

# Silica-Alumina Based Catalytic Cracking of Bio-Oil Using Double Series Reactor

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**Abstract-** Palm oil empty fruit bunches (EFB) which are abundantly present in Indonesia as waste with a low economic value can be processed into bio-oil through pyrolysis process. However, as it contains large molecules, bio-oil generally has a high viscosity which limits the feasibility of its utilization. In this study, the use of silica-alumina as mesoporous catalyst was examined to improve the quality of products from catalytic cracking of bio-oil by breaking down the large molecules. The effect of the catalyst weight (0-40 gram) on the yield and composition of the catalytic cracking product was investigated. Bio-oil derived from EFB was upgraded through double series reactor under atmospheric pressure to minimize coke formation. The results confirmed that the weight of catalyst affects the quality and quantity of oil product. Increasing catalyst weight from 0 to 40 gram reduced the yield of oil from 42.8 to 22.72% but increased the concentration of gasoline and kerosene from 6.61 to 17.02% and 17.53 to 24.53%, respectively. In addition, increasing catalyst weight promoted an increase in the heating value of oil from 32 to 36.7 MJ/kg.

**Keywords** Bio-oil; catalytic cracking; gasoline, kerosene; silica-alumina.

## 1. Introduction

Fuel consumption has increased annually due to the growth in global population. The need for transport and mobility demands the automobile industry to increase accordingly. As a result, high depletion rate of the non-renewable fossil fuels especially for transportation has intensified since the last few decades [1-3]. Moreover, the continuous use of fossil fuels for hydrocarbon and energy sources has caused numerous severe global problems through the increasing concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere [4-6]. It is therefore understandable that alternative energy sources that are renewable and environmentally friendly have gained many interests [7].

Among many alternatives, biomass is a renewable energy source which promotes a net zero CO<sub>2</sub> emission and does not directly contribute to the global warming [8-11]. As an agricultural country, one of the most abundant biomass in Indonesia is palm empty fruit bunches (EFB). This type of

biomass has a very competitive price because it is produced as a solid waste from the palm oil industry. Moreover, EFB contains cellulose, hemicellulose and lignin, all of which can be converted into bio-oil through pyrolysis [12, 13].

On the other hand, bio-oil produced from biomass pyrolysis has not been able to substitute transportation fuel since it contains a high proportion of oxygenated compounds (35-40%wt) [14]. Found in diverse chemical forms, such as aldehydes, alcohols, acids, guaiacol, esters, ketones, phenol and derivatives, these oxygenated compounds have caused various undesired properties on bio-oil such as thermal instability, high viscosity, low heating value and corrosiveness [15-17]. Consequently, prior to being used as an energy source, the effort to upgrade bio-oil quality is required. Reducing the oxygenated compounds in bio-oil can be achieved through catalytic cracking [18].

Catalytic cracking is generally performed using cracking catalysts (zeolites, silica alumina and molecular sieves) at

atmospheric pressure with the temperature ranges from 350 to 650°C [19, 20]. With the absence of hydrogen, oxygen is eliminated in the form of water, carbon monoxide and carbon dioxide. On the other words, cracking is a thermally treated process in which deoxygenation of bio-oil is accomplished through simultaneous dehydration, decarboxylation, decarbonylation, oligomerization, dehydrogenation and isomerization reaction. The products of catalytic cracking process consist of gas, liquid and solid. The gas is combustible, composed of CO, CO<sub>2</sub>, H<sub>2</sub> and light hydrocarbon [21] whereas the liquid product can be divided into two phases, *i.e.*, aqueous and oil phases. The aqueous phase consists of over 95% water and several organic components that are soluble in water [22]. The main composition of oil is aromatic hydrocarbon compounds with a high octane number hence it can be used in gasoline as octane enhancers [23, 24].

One of the challenges in catalytic cracking of bio-oil is coke formation. Coke causes catalyst deactivation by poisoning catalyst acid site and pore blockage hence reducing the yield of oil and selectivity of hydrocarbon [25]. Coke formation can be influenced by chemical composition of feedstock, reaction conditions and catalyst properties [26]. However, according to Ibanez et al. [27], coke is mostly formed by lignin pyrolysis phenol derivatives. While higher coke yields were obtained from catalysts with larger pore size, catalyst with medium pore size resulted in the least formation of coke.

Silica-alumina has been extensively used as catalyst for bio-oil catalytic cracking. It is appropriate due to the fact that the diffusion rate of bio-oil influences the activity and selectivity of catalyst. In addition to several acid sites, silica-alumina also has larger pore size than zeolite. Thus, the catalyst acidity rises with the increasing calcination temperature. The presence of mesoporous silica-alumina contributes the diffusion of reaction molecules inside of catalyst particles pore since large molecules are cracked into smaller molecules by a primary reaction. This catalyst will resist the excess of cracking and will encourage the isomerization [28, 29].

Several studies of crude bio-oil catalytic cracking were conducted using ZSM-5 catalyst in a single fixed bed reactor. Zhu et al. [30] studied catalytic cracking using ZSM-5 catalyst and obtained a yield of oil and coke of 36% and 23.8%, respectively. With an identical type of catalyst, Stefanidis et al. [31] assessed catalytic cracking of biomass pyrolysis vapors and obtained an oil and coke yield of 28.4% and 26.38%, respectively. In addition, Graca et al. [32] used mixture of crude bio-oil and gasoil as raw materials for catalytic cracking and obtained an oil yield and coke of 19.6% and 16%, respectively. However, in these studies, a relatively high amount of coke was generated despite the use of ZSM-5 catalyst, which is more expensive than silica-alumina catalyst.

The objective of this study is to examine the effect of the silica-alumina catalyst weight (0 - 40 g) on the product yield and composition in catalytic cracking of bio-oil. In order to minimize coke formation, double series reactor which is the unification between thermal reactor and catalytic cracking

reactor is employed. The thermal cracking reactor is useful for cracking of lignin pyrolysis phenol derivatives into smaller molecules, so the formation of coke on the catalytic cracking reactor can be minimized. Instead of crude bio-oil, the top phase fraction of bio-oil was used as raw material for catalytic cracking. The raw material itself was a result of decantation crude bio-oil derived from pyrolysis of oil palm empty fruit bunch (EFB). The raw material is present in a homogeneous phase, has a high heating value with a low viscosity and low density.

## 2. Materials and Methods

### 2.1. Materials

Bio-oil was produced by palm empty fruit bunch (EFB) pyrolysis in a fixed bed reactor with capacity of 1 kg/batch at 500 °C. The liquid product was then separated by decantation and its top product was used as raw material of catalytic cracking. The density of the raw material was 0.997 g/mL, its viscosity was 17.906 centipoise (cP) and its heating value was 27.575 MJ/kg. The compositions of raw material comprised of 4.02% acetone, 5.24% acetic acid, 2.69% gasoline (C<sub>5</sub>-C<sub>11</sub>), 6.53% kerosene (C<sub>12</sub>-C<sub>18</sub>), 23.89% phenol, and 57.54% oxygenated organic compounds.

### 2.2. Catalyst Preparation

Silica-alumina powder was obtained from PT. Pertamina, Balongan, Indonesia. The powder was mixed with 5% clay and distilled water, then was formed into cylindrical form with the length of 0.6 cm and diameter of 0.4 cm using pressing equipment. After the pressing, the catalyst was dried at 110 °C for 2 h and then calcined at 500 °C under N<sub>2</sub> purge for 2 hours to activate. Before being used, the catalyst was stored in a desiccator to minimize the adsorption of the atmospheric moisture.

### 2.3. Catalyst Characterization

The calcined catalyst was characterized by Brunauer-Emmett-Teller (BET) Surface Area Analysis to determine the surface area, pore diameter and pore volume. The composition of catalyst material was analyzed using atomic absorption spectroscopy (AAS). Physical properties and composition of the catalyst are shown in Table 1.

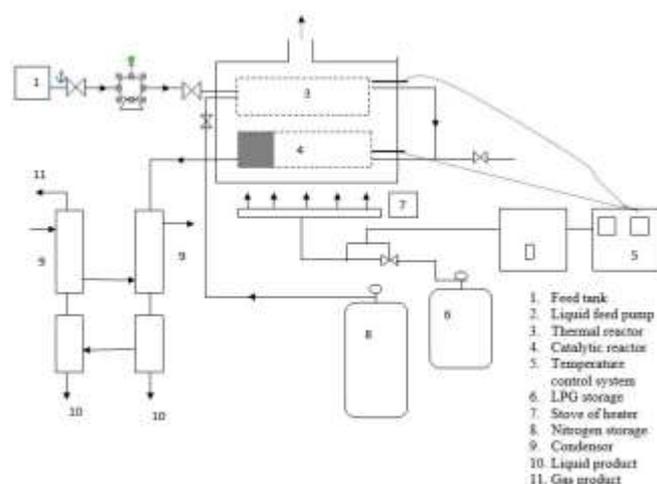
### 2.4. Bio-oil Catalytic Cracking

The catalytic cracking of bio-oil was performed in series of tubular reactors under atmospheric pressure using silica-alumina catalyst. The scheme of the experiment equipment was presented in Fig.1. The system consisted of two tube reactors (inner diameter = 70 mm, length = 300 mm), a liquid feed system, a liquid feed pump, furnace, stove, a gas of LPG system, a condenser and a cooling water pump. Before heating, 10 to 40 g of the silica-alumina catalyst with a particle size of 0.4 x 0.6 cm was uniformly filled in the catalyst bed. The reactor was then heated up with LPG fuel stove until desired temperature (500 °C). Furthermore, N<sub>2</sub>

was flowed with a flow rate of 400 mL/min to completely remove the air throughout the reactor system, then bio-oil was flowed with volumetric rate of 8 mL/min and stopped to volume of 50 mL. The vapor produced was then condensed in water cooled condenser, while liquid product was collected in an Erlenmeyer flask. Finally, the oil and aqueous product were weighed separately.

**Table 1.** Properties of silica-alumina catalyst

Properties	Value
Surface area (m <sup>2</sup> /g)	240.553
Pore volume (cc/g)	0.199
Average pore diameter (nm)	3.3
SiO <sub>2</sub> (%)	51.546
Al <sub>2</sub> O <sub>3</sub> (%)	43.923
Na <sub>2</sub> O (%)	0.48
K <sub>2</sub> O (%)	0.017
CaO (%)	0.035
Fe <sub>2</sub> O <sub>3</sub> (%)	0.282



**Fig. 1.** Schematic diagram the experimental for cracking reaction

### 2.5. Product Analysis

The oil was weighed to determine its yield. The density of bio-oil, oil and aqueous product were measured using pycnometer. Additionally, the calorific value of oil was measured using bomb calorimeter while flash point was measured using flash point PMCC. The composition of bio-oil and oil were measured using gas chromatography-mass spectroscopy (GC-MS) and QP2010S Shimadzu. Besides that, Restek RxiR-5MS; 30 m; 0.25 mm ID was also used as the column using helium as the carrier gas. More specifically, the temperature of the column was adjusted to 50 °C for 5 min and then increased to 280 °C by 5 °C/min. In addition, the injection and temperatures detection were set to be 300 and 280 °C with pressure: 12 kPa; total flow: 40.0 mL/min; column flow: 0.54 mL/min. The composition of gas

product was measured using gas chromatography (GC) (Shimadzu series GC 8A). Analysis of CH<sub>4</sub>, CO and CO<sub>2</sub> content were conducted using column of porapak-Q, column temperature of 40 °C, injection and detection temperatures of 60 °C using helium as carrier gas in this analysis. Analysis of H<sub>2</sub> was conducted using column of molecular sieve ms 5A, column temperature of 60 °C, injection and detection temperatures of 70 °C using nitrogen as the carrier gas.

The yield of oil, coke, aqueous and gas were calculated by using Eq. (1) – (4).

$$Y_{oil} = \frac{W_{oil}}{W_{bio-oil}} \times 100\% \quad (1)$$

$$Y_{coke} = \frac{W_{coke}}{W_{bio-oil}} \times 100\% \quad (2)$$

$$Y_{aqueous} = \frac{W_{aqueous}}{W_{bio-oil}} \times 100\% \quad (3)$$

$$Y_{gas} = \frac{W_{bio-oil} - W_{oil} - W_{coke} - W_{aqueous}}{W_{bio-oil}} \times 100\% \quad (4)$$

Where Y<sub>oil</sub> is the yield of oil product; W<sub>oil</sub> is the weight of oil product; W<sub>bio-oil</sub> is the weight of bio-oil; Y<sub>coke</sub> is the yield of coke; W<sub>coke</sub> is the weight of coke; Y<sub>aqueous</sub> is the yield of aqueous; W<sub>aqueous</sub> is the weight of aqueous; Y<sub>gas</sub> is the yield of gas.

## 3. Results and Discussion

### 3.1. Effect of catalyst weight on the yields of product

The effect of catalyst weight on the product yield during catalytic cracking of the bio-oil with silica-alumina catalyst at 500 °C is shown in Fig. 2. The product of catalytic cracking consists of oil, coke, aqueous and gas. It can be seen that the yield of oil decreased as the weight of catalyst increased. With the rise of catalyst weight from 0 to 40 gram, the yield of oil declined from 42.8 to 22.72%. On the contrary, increasing catalyst weight resulted in an increase in gas yield from 41.49 to 54.47%. Moreover, increasing catalyst weight also increased the reactants residence time in the catalyst bed, leading to the increase in the decomposition of bio-oil into gases with small molecules. Figure 2 also shows that the yield of coke with catalyst was higher than that of without catalyst. With the increase of catalyst weight from 0 to 40 gram, the yield of coke increased from 5.61 to 9.59% due to the secondary cracking of the aromatic hydrocarbons. It is important to note that the coke yield in this study was lower than other previous studies [30-32]. This implies that cracking of the top phase fraction of bio-oil using double series reactor is a feasible method to decrease catalyst coking. The yield of thermal coke and catalytic coke obtained in this study is listed in Table 2. The yield of catalytic coke was lower than yield of thermal coke, implying that the cracking of phenolic compounds has occurred in the thermal reactor. Thus, deactivation of catalyst

can be reduced. The effect of catalyst weight on the product yield in catalytic cracking of bio-oil was comparable to the effect of temperature on the product yield investigated by Sunarno et al. [33].

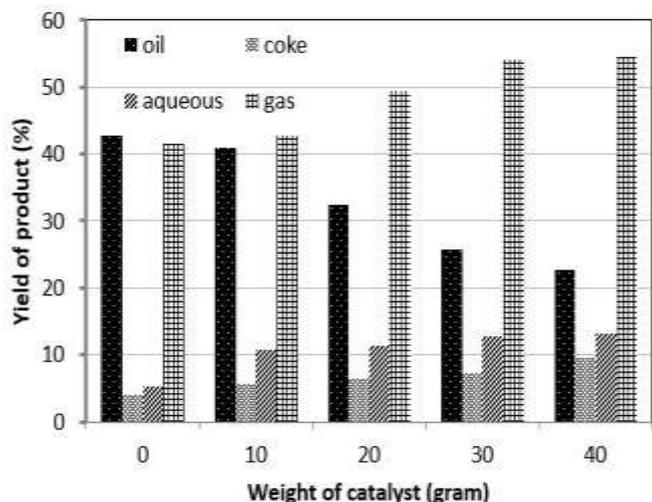


Fig. 2. Effect of catalyst weight on yield of product

Table 2. The effect of catalyst weight on yield of coke

Catalyst weight (gram)	Yield thermal of coke (%)	Yield catalytic of coke (%)
0	4.13	0
10	3.98	2.04
20	4.54	1.63
30	4.98	2.38
40	6.60	1.53

Figure 2 also indicates that with the increase of catalyst weight, the yield of aqueous will also increase. More specifically, this suggests that increasing of catalyst weight will increase the water production, as a result of deoxygenation of bio-oil. The organic component of aqueous products on catalytic cracking using 10 grams catalyst is listed in Table 3. It was found that the aqueous product mainly consisted of acetic acid, followed by phenol and propanoic acid. The density and viscosity of the aqueous product were 1.062 g/mL and 1.078 cP, respectively, which approach the density and viscosity of water.

Table 3. Composition of aqueous product

No.	Compound	Concentration of aqueous (%)
1	Acetone	3.87
2	Acetic acid	55.66
3	Benzeneethanamine	8.92
4	Propanoic acid	13.19
5	Phenol	18.21

### 3.2 Effect of catalyst weight on the composition of oil product

The oil product consists of oxygenated compounds, gasoline, kerosene, phenol, acetic acid and acetone. As shown in Fig. 3, catalyst weight has an effect on composition of oil product. Increasing the catalyst weight reduced the concentration of oxygenated compound in oil product and increased the concentration of gasoline and kerosene as well as phenol concentration. However, the concentration of acetic acid and acetone were relatively constant. This can be ascribed to the effect of catalyst addition that deoxygenated the oxygenated compound into hydrocarbons i.e. gasoline and kerosene. In addition, the cracking of oxygenated compound into phenol also occurred. The increase of catalyst weight from 0 to 40 gram resulted in a decrease in concentration of oxygenated compound from 51.99 to 30.71% and increase in gasoline concentration from 6.61 to 17.02%. Additionally, kerosene and phenol concentration also increased from 17.53 to 24.53% and from 19.68 to 23.91%, respectively.

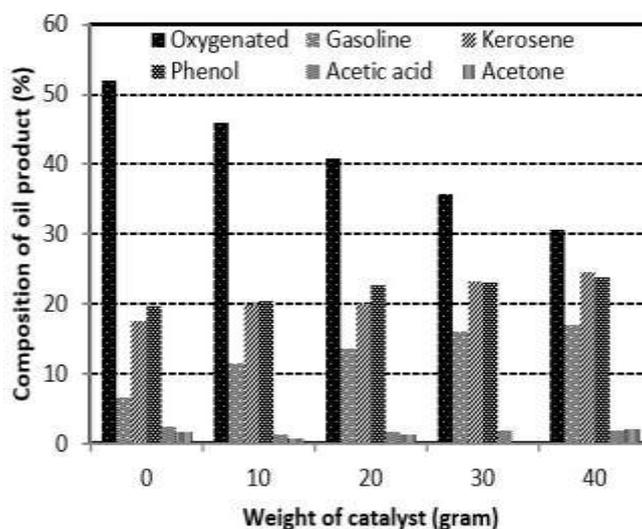
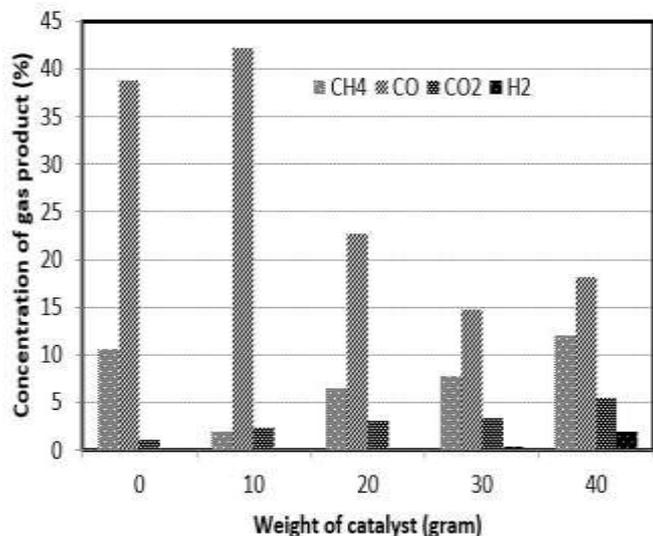


Fig. 3. Effect of catalyst weight on composition of oil product

### 3.3 Effect of catalyst weight on the composition of gas product

Figure 4 shows the effect of catalyst weight on the composition of gas product. The gas product mainly consisted of CO and a smaller quantity of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. Increasing catalyst weight reduced CO concentration but increased CO<sub>2</sub> concentration. This can be explained by several chemical reactions including decarbonylation and decarboxylation occurred during bio-oil cracking. With the increase of catalyst weight, the decarbonylation reaction will decrease, while the decarboxylation reaction will increase. On the other hand, it was observed that H<sub>2</sub> was only produced at the catalyst weight of more than 20 gram, indicating that catalyst weight of more than 20 gram promotes dehydrogenation reaction during catalytic cracking

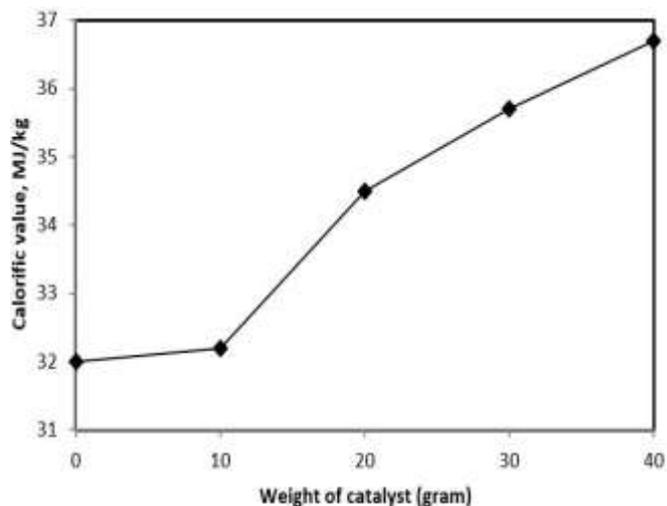
of bio-oil. Overall, with catalyst weight of 0 – 40 gram, CH<sub>4</sub> was produced in the range of 1.978 – 12.012%, CO in the range of 18.174 – 42.303%, CO<sub>2</sub> gas in the range of 1.146 – 5.437% and H<sub>2</sub> in the range of 0.207 – 1.873%. It should be noted that H<sub>2</sub> concentration in the gas product was lower than result of tar decomposition using Fe catalyst previously studied by Wicakso et al. [34].



**Fig. 4.** Effect of catalyst weight on composition of gas product

### 3.4. Effect of catalyst weight on the physical properties of oil product

In addition to the composition of gas and oil product, catalyst weight also showed an effect on physical properties of oil product including heating value, density and viscosity. Figure 5 shows that the heating value of the oil obtained by non-catalytic cracking at 500 °C increased by 16.05% to 32 MJ/kg from 27.575 MJ/kg for bio-oil raw material. With catalyst addition of 10 gram, the heating value only increased by 16.77% to 32.2 MJ/kg. However, when the catalyst weight was further increased from 20 gram to 40 gram, the heating value of oil increased from 34.5 MJ/kg to 36.7 MJ/kg. The heating value of all oil product increased after cracking process as opposed to the raw bio-oil. During the bio-oil cracking, oxygen atoms were removed through deoxidation, decarbonylation, decarboxylation and dehydration reaction which led to the increase of heating value. The heating value of oil produced from catalytic cracking was found to be higher than that of oil produced from non-catalytic cracking. This is because acid sites on silica-alumina catalyst promoted the hydrocarbon production through chemical reactions such as decarbonylation and decarboxylation. As it can be observed from Fig. 3 that gasoline and kerosene produced with catalyst contained a higher hydrocarbon content than of the product without catalyst. As comparison, the heating value of all oil products in this study was notably higher than the heating value of oil via the decomposition of tar (31 MJ/kg) performed by Wicakso et al. [34] and cracking of lignin (24.5 MJ/kg) conducted by Bu et al. [3].



**Fig. 5.** Effect of catalyst weight on heating value of oil product

**Table 4.** Effect of catalyst weight on density and viscosity of oil product

Weight of catalyst (gram)	Density of oil product (g/mL)	Viscosity of oil product (cP)
0	0.9920	9.1457
10	0.9845	6.7153
20	0.9812	4.6199
30	0.9698	4.4574
40	0.9542	3.4325

Oil density is important in the combustion system and it is related to the chemical structure and composition of oil. Table 4 shows the effect of catalyst weight on density and viscosity of oil product. With the increase of catalyst weight from 0 to 40 gram, the oil density reduced from 0.9920 to 0.9542 g/mL. During the cracking process, bio-oil containing oxygenated compounds were decomposed to hydrocarbons such as gasoline and kerosene which have lower density than oxygenated compounds. Viscosity is affected by the chemical structure of the oil such as the oxygenated compounds profile, chain length, oxidation product and degree of unsaturation. The oil product had a much lower viscosity than that of raw bio-oil, mainly because several large and complicated bio-oil molecules had been cracked into smaller and simpler molecules. As seen in Table 4, increasing the catalyst weight from 0 to 40 gram reduced the oil viscosity from 9.1457 to 3.4325 cP. This viscosity value was most likely similar to viscosity of biodiesel and diesel oil.

## 4. Conclusion

The weight of silica-alumina catalyst affected the product yield, composition of oil & gas product, and physical properties of oil product from catalytic cracking. Increasing catalyst weight from 0 to 40 gram caused bio-oil yield to decrease from 42.8 to 22.72% in contrast to the yield of gas,

aqueous phase and coke which underwent a significant increase. In addition, increasing catalyst weight promoted a decrease in the concentration of oxygenated compound from 51.99 to 30.71%, in contrast to the increase of gasoline from 6.61 to 17.02%, kerosene from 17.53 to 24.53% and phenol from 19.68 to 23.91%. Increasing catalyst weight also caused heating value of oil to increase from 32 to 36.7 MJ/kg, meanwhile, both density and viscosity of oil decreased from 0.992 to 0.954 g/mL and from 9.1457 to 3.4325 cP, respectively. Hence, this study has confirmed that catalytic cracking of bio-oil can improve the quality of oil product.

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