst

Several types of catalyst were employed in pyrolysis of biomass to produce fuels or chemicals. Zeolite-based catalysts are the most often used catalyst in pyrolysis, instead of metal oxides, inorganic carbonates, and other organosilicate materials. Table 1 shows catalysts used in bio-oil production for selected biomass feedstock, either in single or dual stage reaction. Catalyst selection is based on the main purpose of the pyrolysis process. Besides the ability of the catalyst to lower the activation energy of the whole process, the selectivity of the catalyst is also important. Zeolitic materials are usually employed to obtain smaller hydrocarbon molecules since the structure of zeolite able to facilitate thermal cracking of large molecules. In order to maximize gas production from biomass pyrolysis, metal oxides, such as calcium oxide and magnesium oxide, may be used as the catalyst [9].

Table 1. Catalyst and biomass feedstock used in catalytic pyrolysis

Catalyst	Feedstock	Reactor type	Reference	
ZSM-5	Rice husk	Fixed bed	[8]	
	Pine sawdust	Fluidised bed	[7], [10]	
	Pine wood chip	Fixed bed	[11]	
	Pine barks	Fixed bed	[12]	
	Aspen wood	Tubular bed	[13]	
	Sawdust	Fluidised bed	[14]	
	EFB	Fixed bed	[15]	
	<i>Nannochloropsis sp.</i>	Fixed bed	[16]	
	Beech wood	Fixed bed	[5]	
	Corn stalks	Fixed bed	[17]	
	Corncob	Fluidised bed	[18]	
	H-beta-zeolite	Pine sawdust	Fluidised bed	[10]
		Oak	Packed bed	[19]
	Mordenite	Pine sawdust	Fluidised bed	[10]
Oak		Packed bed	[19]	
FeO	Sawdust	Fixed bed	[20]	
Al ₂ O ₃	Sawdust	Fixed bed	[20]	
	Olive bagasse	Fixed bed	[21]	
	Hazelnut bagasse	Fixed bed	[21]	
	Beech wood	Fixed bed	[5]	
	Miscanthus giganteus	Fixed bed	[22]	
CaO	Sawdust	Fixed bed	[20]	
	Sewage sludge	Fluidised bed	[23]	
MnO	Sawdust	Fixed bed	[20]	
CuO	Sawdust	Fixed bed	[20]	
Cr ₂ O ₃	Sawdust	Fixed bed	[20]	
La ₂ O ₃	Sewage sludge	Fluidised bed	[23]	
B ₂ O ₃	EFB	Fixed bed	[24]	
ZnO	Rice husk	Fixed bed	[25]	
ZnO	Pine sawdust	Fluidised bed	[26]	
Sodium feldspar	Olive, hazelnut bagasse	Fixed bed	[21]	
Al-MSU-F	Rice husk	Fixed bed	[8]	
Al-MCM-41	Rice husk	Fixed bed	[8]	
Rice husk ash	Rice husk	Fixed bed	[8]	
Na ₂ CO ₃	Microalgae	Fixed bed	[27]	
K ₂ CO ₃	Reed	Fixed bed	[28]	
	Cellulose	Fixed bed	[29]	

Generally, the presence of zeolitic materials in biomass pyrolysis affects the product distribution. Aho et al. investigated the effect of different type of zeolites in product distribution of biomass pyrolysis [10]. As shown in Figure 1, bio-oil yield decreases for all type of zeolites, while aqueous product increases compared to that of non-catalytic pyrolysis. It is likely that the elimination of oxygen occurred through the formation of water molecules. Increase of solid product might be caused by coke formation during high-temperature thermal

treatment. In this study, gas production was relatively uniform and is not affected by types of zeolite. However, some studies indicated the increase of gaseous product due to cracking reaction during thermal treatment of biomass [5], [12], [17], [19], [30].

In the pyrolysis process, zeolite facilitates conversion of oxygenates compounds into aromatics hydrocarbons. Figure 2 illustrates the oxygenated compound present in the bio-oil and aromatics resulted from catalytic pyrolysis on zeolites. According to Bridgwater, aromatisation is an important step in the reactions of hydrocarbons over zeolite catalysts [31]. It is in agreement with some previous studies in catalytic pyrolysis of biomass by using zeolite, which indicated the increase of aromatic hydrocarbon content in bio-oil compared to that of non-catalytic pyrolysis. Application of ZSM-5 on pyrolysis of microalgae increased the content of aromatic carbon almost three-fold, from 19.8 to 50.8% [32]. Wang et al. found that ZSM-5 catalyst increased the aromatic hydrocarbon content from 0.72%, obtained by non-catalytic pyrolysis of Douglas-fir, to 6.89% [33]. Moreover, increasing of aromatic hydrocarbon by about 50% from non-catalytic pyrolysis was achieved in rice husk pyrolysis by using ZSM-5 as catalyst [8]. Aromatisation reaction may be preceded by the Diels–Alder reaction, in which cyclic and aromatic compounds are produced by cracking combine with each other as shown in Equation 1 [34]. C-C bonds cracking are promoted by strong acidity and shape selectivity of ZSM-5. It also determines the shorter chain length of products [35].

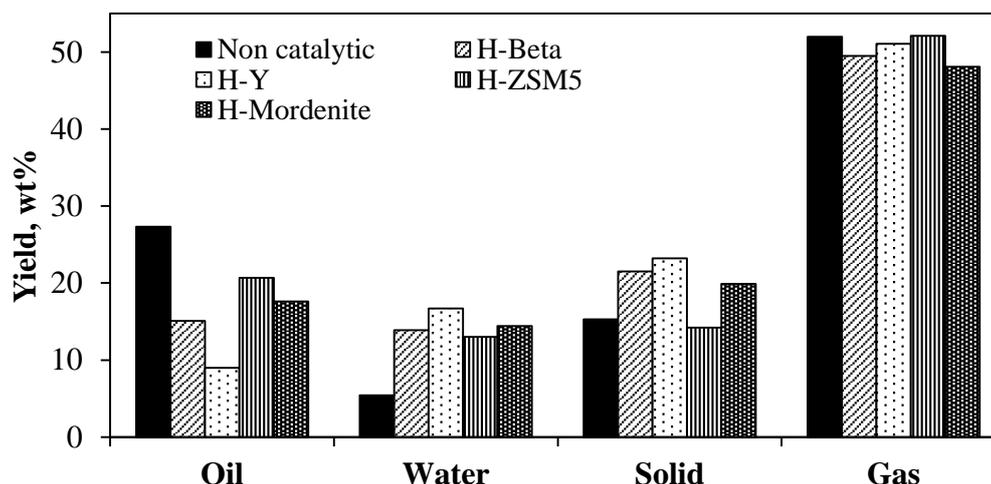


Figure 1. Product distribution of catalytic pyrolysis of pine chips using different zeolite-based catalyst [10]

The deoxygenation of biomass also occurs through reaction of decarbonylation and decarboxylation reaction [36]. Reduction of oxygen content from 33 to 13 % was reported in catalytic pyrolysis using ZSM-5 as the catalyst. The oxygen contained in the feedstock are removed as CO, CO₂ and H₂O [37]. At lower temperature, oxygen removal is in the form of H₂O, while at higher temperatures, it was as CO and CO₂ [38], [39]. Modification of ZSM-5 used as biomass pyrolysis catalysts was attempted to enhance the oxygen rejection. It may be obtained by producing more carbon oxides and less water, thus provide more hydrogen available to be incorporated into hydrocarbon [36]. Moreover, zeolites also effectively increases the C/O ratio and improves the octane number [40], [41]. The presence of transition metal promoted zeolitic materials lead to the production of more hydrocarbons and less coke than that of commercial ZSM-5 catalyst's usage [13]. Thus, some transition metals modified catalysts were employed in pyrolysis to enhance the bio-oil characteristic, such as CeZSM-5, CoZSM-5, CoHZSM-5, GaZSM-5, and NiZSM-5.

Calcium oxide (CaO) is widely known as a potential catalyst for biomass gasification to produce hydrogen and syn-gas. Impregnation of CaO with sawdust successfully increased the rate of hydrogen production in the temperature-programmed gasification [42]. Increase of H₂ yields were also observed in gasification of pine bark [43], pine sawdust [44], the empty palm fruit bunch [45]. Critical review on application of CaO as a catalyst of biomass gasification was also conducted by Udomsirichakorn & Salam [46]. Nevertheless, CaO was also employed as a catalyst in pyrolysis of biomass to produce bio-oil. In the catalytic pyrolysis of white

pine biomass using CaO, [47] reported that the oxygen content in the bio-oil obtained and the contents of formic and acetic acids were lower than those in the bio-oil obtained by pyrolysis of the same biomass material. Presence of CaO in sewage sludge pyrolysis slightly reduced the bio-oil yield from 43 to 39 – 40 wt% due to the catalytic cracking of pyrolysis vapor. However, the chlorine content was effectively reduced from 498 to 73 ppm [23].

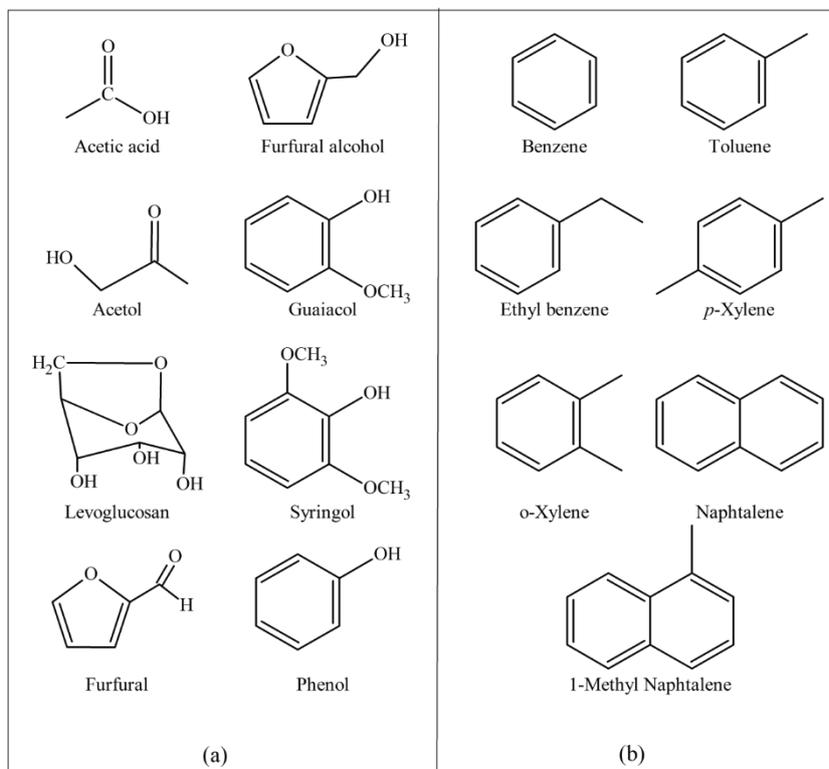


Figure 2. Typical oxygenated compounds associated with fast pyrolysis of biomass (a), and aromatic hydrocarbons produced by catalytic pyrolysis using zeolites (b) [41]

The performance of some other metal oxides as catalyst on catalytic pyrolysis was also studied, either for gasification or bio-oil production purposes. Table 2 summarizes the utilisation of metal oxide as a catalyst for selected biomass pyrolysis. Generally, gaseous product increases while liquid fraction decreases in the presence of metal oxide catalyst. Kuan et al. investigated the pyrolysis of sugarcane bagasse over NiO, CuO, MgO and CaO catalyst [48]. By using microwave heating, gaseous product increased from 58% in non-catalytic pyrolysis to 62 and 65% by addition of CaO and MgO, respectively. At the same time, liquid yield of pyrolysis decreased from 23% to 19% by addition of MgO. Addition of CaO, NiO and CuO enhanced the liquid fraction to 24, 32, and 33%, respectively.

The chemical composition of bio-oils is affected by the application of catalyst. This is because several types of chemical reaction are enhanced by catalyst such as cracking, carbonylation, carboxylation, dehydration, esterification, and isomerisation. Smets et al. (2013) compared the composition of bio-oil derived from rapeseed cake by using γ -Al₂O₃, H-ZSM5 and Na₂CO₃ as catalyst. As shown in Figure 3, H-ZSM5 increased the portion of aromatic hydrocarbon and nitriles in bio-oil produced, but decreased the fraction of carboxylic acid, phenol and esters. γ -Al₂O₃ gave slight effect on reducing the phenolic compounds and aromatics, while Na₂CO₃ perfectly reduced the presence of carboxylic acid from more than 40% to less than 10%. The presence of B₂O₃ as a catalyst reduced the content of methoxy-phenolic group in pyrolysis of empty palm fruit bunch and oil palm frond, from 16% to 12% and from 24% to 10%, respectively. Methoxy-phenolic compounds could be formed at temperature below 400 °C due to the decomposition of holocellulose and lignin structure [24].

Table 2. Comparison of bio-oil yield between non-catalytic and catalytic pyrolysis using CaO and other metal oxides for various biomass feedstock type.

Catalyst	Feedstock	Bio-oil yield, wt%		Reference
		Non-catalytic	Catalytic	
γ -Al ₂ O ₃	Rapeseed cake	47.1	40.8	[49]
CaO	White pine powder	39.4	34.1	[47]
	Sewage sludge	43.0	39.0 – 40.0	[23]
	Sugarcane bagasse	23.0	24.0	[48]
	Pine sawdust	47.0	13.0	[7]
CuO	Sugarcane bagasse	23.0	34.0	[48]
	Pine sawdust	47.0	49.0	[7]
La ₂ O ₃	Sewage sludge	43.0	39.0 – 40.0	[23]
MgO	Sugarcane bagasse	23.0	18.0	[48]
	Pine sawdust	44.0	16.0	[7]
NiO	Sugarcane bagasse	23.0	32.0	[48]
SiO ₂	Pine sawdust	47.0	19.0	[7]
SnO ₂	Pine sawdust	47.0	32.0	[7]
ZnO	Pine sawdust	47.0	47.0	[7]

Acidity of the catalyst has influenced the pyrolysis products. Aho et al. reported the effect of catalyst acidity on pyrolysis of pine wood chips [50]. The acidity of zeolites slightly influenced the formation of different groups of compounds. Decreasing of aldehydes formation was observed with an increasing acidity of the zeolites. Less ketones and phenols were formed in pyrolysis of pine biomass with acidic zeolites as bed material than with quartz sand in the bed. However, the presence of acidic catalyst did not significantly influence the amounts of acids and alcohols formed during the pyrolysis of biomass. Interestingly PAHs were obtained only when zeolites are used. Acid catalysed reactions such as cracking, dimerization, cyclization and dehydrocyclization takes place on Brønsted acid sites [50].

Properties of bio-oil derived from catalytic pyrolysis

The presence of catalyst affects the chemical composition of bio-oil obtained through the pyrolysis process. In general, bio-oil produced by catalytic pyrolysis has higher content of aromatic hydrocarbon and lower oxygen content. In addition, heavy molecules are cracked to form new compounds with smaller molecular weight. Moreover, the chemical composition of bio-oil greatly influences the physicochemical properties of bio-oil. Therefore, catalytic pyrolysis of biomass could enhance bio-oil properties such as oxygen content, moisture content, heating value, viscosity and density of bio-oils. Table 3 compares certain properties of bio-oil produced by non-catalytic and catalytic pyrolysis. Except for catalytic pyrolysis of pine sawdust over ZnO, generally the presence of the catalyst reduced the oxygen content in bio-oil. As the result, calorific value of bio-oil also increased, since the lower oxygen content gave the lower calorific value according to the correlation proposed by Channiwala & Parikh [51].

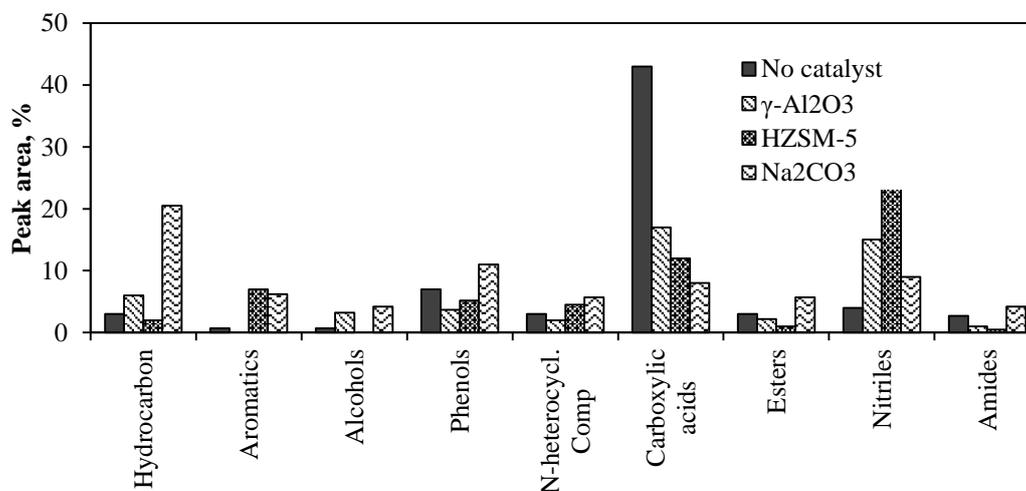


Figure 3. The distribution of different classes of compounds present in the oil fractions of the pyrolysis liquids derived from rapeseed cake by various catalysts [49]

Besides the chemical composition, elemental composition and calorific value, some properties also become important since they can describe the character of the oil obtained by catalytic pyrolysis compared to that of conventional fuels such as gasoline, diesel oil and heavy oil. Good biofuel should have neutral pH to avoid the corrosion problems when the fuel is applied into the internal combustion engine. Fan et al. reported the significant increase in the pH of rape straw bio-oil from 2.30 to 5.15 by using H-ZSM5 as a catalyst [52]. Similar result was also reported for corncob catalytic pyrolysis. By using H-ZSM5, increase of pH from 2.8 (without catalyst) to 5.2 (with catalyst) was achieved [18]. Reduction of acid, ester and alcohol content may contribute to the increase of pH value of bio-oil. The presence of catalyst also enhances the stability of bio-oils. Nokkosmaki et al. studied the stability of bio-oil by artificial aging at 80 °C for 24 h [26]. Kinematic viscosity measurement showed that bio-oil produced by catalytic pyrolysis had better stability. The change by about 55% (from 6 to 9 cSt), compared to 129 % from 9 to 22 cSt for bio-oil produced by non-catalytic pyrolysis.

Table 3. Comparison of oxygen content and HHV of bio-oil obtained by non-catalytic and catalytic pyrolysis

Feedstock	Catalyst	Properties	Non-catal.	Catalytic	Ref(s).
Rape straw	H-ZSM5	O, wt%	49.75	19.07	[53]
		O/C	0.335	0.195	
		H/C	1.426	1.510	
		HHV, MJ/kg	18.30	33.80	
Corncob	H-ZSM5	O, wt%	40.28	14.69	[18]
		O/C	0.58	0.15	
		H/C	1.61	1.51	
		HHV, MJ/kg	18.80	34.60	
Nannochloropsis sp.	H-ZSM5	O, wt%	30.09	19.53	[16]
		O/C	0.40	0.22	
		H/C	1.63	1.89	
		HHV, MJ/kg	24.40	32.20	
Pine wood	H-Beta-25	O, wt%	41.30	32.20	[6]
		O/C	0.62	0.42	
		H/C	1.90	1.99	
		HHV, MJ/kg	30.96	n/a	
Cottonseed cake	Natural zeolite	O, wt%	19.90	14.33	[54], [55]
		O/C	0.23	0.16	
		H/C	1.54	1.52	
		HHV, MJ/kg	30.96	n/a	
Pine sawdust	ZnO	O, wt%	48.00	51.00	[26]
		O/C	0.82	0.91	
		H/C	1.91	2.29	
		HHV, MJ/kg	18.00	18.00	
Cottonseed oil cake	MgO	O, wt%	9.56	4.90	[56]
		O/C	0.10	0.05	
		H/C	1.83	1.87	
		HHV, MJ/kg	39.83	42.91	

Conclusion

Pyrolysis becomes a prospective alternative to convert biomass into fuels and other chemicals, since it able to convert almost of the raw materials into usable product. However, bio-oils derived from biomass through the pyrolysis have low stability and also lower calorific value, particularly due to high oxygenated compounds contained in the oils. Catalytic upgrading becomes option to increase the quality of bio-oil regarding to the high oxygen content. Several studies have been carried out to develop the possibility to conduct upgrading

process in single step through catalytic pyrolysis. Previous studies shown that the application of catalytic pyrolysis able to reduce the oxygen content of bio-oil, and also enhance the properties of bio-oils include the acidity, viscosity, and higher heating value as well. Searching of more effective catalysts, and also process modification of pyrolysis still becomes an attractive challenge, particularly to find out new technology that able to provide alternative energy sources in lower cost and highly sustainable. The mechanism and reaction pathways of biomass pyrolysis process are also interested to be studied in order to enhance the understanding of pyrolysis process.

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