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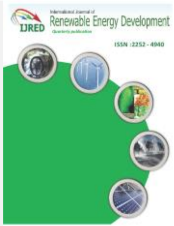

***Research Article***

# Catalytic Co-Pyrolysis of Palm Oil Empty Fruit Bunch and Coal into Liquid Oil

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**Abstract**. The decline in fossil fuel sources has prompted research into finding renewable fuels. One of environmentally friendly energy sources with high efficiency is by producing liquid oil from palm oil empty fruit bunch (EFB) and coal. Pre-treatment of empty fruit bunches using NaOH and various concentrations of $H_2O_2$, various ratios of EFB/coal, the ratio of CaO catalyst, chemical and physical characteristics were studied to produce the better liquid oil yield. The $H_2O_2$ concentrations are 0%, 1%, 2%, and 3%. The ratios of EFB/coal (R) are 0/100, 25/75, 50/50, and 75/25. The ratios of catalyst CaO/raw material are 0%, 3%, 6%, and 9%. It ran at 400 °C with 100 mL/min nitrogen gas flowing during one hour. The results showed that adding sodium hydroxide and hydrogen peroxide in the EFB pre-treatment increased the liquid oil yield. With an increase in the EFB/coal ratio, the liquid oil yield increased. Co-pyrolysis treated EFB and Coal with a ratio of 75:25 produced 32% liquid oil yield, but the liquid oil yield decreased to 19% with the addition of 9% CaO catalyst. However, the addition of CaO catalyst reduces the acidity and increases the calorific value of the liquid oil.

***Keywords:*** coal, CaO catalyst, co-pyrolysis, empty fruit bunches, liquid oil

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## 1. Introduction

The rapid development of the automotive industry has led to an increase in the demand for transportation fuels (Payormhorm *et al.* 2013; Sunarno *et al.* 2018). Until now, petroleum is still a dominant transportation fuel (Liu *et al.* 2014). Petroleum reserves are currently dwindling with the increasing demand for fuel. Besides, petroleum as a fuel also causes air pollution and the greenhouse effect (Chang, 2018; Wicakso *et al.* 2020). Thus, it is necessary to find other sources as alternative energy for transportation fuel.

The coal pyrolysis process is the conversion of coal into liquid fuel at atmospheric pressure. However, the coal pyrolysis process produces a low liquid oil yield. Jilkova *et al.* (2015) performed the pyrolysis of coal at 650 °C for 3 hours. The liquid oil product obtained is 5.03%. Onay and Koca (2015) carried out the pyrolysis of lignite and obtained liquid oil product of 13.26%. Meanwhile, Zhao *et al.* (2018) observed the pyrolysis of lignite in a bench scale fixed bed reactor at a temperature of 800 °C and obtained a liquid oil yield of 5.11%. The gas and solid products still dominated the coal pyrolysis products.

The co-pyrolysis process of coal with other materials with a higher H/C atom ratio can increase the yield of liquid products. Empty fruit bunch (EFB) is biomass with a higher H/C atom ratio compared to coal (Chang, 2018; Huang *et al.* 2019). The hydrogen produced from the rapid pyrolysis of biomass stabilizes large radical structures generated during the early stages of coal pyrolysis (Wang *et al.* 2020). Other researchers worked on the co-pyrolysis of coal and biomass. For example, Yilgin *et al.* (2010) observed co-pyrolysis of lignite and sugar beet pulp with a ratio of 50:50 at 600 °C and obtained a liquid oil yield of 28%. Huang *et al.* (2019), who carried out the co-pyrolysis of bituminous coal and wheat straw with a weight ratio of 25:75 at a temperature of 600 °C and a pressure of 0.3 MPa obtained a liquid oil yield of 18%. These studies used untreated biomass as the raw material. Even though using high temperatures above 500 °C, the yield of liquid oil obtained is low.

Calcium oxide (CaO) is an alkaline earth metal used as a catalyst for biomass pyrolysis. Yu *et al.* (2014) studied CaO on the pyrolysis of sewage sludge under the microwave and found that CaO supports the production of hydrogen gas products. Chen *et al.* (2017) carried out fast pyrolysis of cotton stalk biomass using calcium oxide. The results showed that the acid compounds in the liquid oil decreased while the ketones and hydrocarbons increased. CaO also has a catalytic role in the coal pyrolysis and promotes the release of volatiles (Wang *et al.* 2020).

The co-pyrolysis of coal and EFB in this work was conducted using CaO as the catalyst. Before being used as raw material, the EFB was pre-treated with a mixed solution of NaOH and $H_2O_2$. This pre-treatment resulted

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in a significant decrease in the lignin content in the EFB and an increase in the yield of liquid oil at co-pyrolysis temperatures below 500 °C. The use of CaO catalyst in the co-pyrolysis of EFB and coal can reduce acid compounds in liquid oil and increase the calorific value of liquid oil. The objective of the research is to study the effects of pre-treatment of EFB, ratio of EFB/coal, and concentration of CaO catalyst on the yield and composition of the liquid oil product.

## 2. Materials and Methods

### *2.1 Raw Materials and Catalyst*

The raw materials were empty fruit bunch (EFB) and coal. EFB was obtained from PTPN V PKS Sei. Galuh, Riau Province, Indonesia, while the coal was obtained from Peranap, Indragiri Hulu Regency, Riau Province. The analyses of proximate and ultimate were done at the Central Laboratory of Coal and Geothermal Mineral Resources, Bandung, Indonesia, using TGA Q500IR and a LECO-932 elemental analyzer. The results of EFB and coal analysis are presented in Table 1. Calcium Oxide catalyst was commercial grade (>95%) with particle sizes less than 50 µm. CaO catalyst was analyzed by BET (Brunaur, Emmet and Teller). Analysis of BET was done at Integrated Laboratory of Diponegoro University. The result of the CaO analysis is presented in Table 2.

### *2.2 Pre-treatment of Coal and EFB*

Pre-treatment of coal was carried out by washing with water. After that, it was dried under the sun for 6 hours to reduce the water content. The coal was crushed and sieved by 50 mesh standard screening. Finally, the coal was dried using an oven at 105 °C for 24 hours. EFB from plantations was washed with water and dried in the sun. The dried EFB was cut at a range of 0.5-1 cm size. Fifty grams of EFB were mixed with 100 mL of 10% (w/v) NaOH solution and 100 mL of $H_2O_2$ solution at 200 rpm and 27 °C for 48 hours. The concentration of $H_2O_2$ were varied at 0%; 1%; 2%; 3% (v/v). The treated EFB was filtered and washed with distilled water. Then, it was dried using an oven at 110 °C for 24 hours. The treated EFB was subsequently analyzed for lignocellulosic content with Chesson-Datta Method and pyrolysis tested at 400 °C for one hour.

**Table 1**
The Proximate and Ultimate analysis of EFB and coal

| Sample | | EFB | Coal |
|---|---|---|---|
| Proximate | Volatile (%) | 73.84 | 25.59 |
| | Fixed carbon (%) | 13.5 | 29.25 |
| | Ash (%) | 3.3 | 31.39 |
| | Moisture (%) | 9.36 | 13.79 |
| | Heating value (MJ/kg) | 13.56 | 16.37 |
| Ultimate | Carbon (%) | 47.54 | 60.36 |
| | Hydrogen (%) | 7.11 | 3.1 |
| | Nitrogen (%) | 0.62 | 0.17 |
| | Sulfur (%) | - | 0.18 |
| | Oxygen (%) | 39.82 | 36.19 |

**Table 2**
The BET analysis of calcium oxide (CaO)

| Element | Value |
|---|---|
| Surface Area | 8.563 $m^2$/g |
| Pore Size | 31.56 Å |
| Total Pore Volume | 0.0135 cc/g |

### *2.3 Co-Pyrolysis Methods*

The co-pyrolysis was performed using the calcium oxide catalyst in a packed bed reactor. The schematic diagram of the co-pyrolysis apparatus is presented in Figure 1. This system consists of a tube reactor (inner diameter of 35 mm and length of 240 mm), condenser, separator, temperature controller, nitrogen cylinder, and flowmeter. The treated EFB and the treated coal were mixed with a weight ratio of (0:100, 75:25, 50:50, and 25:75). The mixed EFB and coal were fed into the packed bed reactor and heated at 400 °C as well as the nitrogen gas was flowed at a flow rate of 100 mL/min for one hour. The experiment was repeated with the addition of a CaO catalyst. The mass ratio variables of CaO catalyst to raw materials were 3%, 6%, and 9%. The catalytic co-pyrolysis experiment was repeated with two replicates. The vapor produced was condensed in a partial condenser using water, while the liquid oil product was collected in the Erlenmeyer flask. The products of liquid oil and char were measured by weight. The liquid oil was stored in the sample bottle and tested to determine the chemical percentage of liquid oil.

### *2.4 Products of Co-pyrolysis Analysis*

Liquid oil yield and char were measured by weighing the products separately. The percentage of liquid oil product compounds was tested using gas chromatography-mass spectroscopy (GC-MS/QP2010 SHIMADZU). Densities of liquid oil were determined using pycnometer bottles. Viscosities of liquid oil were tested using an Ostwald viscometer. The acidity of liquid oil was measured using a digital pH meter. The calorific value of liquid oil was determined by a bomb calorimeter (P.H Hilton C200 series). The yield of liquid oil, char, and gas calculation was done using equations 1,2 and 3.

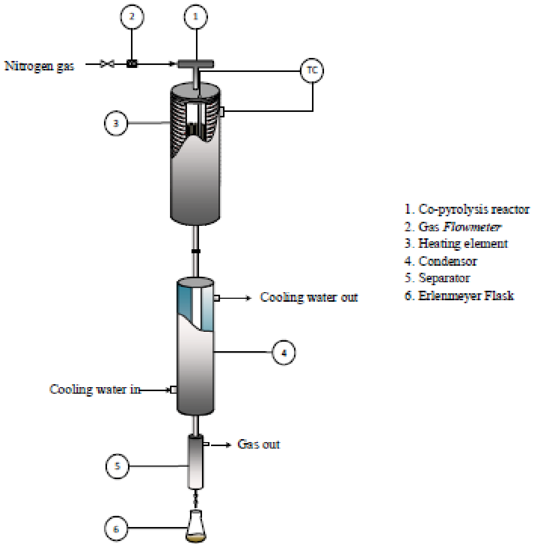

**Fig. 1**. The schematic of the co-pyrolysis apparatus

$$Y_{\text{liquid oil}} = \frac{m_{\text{liquid oil}}}{m_{\text{feed}}} \times 100\% \qquad (1)$$

$$Y_{\text{char}} = \frac{m_{\text{char}}}{m_{\text{feed}}} \times 100\% \qquad (2)$$

$$Y_{\text{gas}} = \frac{m_{\text{feed}} - m_{\text{liquid oil}} - m_{\text{char}}}{m_{\text{feed}}} \times 100\% \qquad (3)$$

Where $Y_{\text{liquid oil}}$ is the product of liquid oil yield, $m_{\text{liquid oil}}$ is the mass of the liquid oil product, $m_{\text{feed}}$ is the mass of reactor feed, $Y_{\text{char}}$ is the char yield, $m_{\text{char}}$ is the mass of char product, $Y_{\text{gas}}$ is the product of gas yield.

## 3. Results and Discussion

### *3.1 Analysis of the influence of $H_2O_2$ concentration and the EFB biomass pre-treatment process on the yield of liquid oil*

Chemical pre-treatment was carried out using sodium hydroxide (10% NaOH) with the addition of Hydrogen Peroxide ($H_2O_2$) concentrations of 1%, 2%, and 3%. The results of the lignocellulose content of each EFB sample were analyzed using the Chesson method. The results can be seen in Fig. 2.

Fig. 2 shows that the pre-treatment decreases the EFB lignin levels. The lignin content in untreated EFB was 13.2%. With the addition of 10% NaOH and 3% $H_2O_2$, the lignin content in EFB decreased to 11.4%. Sodium hydroxide is able to break down the structure of lignin because the hydroxyl group in NaOH will decompose and bind to the constituents of lignin. These hydroxyl ions will accelerate the breaking of the bonds to the basic structure of lignin, so that the lignin will be dissolved more quickly or separated and dissolved from the EFB biomass. In order for the lignin dissolving process to be faster, the $H_2O_2$ compound was added. In addition, NaOH can also reduce hemicellulose content and increase cellulose content. According to Choi *et al.* 2013, NaOH pre-treatment of EFB was highly effective in removing lignin.

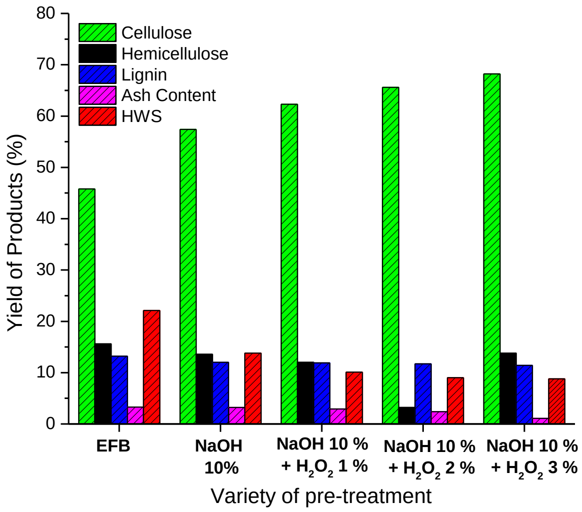

**Fig. 2.** Analysis of lignocellulose content in EFB using the Chesson method

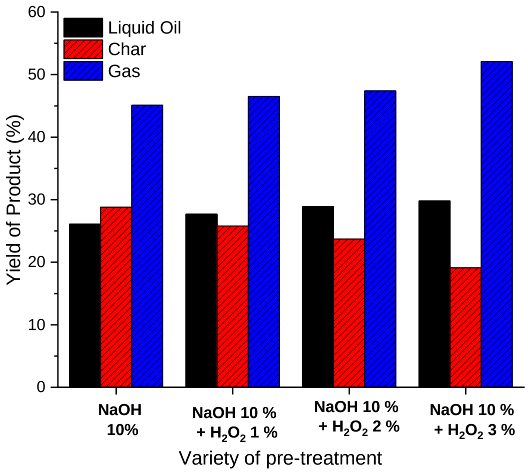

**Fig. 3.** The liquid oil yield based on EFB pre-treatment with NaOH and the addition of various concentration of $H_2O_2$

The addition of $H_2O_2$ helps in accelerating the degradation process. Hydrogen peroxide will act as a decomposition of the hydroxyl ions found in NaOH or a mixture of NaOH and EFB. The hydroxyl ions will bind to the basic structure of lignin so that lignin is more easily dissolved from EFB. Thus cellulose content in EFB increased (Gupta *et al.* 2010).

The effect of EFB pre-treatment with the addition of NaOH and $H_2O_2$ on the yield of liquid oil can be seen in Fig. 3. Pyrolysis of EFB with 10% NaOH pre-treatment resulted in 26.1% liquid oil yield, while EFB with 10% NaOH and 3% $H_2O_2$ pre-treatment produced 29.8% liquid oil yield.

Lignin levels significantly affect the yield of the liquid oil produced. If the lignin level is higher, the liquid oil will be less. It is inversely proportional to the char formed, the number will increase. The presence of lignin in biomass pyrolysis will lead to the charcoal production. Lignin is more difficult to decompose because of its decomposition over a wide temperature range, which is 160 – 900 °C, and the resulting high solid residue (Yang *et al.* 2007).

### *3.2 The influence of empty fruit bunches (EFB) to coal ratio on the yield liquid oil*

The co-pyrolysis process was carried out using EFB pre-treated using 10% NaOH and 3% $H_2O_2$. The co-pyrolysis process was carried out at an operating temperature of 400 °C. The yield of liquid oil using variations in the ratio of raw materials can be seen in Fig. 4

Based on the data obtained, the char yield has decreased along with the enhancement in the blending ratio of EFB to coal. Meanwhile, the liquid oil yield increased. The reason is that with a higher biomass ratio, the availability of hydrogen during the co-pyrolysis process is getting bigger. Based on these results, there is a synergistic influence with the addition of EFB biomass. The hydrogen content in EFB can act as a hydrogen donor during the co-pyrolysis process. Hydrogen is useful for preventing cross-linking and recombination reactions from free radicals/metaplasts, which can increase char formation (Zhang *et al.* 2007).

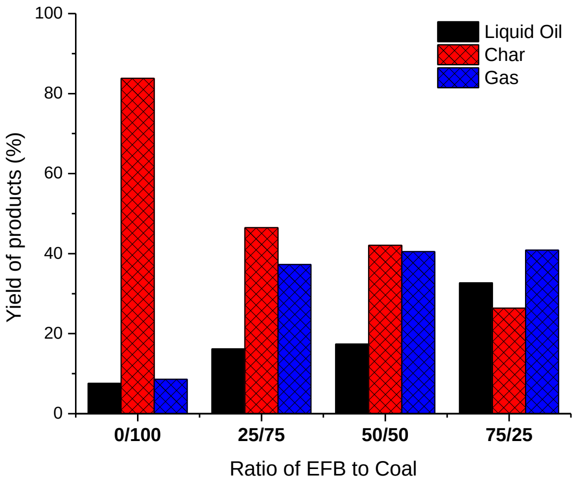

**Fig. 4.** Influence of the ratio of EFB to coal on the yield of liquid oil

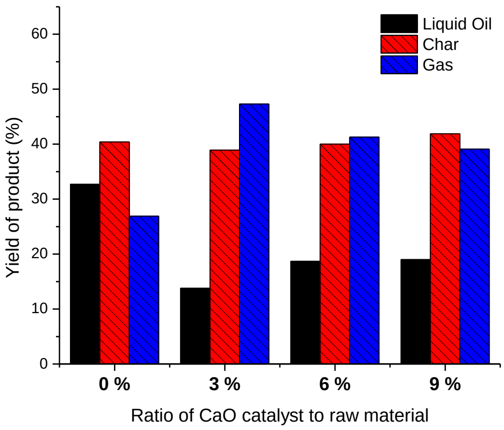

**Fig. 5** Influence of ratio CaO catalyst/raw materials on the yield of liquid oil

Co-pyrolysis of EFB/coal with the ratio of 0/100, there is a significant reduction in the liquid oil yield. This is because there is no hydrogen supply which can reduce the amount of liquid oil produced. In addition, coal has a volatile matter value of 25.59% lower than EFB, which has a volatile matter of 73.84%. The yield of liquid oil has increased with the enhancement in the blending ratio between biomass and coal due to the high content of volatile matter contained in the biomass. This is in accordance with the research of Li *et al.* (2014), which states that tar and gas yields increase with the increase in the biomass blending ratio due to the high volatile matter in biomass. This study is also similar to Huang *et al.* (2019), who conducted co-pyrolysis of bituminous coal and wheat straw at a temperature of 600 °C and a pressure of 0.3 MPa. The results show that with an increase in the ratio of biomass/coal, the yield of liquid oil and gas increases while the yield of char decreases.

### *3.3 The influence of the mass ratio of CaO catalyst to the raw materials on the yield of liquid oil*

The treated EFB (NaOH 10%, $H_2O_2$ 3%) to the coals ratio of 75/25 was used to study the influence of co-pyrolysis using CaO catalyst and without catalyst on the yield of liquid oil. The varied mass ratio of CaO catalyst to raw materials were 3%, 6%, and 9%. Figure 5 shows that the increasing the percentage of CaO catalyst, the produced liquid oil increased. However, the co-pyrolysis process without a CaO catalyst resulted in more liquid oil yield than using a catalyst. In the co-pyrolysis process using CaO, there is cracking of liquid oil into gas products. This happens because CaO acts as a catalyst that decreases the activation energy and increases the reaction rate so that the reaction rate is faster and the cracking of liquid oil occurs (Wang *et al.* 2020).

The reduction of liquid oil yield was also caused by the large number of non-condensable gas products that were formed. When the cracking process occurs, it produces more light hydrocarbon fractions that cannot be condensed. This type of hydrocarbon has a lower boiling point than the ambient temperature.

The increase in the ratio of CaO catalyst to raw materials also affects the increase in the amount of char produced. According to Lin *et al.* (2010), it happens because CaO as a catalyst absorbs $CO_2$ gas during the co-pyrolysis process. The more CaO catalyst used, the more $CO_2$ gas will be absorbed. This causes char production in the co-pyrolysis process to increase while gas production decreases. CaO catalyst reacts with $CO_2$ to form $CaCO_3$, according to the equation below (Xu *et al.* 2018).

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(S)} \qquad (4)$$

### *3.4 Characteristic of liquid oil*

The characteristics of the liquid oil analyzed include physical and chemical characteristics. The analysis of physical characteristics was carried out for the liquid oil that had the highest yield of each variable, namely liquid oil from treated EFB with NaOH 10% and $H_2O_2$ 3%, the treated EFB/coal with a ratio of 75/25, and the treated EFB/coal with a ratio of 75/25 using 9% CaO catalyst.

### *3.4.1 Chemical characteristics of liquid oil*

Chemical characteristics were analyzed by gas chromatography-mass spectroscopy (GC-MS) to determine the chemical components contained in the liquid oil. Chromatogram of liquid oil can be seen in Fig 6. Table 3 shows the composition of liquid oil products from treated EFB and EFB/coal (R = 75/25) with a 9% CaO catalyst. The liquid oil product from EFB/coals (R = 75/25) with 9% CaO catalyst showed that hydrocarbon compounds increased while acid and phenol compounds decreased compared to the liquid oil of treated EFB. The CaO catalyst can significantly reduce the formation of acid and phenol content. Acidic compounds decrease because, during the pyrolysis process, the CaO catalyst neutralizes the acid produced, called deacidification. Deacidification results in the breakdown of O atoms to turn into ketones and furans. Deacidification also impacts increasing the amount of hydrocarbons which is indicated by the increasing calorific value. Decreased phenol compounds can occur because of two possibilities, CaO can react with the acid functional groups in phenol, and CaO can catalyze the decomposition of phenol to produce CO (Wang *et al.* 2020).

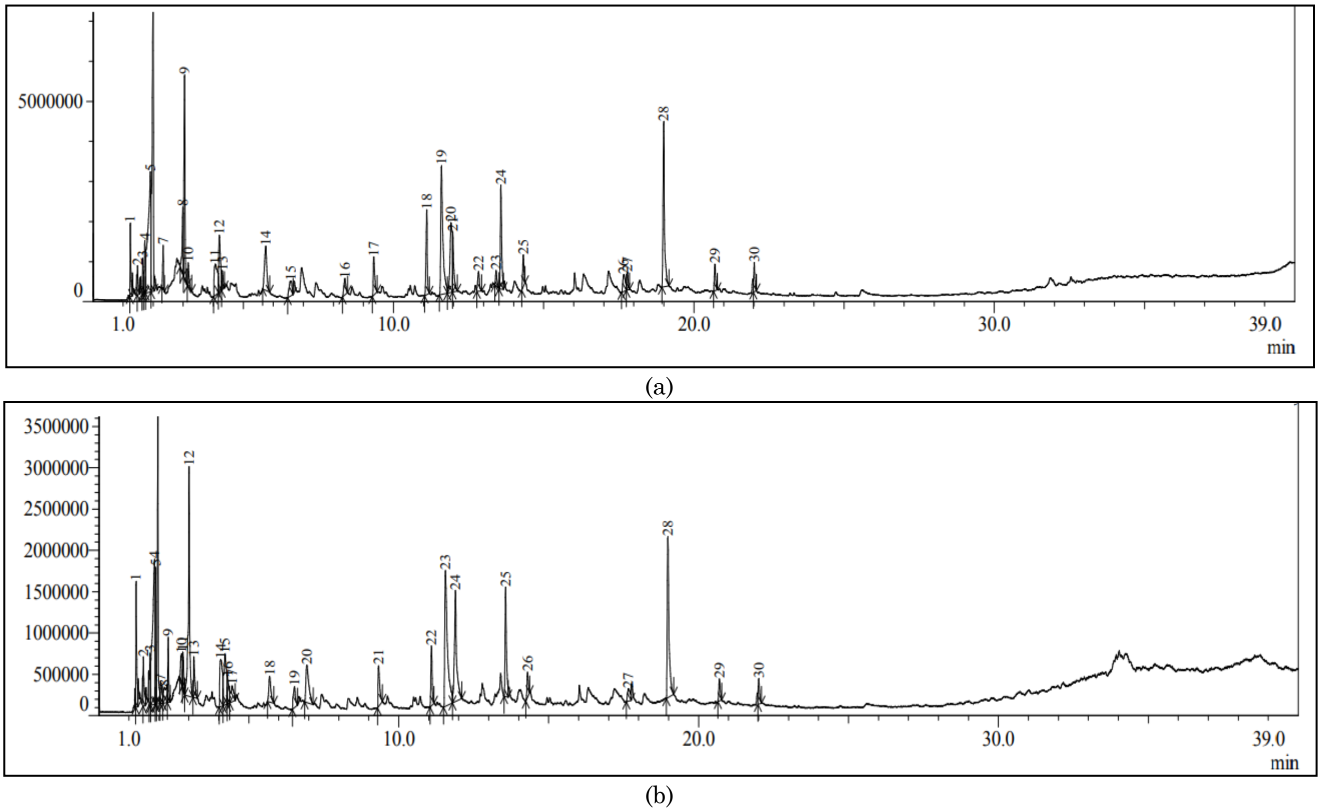

**Fig. 6.** Chromatogram of liquid oil : (a) treated EFB, (b) treated EFB/coal (R=75/25) with 9% CaO catalyst

**Table 3**
Chemical characteristics of liquid oil

| **Components** | **The samples** | |
|---|---|---|
| | **The treated EFB (% Area)** | **EFB/Coals (R = 75/25) using 9% CaO catalyst (% Area)** |
| Hydrocarbons | 3.42 | 4.64 |
| Phenols | 26.69 | 22.84 |
| Acids | 14.87 | 11.96 |
| Ketones | 26.53 | 41.94 |
| Furans | 8.51 | 8.93 |
| Aldehydes | 2.86 | 1.39 |
| Eter and Ester | 17.12 | 8.30 |

**Table 4**
Physical characteristic of liquid oil

| **Parameter** | **Liquid oil products from** | | | **Bio-oil standards** [Dynamotiv, 2012] | **Diesel standards** [Pazylzhan *et al.*2018] |
|---|---|---|---|---|---|
| | **The treated EFB** | **Treated EFB/Coals (R = 75/25)** | **Treated EFB/Coals (R = 75/25) using CaO 9%** | | |
| Density (g/mL) | 1.009 | 1.029 | 1.032 | 0.9 – 1.2 | 0.8512 |
| Viscosity (cSt) | 2 | 2.1 | 2.19 | 4 - 7,8 | 2.3 – 8 |
| Heating value (MJ/kg) | 33.72 | 34.69 | 34.93 | 13 – 19 | 42.75 |
| pH | 1.9 | 2.1 | 2.4 | 2 – 3.3 | 5 |

Liquid oil is derived from hemicellulose, cellulose, and lignin decomposition. In general, the main liquid oil compounds identified are carboxylic acids, alcohols, ketones, aldehydes, ether, esters, phenols, and derivatives compounds (Lu *et al.* 2009). Hydrocarbons are resulted from the synergy and the thermal cracking of coal and biomass. Phenolic compounds are derived from the depolymerization of lignin contained in biomass. Ketone compounds are the product of condensation reactions from carbohydrate compound fractions and decomposition reactions of oxygenated compounds, such as saccharides and furans (Alvarez *et al.* 2019). The formation of these fatty acid ethyl esters and fatty alcohols indicates that there is the participation of biomass derivative radicals in the radical termination reaction (Sharypov *et al.* 2003).

### *3.4.2 Physical characteristics of liquid oil*

The physical characteristics of the liquid oil analyzed are density, viscosity, heating value, and pH. The analysis results are compared with the standard characteristics of bio-oil and diesel oil. This comparison is used to see opportunities the liquid oil produced as fuel. The results of liquid oil's physical characteristics can be seen in Table 4.

The density of the liquid oil product was 1.032 g/mL, in the range of bio-oil standard values. The liquid oil density is influenced by the molecular weight of the compounds contained in the liquid oil. It tends to decrease when the co-pyrolysis temperature increases. This is due to the decomposition of a compound with a large molecular weight into a compound with a lower molecular weight due to the high temperature. The smaller the liquid oil density, the better it will be used as a fuel because it is lighter (Abnisa *et al.* 2011; Abnisa *et al.* 2013).

Viscosity is an important physical property of a fuel that must be considered when designing the storage, processing, and transportation of the fuel. In this study, the viscosity value of 2.19 cSt was obtained. A low viscosity value indicates a high moisture content in the liquid oil. The viscosity of the liquid oil obtained decreased with increasing water content in the liquid oil. The water content in liquid oil comes from the moisture of the raw material and the dehydration reaction that occurs during the co-pyrolysis process (Sunarno *et al.* 2020).

The heating value of combustion shows the calorific energy contained in each mass unit of fuel. The calorific value in this study is 34.93 MJ / kg. As a comparison, the calorific value of liquid oil is higher than the calorific value of product oil produced from the pyrolysis of spirulina platensis residue, which is 25.70 MJ/kg (Jamilatun *et al.* 2019). This calorific value is also above the bio-oil range but below diesel oil. This relatively low calorific value is due to the presence of oxygenate compounds contained in the liquid oil.

Table 4 shows the degree of acidity (pH) of liquid oil resulting from this study of 2.4 which is in the standard of bio-oil acidity (pH) set by Dynamotive (Dynamotive, 2012), namely with a pH ranging from 2 - 3.3 but still below the standard of acidity (pH) for diesel oil, which is around 5. Liquid oil consists of carboxylic acid compounds such as acetic acid and formic acid, which cause liquid oil to be increasingly active acids with a pH between 2–3.

This research has resulted in higher liquid oil yields than previous studies. However, the liquid oil products have a lower pH and calorific value than diesel oil. To improve the quality of liquid oil, future research will be carried out at temperatures above 400 °C and with the addition of CaO catalyst above 9%.

## 4. Conclusions

The pre-treatment of EFB, the ratio of treated EFB to coal, and the addition of CaO catalyst affect the yield and composition of the product. Increasing the ratio of treated EFB to coal can increase liquid oil yield. The addition of a CaO catalyst can reduce acid compounds and increase the calorific value of liquid oil. The catalytic co-pyrolysis process with treated EFB to coal ratio of 75:25 at the temperature of 400 °C and addition 9% CaO catalyst resulted in 19% liquid oil yield consisting of 4.64% hydrocarbon compounds, 22.84% phenols, 11.96% acids, 41.94% ketones, 8.93% furans, 1.39% aldehydes, and 8.3% esters with a heating value of 34.93 MJ / kg, density of 1.032 g/mL, the viscosity of 2.19 cSt, and pH of 2.4. The liquid oil can be considered as an alternative renewable energy source.

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