

Catalytic pyrolysis of palm oil decanter cake using CaO and γ -Al₂O₃ in vacuum fixed bed reactor to produce bio-oil

Nugroho Dewayanto¹, Ruzinah Isha², Mohd Ridzuan Nordin³

¹Faculty of Industrial Sciences and Technology Universiti Malaysia Pahang,
Kuantan, Malaysia, e-mail: nugroho.dewayanto@gmail.com

²Faculty of Chemical and Natural Resources Engineering Universiti Malaysia Pahang,
Kuantan, Malaysia, e-mail: ruzinah@ump.edu.my

³Faculty of Industrial Sciences and Technology Universiti Malaysia Pahang,
Kuantan, Malaysia, e-mail: mridzuan@ump.edu.my

ABSTRACT:

The objective of this paper is to present the influence of catalyst towards the properties of bio-oil produced from Palm oil decanter cake (PDC), a semi-solid waste from palm oil milling plant. The PDC was first dried in oven at 105 °C for 24 hours to remove moisture and then ground to particle size of 0.85 – 2 mm. The dried PDC was then pyrolysed under dynamic vacuum at 500 °C, with temperature increased at 15 °C/min and maintained at the final temperature until no more product were formed. Two catalysts, the basic CaO and acidic γ -Al₂O₃ were used. The catalyst was mixed with decanter cake at various sample to catalyst weight ratio to investigate the effect of catalyst amount towards bio-oil production. In-terms of bio-oil yield and its HHV value, CaO performed better than γ -Al₂O₃. It is also found that 5 wt% of calcium oxide to sample produced the highest yield on bio-oil production. The oil was also characterized using ¹H-NMR, FTIR, CHNS analyzer and GC-MS. The analyses show that bio-oil obtained through catalytic pyrolysis of PDC is slightly different from that produced via non-catalytic process. GC/MS data indicates that the addition of calcium oxide reduced the content of carboxylic acid in bio-oil significantly. In addition, the bio oil produced from PDC has near neutral acidity, with pH value of 6.38, 6 and 8 for non catalytic, γ -Al₂O₃ and CaO catalytic pyrolysis, respectively. It can be deduced from this study that CaO can be used to enhance the production of bio-oil from decanter cake.

Keywords: Catalytic pyrolysis, bio-oil, biomass, palm oil decanter cake, calcium oxide

INTRODUCTION

In 2011, Malaysia retain its position as the world's largest palm oil exporter with total palm oil exports of 17.99 million tons, representing 46% of global palm oil trade. A total of 18.91 million tons of crude palm oil (CPO) and 2.14 million tons of crude palm kernel oil (CPKO) were produced in 2011, an increased of 11.3 % from previous year (MPOC, 2011). With the growth of palm oil production in Malaysia, the amount of residues generated also shows a corresponding increase. Wastes from palm oil industry are in the form of solid biomass residue, water effluent and gas emission. From the processing of fresh fruit bunch (FFB), palm oil milling plant produces 23.5 wt% as CPO, 5.2 wt% as crude palm kernel oil (CPKO) while the other 71.3 wt% is released into the environment in the form of solid or aqueous phase (Chavalparit et al, 2006). In the other hand, every hectare of palm oil plantation generated about 50 – 70 tons of biomass residue. Overall, 85% of biomass in Malaysia are made up of agricultural, forestry and municipal waste and in this category the oil palm industry is the major producer (Shuit et al., 2009).

Utilization of biomass residue as alternative energy sources is increasing in the last decade, due to increasing energy consumption,

uncertainty in price and supply of fossil fuels. Biomass, being a renewable energy source becomes a promising option to solve energy shortage and environmental problems simultaneously. Employing biomass as fuel also contribute to preventing global warming, since biomass fuel is categorized as carbon neutral, because there are no new or additional carbon emitted to the environment during its' combustion (Naik et al., 2010). Biomass can be transformed into energy sources in a number of ways, including direct combustion of solid biomass, hydrolysis, fermentation and thermochemical processes.

Pyrolysis is a thermochemical process involving decomposition of biomass at high temperature in the absence of oxygen. This process transforms biomass into solid, liquid and gas fractions; the proportion of these fractions depends on the mode of pyrolysis employed. Fast pyrolysis (residence time less than 2 s) at 400 – 600 °C produces up to 75% liquid fraction, while slow pyrolysis generates lesser liquid fraction and more solid fraction. A high temperature process, gasification, converts almost 90% of biomass into gas fraction (Bulushev & Ross, 2011). Pyrolysis for liquids production is currently of particular interest as the liquid can be stored and transported, and used for chemicals synthesis or as an energy carrier (Bridgwater, 2012). Vacuum pyrolysis is usually conducted in slow or intermediate pyrolysis mode.

Vacuum pump is employed to evacuate the oxygen before heat treatment of biomass and withdraw the vapour during thermal decomposition of biomass. Typically, liquid yield of vacuum pyrolysis is about 20 to 40%, comparable with that of slow pyrolysis (Carrier et al., 2011). Simple reactor design and no requirement of inert gas made up the advantage of vacuum pyrolysis compared to fast pyrolysis mode.

The chemical composition of bio-oils is very complex. According to Mortensen et al. 2011, bio-oil typically consisted of 55 – 65 wt% C, 5 – 7% H, 28 – 40% O and small amount of N and S (less than 0.5%). Generally, bio-oil compounds can be classified into acids, esters, linear aldehydes and ketones, cyclic ketones, furans, alcohols and sugars, ethers, phenols, phenolic ethers, oxygenated cyclic compounds, hydrocarbons and derivatives, and nitrogen compounds (Bertero et al., 2012). High oxygen content of bio-oil is a major concern since it causes the instability of bio-oil, low calorific value and high acidity (Zheng, 2008). Therefore, upgrading process of bio-oil is required before its utilization as fuel. Hydrotreatment, particularly hydrodeoxygenation (HDO), is the most common process in bio-oil upgrading. Typically, HDO process using heterogeneous catalyst will produce lower oxygen content in bio-oil and better physicochemical properties of bio-oils.

Instead of the two step processes being pyrolysis followed by catalytic hydrotreatment, catalytic pyrolysis was proposed to enhance the properties of bio-oil produced. Better characteristic of bio-oil can be obtained by oxygen rejection and cracking reaction to form smaller molecules through catalytic activity during pyrolysis process. Typically, bio-oil yield obtained from catalytic pyrolysis was not significantly higher and, even in some cases they were lower than that of the thermal process such as the pyrolysis on zeolitic material (Abu Bakar & Titiloye, 2012; Aho et al., 2007; Compton et al., 2011; Pan et al., 2010), sodium carbonate (Babich et al., 2011), alumina, and sodium feldspar (Demiral & Sensöz, 2008). The lower bio-oil yield could be a result of the cracking abilities of the catalyst. Utilization of metal oxides as catalyst, such as CaO, CuO, MnO, Al₂O₃, FeO and Cr₂O₃ could increase gas yield from biomass pyrolysis. Therefore, these oxides are considered for application in catalytic pyrolysis, particularly for hydrogen production.

In this study, palm oil milling plant decanter cake (PDC) was used as raw material to produce bio-oil. PDC is generated by palm oil milling plant from the 3-phase CPO purification

step. The production rate of PDC amount to about 4 – 5 wt % of fresh fruit bunch processed. Catalytic pyrolysis using CaO and γ -Al₂O₃ as catalyst was carried out in dynamic vacuum condition. The effects of catalyst loading on the pyrolysis conversion, product yields and compositions were also investigated.

EXPERIMENTAL

PDC was collected from LKPP Sdn. Bhd. palm oil milling plant in Lepar Hilir, Kuantan, Pahang. All materials were dried in oven at 105 °C for 24 hours to remove moisture. Dried decanter cake was then ground and sieved to obtain the particle size of 0.85 – 2 mm. CaO powder was purchased from R & M Chemicals, while γ -Al₂O₃ was purchased from Merck.

The pyrolysis of biomass was carried out in a cylindrical stainless steel reactor with inner diameter of 6.5 cm and height of 12 cm. The pyrolysis apparatus is illustrated in Fig. 1. About 300 g of biomass could be loaded into the reactor. To investigate the effects of catalyst presence, an amount of catalyst were added and premixed in various weight ratios (5, 10, 15 and 20 %) of catalyst to biomass. The reactor was then sealed and positioned into a muffle furnace. A vacuum pump was used to evacuate the air inside the reactor and keep the pressure below 30 kPa. The reactor was heated at 15 °C/min to obtain the final temperature of 500 °C. Vapour generated from pyrolysis process was withdrawn by vacuum pump and condensed using water condenser to obtain 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 processes was terminated after about an hour at final temperature or when liquid was not produced anymore. The liquid product exists in two phases: organic and aqueous phase. The organic phase obtained was separated from the aqueous phase and identified as the bio-oil. The bio-oils obtained are labelled as shown in Table 1. All of the bio-oil samples were then analysed to determine their properties and chemical compositions.

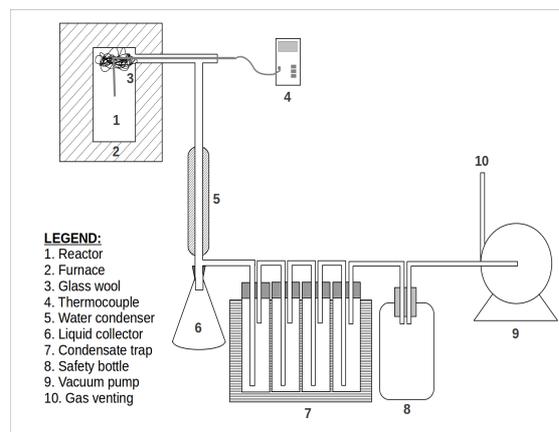


Fig. 1. Illustration of equipment used for vacuum pyrolysis

Table 1. Labelling of bio-oil sample

Label	Pyrolytic condition
PDC-0	Non-catalytic pyrolysis
PDC-A05	5 wt% of γ -Al ₂ O ₃ loading
PDC-A10	10 wt% of γ -Al ₂ O ₃ loading
PDC-A15	15 wt% of γ -Al ₂ O ₃ loading
PDC-A20	20 wt% of γ -Al ₂ O ₃ loading
PDC-C05	5 wt% of CaO loading
PDC-C10	10 wt% of CaO loading
PDC-C15	15 wt% of CaO loading
PDC-C20	20 wt% of CaO loading

The calorific value of bio-oils was measured by IKA C-200 oxygen bomb calorimeter. Mettler Toledo SevenEasy pH meter was used to determine the pH of bio-oil. Karl Fisher titration method was used to determine moisture content of bio-oil. FTIR spectra of the bio-oils were obtained by Perkin Elmer Spectrometer. A thin film of bio-oil was placed between KBr plates and its FTIR spectrum obtained, accumulating 100 scans from 400 – 4000 cm⁻¹ wavenumber. The composition of different type of hydrogen in the bio-oil molecules being aliphatic, olefinic and aromatic were determined by Bruker NMR, using deuterated chloroform as solvent. Analysis of bio-oil composition was performed on HP 6895 GC-FID while the identification of individual molecule was done using another GC equipped with Agilent 5973 mass selective detector. An HP DB-Wax capillary column (30 m x 0.25 mm x 0.25 μ m) was employed to separate the constituents. A 1 μ l sample of bio-oil was injected into the column at 250 °C. Helium

was used as carrier gas at flow of 1 ml.min⁻¹. The oven temperature was programmed from 40 to 250 °C with heat ramp 8 C.min⁻¹, held at initial and final temperature for 10 min.

RESULTS AND DISCUSSIONS

Fig. 2 presents the plots of the pyrolysis product yields versus the catalyst loading from the catalytic pyrolysis of PDC. When the amount of γ -Al₂O₃ in PDC was increased, the liquid yield decreased. The liquid fraction is composed of aqueous and bio-oil phases. The pyrolytic aqueous phase consists of water coming from the feedstock and biomass pyrolysis reactions and water-soluble organic compounds. The portion of aqueous component in liquid fraction increased by addition of γ -Al₂O₃, while the bio-oil/organic phase portion decreased from 21.46 % in non-catalytic pyrolysis to 17.57 % for 20% γ -Al₂O₃ loading. This finding is similar with that of other study on catalytic pyrolysis using other type of biomass (Azura et al., 2013; Yorgun & Simşek, 2008). The lower bio-oil yield can be due to the presence of acid sites on alumina catalyst that accelerate the decarbonylation, dehydration, cracking and hydrogenation reactions during the pyrolysis processes (Samolada et al., 2000). Decrease of liquid yield with the increase of catalyst loading also occurs in catalytic pyrolysis of PDC over CaO (Fig. 2b.). The portion of bio-oil/organic phase increased from 21.46% to 26.21% for 5% CaO loading, but decreased consistently for higher CaO loading. The lowest bio-oil yield of 17.21 was achieved at 15% CaO loading. Addition of CaO increased the gaseous portion of the product such as methane, CO, and CO₂ (Han et al., 2010; Wang, Xiao, Zhang, & He, 2010). Char production of catalytic pyrolysis over CaO was relatively constant at various CaO loading. Based on the bio-oil yield from 5% catalyst loading, it can be concluded that CaO gave better result than that of γ -Al₂O₃ illustrated in Fig. 3.

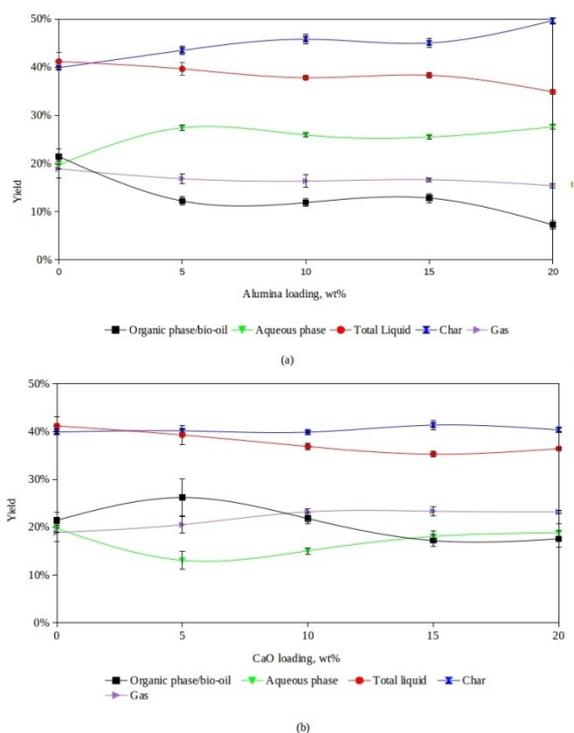


Fig. 2. Effect of catalyst loading on yield of product fraction for $\gamma\text{-Al}_2\text{O}_3$ (a) and CaO (b)

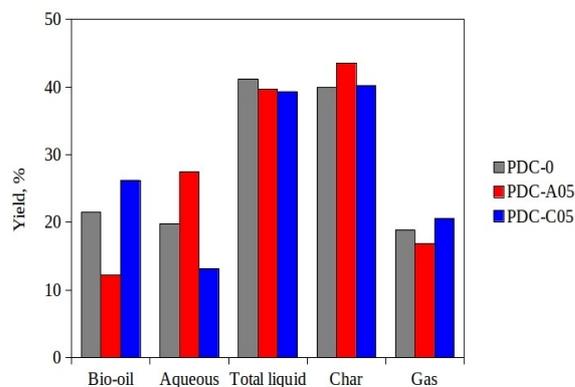


Fig. 3. Comparison of the yield of different fractions from non-catalytic pyrolysis (PDC-0), and catalytic pyrolysis on $\gamma\text{-Al}_2\text{O}_3$ (PDC-A05) and CaO (PDC-C05)

Fig. 4. shows the effect of catalyst used and its loading on the heating value and pH of bio-oil produced. In general, the HHV of bio-oil produced by catalytic pyrolysis were within the range of 36 – 39 MJ/kg, distinctly different from the heating value of PDC-0 that is from non-catalytic pyrolysis, which is 36.79 MJ/kg. These values were higher than HHV of other bio-oils derived from cellulosic biomass, typically lower than 30 MJ/kg (Mortensen et al., 2011). This could be due to high oil content in PDC, as observed for bio-oil produced from soybean oil cake (33.6

MJ/kg) (Şensöz & Kaynar, 2006). These values are also comparable to the calorific value of petroleum fuels, being 47.3, 45.7 and 42.9 MJ/kg for gasoline, diesel oil and heavy fuel oil, respectively (Channiwala & Parikh, 2002). The pH measurement of bio-oils showed that the catalyst affected the acidity of bio-oils. Catalytic pyrolysis over CaO produced bio-oil with high pH value (around 8), while presence of $\gamma\text{-Al}_2\text{O}_3$ decreased pH value of bio-oil. As shown in Fig 4. (b), the pH of bio-oil increased with higher loading of CaO, and decreased with higher loading of $\gamma\text{-Al}_2\text{O}_3$. Since $\gamma\text{-Al}_2\text{O}_3$ is known as acidic, while CaO is basic catalyst, it can be concluded that the acidity-basicity of catalyst influence the pH value of bio-oil produced. However, the pH of bio-oils produced from catalytic pyrolysis of PDC over $\gamma\text{-Al}_2\text{O}_3$ still showed higher pH compared to that of other common bio-oils (pH range 2 – 4) (Mortensen et al., 2011).

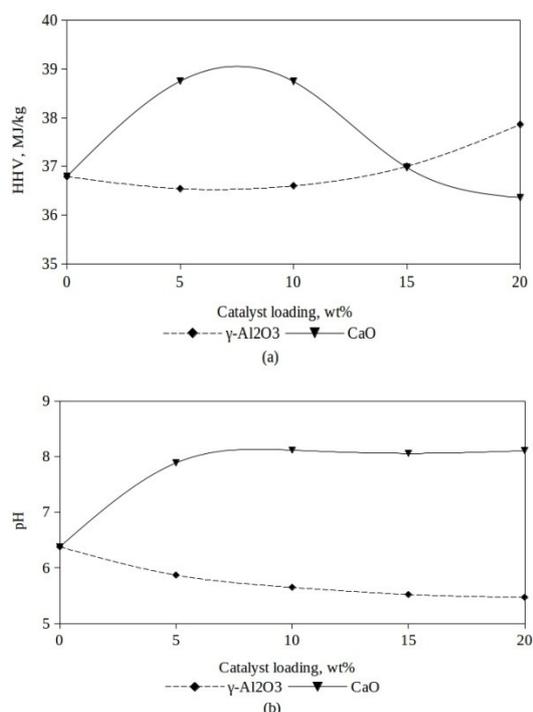


Fig. 4. Effect of catalyst loading on HHV (a) and pH (b) of bio-oil produced

The FTIR spectra of bio-oil are shown in Fig. 5. The presence of water impurities and other polymeric O-H in the oil were indicated by the broad absorbance peak of O-H stretching vibration between 4000 and 3500 cm^{-1} . The presence of alkanes was indicated by the strong absorbance peak of C-H vibrations at 2922 and 2852 cm^{-1} . Vibration at 1707 cm^{-1} represent C=O stretch, indicating the presence of ketones and carboxylic

acids. The presence of aromatics was indicated by the absorbance peaks at 1460 and 721 cm^{-1} . Based on the FTIR spectra, qualitatively all of the bio-oils contained the same functional groups dominated by alkanes. Fig. 6 shows the $^1\text{H-NMR}$ spectra of bio-oil that can be divided into three main regions: aromatic, olefinic, and aliphatic, based on the chemical shifts of specific proton types. The aromatic, olefinic, and aliphatic resonances occur in the chemical shift regions of 9.0–6.0, 6.0–4.0, and 3.0–0.5 ppm, respectively (Uzun, Pütün, & Pütün, 2006). 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. Highest portion of aliphatic proton for bio-oil derived using CaO indicate that the reaction over CaO tend 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 bio-oil derived from $\gamma\text{-Al}_2\text{O}_3$ suggests that the reaction involving carbon backbone occurs due to the acidic nature of the catalyst.

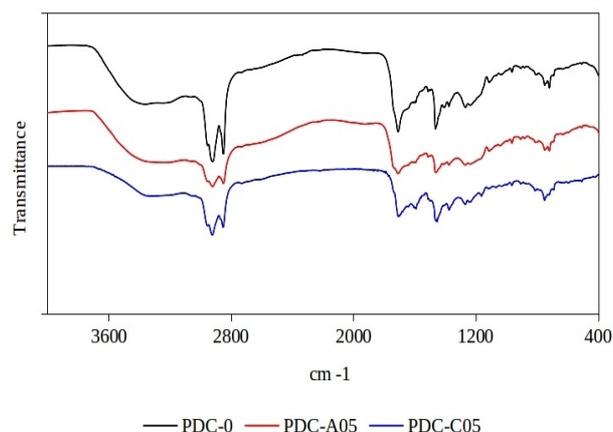


Fig. 5. FTIR spectra of bio-oil produced by non-catalytic pyrolysis (PDC-0) and catalytic pyrolysis (PDC-A05 and PDC-C05)

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

Type of hydrogen	Chemical shift, ppm	Non-catalytic, %area	Catalytic (CaO), %area	Catalytic ($\gamma\text{-Al}_2\text{O}_3$), %area
Aromatic	9.0 – 6.0	10.82	3.78	8.85
Olefinic	6.0 – 4.0	1.44	2.51	5.38
Aliphatic	3.0 – 0.5	85.76	93.20	84.82

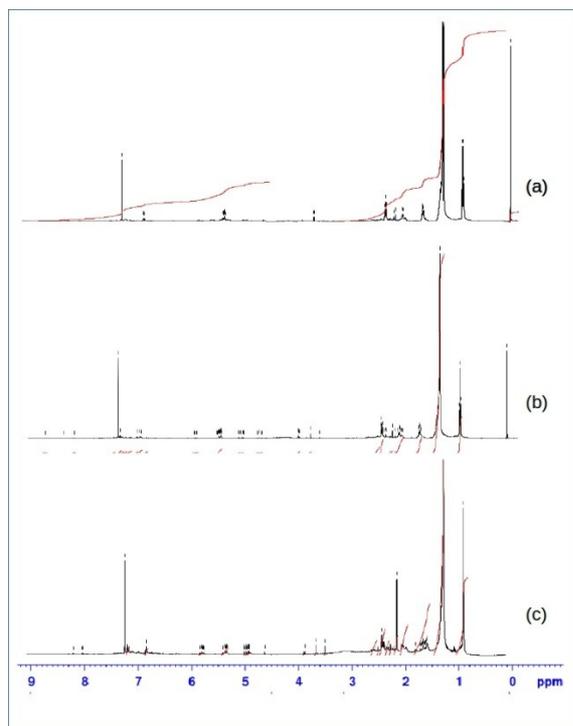


Fig. 6. NMR spectra of bio-oils (a) PDC-0, (b) PDC-A05 and (c) PDC-C05

GC-MS was also employed to identify the chemical compounds present in bio-oil. Fig. 7 shows the chromatograph of bio-oil, while Table 3 provides the major chemical constituents of bio-oils. Major component of PDC-0 was aliphatic hydrocarbon and aliphatic carboxylic acid with number of C atom between 16 and 18 (hexadecanoic acid and octadecanoic acid). This is consistent with the fact that the raw material has high content of fatty acid from crude palm oil. Catalytic pyrolysis over γ - Al_2O_3 catalyst significantly decreased the level of hexadecanoic acid and octadecanoic acid from 34.35 % to 5.00 % and 28.83 % to 7.31 %, respectively. The same phenomenon was also observed in catalytic pyrolysis over CaO catalyst, which has decreased the content of hexadecanoic acid and octadecanoic acid to 6.14 % and 2.01 %, respectively. High content of methyl ester in PDC-C05 indicated that CaO presence in pyrolysis enhanced transesterification reaction of hexadecanoic acid into hexadecanoic methyl ester, while γ - Al_2O_3 enhanced cracking reaction to form smaller molecules.

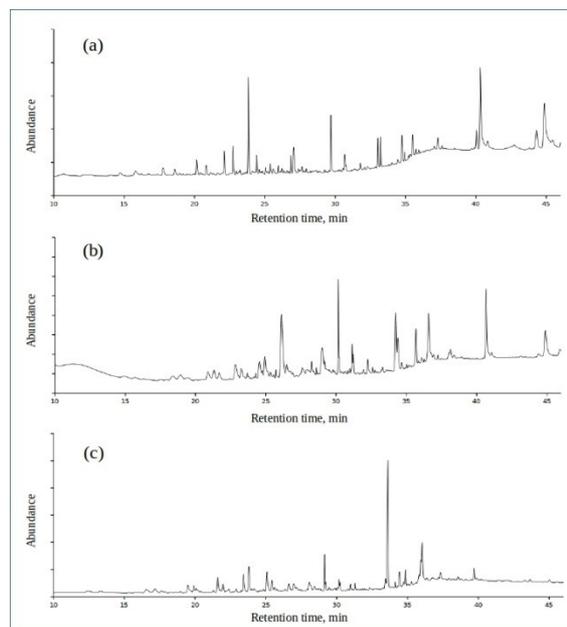


Fig. 7. GC/MS spectra for bio-oils: (a) PDC-0, (b) PDC-A05 and (c) PDC-C05

CONCLUSION

In this study, the effect of CaO and γ - Al_2O_3 addition in vacuum pyrolysis of palm oil decanter cake was investigated. Generally, the presence of the catalyst decreased the yield of bio-oil, except for the addition 5% of CaO where the yield of bio-oil increased from 21.46 % to 26.21%. The HHV of bio-oil from catalytic pyrolysis is higher for CaO but lower for that from γ - Al_2O_3 , except at 20% catalyst loading. The pH value of bio-oil was lower in the presence of γ - Al_2O_3 , while CaO caused increased in pH value. This clearly indicated that the acidity-basicity of catalyst affected the pH of bio-oil produced. The bio-oil composition was primarily comprised of aliphatic structure and alkenes functional groups, according to NMR and FTIR analysis. GC-MS analysis showed significant reduction of octadecanoic acid and hexadecanoic acid by catalytic pyrolysis. CaO caused the amount of hexadecanoic acid methyl ester to increase by seven-fold. It indicated an intensive transesterification reaction occurred during pyrolysis process. This phenomenon was not observed in catalytic pyrolysis over γ - Al_2O_3 . The main advantage of bio-oil derived from palm oil decanter cake is its high calorific value of about 37 MJ/kg, which is close to those of petroleum calorific value, and its pH value that is close to neutral. Thus, bio-oil obtained in this investigation has huge potential

to be used as fuel. It may either be used directly or as an additive to the conventional fuels.

Table 3. Chemical composition of bio-oils determined by GC-MS

Chemical compound	RT, min	% Area		
		PDC-0	PDC-A05	PDC-C05
Tridecane	20.9	0.45	1.04	2.59
1-Tridecene	21.3	-	1.15	1.47
Tetradecane	22.8	0.80	1.88	4.03
2-Tetradecene	23.2	0.75	1.19	1.30
Pentadecane	24.5	2.48	1.58	3.66
Cyclopentadecane	24.9	0.51	1.67	3.71
Cyclohexadecane	26.1	0.30	6.0	6.03
Heptadecane	26.5	0.77	1.03	2.24
8-Heptadecene	27.6	1.75	1.15	1.61
1,2-Cyclopentanedione, 3-methyl	27.9	0.23	1.06	1.61
2,6 Dimethylphenol	29.0	-	2.65	3.04
Phenol	30.1	1.24	3.88	2.35
Phenol, 4-methyl-	31.1	0.54	1.20	1.22
Phenol, 2,6-dimethoxy-	34.2	-	1.42	2.00
Hexadecanoic acid, methyl ester	34.4	2.70	2.09	14.78
Pentadecanenitrile	35.7	2.90	2.72	1.66
Octadecanoic acid, methyl ester	36.7	0.79	2.93	1.89
1,15-Hexadecadiene	36.8	-	1.31	1.82
Homovanillyl alcohol	37.0	0.90	1.21	2.62
9-Nonadecene	37.6	-	1.60	1.82
Tetradecanoic acid	38.1	0.94	3.10	6.33
Hexadecanoic acid	40.7	34.35	5.00	6.14
Octadecanoic acid	44.9	28.83	7.31	2.01
Total % area identified		81.25	75.92	54.16

REFERENCES

- Abu Bakar, M. S., & Titiloye, J. O. (2012). Catalytic pyrolysis of rice husk for bio-oil production. *Journal of Analytical and Applied Pyrolysis*.
- Aho, A., Kumar, N., Eränen, K., Salmi, T., Hupa, M., & Murzin, D. Y. (2007). Catalytic Pyrolysis of Biomass in a Fluidized Bed Reactor. *Process Safety and Environmental Protection*, 85(5), 473–480.
- Azuara, M., Fonts, I., Barcelona, P., Murillo, M. B., & Gea, G. (2013). Study of catalytic post-treatment of the vapours from sewage sludge pyrolysis by means of γ -Al₂O₃. *Fuel*, 107, 113–121.
- Babich, I. V., Van der Hulst, M., Lefferts, L., Moulijn, J. a., O'Connor, P., & Seshan, K. (2011). Catalytic pyrolysis of microalgae to high-quality liquid bio-fuels. *Biomass and Bioenergy*, 35(7), 3199–3207.
- Bertero, M., De la Puente, G., & Sedran, U. (2012). Fuels from bio-oils: Bio-oil production from different residual sources, characterization and thermal conditioning. *Fuel*, 95, 263–271.
- Bridgwater, a. V. (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*, 38, 68–94.
- Bulushev, D. a., & Ross, J. R. H. (2011). Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review. *Catalysis Today*, 171(1), 1–13.
- Carrier, M., Hugo, T., Gorgens, J., & Knoetze, H. (2011). Comparison of slow and vacuum pyrolysis of sugar cane bagasse. *Journal of Analytical and Applied Pyrolysis*, 90(1), 18–26.
- Channiwala, S. A., & Parikh, P. P. (2002). A unified correlation for estimating HHV of solid , liquid and gaseous fuels. *Fuel*, 81, 1051–1063.
- Chavalparit, O., Rulkens, W. H., Mol, a. P. J., & Khaodhair, S. (2006). Options for Environmental Sustainability of the Crude Palm Oil Industry in Thailand Through Enhancement of Industrial Ecosystems. *Environment, Development and Sustainability*, 8(2), 271–287.
- Compton, D. L., Jackson, M. a., Mihalcik, D. J., Mullen, C. a., & Boateng, A. a. (2011). Catalytic pyrolysis of oak via pyroprobe and bench scale, packed bed pyrolysis reactors. *Journal of Analytical and Applied Pyrolysis*, 90(2), 174–181.
- Demiral, I., & Sensöz, S. (2008). The effects of different catalysts on the pyrolysis of industrial wastes (olive and hazelnut bagasse). *Bioresource technology*, 99(17), 8002–7.
- Han, L., Wang, Q., Ma, Q., Yu, C., Luo, Z., & Cen, K. (2010). Influence of CaO additives on wheat-straw pyrolysis as determined by TG-FTIR analysis. *Journal of Analytical and Applied Pyrolysis*, 88(2), 199–206.
- Mortensen, P. M., Grunwaldt, J.-D., Jensen, P. a., Knudsen, K. G., & Jensen, a. D. (2011). A review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General*, 407(1-2), 1–19.
- MPOC. (2011). *Malaysian Palm Oil Council Annual Report 2011*. Kelana Jaya.
- Naik, S. N., Goud, V. V., Rout, P. K., & Dalai, A. K. (2010). Production of first and second generation biofuels: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 14(2), 578–597.
- Pan, P., Hu, C., Yang, W., Li, Y., Dong, L., Zhu, L., Tong, D., et al. (2010). The direct pyrolysis and catalytic pyrolysis of Nannochloropsis sp. residue for renewable bio-oils. *Bioresource technology*, 101(12), 4593–9.
- Samolada, M. C., Papafotica, A., & Vasalos, I. A. (2000). Catalyst Evaluation for Catalytic Biomass Pyrolysis. *Energy & Fuels*, 14, 1161–1167.
- Sensoz, S., & Kaynar, (2006). Bio-oil production from soybean (*Glycine max L.*); fuel properties of Bio-oil. *Industrial Crops and Products*, 23(1), 99–105.
- Shuit, S. H., Tan, K. T., Lee, K. T., & Kamaruddin, a. H. (2009). Oil palm biomass as a sustainable energy source: A Malaysian case study. *Energy*, 34(9), 1225–1235.
- Uzun, B. B., Pütün, A. E., & Pütün, E. (2006). Fast pyrolysis of soybean cake: product yields and compositions. *Bioresource technology*, 97(4), 569–76.
- Wang, D., Xiao, R., Zhang, H., & He, G. (2010). Comparison of catalytic pyrolysis of biomass with MCM-41 and CaO catalysts by using TGA–FTIR analysis. *Journal of Analytical and Applied Pyrolysis*, 89(2), 171–177.
- Yorgun, S., & Simşek, Y. E. (2008). Catalytic pyrolysis of *Miscanthus x giganteus* over activated alumina. *Bioresource technology*, 99(17), 8095–100.
- Zheng, J.-L. (2008). Pyrolysis oil from fast pyrolysis of maize stalk. *Journal of Analytical and Applied Pyrolysis*, 83(2), 205–212.

