Production Of Liquid Biofuel From Sludge Palm Oil (SPO) Using Heterogeneous Catalytic Pyrolysis

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Sludge palm oil (SPO) is waste generated in the palm oil industry. The discharge of SPO together with palm oil mill effluent has created a major problem due to its difficulty in the treatment process. The feasibility of SPO as a raw material for biofuel production was investigated via catalytic pyrolysis process using heterogeneous Malaysian dolomite catalyst. The effects of operating temperatures and reaction times in the catalytic pyrolysis using Malaysian dolomite catalyst were assessed. The condition for the reaction parameters investigated is as followed: operating temperatures of 350 °C, 400 °C, and 450 °C, reaction times of 30, 45 and 60 minutes, under a constant of 100 ml/min of nitrogen flow rate and 5 wt.% catalyst loading. At a reaction temperature of 350 °C the SPO conversion was very low even at longer reaction times. The longer reaction times gave higher SPO conversion at an operating temperature of 400 °C with the range of conversion between 45.7 to 58.3 wt.%. At temperature 450 °C the conversion achieved an average of 93.1 ± 1.0 wt.%. Only a slight change at longer times was observed at this temperature. At a temperature of 400 °C and 45 min of reaction times, the pyro-oil obtained from the process contained the highest hydrocarbon content (83.90 %) and lowest oxygenated compound content (16.10 %), even though the conversion was lower than at 450 °C. The product selectivity was highest in the diesel range at the reaction temperature of 400 °C. Thus, with further improvement in catalyst modification together with optimized operating conditions, SPO can be used as a feedstock in the catalytic pyrolysis for producing biofuel in the range carbon number of diesel, gasoline and kerosene.

Keywords: Sludge Palm Oil (SPO), Pyro-oil, Malaysian Dolomite Catalyst, Biofuel

1. Introduction

For today's production of the biofuel industry, the main concern toward this production is the impact that petroleum-based diesel makes on the environment. With the increase in fuel prices and gradual diminishing of petroleum reserves and the raising of public awareness of the environmental impact of using petroleum-based diesel, concerns about the need for alternative renewable fuel such as liquid biofuel have been fast-tracked, it becomes the driving forces behind the upsurge interest towards liquid biofuels productions. Liquid biofuels are energy sources made from grown biomass and it is renewable as they are continually replenished. It can be used in existing diesel engines, and as it does not contain sulfur, SOx will not be emitted. Besides that, it can reduce emissions of hydrocarbons (HCs), CO, and black smoke due to achieving complete combustion and higher flash point [1]. Bioenergy derived from biomass is of particular interest due to its potential for mass production within a relatively short period

of time and because of its carbon-neutral, renewability and biodegradability that can mitigate the environmental effect raised by the use of fossil fuel.

For the production of liquid biofuels, usually, the feedstocks are taken from food biomass such as vegetable oils and non-food biomass [2, 3]. Presently, the liquid biofuel industry desires vegetable oils such as crude palm oil (CPO) and soybean oil. However, due to the cost of feedstock and limited availability of edible vegetable oils, it always becomes critical issues for biofuel production [4]. Therefore, biodiesel production from waste oil and post-consumer fat and oil such as waste cooking oil is sought after.

Sludge palm oil (SPO) is waste oil that is recovered from palm oil mill production which contributed to low milling efficiency. SPO is a floating residual oil contained in the initial stage of palm oil mill effluent (POME), which is separated before the discharge of POME to the open pond. The SPO contains a small amount of oil that fails to be extracted as CPO together with the oil that leaches out from various stages during the milling process, particularly in the sterilizer and sludge separator [5]. It will be collected in a sludge pit and the oil will end up as poor-quality oil with a concentration around 4000-9000 ppm [6]. In the conventional method, they use hot water to leach out the oil, which also explains the large consumption of water resources for milling processes and the concomitant large production of wastewater [7]. Malaysia currently is the world's second-largest producer of palm oil accounting for 39% of world palm oil production and 44% of world export. With the growing global needs, it is expected that around 18 million tonnes of palm oil are produced per year, and most of it is exported to other countries. Thus, SPO has higher availability as around 2% of total palm oil production is the amount of SPO generated from the process [8]. There are similarities between SPO and vegetable oils as they are composed of triglycerides and long-chain carbon fatty acids, however, SPO is considered a third-grade oil due to its high free fatty acid (FFA), high moisture and impurities contents [9]. Theoretically, the FFA content of palm sludge oil is usually between 33-37% and several FFA are palmitic acid, C16:0 (49.11 %), oleic acid, C18:1 (36.93 %), linoleic acid, C18:2 (98.31 %) and stearic acid, C18:0 (3.76 %) [10]. A similar result was shown in two studies done by Hayyan et al. [11] and Thinagaran et al. [12] in which the highest fatty acids found in the composition of SPO were palmitic (42-64 %), oleic acid (14-39 %), stearic acid (4-9 %) and linoleic (2-9 %). The SPO is more saturated than vegetable oil causing it to be retained in the solid phase at room temperature and categorised under sludge oil as it exhibits high free fatty acids (FFA) and very low deterioration of bleachability

index (DOBI) values. Therefore, SPO is sold at discounted 40-60% of CPO's price. Consequently, the use of SPO can significantly lower the biodiesel production price hence SPO itself presents a promising alternative resource and be a great substitute for the biofuel production's feedstock [11].

Basically, biodiesel comprises fatty acid methyl esters (FAMEs), which are produced by the transesterification of triacylglycerol (TGs), the main component of fats and oils with methanol or ethanol, in the presence of a basic catalyst to chemically break the molecule of the raw bio-oil into methyl or ethyl esters of the bio-oil with glycerol as a by-product [1, 13]. Due to higher free fatty acids in feedstock, esterification is usually conducted with the same alcohols in the presence of an acidic catalyst to lower the free fatty acids of the raw feedstock [14]. The transesterification process has some drawbacks as fatty acid methyl ester (FAME) biodiesel usually requires blending with petroleum diesel fuel to give a partially renewable fuel which is not economically attractive [15]. Blending is required as FAME has many undesirable physical-chemical properties relative to petroleum diesel. According to previous researchers [16–18], the FAME produced from the transesterification process has low energy density, higher viscosity, high cloud point, poor storage stability, high emissions of NOx and a tendency to form deposits in the fuel injection systems. Apart from that, this process is not favourable due to its relatively higher oxygenated content in the final product. It is less stable and can cause serious damage to the engine plug, filter, and corrosion to the metal part of the process engine [19, 20].

Therefore, pyrolysis has been examined as an attractive alternative technology applied for the conversion of waste to biofuel production [21]. The pyrolysis or cracking of vegetable oils or animals fats consists of the thermal decomposition of triacylglycerides in the absence of oxygen to degrade biomass into liquid (bio-oil), gaseous and solid (char) fractions where different pyrolysis conditions will lead to different yields of products. With the presence of catalysts in the pyrolysis process, it will result in a complex mixture of hydrocarbons, mostly consisting of linear chains [22]. The removal of oxygen from the triglyceride from the catalytic pyrolysis will obtain a high-grade fuel product that provides a wide range of biofuels with lower oxygen content not only in the range of gasoline and diesel but also in the range of fuel oil or kerosene [4, 23]. Apart from that, the elimination of the oxygenated compounds improves its stability and enhances its utilization potential. To achieve high conversion in liquid fuel products, it is strongly dependent on the properties of the catalyst due to its ability

to provide sites that promote the cracking of the feedstock chain. Catalytic pyrolysis reduces the oxygen content of liquid fuel and increases the calorific value in comparison with thermal pyrolysis [24]. However, this NiO-Malaysian dolomite catalyst has not been tested in the catalytic pyrolysis reaction of SPO. Nickel-dolomite catalyst was prepared using the precipitation method of metal-doped calcined Malaysian dolomite [25, 26]. As reported by Hafriz et al. [26], NiO-CMD catalysts have been considered for deoxygenation reaction (main reaction of oxygen removal), owing to promising chemical and textural properties which are as follows: greater textural mesoporosity creating more pathways of deoxygenation reaction to occur, synergistic effects of bi-functional acid-base (NiO-CaO/MgO) properties, whereas the addition of NiO species promotes acidic site in the catalyst system and high adsorption for hydrocarbon storage with strong resistance to deactivation which favours cracking of the waste cooking oil. Herein, in this study, efficient reaction parameters towards SPO catalytic pyrolysis using NiO-Malaysian dolomite catalyst were further investigated. The yield of pyro-oil, as well as the selectivity of the hydrocarbon fuel produced from the SPO catalytic pyrolysis, was evaluated.

2. Experimental setup

2.1. Materials

Raw sludge palm oil (SPO) was acquired from a local palm oil mill factory, Felda Palm Industries Sdn Bhd, Kelantan, Malaysia and the oil was filtered and centrifuged at 6000 rpm for 30 minutes to remove any impurities. The oil was stored at 4 °C and was preheated in an oven at 80 °C overnight prior to use. The free fatty acid of the SPO was evaluated via titration method with a content of 11.23 %. Industrial nitrogen gas was supplied by Smart Biogas Sdn. Bhd.

2.2. NiO-Malaysian dolomite catalyst synthesis by precipitation

NiO-Malaysian dolomite catalyst was synthesized by using the liquid-liquid blending precipitation method. Calcined Malaysian Dolomite (14 g) was dispersed into 100 ml of deionized water at 60 °C with continuous stirring and an appropriate amount of $Ni(NO_3)_2.6H_2O$ was dissolved in 10 ml of deionized water. $Ni(NO_3)_2.6H_2O$ solution was then added drop-wise into calcination Malaysian dolomite suspension with stirring at 60 °C for 4 hours. The precipitated product was washed with deionized water and obtained by filtration using filter paper. The obtained product was dried at 120 °C overnight and further calcined at 900 °C for 4 hours.

2.3. Catalytic pyrolysis of sludge palm oil

The pyrolysis of SPO was executed in a laboratory-scale fractionated cracking system as shown in Fig. 1. In the system, three mouthed round bottom flask was connected to a 44 cm condenser, thermocouple and industrial nitrogen gas cylinder. The temperature was controlled and heated by an integral magnetic stirring mantle. Prior to the pyrolysis reaction of SPO, 150 g of SPO was loaded into the bottom flask reactor together with nickel-dolomite catalyst (5 wt.% based on the weight of SPO) was stirred together by the integral magnetic stirring mantle. Before the reaction was started, nitrogen gas was purged at a rate of l00 ml/min for 10 minutes to remove all oxygen and air in the system and the reaction temperatures of 350 °C, 400 °C and 450 °C were chosen. The reaction was started by a continuous flow of nitrogen gas, and the reaction temperature was kept constant for 30 minutes after the desired temperature was achieved. The liquid and gaseous product left the bottom flask reactor. The liquid product was condensed in a condenser with a room temperature of water flowing through it and collected in a collected flask. The liquid product contains pyro-oil and soap has been separated using filter paper. Meanwhile, the gaseous product was released from the reaction system without further analysis. The gaseous weight was estimated through mass balance when the feedstock, catalyst used, pyro-oil, and by-product (such as acid phase, soap, coke, or the remaining unreacted oil) were determined and weighed. The effect of several reaction times on pyrolysis of SPO was carried out by using temperatures with the highest yield of pyro-oil. The reaction times were varied at 30, 45 and 60 minutes while nitrogen gas was kept flowing at 100 ml/min, fixed stirring rate and the same catalyst loading (5 wt.% based on the weight of SPO). Once the optimum temperature was reached, the reaction time was started and the respective amount of the liquid product and residual oil-coke were measured by using mass balance Eqs. (1) to (3):

Yield of pyro-oil $(wt.\%) =$
(Weight of pyro-oil)/(Total weight of SPO) $\times 100\%$ (1)

$Coke(wt.\%) =$
(Weight of $(w_1 - w_2)$)/(Total weight of SPO) $\times 100\%$ (2)

Conversion SPO$(wt.\%) =$
(Weight of (SPO-coke))/(Total weight of SPO) $\times 100\%$ (3)

Where w_1 is the residue in the bottom flask reactor after the reaction which includes catalyst after use, coke formation

and some amount of unreacted oil and w_2 is the weight of catalyst before the reaction.

2.4. Second fractional distillation

The pyro-oil collected from the pyrolysis of SPO was further investigated by the changes in the amount of hydrocarbon and total oxygenated compound (improve selectivity at a certain temperature) produced after the second stage of the fractional distillation process. The set-up for the process was similar to the pyrolysis of SPO and the operating parameters were set as reaction temperature of 200 °C, nitrogen gas flow of 100 ml/min and reaction time of 45 minutes. For this stage, no catalyst was added, and the feed from the highest yields of pyro-oils from the first stage of catalytic pyrolysis of SPO was used.

2.5. Chemical analysis of pyro-oil

The composition of pyro-oil from the first stage and second stage of fractional distillation was analysed using Gas Chromatography-Mass Spectrometry (GC-MS). The analysis was accomplished in a non-polar ZB-5MS column (30 m × 0.25 mm I.D × 0.25 μm film thickness) in a split mode using Helium as carrier gas which flowed at 3.0 mL/min and the injector temperature was set at 250 °C. The oven temperature was held at 40 °C for 3 min, ramp at 7 °C/min to 300 °C and held at 300 °C for 5 min. Total product yield and product selectivity were determined by comparing the peak area in percentage (%) of obtained spectra presented [25]. It is calculated based on Eqs. (4) and (5):

$$\text{Product yield } (\%) = $$
$$(\text{Area of } C_8 - C_{24})/(\text{Total area of product}) \times 100\% \quad (4)$$

Product selectivity (%) =
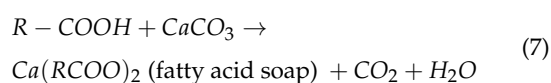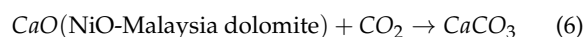(Area of desired product)/(Total area of product) × 100%
$$(5)$$

3. Result and discussions

3.1. Catalytic Pyrolysis of SPO

3.1.1. *Effect of temperature*

The effect of temperatures in catalytic pyrolysis of sludge palm oil (SPO) was investigated by varying the reaction temperatures. The optimum temperature was determined by calculating the highest yield of pyro-oil from each pyrolysis process. Based on product distribution in Fig. 2, the product distribution of SPO generated at a temperature of 450 °C gave the highest conversion (92.14 wt.%) followed by 400 °C (45.74 wt.%) > 350 °C (14.24 wt.%). The yield of liquid products was in the order of temperature 450 °C (72.66 wt.%%) > 400 °C (35.36 wt.%) > 350 °C (4.00 wt.%).

Even though the liquid product at 450 °C (reaction time; 30 minutes) was higher, the formation of soap was rapidly increased by 7 times as compared to the reaction at 400 °C and it gave an effect on the yield of the pyro-oil produced. The formation of soap (fatty acid salt) as shown in Fig. 3 was caused by a side reaction of hydrolysis (saponification) of fatty acid with the base catalyst used during the pyrolysis process [25]. During the lignin pyrolysis process using various kinds of potassium salts conducted by Yang et al. [26], K_2CO_3 and KOH were found to react with phenolic hydroxyl groups to form organic-K salts or soap. As reported by Hafriz et al. [25], the calcium carbonate ($CaCO_3$) was generated during the absorption of carbon dioxide (CO_2) by calcium oxide (CaO) due to the high formation of CaO composition in calcined Malaysian dolomite as shown in Eq. (6). Based on Eq. (7), oxygenates such as carboxylic acid (RCOOH) were speculated to have reacted with calcium carbonate ($CaCO_3$) in producing fatty acid soap ($Ca(RCOO)_2$). At a reaction temperature of 450 °C the high temperature will increase the rate of collision between reactant molecules of SPO with the catalyst and it will increase the possibility of high formation of soap (34.12 %) in this reaction.

$$CaO(\text{NiO-Malaysia dolomite}) + CO_2 \rightarrow CaCO_3 \quad (6)$$

$$R - COOH + CaCO_3 \rightarrow$$
$$Ca(RCOO)_2 \text{ (fatty acid soap) } + CO_2 + H_2O \quad (7)$$

Meanwhile, the coke formation at the end of the reaction was greater at 350 °C (85.75 %) due to less conversion of SPO in the catalytic cracking affecting the product distribution. The coke formation was suspected to be higher due to some amount of unreacted SPO in the reactor resulting from the temperature being too low for the conversion of SPO to take place.

3.1.2. *Effect of reaction time*

The effects of several reaction times on pyrolysis of SPO were carried out by using temperatures with the highest yield of pyro-oil. Based on Fig. 2, temperatures at 400 °C and 450 °C were chosen for the reaction process and the reaction took place for 30, 45 and 60 minutes. Based on the result in Fig. 2, the conversion of SPO remained higher at 450 °C than 400 °C even after prolonged reaction time. The liquid product obtained at 450 °C showed a slight increase from 30 minutes reaction times and remained the same at 45 and 60 minutes. The pyro-oils obtained at 450 °C also increase as the times increased giving 38.54 wt.% (30 minutes) < 57.32 wt.% (45 minutes) < 66.64 wt.% (60 minutes). Double the reaction times resulted in almost doubled the percentage of pyro-oil obtained. At a lower temperature of 400 °C, only a slight change was observed. The
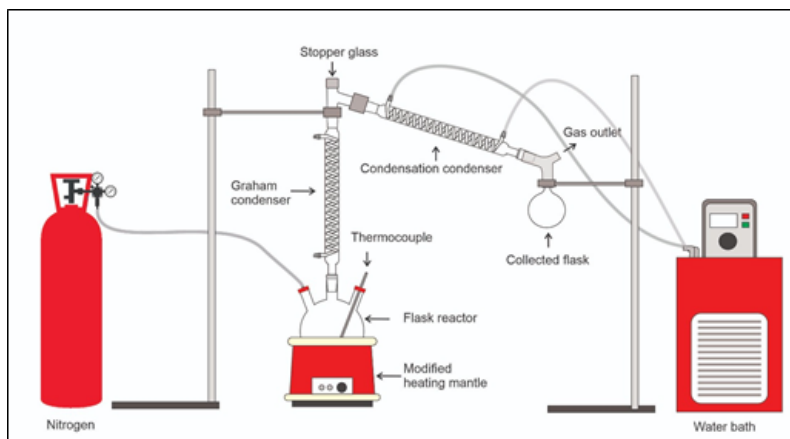
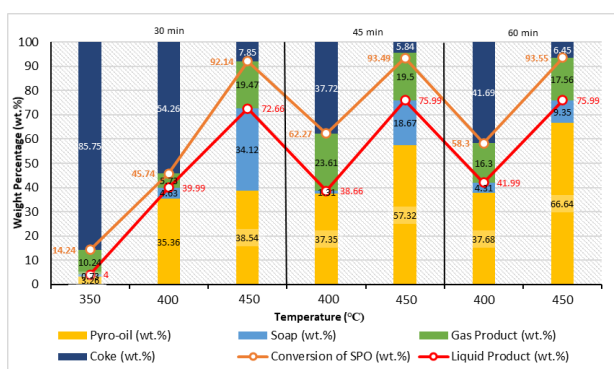**Fig. 1.** A laboratory-scale fractionated cracking system.

Fig. 2. Pyrolysis of SPO product distribution at various reaction times and temperatures (N$_2$: 100 ml/min, 5wt.% Nickel dolomite catalyst: 150g SPO).
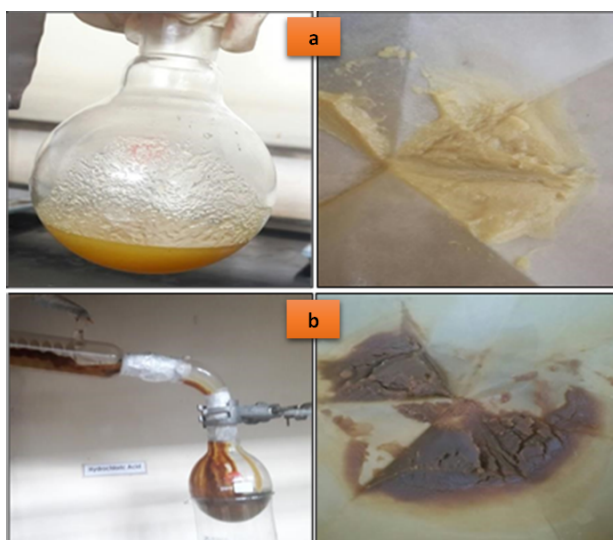

Fig. 3. The soap formation after catalytic pyrolysis of SPO using NiO-Malaysian dolomite catalyst at a) 400 °C and b) 450 °C.

pyro-oil obtained was only increased from 35.36 wt.% (30 minutes) to 37.68 wt.% (60 minutes). A higher temperature was needed to have better cracking of the feedstock in the catalytic pyrolysis process [25]. For reaction temperature at 400 °C, 45 minutes showed to be the potential reaction time meanwhile, 60 minutes reaction time was likely for 450 °C. Both reaction times gave higher conversion of SPO, a greater yield of pyro-oil and a smaller amount of soap and coke formation. The increase of gas product at 350 °C could be due to condensation efficiency resulting in a low yield of pyro-oil as compared to a reaction temperature of 400 °C The study showed that with the aid of 5 wt.% NiO-Malaysian dolomite catalyst in the catalytic pyrolysis of SPO, higher pyro-oil was generated at 400 °C(35.36 wt.%). However, as reported by Thangalazhy-Gopakumar et al. [27], though no catalyst was added in the pyrolysis of sludge palm oil, the pyro-oil yielded was quite high with 27.4 wt.% owing to the high operating temperature used at 550 °C

3.2. Chemical Analysis of Pyro-oil

3.2.1. Composition of liquid hydrocarbon and oxygenated compound

The data shown in Table 1 was the composition of pyro-oil which comprises alkanes, alkenes, diene, alkyne, cycloalkane, cycloalkenes and aromatic group. Meanwhile, the composition of oxygenated compounds includes ester, carboxylic acid, ketone, alcohol and others. The high amount of oxygenated compound especially carboxylic acid gives a higher acid value to the biofuel. The higher acid value has a large effect on the corrosion value, cold filter plugging point and freezing point of pyrolysis oil [28].

The presence of alkanes and alkenes in pyro-oil proves that the deoxygenation reaction is possible to occur in catalytic pyrolysis of SPO as shown in Fig. 4. As reported by

Table 1. Composition of pyro-oil at different temperature (reaction time: 30 minutes, N_2: 100 ml/min, 5wt.% Nickel dolomite catalyst: 150g SPO).

| Pyro-oil Composition / Temperature (°C)	350	400	450
Total Hydrocarbon Product (%)	*63.86*	*83.90*	*74.48*
Alkanes (%)	**37.41**	**43.70**	**19.07**
Alkenes (%)	**22.41**	**35.66**	**49.31**
Diene (%)	0.19	0.24	1.00
Alkyne (%)	0.30	1.80	0.71
Cycloalkane (%)	3.12	2.15	2.68
Cycloalkene (%)	0.08	0.19	1.70
Aromatic (%)	0.34	0.17	0.00
Total Oxygenated Product (%)	*36.14*	*16.10*	*25.52*
Ester (%)	2.63	0.46	0.36
Carboxylic Acid (%)	21.95	6.28	3.19
Ketone (%)	4.02	3.76	14.96
Alcohol (%)	7.27	5.55	7.01
Others (%)	0.27	0.00	0.00
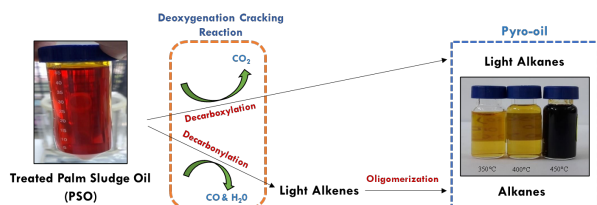
Fig. 4. Deoxygenation reaction in catalytic pyrolysis of SPO using NiO-Malaysian dolomite.

Oi et al. [29], there are various mechanisms for deoxygenation reaction to be occurred in the green organic synthesis using TiO_2 catalyst such as decarboxylation that removes carboxyl groups to yield paraffin (alkanes) and CO_2 and decarbonylation that yields olefins (alkenes), CO and water as a by-product. Based on Faten et al. [30] and Hafriz et al. [31], the decarboxylation reaction would eliminate the carbonyl group by releasing CO_2 to produce light alkanes, while the decarbonylation reaction would remove the carbonyl group in neutral lipids to produce light alkenes by releasing CO and by-product of H_2O. Then the light alkenes were undergone oligomerization to form alkanes.

Based on the result presented in Table 1, pyro-oil produced at 400 °C shows a high amount of total hydrocarbon (83.90 %) and a lower oxygenated compound (16.10 %). Even though the conversion of SPO at 450 °C was the highest, a lower total hydrocarbon (74.48 %) and higher amount of oxygenated compound (25.52 %) were obtained. Similarly, at temperatures of 350 °C, the amount of hydrocarbon was the lowest (63.86 %) giving the highest amount of oxygenated carbon (36.14 %). This indicates that pyro-oil at 350 °C was the least favourable not only due to poor conversion and lower total hydrocarbon content but also due to the high amount of carboxylic acid in the pyro-oil, resulting

in higher acid value on the product fuel. The higher acid value has a large effect on the corrosion value, cold filter plugging point and freezing point of pyro-oil [24]. Based on the composition profile of hydrocarbon in Table 1, the presence of straight alkanes at a reaction temperature of 400 °C was higher at 43.70 %. As compared to the higher temperature of 450 °C the amount of alkanes was reduced (19.07 %) yet giving higher alkenes composition (49.31 %). Meanwhile, a higher amount of soap formation was found related to the amount of ketones. By comparing Fig. 3 and Table 1, it shows that catalytic pyrolysis of SPO at 450 °C with 30 minutes reaction time generated the highest soap formation in the liquid product (34.12 %) due to higher ketones content (14.96 %) whereas the operating temperature of 400 °C yielded the lowest amount of ketone (3.76 %).

3.2.2. Product selectivity

The analysis of carbon distribution could be obtained from GC-MS analysis and the selectivity in SPO derived pyro-oil at various temperatures could also be calculated. The selectivity of the pyro-oil product was determined by the range of hydrocarbon. The carbon distribution for all pyro-oil in different reaction temperatures was in the range of C_8-C_{24}. From Fig. 5, the hydrocarbon product generated from different reaction temperatures was more favoured in the diesel range (C_{14}-C_{20}). At 400 °C reaction temperature, it exhibited high degree of selectivity (68.11 %) of diesel fraction compared to 450 °C (52.52 %) and 350 °C (49.79 %). This was likely due to the 400 °C reaction temperature producing more hydrocarbon than 350 °C and 450 °C. The selectivity for gasoline fractions (C_8-C_{12}) were in the following sequences: 16.92 % (450 °C) > 13.38 % (350 °C > 12.15 % (400 °C). Meanwhile, for kerosene fraction (C_{11}-C_{13}), the selectivity was in the order of 11.92 % (450
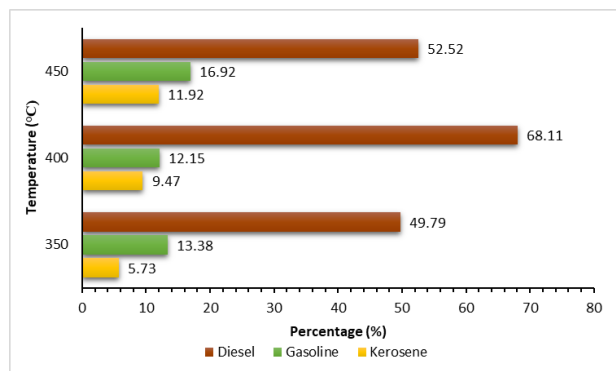
Fig. 5. Product selectivity in liquid hydrocarbon at different temperatures.

°C) > 9.47 % (400 °C) > 5.73 % (350 °C).

3.3. Second Stage Fractional Distillation

3.3.1. *Composition analysis before and after second fractional distillation*

Pyro-oils generated from temperatures 400 °C and 450 °C were selected for second fractional distillation (temperature: 200 °C time: 45 minutes, nitrogen flow: 100 ml/min, no catalyst) due to higher conversion of SPO and higher composition of hydrocarbon as shown in Fig. 6. Based on Table 2, the compositions of hydrocarbon after the second fractional distillation were slightly increased leading to a slight reduction in the total oxygenated compounds at both reaction temperatures. For pyro-oil generated at 400 °C, the comparison of total hydrocarbon before and after the second fractional distillation was 83.90 % to 84.06 %, and at 450 °C, the amount was 74.48 % to 77.60 %, respectively. At a high temperature of 450 °C the oligomerization of alkenes compound to form alkanes compound could be observed by an increase of alkanes compound and a decrease of alkenes compound after second fractional distillation. Even though only a trivial increment was observed, it still demonstrated that second fractional distillation helped to increase hydrocarbon content in the pyro-oil and it was possibly due to further cracking as a result of secondary reaction leading to a decrease mainly in alcohol fraction in both reactions temperatures.

3.3.2. *Product selectivity before and after fractional distillation*

The product selectivity for both reaction processes exhibited some changes possibly due to the increase in hydrocarbon contents after the second fractional distillation. As displayed in Fig. 7, the range of diesel hydrocarbon (C_{14}-C_{20}) was higher after the second fractional distillation and could be contributed by the decrease of the oxygenated compound during the reaction process. For pyro-oil pro-
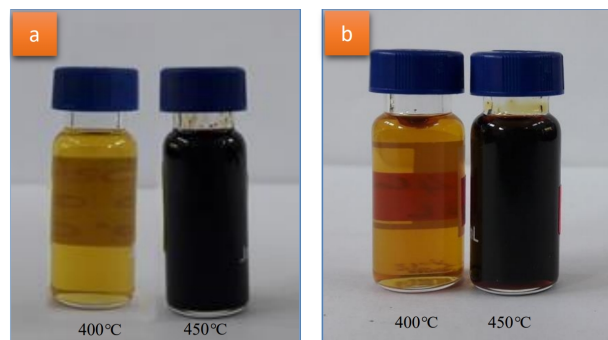

Fig. 6. Pyro-oil a) before and b) after second fractional distillation process.
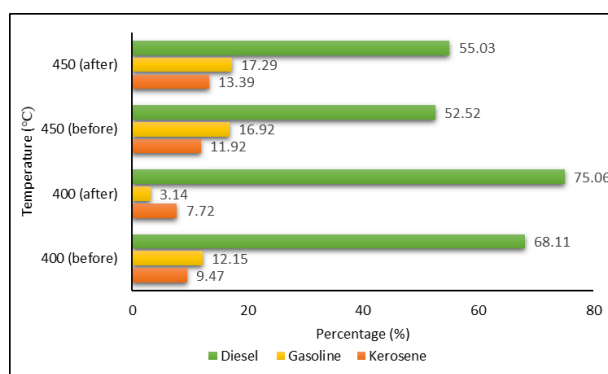

Fig. 7. Product selectivity in liquid hydrocarbon at different temperatures before and after second fractional distillation.

duced at a temperature of 400 °C, the diesel range was increased to almost 7.0 % while it was a 2.5 % increase for pyro-oil produced at 450 °C. Although this study proved that second fractional distillation could lessen the amount of oxygenated compounds, it could be said that there was no significance in doing this study as the changes in the amount of oxygenated compounds were relatively small.

4. Conclusions

Pyro-oil from the process of catalytic pyrolysis of palm sludge oil showed good potential as a biofuel and it proves that SPO was potentially to become alternative raw material for biofuel production. Based on the effect of reaction temperature and reaction times, such results indicated that pyro-oil generated from SPO catalytic pyrolysis at 400 °C and 45 minutes gave the best results due to higher hydrocarbon content (83.90 %) and the lowest oxygenated compound (16.10 %) with higher content of diesel range (68.11 %). Apart from that, it also had a lower amount of soap formation due to the lower value of ketones (3.76 %) and slightly higher carboxylic acid (6.28 %) than that off at 450

Table 2. Composition of pyro-oil at different temperature before and after second fractional distillation.

Pyro-oil Composition / Temperature (°C)	400	400	450		450
Product Composition	**Before**	**After**	**Before**		**After**
Total Hydrocarbon Product (%)	*83.90*	*84.06*	*74.48*		*77.60*
Alkanes (%)	43.70	42.64	**19.07**	→	**35.55**
Alkenes (%)	35.67	36.56	**49.32**	→	**37.67**
Diene (%)	0.20	0.26	1.00		0.73
Alkyne (%)	1.80	1.11	0.71		1.03
Cycloalkane (%)	2.16	2.28	2.68		1.68
Cycloalkene	0.20	1.09	1.70		0.89
Aromatic (%)	0.17	0.12	0.00		0.00
Total Oxygenated Product (%)	*16.10*	*15.94*	*25.52*		*22.40*
Ester (%)	0.46	0.38	0.36		0.31
Carboxylic Acid (%)	6.28	8.51	3.19		3.41
Ketone (%)	3.76	4.15	14.96		15.28
Alcohol (%)	5.60	2.74	7.01		3.40
Others (%)	0.00	0.16	0.00		0.00

°C. In the second fractional distillation process, the changes in the amount of hydrocarbon and oxygenated compound produced were smaller at the reaction temperature of 200 °C however, it improved the amount of saturated hydrocarbon (alkanes) by oligomerization of alkenes compounds in pyro-oil.

Acknowledgements

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