Catalytic co-pyrolysis palm oil empty fruit bunch and low-density polyethylene of plastic waste into high grade bio-oil

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Abstract. Bio-oil produced from biomass pyrolysis is still acidic and has a low heating value. Co-pyrolysis is a process of pyrolysis of biomass and material that has a higher (H/C) effective. Low-density polyethylene (LDPE) is a type of plastic waste that has a higher hydrogen index than empty fruit bunch (EFB). To improve the quality of bio-oil, it is necessary to co-pyrolysis EFB and LDPE using a calcium oxide catalyst. The purpose of this research is to produce bio-oil from a mixture of EFB and LDPE, to determine the effect of the CaO catalyst ratio and temperature on the bio-oil yield, and to determine the physical and chemical characteristics of the bio-oil product. The catalytic co-pyrolysis process uses 10 grams of EFB/LDPE mixture (EFB/LDPE ratio 50%:50%), CaO catalyst with a variation of CaO/raw material ratio (1%, 2%, 3%, 4%, and 5% w/w) and temperature variations (400°C, 450°C, 500°C, 550 and 600 °C), with nitrogen gas flowing at a flow rate of 400 mL/min for 45 minutes. The highest yield generated on the use of CaO/raw material ratio of 5% w/w and temperature of 550 °C was 35.2%. The characteristics of the bio-oil obtained were the density of 0.948 g/mL, the viscosity of 4.18 cSt, pH of 4.04, and heating value of 43.4 MJ/Kg. The results of GC-MS analysis showed that bio-oil contained 37.05% phenol compounds, 27.88% hydrocarbon, 20.27% ketones, 7.21% alcohol, 4.36% aldehydes, and 1.08% ester.

1. Introduction
Biomass is an auspicious alternative energy source. One of the abundant biomass in Indonesia is empty fruit bunch (EFB) of palm oil, as solid waste from the palm oil industry [1,2]. This waste can be converted into liquid fuel (bio-oil) through pyrolysis technology. However, bio-oil produced from EFB pyrolysis has a low heating value, acidic and contains high oxygenate compounds [3,4]. Improving the quality of bio-oil can be done with hydrodeoxygenation (HDO) and catalytic cracking of bio-oil [5,6].

HDO and catalytic cracking are two-step processes for producing biofuel from biomass. Both of these processes require a catalyst, but the HDO process requires hydrogen gas and high pressure, so the operational cost is higher [7, 8]. The catalytic pyrolysis process is a one-step bio-oil upgrading process by pyrolysis of biomass using a catalyst [9,10]. The catalyst used is zeolite, such as ZSM-5 and ZSM-5...
modification. Zhang et al. [11] have conducted catalytic pyrolysis pre-treated rice husk with catalysts ZSM-5 and Fe/ZSM-5, produced bio-oils containing hydrocarbons respectively 44.19% and 49.97%, but bio-oil contains phenol compounds of 32% and 25%.

Another bio-oil upgrading process with a one-step process is co-pyrolysis, which is pyrolysis of biomass with materials that have a higher hydrogen index [12,13]. Some researchers have conducted co-pyrolysis of biomass and materials such as rubber and plastic. Sunarno et al. [14] have conducted co-pyrolysis of EFB using tires with a ratio of 25%: 75% at 500 °C, obtained bio-oil containing 59.55% hydrocarbons, 8.16% phenol, 5.63% acetic acid, 2.45% methanol and 24.19% oxygenate compounds with a bio-oil heating value of 33.1 MJ/kg. Abnisa et al. [15] has studied co-pyrolysis of palm shell and plastic polystyrene with a ratio of 50%: 50% at a temperature of 500 °C, and has obtained bio-oil with a heating value of 38.01 MJ/kg. The heating value of bio-oil produced in co-pyrolysis is still below the heating value of conventional liquid fuels, and bio-oil contains acid.

The purpose of this research is to study the effect of CaO catalyst concentration, and temperature of co-pyrolysis treated EFB and LDPE on bio-oil yields, bio-oil characterization of the best process conditions. The catalyst plays a role to increase the reaction rate and product selectivity [16,17]. Calcium oxide catalyst is relatively cheap and is widely used for the reaction of making biodiesel [18,19]. The use of CaO catalyst for co-pyrolysis treated EFB and LDPE can increase the heating value and reduce the acidity of bio-oil.

2. Materials and Method

Materials
Empty fruit bunch (EFB) of palm oil taken from PTPN V Riau, Indonesia. Plastic of low-density polyethylene (LDPE), NaOH, CaO, nitrogen and distilled water were used.

Methodology
EFB was washed with water, then dried in the sun. The dried EFB was cut into 1 cm size and soaked into 0.1 molar NaOH solution at 30 °C for 24 hours, with a weight ratio of EFB and sodium hydroxide solution of 1:5. EFB was filtered and washed with distilled water, then dried using an oven at 110 °C for 3 hours. Treated EFB was analyzed for lignocellulosic content. EFB contains 32.2% hemicellulose, 58.5% cellulose and 9.4% lignin. Low-density polyethylene (LDPE) obtained from plastic waste is washed and dried using the sun. Dried LDPE is cut into 1x1 cm.

Calcium oxide catalyst was carried out calcination process before being used in the process of co-pyrolysis. Calcium oxide powder is calcined into the furnace at 600 °C for 2 hours. Calcined CaO was analyzed with a Scanning Electron Microscope (SEM EDX) and Brunauer Emmet Teller (BET). The surface area of the catalyst is 46.116 m²/g. The composition of catalyst is shown in Table 1.

Table 1. Composition of Calcium Oxide Catalyst

| Compound | Value (%) |
|----------|-----------|
| Carbon   | 42.57     |
| MgO      | 0.33      |
| CaO      | 21.40     |
| CuO      | 0.57      |

The catalytic co-pyrolysis was carried out in the fixed-bed reactor under atmospheric pressure on a calcium oxide catalyst. The scheme of the experiment equipment was presented on Fig. 1. This system consists of tube reactors (inner diameter = 30 mm, length = 300 mm), condenser, separator, temperature controller, nitrogen cylinder and flowmeter. The treated EFB and pieces of LDPE waste with a weight
ratio of 50% : 50% was mixed calcium oxide with a concentration of 1, 2, 3, 4 and 5%. The mixed raw materials and catalyst were put into the co-pyrolysis reactor and heated at 500°C as well as the nitrogen gas was flowed at a flow rate of 400 mL/min for 45 minutes. The experiment was repeated at temperatures of 400, 450, 550 and 600°C. The vapour produced was condensed in a water-cooled condenser, while the liquid product was collected in the Erlenmeyer flask. Finally, the bio-oil and char product was weighed separately.

![Schematic diagram the experimental for catalytic co-pyrolysis.](image)

**Figure 1.** Schematic diagram the experimental for catalytic co-pyrolysis. 
(1)-nitrogen cylinder; (2)-reactor; (3)-temperature controller; (4)-condenser; (5)-separator; (6)-electric current source; (7)-bio-oil storage

The product of catalytic co-pyrolysis consists of bio-oil, char and non-condensable gases. The bio-oil and char were weighed to determine its yields. Heating value, acidity and viscosity of bio-oil were measured using bomb calorimeter, pH and viscometer, respectively. Compound composition of bio-oil was measured using gas chromatography-mass spectroscopy (GC-MS), QP2010S Shimadzu was used. Restek RxiR-5MS; 30 m; 0.25 mm ID was used as the column and the carrier gas was Helium. The temperature of the column was adjusted to 50°C for 5 min and then increased to 280°C by 5 °C/min. The injection and detection temperatures were set to be 300 and 280°C. Pressure: 12 kPa; Total flow: 40.0 mL/min; Column flow: 0.54 mL/min.

The equation used to calculate the yield of bio-oil, char and gas are as follow:

$$Y_{bio-oil} = \frac{W_{bio-oil}}{W_{raw-material}} \times 100\%$$  \hspace{1cm} (1) 

$$Y_{char} = \frac{W_{char}}{W_{raw-material}} \times 100\%$$  \hspace{1cm} (2)
\[ Y_{\text{gas}} = \frac{W_{\text{raw-material}} - W_{\text{bio-oil}} - W_{\text{char}}}{W_{\text{raw-material}}} \times 100\% \]  

(3)

Where \( Y_{\text{bio-oil}} \) is the yield of the bio-oil product; \( W_{\text{bio-oil}} \) is the weight of the bio-oil product; \( W_{\text{raw-material}} \) is the weight of raw-material; \( Y_{\text{char}} \) is the yield of char; \( W_{\text{char}} \) is the weight of char; \( Y_{\text{gas}} \) is the yield of gas.

3. Results and Discussion

The effect of catalyst concentration was studied on catalytic co-pyrolysis mix of empty fruit bunch (EFB) and low-density polyethylene (LDPE) with a ratio of 50% : 50% and at a temperature of 500 °C using calcium oxide catalyst. The product of the catalytic cracking process consists of bio-oil, char, and gas. Figure 2 shows the effect of CaO catalyst concentration on yield product of catalytic co-pyrolysis mix EFB and LDPE in the concentration range studied (1, 2, 3, 4, 5 wt.%). With the increase of calcium oxide concentration, the yield of bio-oil tends to increase. On the contrary, for the yield of char and gas, with increasing CaO concentration, the yield of char and gas show a decrease. As the concentration of calcium oxide increases, the activity of catalyst will increase, leading to an increase in the decomposition of raw materials of EFB and LDPE into bio-oil. With an increase in the concentration of CaO catalyst from 1 to 5%, the yield of bio-oil increased from 20.2% to 32.8%, while the gas yield decreased from 67.5% to 57.4% and the char yield fell from 12.3% to 9.8%. This study is similar to Lin et al. [20] which states that with an increase in CaO catalyst concentration of 5%, an increase in bio-oil yield of 11.3%.

![Figure 2](image)

**Figure 2.** The Effect of concentration of CaO Catalyst on yield of product

The raw material with EFB and LDPE ratio of 50% : 50% as well as catalyst concentration of 5% at 400-600 °C was used to study the effect of catalytic co-pyrolysis temperature on product yield. Fig.3 shows that with an increase in temperature from 400 to 550 °C, the yield of bio-oil increased, but at temperatures above 550 °C the yield decreases. This shows with an increase in temperature up to 550 °C raw material decomposed into bio-oil. However, at temperatures above 550°C, the formed bio-oil decomposed into gas. Bio-oil yield at EFB and LDPE ratio 1:1, catalyst concentration of 5% and temperature of 550°C were of 35.2%. As a comparison, Veses et al. [21] carried out catalytic pyrolysis of
pinewood chip using bentonite catalyst at a temperature range of 400-500 °C and the results showed that with an increase in temperature, the bio-oil yield increased, but the gas and char yield decreased.

![Figure 3. Effect of temperature on yield product](image)

The bio-oil product from catalytic co-pyrolysis EFB and LDPE with a ratio of 1:1 at a temperature of 550 °C and a catalyst concentration of 5% was analyzed by GC-MS. The chromatogram results of bio-oil can be seen in Figure 4. The composition of bio-oil was showed in Table 2. The compounds contained in bio-oil consists of 27.88% hydrocarbons, 37.05% phenol, 20.27% ketones, 7.21% alcohol, 4.37% aldehyde and 1.08% ester.

![Figure 4. Chromatogram of bio-oil composition profile from co-pyrolysis EFB and LDPE](image)
Table 2. Composition of bio-oil from co-pyrolysis of EFB and LDPE (1: 1) with a catalyst concentration of 5% at 550 °C

| Compounds                  | % Area |
|----------------------------|--------|
| **Hydrocarbons**           | 27.88  |
| 1-methyl-3- Benzene        | 2.5    |
| Buthyl- benzene            | 2.24   |
| 1-methyl-4- cyclohexene    | 1.06   |
| 1-methyl-4- benzene        | 3.15   |
| Hexane-isopropylidene-1-Methyl- Bicyclo | 1.85 |
| 3-methylene-4- cyclohexene | 0.45   |
| Penthyl- benzene           | 3.22   |
| 1,2-dihydro-3-methyl- Naphthalene | 1.08 |
| 1-cyclopentene-1-yl- Benzene | 2.45  |
| 3,3,5-trimethyl1,4-Hexadiene | 2.33  |
| Hexane (CAS)               | 2.73   |
| Methyl- cyclopentane       | 1.04   |
| Trans- 4,4-dideutero cyclopentene-3,5-diol | 0.45 |
| 1-Penten-3-ol (CAS)        | 1.32   |
| Cyclohexane, (ethylthio)- (CAS) | 0.97 |
| Toluene                    | 1.04   |
| **Phenols**                | 37.05  |
| Phenol                     | 34.50  |
| 2,6-dimethoxy- Phenol      | 2.55   |
| **Alcohols**               | 7.21   |
| Methyl alcohol             | 4.26   |
| 1,1,1,2,3,3-hexadeutero-2-butanol | 2.47 |
| 2-[6-chloro-4-(4-methyl-1-piperidyl)-1,3,5-triazin-2-ylamino]- Ethanol | 0.48 |
| **Ketones**                | 20.27  |
| 1-Hydroxy-2-butane         | 14.57  |
| 2-propanone                | 5.10   |
| Ethanone, 1-[2-(dimethylamino)phenyl]- (spectrum disagrees) (CAS) | 0.6 |
| **Aldehyde**               | 4.37   |
| n-Pentanal                 | 4.37   |
| **Esters**                 | 1.08   |
| Butanoic acid, 2-propenyl ester | 0.59 |
| Alpha-,(2,4,5-trichlorophenoxy)propionic acid, n-butyl ester | 0.49 |
| **Others**                 | 2.14   |
| Hexaacetyladrepine         | 0.95   |
| 8a-dimethyl- (3s,3ar,8ar,9ar)-3- {[4-(3-chlorophenyl)-1-piperazinyl]methyl} -5 | 0.67 |
| Curan-19,20-diol, 16,17-didehydro-, (19S)- (CAS) | 0.52 |
The physical characterization of bio-oil product from the catalytic co-pyrolysis process from a mixture of EFB and LDPE using a 5% CaO catalyst at a temperature of 550 °C can be seen in Table 3. The properties of the bio-oil product consists of the density of 0.948 g/mL, the viscosity of 4.178 cSt, pH of 4.04 and heating value of 43.4 MJ/kg. The density and viscosity of the bio-oil obtained from this study were lower than the density and viscosity of bio-oil from biomass pyrolysis. This shows that the carbon chain of bio-oil from catalytic co-pyrolysis is shorter than the oil from biomass pyrolysis. The pH and heating value of the bio-oil obtained from this study were higher than bio-oil from biomass pyrolysis. This indicates that the addition of LDPE and CaO catalyst can reduce acid compounds and increase hydrocarbon compounds in bio-oil. Thus, the bio-oil properties of catalytic co-pyrolysis EFB and LDPE using CaO catalysts are close to those of diesel oil.

Table 3. Comparison between properties of bio-oil and diesel oil

| No. | Properties               | Bio-oil of this study | Bio-oil [22] | Diesel oil [23] |
|-----|--------------------------|-----------------------|--------------|----------------|
| 1   | Density (g/mL)           | 0.948                 | 1.11-1.30    | 0.84           |
| 2   | Viscosity (cSt)          | 4.178                 | 15-40        | 6              |
| 3   | pH                       | 4.04                  | 2-3          | 5              |
| 4   | Heating value (MJ/kg)    | 43.4                  | 14-19        | 42-46          |

4. Conclusion
The concentration of calcium oxide catalyst and co-pyrolysis temperature plays a role in product yield of catalytic co-pyrolysis of EFB and LDPE. With the increase CaO concentration (1 – 5 wt.%), the yield of bio-oil rose, while the yield of char and gas decreased. With the raw materials EFB to LDPE ratio of 1 : 1 and 5% CaO catalyst at a temperature of 550 °C, the bio-oil yield obtained is 35.2%. The characteristics of the bio-oil obtained were the density of 0.948 g/mL, the viscosity of 4.18 cSt, pH of 4.04, and heating value of 43.4 MJ/Kg. The results of GC-MS analysis showed that bio-oil contained 37.05% phenol compounds, 27.88% hydrocarbon, 20.27% ketones, 7.21% alcohol, 4.36% aldehydes, and 1.08% ester.

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