Improving characteristic of bio-oil by esterification method

R C Sondakh¹, E Hambali¹,² and N S Indrasti¹

¹ Department Agro-industrial Technology, Faculty of Agricultural Technology, Bogor Agricultural University, Bogor, Indonesia
² Surfactant Bioenergy Research Center LPPM IPB, Bogor, Indonesia

E-mail: riansondakh@gmail.com

Abstract. Bio-oil is one of the promising renewable energy that raw materials are sourced from agricultural waste and industrial waste but the quality of bio-oil is still not good for fuel use. One of the methods to upgrading bio-oil is using esterification. Esterification method reduces viscosity, water content, and improving heating value. The purpose of this research was to improving bio-oil quality by type and concentration acid catalyst. Catalyst used was H₂SO₄ and HCl. The result showed 1% catalyst concentration of bio-oil which the best in improving the characteristic of bio-oil. The bio-oil after esterification shows viscosity kinematic 3.06 and 3.03 cSt @40°C, density 1.20 and 1.23 kg/dm³ @20°C, calorific value 20.17 and 18.31 MJ/kg, water content 0.83 and 0.84 wt%, ash content 0.0003 and 0.0001 wt%, pH value 3.28 and 2.99, acid number 0.27 and 1.04 mg-KOH/g. H₂SO₄ catalyst found more suitable with 1% catalyst concentration because has better impact to bio-oil characteristic. The process conducted that organic acids can be converted to esters over H₂SO₄ and HCl catalyst indicating its high activity.

1. Introduction
Bio-oil is one of the promising renewable energy where raw materials are sourced from agricultural waste and industrial waste. There are many methods to produce bio-oils such as using fast pyrolysis or hydrothermal liquefaction [1]. Fast pyrolysis is designed to maximize bio-oil yield by the rate of heating used potential. However, there are many issues of bio-oil like high water content in bio-oil affects the value of heating and viscosity, while high acidity causes bio-oil to become highly corrosive and unstable and high oxygen content causes low energy density and insoluble with hydrocarbons. The problems of low quality bio-oil as fuel becomes main issues, but the quality bio-oil can be improved through several efforts, known as upgrading bio-oil. There are several methods to improve the quality of bio-oil to be better including hydro-cracking, supercritical fluids (SCFs), esterification process, and emulsification [2].

Esterification is the best method of choice for converting reactive organic acids in bio-oil to a more stable ester. The reaction conditions for acid esterification in bio-oil is the presence of an acid catalyst in a mixture of bio-oil and alcohol complexes, are also suitable / conducive to many other reactions. Esterification is a heating process involving an acid catalyst (acid catalysts) mixed with a polar solvent. This process takes place at a temperature of 55°C - 60°C within 1-4 hours [3]. Chemical reactions between bio-oil and methanol / ethanol in the esterification process, beside to reduce viscosity in the same time reduce acidity, increase volatility, increase heating value, and also better in mixing with diesel fuel. The chemical reaction between bio-oil and alcohol are R—COOH + R’—OH —> R—
COO—R’ + H₂O. The esterification process uses several catalysts such as heterogeneous catalysts, solid acid catalysts, solid base catalysts, ionic liquid catalysts, HZSM-5 and aluminum silicate [4].

This paper reports how to improve the characteristic of bio-oil by treating the type and concentration of catalysts in the esterification reaction and obtain the characteristic of bio-oil according to standards.

2. Method

2.1. Material and chemical

The raw material of bio-oil comes from woods pellet produced by fast pyrolysis reaction from the Agency Assessment and Application of Technology (BPPT), Indonesia. H₂SO₄ (96%) and HCl (37%) were used as catalyst, Ethanol (97%) was used for solvent. The catalyst and solvent are from the Laboratory of Surfactant and Bioenergy Research Center LPPM IPB, Bogor.

2.2. Characterization of bio-oil

Bio-oil preparation before esterification was carried out by the characteristic analysis of bio-oil, so after esterification it could be seen that bio-oil characteristic was improve according to standard pyrolysis liquid bio-fuel, can be seen in Table 1. The analysis in bio-oil sample carried out was an analysis of physical-chemical properties such as acid number (FBI-A01-03 titration), density (4500 M Anton Paar DMA density meter), kinematic viscosity (Brookfield DV III Ultra Rheometer), pH (pH Meter Schoot HandyLab), bomb calorimeter (parr 6200), water content (distillation), ash (ASTM D 874 furnace).

2.3. Esterification reaction

Before entering esterification process, first thing to do was preparing bio-oil sample of 50 ml using a measuring cup and solvent used was ethanol by 50% (w/w) [3]. In this research was carried out at temperature 60°C [4] with a reaction time of 240 minutes [5] which produces yields more than 70%. The catalyst used in this research was commercial catalyst such as sulfuric acid (H₂SO₄ 96%) and hydrochloric acid (HCl 37%). The catalyst concentration used varies 1%, 3%, 5% from the sample weight. After the esterification process, separation was carried out using 0.1 N KOH liquid to separate ethanol and unreacted catalyst and then purification using sodium sulfate (Na₂SO₄) to separate water from bio-oil, the next stage was decanting and filtration to separate sodium sulfate, water and bio-oil.

2.4. Characterization of bio-oil after esterification reaction

After esterification analysis performed was analysis physical-chemical properties. Characteristics bio-oil refers to standard specification for pyrolysis liquid bio-fuel by American Standard Test and Material (ASTM D7544) can be seen at Table 1. In this research some characteristic were determined use test method like density (DMA density 4500 M Anton Paar), kinematic viscosity (Brookfield DV III Ultra Rheometer), pH (pH Meter Schoot HandyLab), calorific value (bomb calorimeter parr 6200), water content (distillation), ash (furnace), acid number (Titration FBI-A01-03).

| Characteristics                  | Value limit | Test method  |
|----------------------------------|-------------|--------------|
| Density 20°C, kg/dm³             | 1.1         | ASTM D 4052  |
| Viscosity kinematic 40 °C, mm²/s (cSt) | 125 max     | ASTM D 445   |
| Calorific value MJ/kg            | 15 min      | ASTM D 240   |
| Water content wt%                | 30 max      | ASTM E203    |
| pH                               | Report       | ASTM E70     |
| Ash content wt%                  | 0.25 max    | ASTM 482     |
| Acid number                      | 0.8         | FBI-A01-03   |

Table 1. Standard specification of pyrolysis liquid bio-fuel (ASTM D7544).
3. Results and Discussion

3.1. Characterization of bio-oil

Bio-oil used in this research has a color dark-brown and was produced through the process of fast pyrolysis with raw materials made from pine wood in the form of pellets. Furthermore, physical-chemical analysis of bio-oil is carried out before esterification. The results of bio-oil analysis can be seen in Table 2.

| Characteristic       | Unit         | Value  |
|----------------------|--------------|--------|
| Viscosity kinematic  | cSt @40°C    | 41.31  |
| Density              | kg/dm³ @20°C | 1.51   |
| Water content        | wt%          | 25     |
| pH                   | -            | 2.32   |
| Acid Number          | mg-KOH/g     | 12.09  |
| Ash                  | wt%          | 0.02   |
| calorific value      | MJ/kg        | 13.12  |

Table 2 shows bio-oil has considerable viscosity and low calorific values, the average characteristics of bio-oil do not meet applicable standards. According to Zhang [5] bio-oil from wood has a heating value of 20 MJ/kg much different from the results of this study which was only 13.12 MJ/kg which does not meet the standards. An increase in bio-oil viscosity is usually due to poor storage and in the certain temperature with the addition of low solvent concentrations. The density in this study was quite large 1.51 kg/dm³ @20°C because there are still many impurity particles or water content in bio-oil. Water content was 25 wt% which means low calorific value. The pH is quite low in this study was 2.32 due to organic acid components in bio-oil [6]. The acid number was 12.09 mg-KOH/g is the amount of organic acid in bio-oil [7]. Ash content of 0.02 wt% was quite low and meets to standard.

3.2. Bio-oil Analysis Results After Esterification

Bio-oil after the esterification reaction with 50% ethanol (w/w) and acid catalyst types including H₂SO₄ (K1) and HCl (K2) was carried out with a variety of concentrations including 1% (A1), 3% (A2), 5% (A3) shows a significant change in the characteristics of bio-oil such as reducing kinematic viscosity, density, ash and acid numbers and increasing the calorific value [6]. More can be seen in Table 3.

| Treatment | Viscosity kinematic cSt @40°C | Density kg/dm³ @20°C | Calorific value MJ/kg | Water content wt% | Ash content wt% | pH value | Acid number mg-KOH/g |
|-----------|-------------------------------|-----------------------|-----------------------|-------------------|-----------------|----------|----------------------|
| K1A1      | 3.06                          | 1.20                  | 20.17                 | 0.83              | 0.0003          | 3.28     | 0.27                 |
| K1A2      | 3.10                          | 1.24                  | 16.65                 | 0.84              | 0.0004          | 2.88     | 0.56                 |
| K1A3      | 3.13                          | 1.26                  | 15.90                 | 0.85              | 0.0006          | 1.56     | 0.70                 |
| K2A1      | 3.03                          | 1.23                  | 18.31                 | 0.84              | 0.0001          | 2.99     | 1.04                 |
| K2A2      | 3.07                          | 1.23                  | 17.23                 | 0.85              | 0.0006          | 2.79     | 1.64                 |
| K2A3      | 3.22                          | 1.25                  | 15.23                 | 0.86              | 0.0008          | 2.42     | 1.89                 |

The treatment of H₂SO₄ (K1) with catalyst concentrations 1%, 3%, and 5% showed better quality
of bio-oil in reducing viscosity, density, ash and acid numbers and increasing calorific value. Table 3 shows the greater the concentration catalyst was given much higher the viscosity produced, same as well with density, ash and acid numbers. Providing H$_2$SO$_4$ catalyst at concentration 1% found an increasing calorific value much better than the other amounted to 20.17 MJ/kg and lower viscosity value 3.06 cSt @40°C. HCl (K2) catalyst concentrations 1%, 3% and 5% have similar results in characteristic bio-oil with H$_2$SO$_4$ catalyst which can reduce viscosity, density, ash, and acid numbers and increase calorific value. The concentration of 1% HCl has a better impact than other concentrations in reducing the ash content to 0.0001 wt% from the previous 0.02 wt% and can reduce the viscosity 3.03 cSt @40°C, density 1.23 kg/dm$^3$ @20°C, and acid numbers 1.04 mg-KOH/g.

3.2.1. Effect of type and concentration of catalyst on bio-oil viscosity and density
Viscosity is the resistance possessed by the liquid flowing in a particular process, if the viscosity is higher and then the flow resistance will be higher [8]. This means the lower viscosity value will be better [8]. This research showed that more catalyst concentration, the greater viscosity value. The effect of the type of catalyst is quite significant in value of viscosity, can be seen in Figure 1. HCl catalyst at 1% concentration has a smaller viscosity value 3.03 cSt @40°C and does not significant differences with H$_2$SO$_4$ was 3.06 cSt @40°C.

![Figure 1. Effect of type and concentration of catalyst on bio-oil viscosity (A) and density (B).](image)

The effect of density will increase the calorific value where low density will produce a high calorific value [9]. Catalyst concentrations of 1%, 3%, and 5% showed changes in the density of bio-oil for all catalysts H$_2$SO$_4$ and HCl. The concentration catalyst 1% gets changes in density smaller than it should be seen in figure 2. Catalyst H$_2$SO$_4$ concentration 1% was get the smallest density than another catalyst 1.20 kg/dm$^3$ @20°C, HCl catalyst was 1.23 kg/dm$^3$ @20°C, but all two catalysts had quality density that conforms to the applicable standard can be seen in figure 1.

3.2.2. Effect of type and concentration of catalyst on bio-oil calorific value and water content
Giving 1% catalyst concentration has a better impact on the characteristic bio oil. Calorific value at 1% concentration of H$_2$SO$_4$ and HCl catalysts get a better heating value of 20.17 and 18.31 MJ/kg, which has increased from previously only 13.12 MJ/kg. Giving 1% catalyst concentration was enough to improve the characteristic bio-oil that meets applicable standards can be seen in Figure 2.

Bio-oil has a large water content of 15-30% depending on the raw materials used and during the storage period. After esterification water content was decreased in two catalysts used, this makes sense because at the same time increasing the calorific value will be reduced water content [10]. In this study found 25 wt% moisture content before esterification, at the time after esterification H$_2$SO$_4$ catalyst was obtained 0.83 wt% with concentration of 1% catalyst which had water content smaller than HCl catalysts and other concentrations. Nevertheless, HCl catalyst was got good quality 0.84 wt% which in
accordance with the applicable standards, can be seen in full in Figure 2.

![Figure 2](image)

**Figure 2.** Effect of type and concentration of catalyst on bio-oil calorific value (A) and water content (B)

### 3.2.3. Effect of type and concentration of catalyst on bio-oil pH value and ash content

H$_2$SO$_4$ and HCl catalysts had pH values 3.28 and 2.99. The acidity of bio-oil is caused by the content of organic acid compounds in bio-oil [11], but according to ASTM D7544 standards pyrolysis liquid bio-fuel will not have an impact on its use as industrial fuel. The pH value data can be seen in Figure 3.

The greater ash content will result in erosion, corrosion, and problems in engine valve and decreases the quality of bio-oil [12]. Before esterification the ash content was quite small 0.02 wt% and after esterification shows a changed. H$_2$SO$_4$ catalyst at the most promising 1% concentration was 0.0003 wt%, HCl 0.0001 wt% catalyst. The two catalysts have decreased ash content and are better seen in figure 3.

![Figure 3](image)

**Figure 3.** Effect of type and concentration of catalyst on bio-oil pH value (A) and ash content (B)

### 3.2.4. Effect of type and concentration of catalyst on bio-oil acid number

Acid numbers in this study showed the amount of organic acids in bio-oil, before esterification there was 12.09 mg-KOH/g. The H$_2$SO$_4$ catalyst was 0.27 mg-KOH/g which is the smallest than HCl catalysts at concentration 1%. The HCl catalyst obtained an acid number 1.04 mg-KOH/g. This study found much more catalyst concentration was used much greater the value of acid number. The 1% concentration in the catalyst H$_2$SO$_4$ and HCl was enough to converted organic acids in bio-oil to ester content. The use of acid catalysts shows high activity in conversion of organic acids into bio-oil [13]. The explanation above can be seen in Figure 4.
Figure 4. Effect of type and concentration of catalyst on bio-oil acid number

4. Conclusion
The results showed that H₂SO₄ catalyst with concentration catalyst of 1% (K1A1) was better because it reduced kinematic viscosity from 41.31 to 3.06 cSt @40°C, density from 1.51 to 1.20 kg/dm³ @20°C, water content from 25 wt% to 0.83 wt%, ash from 0.02 to 0.0003 wt%, the acid number from 12.09 to 0.27 mg-KOH/g, the heating value increase from 13.12 to 20.17 MJ/kg and shows characteristic of bio-oil according to applicable standards.

References
[1] Xiu S, Shahbazi A 2012 Bio-oil production and upgrading research: A review Renewable and Sustain. Energy Rev. 16 4406–4414.
[2] Oasmaa A, Kuoppala E, Selin J F, Gust S, Solantausta Y 2004 Fast pyrolysis of Forestry residue and pine, Improvement of the product quality by solvent addition Energy Fuels 18 5 78–83.
[3] Hambali E, Mujdalipah S, Tambunan P A H, Pattiwiri A W, Hendroko R 2008 Teknologi Bioenergi Agromedia Pustaka Jakarta Indonesia. [In Indonesian]
[4] Zhang Q, Chang J, Wang T J 2006 Upgrading bio-oil over different solid catalysts Energy Fuels 20 2717–2720.
[5] Wang J J, Chang J, Fan J 2010 Upgrading bio-oil by catalytic esterification and determination of acid number for evaluating esterification degree Energy Fuels 24 3251–3255.
[6] Tang Y, Yu W, Mo L, Lou H, Zheng X 2008 One-step hydrogenation-esterification of aldehyde and acid to ester over bifunctional pt catalysts: A model reaction as novel route for catalytic upgrading of fast pyrolysis bio-oil Energy Fuels 22 5 3484–3488.
[7] Diebold J P 2000 A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oil No. NREL/SR-570-27613 National Renewable Energy Laboratory Colorado USA.
[8] Aziz I, Nurbayti S, Ulum B 2011 Pembuatan produk bio-diesel dari minyak goreng bekas dengan cara esterifikasi dan transesterifikasi Valensi 2 3 443-448. [In Indonesian]
[9] Xiu S, Shahbazi A, Wang L, Wallace C 2010 Supercritical ethanol liquefaction of swine manure for bio-oils production Ame. J. Eng. Appl. Sci. 3 2 494–500.
[10] Lu Q, Tang Y, Zhang Y, Zhu X F, Guo Q X 2009 One step bio-oil upgrading through hydrotreatment, esterification and cracking Ind. Eng. Chem. Res. 48 6923–6929.
[11] Cheng D, Wang L, Shahbazi A, Xiu S, Zhang B 2014 Catalytic cracking of crude bio-oil from glycerol-assisted liquefaction of swine manure Energy Convers. Manag. 87 378–384.
[12] Chong Y, Gopakmar S, Kiat H, Ganesan BP, Gan S, Lee L Y, Manickavel V S, Ong C M, Himai H S R A 2017 Emulsification of bio-oil and diesel Chem. Eng. Trans. 56 1801-1806.
[13] Jiang X, Ellis N 2010 Upgrading bio-oil through emulsification with biodiesel: mixture production Energy Fuels 24 1358–1364.