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Original Article

Using reactive distillation for upgrading bio-oil from co-pyrolysis of palm kernel shell and palm empty fruit bunches

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Abstract

Due to the poor physical properties of raw bio-oil from pyrolysis, in this work reactive distillation was used to upgrade vaporized bio-oil from selected co-pyrolysis of palm kernel shell and palm empty fruit bunches at 75%/25% mixing ratio by using 10%Ni/HZSM-5 catalyst and ethanol at various reboiler temperatures. In the pyrolysis process, the feed temperature (bio-oil vapor and non-condensable gas) was in the range between 35 and 230 °C. The reboiler temperature not only influenced the separation of heavy oil from raw bio-oil, which would help minimize catalyst deactivation, but also possibly affected contact time of reactants with catalyst via the residence time. The vaporized bio-oil was upgraded by esterification and acetalization reactions producing levulinic acid ethyl ester, nonanoic acid ethyl ester, and 1,1-diethoxyethane. The physical characteristics density, kinematic viscosity, water content, and pH were improved from those of the raw bio-oil.

Keywords: reactive distillation, co-pyrolysis, palm kernel shell, empty fruit bunches, upgrading bio-oil

1. Introduction

It is known that the greenhouse gas (GHG) emissions from fossil fuel combustion contribute to climate change, air pollution, and to human health risks (Perera, 2018). Combustion of biomass or biofuel is an alternative to address this problem.

Biofuel oil can be produced by pyrolyzing biomass in the absence of oxygen. Pyrolysis is of great interest as quality and selectivity of product could be easily controlled by regulating the processing parameters (Amin, Chetpattana nondh & Ratanawilai, 2019). Biofuel oil is typically used in furnaces, boilers, and gas turbines (Zheng & Kong, 2010). In Thailand, especially in the south, an attractive sustainable biomass feedstock for biofuel production is the wastes generated by the palm oil industry. Theses wastes include palm kernel shell (PKS), empty fruit bunches (EFB), palm tree trunks, and mesocarp fiber from the fruit. EFB is the largest component of solid wastes from fresh oil palm fruit bunches (Chang, 2014). EFB has a high content of volatile matter, contributing to a high yield of bio-oil with a high calorific value (Ruengvilairat, Tanatavikorn, & Vitidsant, 2012), while PKS has the highest lignin content (Shivastava, Khongphakdi, Palamanit, Kumar, & Tekasakul, 2020). Decomposition of lignin provides phenol and phenolic compounds such as catechol, syringol and guaiacol, which can be used as feedstocks to produce resins, adhesives and plasticizers (Azadi, Oliver, Inderwildi, Farnood & King, 2013). Furthermore, it can be converted to aromatic hydrocarbons (Rezaei, Shafaghat & Daud, 2014). However, PKS has a higher cost than EFB. Using a mixture of PKS and EFB as feedstock for bio-oil should be considered.

Unfortunately, the bio-oil from biomass cannot be directly used as vehicle fuel due to its high content of oxygenated compounds, low heating value, high water content, strong corrosiveness, and instability (Czernik & Bridgwater, 2004). The high molecular weight compounds in bio-oil are the cause of these problems, causing catalyst deactivation and deposits on equipment surfaces. The use of reactive distillation (RD) could avoid or minimize catalyst deactivation (Praveen, Lakshmi, Ganesh & Mahajani, 2015). In addition, this technique also benefits from the combination

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of catalytic chemical reactions and undesired product separation in a single unit. There are many studies of bio-oil upgrading by reacting the bio-oil with various types of alcohol and acid catalysts. Results show that acidic compounds are significantly reduced by esterification reactions, and water is partially removed from the bio-oil (Junming, Jianchun, Yunjuan & Yanju, 2008; Mahfud, Melia´n-Cabrera, Manurung & Heeres, 2007; Wang, Hu, Chen, Lv & Jia, 2013). In the RD process, the reboiler temperature is an important parameter to select for the desired reactions. Commonly, the reboiler operating temperature is in the range 80-120 °C in which esterification and transesterification reactions can occur. Higher temperatures lead to decreased product purity (Akkaravathasinp, Narataruksa & Prapainainar, 2019) and promote undesired reactions such as saponification (Prasertsit, Mueanmas & Tongurai, 2013).

The HZSM-5 catalyst (Zeolite Socony Mobil-5) is widely used for upgrading pyrolysis of bio-oil through deoxygenation reactions, because it has several advantages including high yield of hydrocarbons, low coke formation, no hydrogen gas requirement and operation under atmospheric pressure (Liu *et al.*, 2017). Besides, modification of HZSM-5 with nickel metal enhances stability and activity for deoxygenation reactions (Ma *et al.*, 2017; Liu *et al.*, 2017; Yung *et al.*, 2016). Ethanol is an alcohol mainly produced from agricultural materials or waste, such as corn, sugarcane and molasses. It is widely used as a reactant to increase the cracking of bio-oil (Wang, Wang, Cai, & Guo, 2014) and can also be an additive in a transport fuel (Ma *et al.*, 2017). Furthermore, the stability of reactive compounds in bio-oil is effectively improved (Zhang, Yin, Mei, Liu, & Yu, 2016).

However, there are only a few studies focusing on simultaneous upgrading of pyrolysis vapors by using RD. Therefore, the purpose of this work was to study the possibility of using RD to upgrade bio-oil from pyrolysis of the selected co-feeding of PSK and EFB. It could be beneficial in terms of reduction of energy consumption (Huang, Hsu, Hou & Kuo, 2018) and a high temperature of bio-oil vapor may favor catalytic reactions in upgrading bio-oil. The influence of reboiler temperature on upgrading bio-oil was investigated.

2. Materials and Methods

2.1 Raw material preparation and characterization

The empty palm fruit bunches (EFB) and palm kernel shells (PKS) were provided from the Krabi oil palm farmer cooperative federation limited (Thailand). EFB was ground and sieved to 1 cm particle size and PKS was pulverized and sieved to 2-4 mm particle size. These sizes of the raw materials were different from each other due to equipment limitations. All raw materials were dried in an oven at 105 °C for 24 hrs before each experiment.

The ultimate analysis of EFB and PKS was carried out by using a CHNS/O analyzer (Thermo Quest; FlashEA 1112, Italy) to analyze the elemental contents of carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S). Proximate analysis was used to measure moisture content, volatile matter, fixed carbon and ash content according to ASTM E1131 standard methods by using a Thermo gravimetric Analyzer (TGA; Macro TGA 701, LECO, USA) at the Scientific Equipment Center of Prince of Songkla University.

2.2 Chemicals

The NH_4-ZSM-5 catalyst powder was purchased from Zeolyst International (USA) with a silica to alumina ratio (SAR) of 30 and a specific surface area of 405 m^2/g. Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\bullet}6H_2O$) was obtained from LOBA Chemie (India) and Ethanol (95 %wt.) was purchased from Merck (Thailand).

2.3 Catalyst preparation and characterization

The HZSM-5 catalyst with a low silica-to-alumina ratio of 30 was chosen because of the strong Brønsted sites and promoting the highest aromatic yield (Zandonai, Yassue-Cordeiro, Castellã-Pergher, Scaliante & Fernandes-Machado, 2016; Engtrakul *et al.*, 2015). To prepare 10 g of 10%Ni/HZSM-5 catalyst, NH_4-ZSM-5 was calcined in an air atmosphere at 550 °C for 5 h to generate 9 g of HZSM-5 (Saad, Ratanawilai & Tongurai, 2015). The low metal loading of 10 wt.% Ni on support was prepared via wet impregnation method. In the first step, 4.95 g of $Ni(NO_3)_2{\bullet}6H_2O$ crystals (equivalent to 1 g of Ni) was dissolved in 12.26 g of deionized water (wet point of HZSM-5) and was stirred at 25 °C until complete dissolution. Afterwards, HZSM-5 was mixed with the aqueous solution and stirred at ambient temperature for 1 h. The mixture was dried at 105 °C for 12 h. Finally, the sample was calcined at 600 °C under air atmosphere for 5 h (Miskolczi, Juzsakova & Sója, 2019) and stored in a desiccator. Elemental composition of the 10% Ni/HZSM-5 catalyst was analyzed by X-Ray Fluorescence spectrometer (XRF; ZETIUM, PANalytical, Netherlands) at the Scientific Equipment Center of Prince of Songkla University by weighing a sample of about 2-3 grams that was compressed with a hydraulic machine (press 10 torr for 30 s) to a powder disk. The instrument was calibrated with standard samples and quantitative software (SuperQ software), and elemental contents were normalized to 100% with balancing organic compounds (C, H, N and O) measured by the TGA technique. The results indicate that the actual Ni loading was 10.098% wt (for more details see the supplementary file).

2.4 Apparatus and experimental procedures

A schematic diagram of the pyrolysis reactor connected with the constructed RD column is shown in Figure 1(a). The experimental system was divided into two main units. In the first one, a bench-scale tubular pyrolysis furnace is made of 304L stainless steel with 8 cm internal diameter and 80 cm length. In the second process, an RD column constructed with 304L stainless steel has a 3 cm-diameter and a 70 cm-length. Within it, 840 g of 6 mm-diameter glass beads were used as the packing and heat transfer medium. Glass wool was used to support the catalyst and separate the char from volatiles. An inert atmosphere in the pyrolyzer and the RD column was maintained by nitrogen gas (99.99%) as flushing or carrier gas, with a rate of 200 mL/min. The nozzle heater and thermal insulator were installed to provide and maintain heat energy to the reactive zone (isothermal zone) of the RD column (Prasertsit, Ratanawilai, & Thummasaneh,

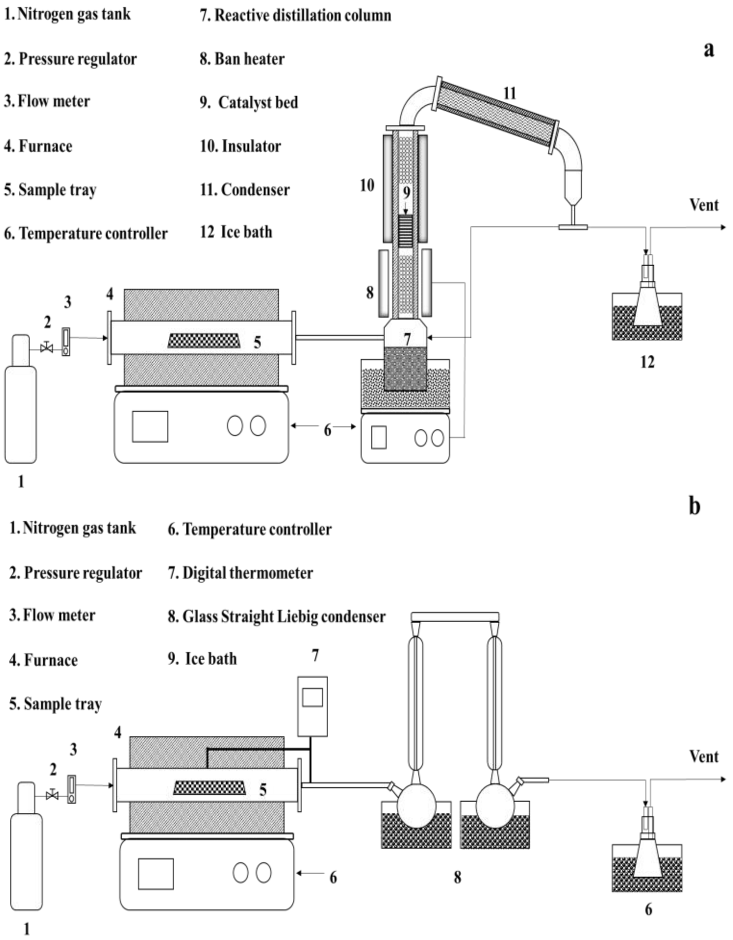

Figure 1. Diagram of pyrolysis furnace and reactive distillation system (a) and pyrolysis furnace without reactive distillation (b)

2017). The temperature inside the column was monitored by using an RTD PT100 sensor and was controlled by a PID controller. The stainless shell and tube heat exchanger and the ice bath were employed to condense all condensable compounds at 5 °C and 0 °C, respectively.

Before upgrading the biofuel oil, the ratio between EFB and PKS needs to be evaluated for best choice by considering product yield and cost. The ratios tested were 100:0, 75:25, 25:75 and 0:100. Raw bio-oil was produced at 20 °C/min heating rate, 550 °C of temperature and 1 hr reaction time by using the previously mentioned pyrolyzer and Glass Straight Liebig condenser (5 °C) connected to an ice bath (0 °C) to collect the raw bio-oil, as shown in Figure 1(b). In order to measure the feed temperature (exit gas temperature of gaseous product entering to RD column) related to pyrolysis time, the digital thermometer with two PT100 sensors was used to continuously measure the feed temperature at the tube outlet and heater wall temperature during the pyrolysis process. The yields of bio-oil were calculated from the following equation.

$$Y_B = \frac{W_B}{W_F} \text{ x } 100\% \qquad (1)$$

where Y_B denotes the yield of bio-oil, W_B denotes the weight of bio-oil, and W_F is the weight of the feedstock.

Prior to pyrolysis, 200 g of ethanol filled in the reboiler was heated at 80 °C and 100 °C in atmospheric pressure to avoid the polymerization of bio-oil during distillation (Dhyani, V. & Bhaskar, T., 2018) at atmospheric pressure. The reactive zone of RD column was packed with 7 g of catalyst (1:12 of catalyst to packing mass ratio) at the top position and was constantly heated to 260 °C (outer surface temperature) for 1 hour. After that, 200 g of biomass (at the selected ratio) was pyrolyzed with 20 °C/min heating rate to 550 °C (outer heater wall temperature) as the final temperature for 1 hour pyrolysis period. RD was operated under total reflux condition until pyrolysis was finished. The vapor of bio-oil from pyrolysis became mixed with the vapor of ethanol before passing through the catalyst bed, assuming it was the gas-phase reaction. The distillate fraction at the top of the column condensed in the shell side and was collected in the receiver flask while the tube side exchanger was connected to an ice bath. This fraction was assumed to be an undesired product since it contained low molecular weight compounds and water. The bottom fraction in the reboiler was rapidly cooled down to room temperature to minimize aging effects. When finished the upgraded bio-oil was stored at 5 °C in a fridge to avoid further reactions. The chemical compositions and physical properties of the bottom fraction from the RD process were characterized to compare with raw bio-oil. The yields of distillate fraction and bottom fraction were calculated by mass balance with the following equations:

$$W_{Volatile} = W_{Raw\ material} - W_{Char} \quad (1)$$

$$W_{Feed} = W_{Volatile} + W_{Ethanol} \quad (2)$$

$$Y_{Distillate} = \frac{W_{Distillate}}{W_{Feed}} \times 100\% \quad (3)$$

$$Y_{Bottom} = \frac{W_{Bottom}}{W_{Feed}} \times 100\% \quad (4)$$

where W denotes the mass in grams (g) and Y denotes the yield (%.)

2.5 Analytical methods

The liquid products were analyzed using gas chromatography (7890B, Agilent, USA) coupled with a mass spectrometer (5977A, Agilent, USA) equipped with HP-5MS column (30 m × 0.32 mm × 0.25 µm, Agilent, USA) and helium as the carrier gas with a flow rate of 0.6 mL/min. The oven temperature program started at 50 °C (hold for 1 min) and was ramped at 10 °C /min to 240 °C (hold for 5 min) and then at 4 °C/min to 300 °C (hold for 10 min). Chemical compositions of the products were identified by comparing with NIST14 and WILEY10 libraries, and the ratio of peak area to the total peak area is used as estimate of content. The pH of upgraded bio-oil was measured by using a digital pH meter (Sartorius DOCU-pH+, Germany). The density of products was determined by using a pycnometer at 25 °C. The kinematic viscosity measurement was carried out with Ostwald's viscometer at 40 °C in accordance with ASTM D445. The water content in the product was quantified by a Volumetric Karl Fisher titrator (Metrohm Toledo V30S, Taiwan) according to ASTM E203.

3. Results and Discussion

3.1 Raw material characterization

The characteristics of PKS and EFB are summarized in Table 1. Both raw materials had high volatile contents with potential to produce liquid fuel (Demirbas, 2004). The water content in EFB was higher than in PKS because of water absorption capacity from strong cell walls of EFB (Omar, Idris, Yunus, Khalid & Aida Isma, 2011). The oxygen contents of biomasses were considerably higher than 40%wt. which gave low higher heating values, an important property of the solid fuel biomass. The low sulfur and nitrogen contents resulted in low NO and SO_2 emissions, possibly reducing greenhouse gas emissions (Kraszkiewicz, Przywara, Kachel-Jakubowska & Lorencowicz, 2015). These values were similar to those reported in prior literature (Kim, Jung & Kim, 2010; Abnisa, Arami-Niya, Wan Daud & Sahu, 2013).

3.2 Pyrolysis and reactive distillation

Pyrolysis of the various ratios of PKS and EFB in the feed was performed in a pyrolyzer at 550 °C and heating rate of 20 °C/min for 1 hr reaction time, in order to produce raw bio-oil. The yield of bio-oil for each ratio is shown in Figure 2. The pure PKS gave the highest bio-oil yield, while the yield of PKS:EFB at 75:25 was slightly decreased. Since the cost of PKS (4,500 Baht/ton) is much higher than of EFB (150 Baht/ton) (DEDE, 2016), the ratio 75:25 was selected for the next experiment.

In addition, the feed temperature (gaseous product) and the heater wall temperature in the entire pyrolysis process at each ratio are shown in Figure 3. After 20 min of pyrolysis, there was an initial increase in feed temperature and the first drop of bio-oil fell from the condenser to bottom flask, while the heater wall temperature was about 400 °C. This was due to the starting thermal decomposition of the raw materials. Afterwards, the feed temperature gradually increased to a maximum of about 230 °C, then gradually dropped and was constant at about 65 °C after 40 min of pyrolysis. The results suggest that this could be the endpoint of biomass decomposition at pyrolysis temperature of 550 ºC. From the composition analyses in Table 2 before and after upgrading, the main components in raw bio-oil were acetic acid, nonanoic acid, levulinic acid, phenols and furfural, in agreement with the work of Yang *et al.* (2007). They found that if the products from pyrolysis were organic compounds such as acids, aldehydes (C-O), alkanes (C–C), or ethers (C–O–C) with some water, then gas products would be released at 200-400 ºC. As a result, the varying feed temperature over time was a limitation of this study. The difference between feed temperature and heater wall temperature might depend on the thermal degradation behavior of feedstock and on heat transfer (Abdullah, Novianti, Hakim, Putra, & Koestoer, 2018).

Table 1. Proximate and ultimate analysis of PKS and EFB

Method	PKS	EFB
Proximate analysis (%wt., dry basis)		
Moisture	4.87	8.43
Volatile matter	71.07	71.83
Fixed carbon	22.77	15.44
Ash	1.29	3.80
Ultimate analysis (%wt., dry basis)		
C	42.55	45.91
H	5.20	5.87
N	0.31	0.1
O	37.47	40.55
S	<0.01	<0.10

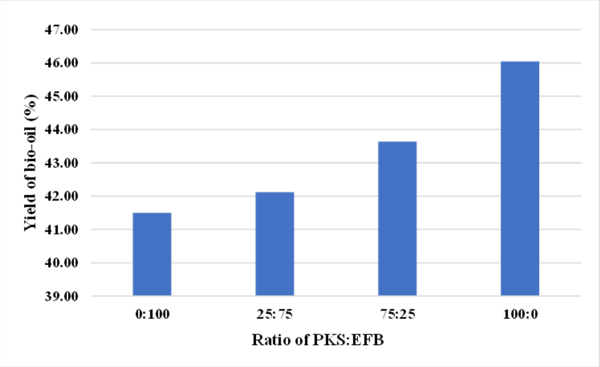

Figure 2. Yield of bio-oil at various ratio of PKS and EFB and 550 °C of reaction temperature

Table 2. Chemical compositions of raw bio-oil and upgraded bio-oil obtained from the bottom fraction produced at reboiler temperature of 80 °C

Products	Relative content (%)	
	Raw bio-oil	Upgraded bio-oil
Acids	48.09	29.44
Acetic acid	37.3	24.78
Propanoic acid	1.14	0.67
Hexanoic acid	0.05	0.19
Octanoic acid	0.19	0.20
Nonanoic acid	5.72	2.53
Levulinic acid	3.7	1.07
Esters	0.14	0.67
Dodecanoic acid, methyl ester	0.14	0.31
Nonanoic acid, ethyl ester	-	0.16
Levulinic acid, ethyl ester	-	0.20
Phenolic compounds	40.54	53.30
Phenol	24.72	31.08
Phenol, 2-methoxy-	3.93	4.17
Phenol, 4-methyl-	1.06	1.03
m-Cresol	0.78	0.63
4-methoxy-2-methylphenol	0.2	0.24
Phenol, 2,6-dimethoxy-	3.95	6.07
Phenol, 4-ethyl-2-methoxy-	1.66	2.15
2-Methoxy-4-vinylphenol	0.35	0.64
3,5-Dimethoxy-4-hydroxytoluene	1.93	4.25
Phenol, 2-methoxy-4-propyl-	0.31	0.61
Eugenol	0.1	0.67
4 - propyl - syringol	0.45	1.07
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.19	0.41
(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl) phenol	0.92	0.29
Ketones	3.43	5.60
1-Hydroxy-2-butanone	0.75	0.50
2-Cyclopenten-1-one	0.63	0.49
1,2-Cyclopentanedione	0.65	0.51
2-Cyclopenten-1-one, 2-methyl-	0.39	2.96
2-Cyclopenten-1-one, 3-methyl-	0.37	0.28
3,5- dimethyl cyclopentenolone	0.17	0.14
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	0.26	0.25
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.21	0.48
Aldehyde	3.94	3.95
Furfural	3.67	3.43
Benzaldehyde, 4-hydroxy-3-methoxy-	0.26	0.53
Furan	1.59	1.42
2-Furanmethanol	1.08	0.99
2(5H)-Furanone	0.21	0.26
2-Furancarboxaldehyde, 5-methyl-	0.30	0.17
Saccharides	1.59	3.84
1,4:3,6-Dianhydro-alpha-d-glucopyranose	0.31	0.59
Beta-D-Glucopyranose, 1,6-anhydro-	1.28	3.25
Nitrogen compound	0.68	0.6
3-Pyridinol	0.68	0.6
Acetals	-	1.19
1,1-Diethoxyethane	-	1.19

The RD of vaporized bio-oil and ethanol gave two fractions at different reboiler temperatures, but with the same reaction time, as shown in Figure 4. At 80 °C reboiler temperature, the yields of the distillate fraction and the bottom fraction were 32.56 wt% and 48.33 wt%, respectively. On increasing reboiler temperature to 100 °C, the distillate fraction was up to 62.41 wt% and the bottom fraction decreased to 19.65 wt%., because of the increase rate of ethanol vaporization which led to ethanol enrichment in the top product.

After finishing the RD process Figure 5(a) and (b) show photographs of the deposition of heavy oil on packing in an RD column at 80 °C and at 100 °C reboiler temperatures.

The lower 80 ºC reboiler temperature caused a lower ethanol evaporation rate, which provided a longer residence time in the column and took less deposition of heavy oil on catalyst surface, as shown in Figure 5(a). However, the separation efficiency was poor (Cheremisinoff, 2000), while at the 100 °C reboiler temperature, ethanol vaporization rate was larger and it carried heavy oil up the RD

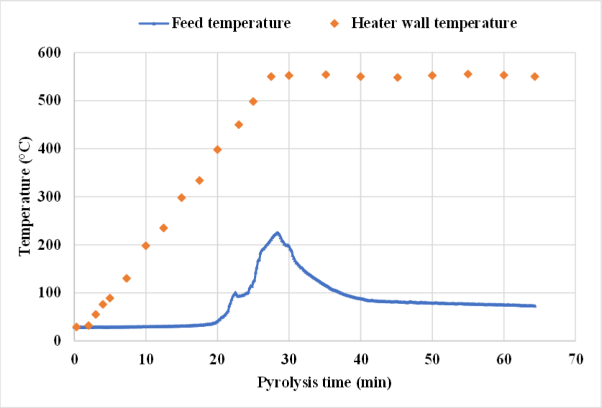

Figure 3. Temperature profile of pyrolysis process at 550 °C and 1 hr time

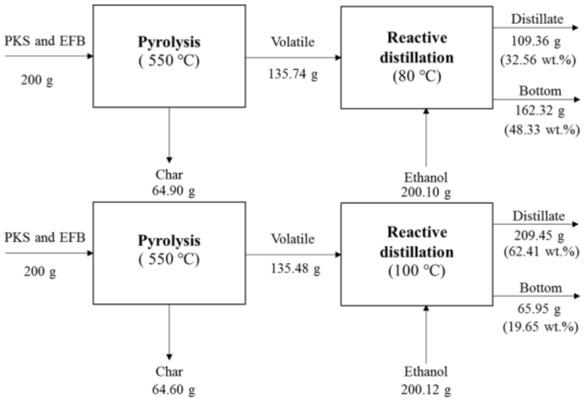

Figure 4. Mass balance at 80 °C and 100 °C of reboiler temperature

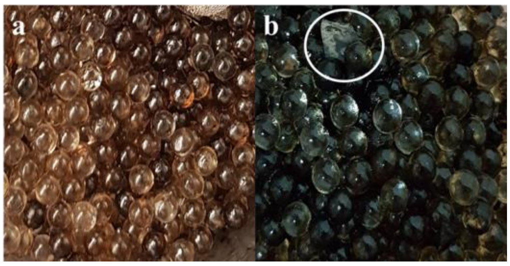

Figure 5. Photographs of deposition of heavy oil on packing at 80 °C (a) and 100 °C of reboiler temperature (b)

column and made more deposits of heavy oil on the catalyst surfaces, as shown in the circle in Figure 5(b). This eventually reduced catalyst activity. Moreover, this provided a short retention and contact time between reactants and catalyst.

It is generally true that a longer residence time is favorable for reaction in the zone containing the catalyst (Lv, *et al.*, 2019). Thus, this suggests that the lower reboiler temperature would give a better separation of heavy oil as well as increase the contact time or reactants with catalyst, by reducing the vapor velocity in the RD column.

3.3 Comparison of chemical compositions

Due to the deposition of heavy oil on packing, the bottom fraction produced at a lower reboiler temperature of 80 °C was analyzed by the GC-MS technique. The peak area percentages in GC-MS chromatogram were used for the quantification. Table 2 shows the chemical components of products classified by functional groups, including acids, phenolic compounds, ketones, aldehydes, furans, nitrogen compounds, esters, acetals, and saccharides. The acid content in raw bio-oil consisted of acetic acid (37.3%) and fatty acids (10.8%), which mainly come from empty fruit bunches (Sembiring, Rinaldi & Simanungkalit, 2015). The high phenolic compound contents (40.54%) mainly resulted from high lignin content in palm shell kernel (Kim, Jung & Kim, 2010).

After upgrading the acid content was clearly decreased from 48.09% to 29.44% as a result of separating low boiling point compounds such as acetic acid (Junming, Jianchun, Yunjuan & Yanju, 2008). The phenolic compounds had no significant change below 400 °C reaction temperature (Gayubo, Aguayo, Atutxa, Aguado & Bilbao, 2004). However, the phenolic compounds in upgraded bio-oil (53.30%) were relatively higher than in raw bio-oil (40.54%) because of the reduction in acids content from normalizing products. Due to limited reaction temperatures and Brønsted acid sites of 10%Ni/HZSM-5 in the presence of alcohol, the esterification reactions of levulinic acid and nonanoic acid generated levulinic acid ethyl ester and nonanoic acid ethyl ester. In addition, the acetaldehyde was converted to 1,1 diethoxyethane products (acetals) through acetalization reactions. However, acetaldehyde could not be identified in the raw bio-oil due to limitations of the GC column (Hilten, Bibens, Kastner & Das, 2009). There no other chemical components were significantly changed and no new chemical compounds were formed because of the low reactivity on HZSM-5 zeolite at these operating conditions (Gayubo, Aguayo, Atutxa, Aguado & Bilbao, 2004).

3.4 Comparison of physical properties

The physical properties of raw bio-oil and upgraded bio-oil are shown in Table 3. Results show that the density decreased from 1.07 g/cm^3 to 0.91 g/cm^3, the pH increased from 2.48 to 3.67, the kinematic viscosity decreased from 3.36 cSt to 1.96 cSt and the water content decreased from 65.96 wt.% to 24.16 wt.%. Low pH from acidic compounds such as acetic acid and fatty acids would cause corrosion of storage tanks and pipelines. The viscosity of upgraded bio-oil was decreased significantly, which is helpful for transportation and for fuel injection in a combustion engine. The decreased water content in bio-oil contributed to improved heating value and ignition of biofuel. This improvement is likely due to the separation and the diluting effect of ethanol.

Table 3. Physical properties of raw bio-oil and upgraded bio-oil

Properties	Raw bio-oil	Upgraded bio-oil
pH	2.48	3.67
Density (g/cm^3)	1.073	0.909
Viscosity (cSt)	3.36	1.96
Moisture (wt%)	65.96	24.16

4. Conclusions

Upgrading bio-oil from pyrolysis of PKS and EFB at 75%/25% ratio by using a constructed RD column with 10%Ni/HZSM-5 catalyst in the presence of ethanol was investigated experimentally. The reboiler temperature influenced the separation of heavy oil in bio-oil and the vapor velocity in the reactor, which affected residence time of reactants in the reactive zone with catalyst. The results implied that 80 °C reboiler temperature enabled good separation of heavy oil in bio-oil, so that catalyst deactivation was avoided, and this also increased the residence time when compared to 100 °C reboiler temperature. Due to variations in feed temperature and temperature of the reactive zone in the presence of 10%Ni/HZSM-5 catalyst, bio-oil was upgraded by esterification and acetalization reactions. Compared to raw bio-oil the upgrading also improved the physical characteristics. Regarding use as an alternative fuel, a higher reaction temperature and further treatment are needed to upgrade highly oxygenated compounds in bio-oil and improve its physical properties.

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