

EFFECT OF CATALYST TYPE ON YIELD AND PROPERTIES OF BIO-OIL DERIVED FROM PALM OIL DECANTER CAKE

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ABSTRACT

Palm oil milling plant generates about 4 – 5 wt % of decanter cake from the total weight of fresh fruit bunch processed and it has potential to be converted into energy source through pyrolysis process. In this investigation, the catalyst was mixed with biomass prior to loading into the pyrolysis reactor. Two base catalysts (CaO and MgO) and two acidic catalyst (γ -Al₂O₃ and H-ZSM5) were employed to investigate the effect of the catalyst on the bio-oil produced. The catalytic pyrolysis was conducted through the vacuum pyrolysis at final temperature of 500 °C. The final temperature was chosen based on TGA analysis of the biomass sample. Chemical composition of bio-oil produced were evaluated by using CHONS analyzer, FTIR, GCMS and NMR, while the properties of bio-oil particularly viscosity, density, moisture content, pH and heating value were also evaluated. In general, addition of catalyst able to enhance the quality of bio-oil in term of lower oxygen content, higher pH and heating value of bio-oil.

Keywords: Bio-oil, catalytic pyrolysis, decanter cake, palm oil, renewable energy.

INTRODUCTION

World's energy consumption has been rapidly increasing in the last three decades, caused mainly by the population growth and economic activities. In the other hand, modern lifestyle which is required better health and environmental provision, accessibility and mobility, also contribute to energy consumption rising worldwide. Energy consumption in Malaysia shows rapid growth from 143 mboe (million barrels of oil equivalent) in 1990 to 503 mboe in 2011, and will reach almost 870 mboe in 2035 with the annual growth rate of 2.3% [1]. In line with the depletion of fossil fuel resources, demand for renewable energy is forecasted to increase its sharing in primary energy source from 13% in 2011 to 18% in 2035 [2]. Compared to the fossil fuels, renewable energy provides advantages on the more secure, reliable and sustainable energy path. Moreover, utilisations of renewable energy in long term offers benefit in reducing CO₂ emission and dependence on imported oil. Among the other renewable energy, such as hydro, wind, and solar photovoltaic, biomass is widely utilised due to its local availability at relatively low price. Biomass is the third largest primary energy source in the world, after coal and oil. It remains the primary source of energy for more than half of the world's population, and provides about 1250 million tons oil equivalent (Mtoe) of primary energy, which is about 14% of the world's annual energy consumption [3].

Abundant source of biomass in Malaysia come from palm oil industries. As second world's largest palm oil producer and exporter, Malaysia produced 18.911 million tonnes of crude palm oil (CPO) from 5.0 million ha of plantation area in 2011 [4]. In the processing of oil palm fruit bunch into CPO, biomass wastes are generated in form of empty fruit bunch, oil palm fibre, palm kernel shell and palm oil decanter cake (PDC). PDC is a semisolid by-product from palm oil milling decantation process. The production rate of the decanter cake amount to about 4 – 5 wt % of the fresh fruit bunch processed. The composition of decanter cake varies by plant site location. Its' major constituents are carbon, hydrogen, oxygen, and nitrogen. Decanter cake may also contain phosphorus and magnesium [5]. The oil content of PDC was reported to be about 11.5 wt% [6]. Substantial amount of PDC generation may lead environmental problem unless properly treated or converted into value added by-product. Conversion of PDC into biofuel through pyrolysis become an option to reduce the adverse effect of solid waste generation. Study of the kinetic of catalytic pyrolysis of PDC has been conducted by using thermogravimetry data [7].

Conversion of biomass into biofuel, particularly through pyrolysis process has drawn attention in last two decades. The advantage of this thermal treatment is ability to convert almost all of the component in the biomass, include cellulose and lignin, into the products. Basically, pyrolysis process will convert biomass into pyrolytic liquid, solid char and gas. Distribution of the products is depended on the mode and operating condition of the pyrolysis. Pyrolytic oil, commonly known as bio-oil, can be considered as potential renewable fuel. However, bio-oil has several drawbacks in its utilization as fuel due to its stability, poor calorific value, high acidity and improper viscosity. It is mostly caused by high oxygenated compounds found in the bio-oil. Thus, upgrading process of bio-oil in order to reduce the oxygen content is definitely required [8]. Some catalysts had been studied and investigated on their capability to reduce oxygen content and increase the property of bio-oil [9]. 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 [10-13]. In this study, some types of catalyst will be investigated to enhance the bio-oil properties obtained from PDC through the vacuum pyrolysis process.

METHODOLOGY

Palm oil decanter cake (PDC) was obtained from local palm oil milling plant LKPP Corporation, Sdn. Bhd. located in Kompleks Kilang LKPP Lepar, KM 43.5 Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang Darul Makmur, Malaysia. Drying process of PDC was conducted in laboratory oven (Memmert) at 105 °C for 18 hours to obtain the final moisture content of 5 – 8 %. Prior to the experiments, dried PDC was ground and sieved to obtain the particle size of decanter cake within the range of 0.8 – 2.0 mm. CaO and MgO (reagent grade) were purchased from Sigma-Aldrich, while γ -Al₂O₃ (analytical grade) was purchased from Merck. H-ZSM5 (Si/Al = 30) was supplied by Zeolyst International. All of the catalysts were calcined at 550 °C for 3 h prior to the experiments, except CaO was at 900 °C. Catalyst was pre-mixed with PDC prior to the experiment. The amount of catalysts were varied from 5, 10, 15 and 20 wt% of total feed.

Pyrolysis experiments were conducted by loaded 300 g of mixture into the reactor and put into a muffle furnace. A vacuum pump was used to evacuate the air inside the reactor and kept the pressure below 30 kPa. The reactor was heated at 15 °C/min heating rate to obtain the final temperature of 500 °C. Arrangement of pyrolysis equipment is illustrated in Fig. 1. Vapour generated from the pyrolysis process was withdrawn by the vacuum pump and condensed using the water condenser to obtain the liquid product. The uncondensed vapours were condensed with water-ice condensate trap. Uncondensed vapours and gases were pumped out and discharged into air properly. The pyrolysis process was terminated either after an hour at final temperature or when liquid was not produced anymore. Liquid product consisted of organic and aqueous phase. The lower density top layer product was the organic phase, while the aqueous phase was the denser layer. The two phases were separated by using separating funnel. Organic phase was defined as bio-oil and used for further analysis. Yield of bio-oil was determined by wt% basis. Bio-oil and aqueous phase separated from liquid fraction were weighed using analytical balance. Char product was collected from pyrolysis reactor and weighed using analytical balance. Gas fraction yield was calculated by difference from the biomass mass balance.

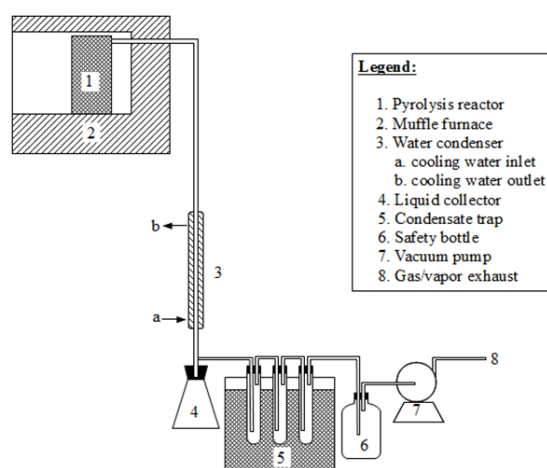


Figure 1. Apparatus arrangement for catalytic pyrolysis using single stage reactor

Determination of C, H, and N composition in bio-oil was carried out by elemental analysis using a Macro Elemental Analyser CHNSO provided by Elementar. Oxygen content of bio-oil was determined by difference. FTIR spectra of the bio-oils were obtained by Perkin Elmer Spectrometry 100. It was achieved using thin films of bio-oil between KBr plates and accumulating 100 scans at 400 – 4000 cm⁻¹ wavenumber. The nature of hydrogen in the bio-oil and the aliphatic, olefinic and aromatic composition in bio oils were examined by ¹H-NMR using deuterated chloroform as solvent. Bruker AVANCE III, 500 MHz FT NMR Spectrometer was employed for this purpose. Analysis of bio-oil composition was performed on HP 6895 GC-MS equipped by Agilent 5973 mass selective detector. A HP DB-Wax capillary column (30 m x 0.25 mm x 0.5 m) was used to separate the constituents. Bio-oil sample was diluted 100 times by using hexane (Merck, chromatography grade) as solvent. One μ L sample of diluted bio-oil was injected into the column at 250 °C. Helium was used as carrier gas at flow of 1 mL.min⁻¹. Oven temperature was programmed from 40 to 250 °C with heat ramp at 8 °C/min, held at initial and final temperature for 10 min. NIST database was used as reference in identifying chemical compounds found. pH of bio-oil was measured using Mettler Toledo SevenEasy, while higher heating value (HHV) of bio-oil was determined by using IKA C-200 Oxygen Bomb Calorimeter. A Metrohm Karl Fisher titration was also employed to determine the moisture content of the bio-oil. Dynamic viscosity of bio-oils was determined by Brookfields DV-II+ viscometer equipped with Small Sample Adapter, while the density of bio-oil was measured using KEM-1 Densitometer.

RESULTS AND DISCUSSION

Effect of catalyst loading on pyrolysis product distribution

The effect of catalyst loading on product distribution of PDC pyrolysis is shown in Figure 2. The bio-oil yield consistently decreased for higher catalyst loading, from 23.38 wt% for non-catalytic pyrolysis to 17.16 and 15.22 wt% for catalytic pyrolysis over 20 wt% CaO and MgO, respectively, as shown in Figure 2a and 2b. In contrary, gas production increased from 17.09 wt% (non-catalytic) to 23.63 wt% (20% CaO loading) and 21.75 wt% (20% MgO loading). Hence, the presence of metal oxide as the catalyst decreased the yield of total liquid and bio-oil, while the gas yield increased gradually. CaO and MgO are commonly employed as the catalyst in the gasification process to increase hydrogen production. Addition of CaO and MgO increased the gaseous portion of the product such as methane, CO, and CO₂ due to catalytic cracking of pyrolysis vapour [14-16]. Char production of catalytic pyrolysis over CaO and MgO was relatively constant at various

catalysts loading. It indicates there was no significant increase in coke deposition in the presence of CaO and MgO catalyst. Addition of $\gamma\text{-Al}_2\text{O}_3$ in PDC pyrolysis decreased the bio-oil yield from 23.28 wt% for non catalytic pyrolysis to 7.28 wt% for catalytic pyrolysis with 20 wt% $\gamma\text{-Al}_2\text{O}_3$ loading. In the other hand, the aqueous fraction of liquid product increased from 19.55 (non-catalytic) to 27.62 wt% (20 wt% $\gamma\text{-Al}_2\text{O}_3$ loading) as illustrated in Figure 2c. The pyrolytic aqueous phase consists of water coming from the feedstock and biomass pyrolysis reactions and water-soluble organic compounds. Small portion of H_2O may be formed from the decomposition of cellulose to form anhydrosugars, dehydration, oligomerisation, decarboxylation and decarbonylation reaction. However, this contributed fewer significant portion of H_2O formation due to low cellulose content of raw material. The water-soluble organic compounds are mainly formic and acetic acids, and contain low molecular weight oxygenated organic compounds such as aldehydes, ketones, alcohols, ethers and others [17-20]. This finding is similar with that of other studies on catalytic pyrolysis using other types of biomass [17], [21]. As illustrated in Figure 2d, the presence of H-ZSM5 decreased the bio-oil yield from 23.28 to 18.16 and 17.52 wt% for 5 and 10 wt% catalyst loading respectively. As 15 and 20 wt% of catalyst was present, bio-oil yield tend to remain constant at around 16.55 wt%. Low yield of bio-oils from pyrolysis using H-ZSM5 was also observed by previous researchers [22-25]. Kim et al. [26] reported the oil yield of palm kernel shell pyrolysis was reduced remarkably from 23.1 wt% without catalyst to 14.4 wt% with H-ZSM5 catalysts. In addition, Other study observed the reduction of bio-oil yield from 37.37 wt% for non-catalytic to 20.82 wt% for H-ZSM5 catalytic pyrolysis of lignocellulosic biomass [11]. Gas and char production was consistently increasing with the amount of the catalyst loaded into the feedstock. Increasing of solid product may correspond to coke formation.

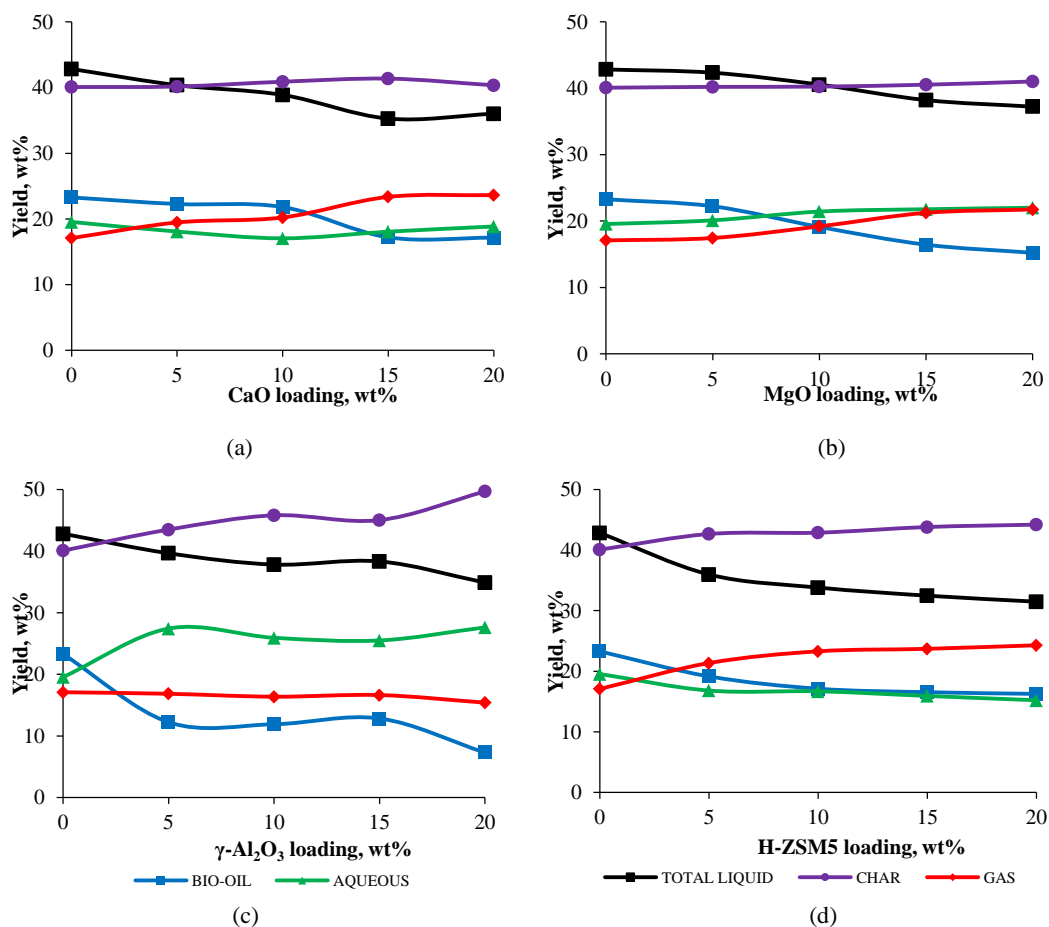


Figure 2. Effect of CaO (a), MgO (b), $\gamma\text{-Al}_2\text{O}_3$ (c) and H-ZSM5 (d) loading on product distribution of PDC pyrolysis

Chemical composition of bio-oils

Elemental composition of bio-oils derived from catalytic pyrolysis was summarised in Table 1. Oxygen content was determined by calculating the difference between total C, H and N with 100%. Catalytic pyrolysis on PDC reduced oxygen content from 17.44 wt% for non-catalytic pyrolysis to 8.54 – 14.78 wt%. Lowest oxygen content in bio-oils was obtained by using H-ZSM5 as a catalyst (8.54 wt%). This implies that during the pyrolysis of PDC over H-ZSM5, the triglycerides firstly decomposed into fatty acid. Further, the fatty acid was deoxygenated via decarboxylation and/or decarbonylation. The primary products are further transformed into the cracked products [27]. This phenomenon was also observed in pyrolysis of oleic acid [28] and that the primary products, mainly those with unsaturated double C=C bonds are further transformed into cracked products. H/C of bio-oil derived from PDC was within the range 1.365 to 1.874, and found to be similar with those of light petroleum products (1.50–1.90) [17].

Functional groups contained in bio-oils were identified by FTIR. The IR spectrums of the bio-oils are presented in Figure 3. The broad adsorption band between 3600 and 3200 cm^{-1} corresponds to the O-H stretching vibration of residual water. The presence of carboxylic acids and alcohols was also indicated by the O-H stretching vibrations. This vibration

maybe also represents some amount of phenols. The C-H stretching vibration between 2850 and 2660 cm^{-1} indicates the presence of alkanes. Together with C-H bending at 1382 cm^{-1} and CH_2 rocking at 724 cm^{-1} , is due to long aliphatic chain, e.g. triglycerides or fatty acids. C=O stretching vibration occurred at around 1715 relates to ketones and carboxylic acids. The presence of carboxylic acids and esters is indicated by C-O stretching vibration between 1280 and 1000 cm^{-1} . The absorption bands between 1610 and 1460 cm^{-1} and the band at 900 – 700 cm^{-1} , representing the C=C stretching and the C-H bending vibrations respectively, are the indication for internal alkenes and aromatics.

Table 1. Elemental composition of bio-oils obtained by catalytic pyrolysis

Catalyst	Elemental constituent, wt%				O/C, mol fraction	H/C, mol fraction
	C	H	O	N		
No catalyst	68.91	10.65	17.44	3.00	0.190	1.855
CaO	78.83	8.97	9.75	2.45	0.093	1.365
MgO	74.12	10.45	12.67	2.76	0.128	1.692
$\gamma\text{-Al}_2\text{O}_3$	71.22	11.12	14.78	2.88	0.156	1.874
H-ZSM5	76.71	11.83	8.54	2.92	0.083	1.851

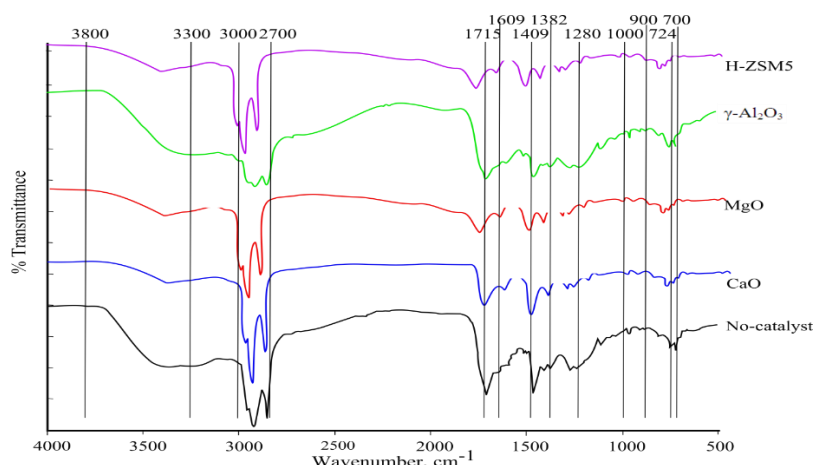


Figure 3. FTIR spectra of PDC bio-oil obtained by catalytic pyrolysis

$^1\text{H-NMR}$ was utilized to generate the spectra of bio-oil derived from catalytic pyrolysis of PDC. The distribution of various types of proton is summarised in Table 2. The results show that most of the protons are with aliphatic structural units existed in the bio-oils derived from PDC. This is because of the nature of the feedstock where PDC is dominated by triglycerides. Highest portion of aliphatic proton for PDC - CaO indicated that the reaction over CaO tended to involve the carboxylate end of bio-oil. This is consistent with the basic nature of CaO. On the other hand, the higher portion for olefinic proton for PDC - $\gamma\text{-Al}_2\text{O}_3$ suggested that the reaction involving carbon backbone occurs due to the acidic nature of the catalyst. H-ZSM5 shows highest content of aromatic protons for bio-oil compare to that of other catalysts. Ability of H-ZSM5 in increasing of aromatic compounds during biomass pyrolysis was also reported by several researchers [29-31]. Adjaye & Bakshi [32] reported that HZSM-5 catalyst in biomass pyrolysis could upgrade the bio-oil to produce hydrocarbons with aromatic yields up to 27 wt%. They also suggested that Brønsted acid sites in HZSM-5 have a critical role in the upgrading reactions. Foster et al. [33] proposed the aromatisation is started by dehydration reaction of cellulose to form anhydrosugars. Decarbonylation and oligomerisation reactions of furans then occur inside the H-ZSM5 catalyst to form a carbocation hydrocarbon pool and carbon monoxide. Non-oxygenated olefins, monocyclic aromatics and polycyclic aromatics can be formed from this hydrocarbon pool.

Table 2. The distribution of hydrogen in different proton environment based on $^1\text{H-NMR}$ of bio-oil obtained by vacuum catalytic pyrolysis of PDC

Catalyst	% area of type of hydrogen (chemical shift, ppm)		
	Aliphatic (0.5 – 3.0)	Olefinic (4.0 – 6.0)	Aromatic (6.0 – 9.0)
No catalyst	85.76	1.44	10.82
CaO	93.20	2.51	4.78
MgO	86.67	2.14	5.56
$\gamma\text{-Al}_2\text{O}_3$	84.82	5.38	8.85
H-ZSM5	80.33	2.55	11.31

Based on the GC-MS spectra, chemical compounds identified in PDC bio-oils can be classified into seven groups: aliphatics hydrocarbon, aromatics compounds, phenols, aldehydes, ketones, carboxylic acid, and esters. Table 3 summarizes the group of chemical compounds in bio-oils based on their functional groups. It was observed that the non-catalytic pyrolysis produced 64.12 % of peak area of fatty acid. Interestingly, the amount of fatty acids decreased to 10.27 – 15.41 % of peak area when the catalysts were used. Content of hydrocarbons increased in catalytic pyrolysis as the result of fatty acid decomposition. Interestingly, catalytic pyrolysis over CaO and MgO increased the level of esters from 3.49 % (non-catalytic)

to 26.67 and 17.55 % of peak area respectively. Ester component was slightly increasing with the presence of acidic catalyst. However, phenolic compound content in bio-oil increased by catalytic pyrolysis, with the largest amount was achieved by H-ZSM5.

Table 3. Composition of PDC bio-oils classified into their functional groups

Chemical groups	% area				
	No catalyst	CaO	MgO	γ -Al ₂ O ₃	H-ZSM5
Aliphatics hydrocarbon	7.81	27.28	28.55	22.6	25.5
Aromatics compounds	1.94	2.97	2.79	3.94	4.13
Phenols	1.78	8.61	7.49	9.15	11.37
Aldehydes	2.90	1.66	1.87	2.72	2.12
Ketones	0.23	1.61	1.02	1.06	1.58
Carboxylic acid	64.12	14.48	11.14	15.41	10.27
Esters	3.49	26.67	17.55	5.02	7.82

Physical properties of bio-oils

Effect of catalyst addition on physical properties of bio-oil produced is summarized in Table 4. Acidity and alkalinity of the catalyst noticeably determined the pH of the bio-oil, particularly observed in PDC bio-oil. CaO and MgO catalyst brought up the pH of bio-oil from 6.38 for non-catalytic pyrolysis to 7.89 and 6.85 for 5 % catalyst loading. The trend of pH increasing still remained at higher catalyst loading. Adverse effect was observed in presence of acidic catalysts. Both γ -Al₂O₃ and H-ZSM5 addition reduced the pH to below 6. HHV of PDC bio-oil produced increased up to 5.3 %, from 36.79 MJ/kg for non-catalytic pyrolysis to 38.75 MJ/kg for catalytic pyrolysis by 5 wt % loading of CaO. Heating value of bio-oil closely related to the elemental composition of bio-oil, particularly oxygen content. In this study, γ -Al₂O₃ gave the highest O/C mole ratio (0.156). Therefore, its HHV was relatively lower than that of other bio-oils as listed in Table 4. Other important properties of bio-oils are viscosity, density and moisture content. The viscosities of the bio-oils at 25 °C were found to range from 84.2 to 96.3 cP. Lower viscosity is preferred to achieve better atomization and combustion properties when the bio-oils are used as a fuel for gas turbine or engine applications. However, higher moisture content was observed in bio-oils produced through catalytic pyrolysis than that of non-catalytic. The formation of H₂O during the deoxygenation process may be responsible for this matter. In this study, the viscosity showed a negative relationship with the water content. An increase in the moisture content reduces the oil viscosity, as shown in Table 4. Same trend was also reported by Nolte & Liberatore in their study of the viscosity of biomass pyrolysis oils from various feedstock [34]. Furthermore, the viscosity of oil can increase during the storage time due to the polymerisation of the reactive species, as shown in stability test in previous section of this study. According to the previous study by Abnisa et al., the presence of water in bio-oil also affects the density [35]. Typically, high-water content leads to a decrease in the bio-oil density. However, this trend was not clearly observed in this study, due to the slight differences between the density of bio-oils.

Table 4.12: Physical properties of PDC bio-oil derived from catalytic vacuum pyrolysis

Biomass	pH	HHV, MJ/kg	Viscosity, cP	Density, g/cm ³	Moisture content, wt%
No catalyst	6.38	36.79	96.3	1.0496	6.32
CaO	7.98	38.75	84.2	1.0212	11.02
MgO	6.85	37.88	91.2	1.0023	6.87
γ -Al ₂ O ₃	5.87	36.54	90.5	1.0473	7.12
H-ZSM5	5.84	37.71	87.8	1.0582	9.13

CONCLUSION

Generally, the presence of catalyst reduced the bio-oil fraction and increased the gas production. At higher catalyst loading, bio-oil yield consistently decreased as well as gas yield increased. Oxygen content and O/C ratio of bio-oil was decreased in catalytic pyrolysis compared to that of non-catalytic pyrolysis. Catalytic activity of CaO and MgO enhanced the formation of methyl ester through the transesterification reaction of fatty acid, which was produced from decomposition of PDC. In addition, H-ZSM5 provides better oxygen content reduction than that of other catalysts. Bio-oils produced from PDC catalytic pyrolysis has relatively high calorific value than that of other bio-oils, and comparable to the HHV of petroleum fuels. Therefore, PDC bio-oil can be considered as potential alternative fuel.

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