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Esterification Bio-oil using Acid Catalyst and Ethanol

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ABSTRACT

Fuel energy sources are limited. It is necessary to obtain alternative energy that can be reached. Bio-oil is one of the promising renewable energy that production of bio-oil derived from agricultural wastes and industrial wastes by fast pyrolysis process but the quality bio-oil is not good as bio-fuel it needs upgrading method. One of the methods to upgrading bio-oil is using esterification. Esterfication method reduces viscosity, density, and ash. The purpose of this research was to increasing bio-oil quality by type of acid catalyst. Catalyst used was H_2SO_4, HCl and citric acid, concentration catalyst was used according to free fatty acid (FFA) and free fatty acid was 5.09 before esterification. The bio-oil after esterification show FFA lower than 2.00 and indicate it worked. Esterification with acid catalyst shows some critical change like acid number, viscosity kinematic, density, pH, and ash. The result found acid number 0.64, 1.02 and 3.39 Mg of KOH/g, viscosity kinematic 11.61, 11.83, and 13.64 cSt @40^{o}C, density 1.11, 1.12 and 1.21 kg/dm^3 @20^{o}C, pH values 2.05, 2.33 and 3.06, ash 0.0003, 0 and 0.004. The concentration catalyst according to FFA with esterification process has a good impact on bio-oil characteristics according to standards and its high activity.

***Keywords*--** Bio-Oil, Esterification, Acidcatalyst, Bioenergy, Bio-Fuel

I. INTRODUCTION

Oil crisis and environmental concern on the release of green gas house emission from fossil fuel burning has led to an increase in research on development of renewable energy which plays an important role for future energy supply. The plentiful of renewable energy sources are widely available like biomass. Biomass is widely available from agriculture residues and industrial waste. 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 pyrolisis or hydrothermal liquefaction. 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 [4].

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. Esterfication is a heating process involving an acid catalyst (acid catalysts) mixed with a polar solvent. This process takes place at a temperature of 55^{o}C - 60^{o}C within 1-4 hours [1]. 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' + H_2O. The esterification process uses several catalysts such as heterogeneous catalysts, solid acid catalysts, solid base

catalysts, ionic liquid catalysts, HZSM-5 and aluminum silicate [10].
The purpose of this research is to improve the quality of bio-oil by treating the type of catalysts in the esterification process and obtain the characteristics of bio-oil according to standards.

II. MATERIALS AND METHODS

Material and chemical

The raw material of bio-oil comes from the Agency Assessment and Application of Technology, Puspiptek Serpong. The process of producing bio-oil through a commercial-scale fast pyrolisis process with 2 ton/hour bio-oil yield provided by BTG Bio-liquid Netherlands and the catalyst used was H_2SO_4, HCl and citric acid from the laboratory of Surfactant and Bioenergy Research Center Bogor, and ethanol 95%.

Bio-oil analysis

Before the esterification first thing to do is analysis of bio-oil characteristics performed so that after esterification can be seen the improvement of quality of bio-oil. Sample of bio-oil was analyzed chemical properties such as acid number (Titration FBI-A01-03), Free fatty acid (Titration) and analysis of physical properties such as density (Density meter DMA 4500 M Anton Paar ASTM D4052), kinematic viscosity 40^{o}C (Rheometer Brookfield DV III Ultra ASTM D 445), and ash (Tanur ASTM D 874),

Bio-Oil Esterification Process

Esterification process is carried out at 60^{o}C and 50% (w/w) ethanol with reaction time of 240 minutes according to the reference the yield more than 70%. The catalysts used in this study in the esterification process were sulfuric acid (H_2SO_4), HCl hydrochloric acid and citric acid. The catalyst concentration used according to *free fatty acid* of the sample weight. After esterification, to separate ethanol and unreacted catalysts were performed by simple decantation can be seen at Figure 1. The purpose of this phase is to optimize the esterification process and get better bio-oil quality.

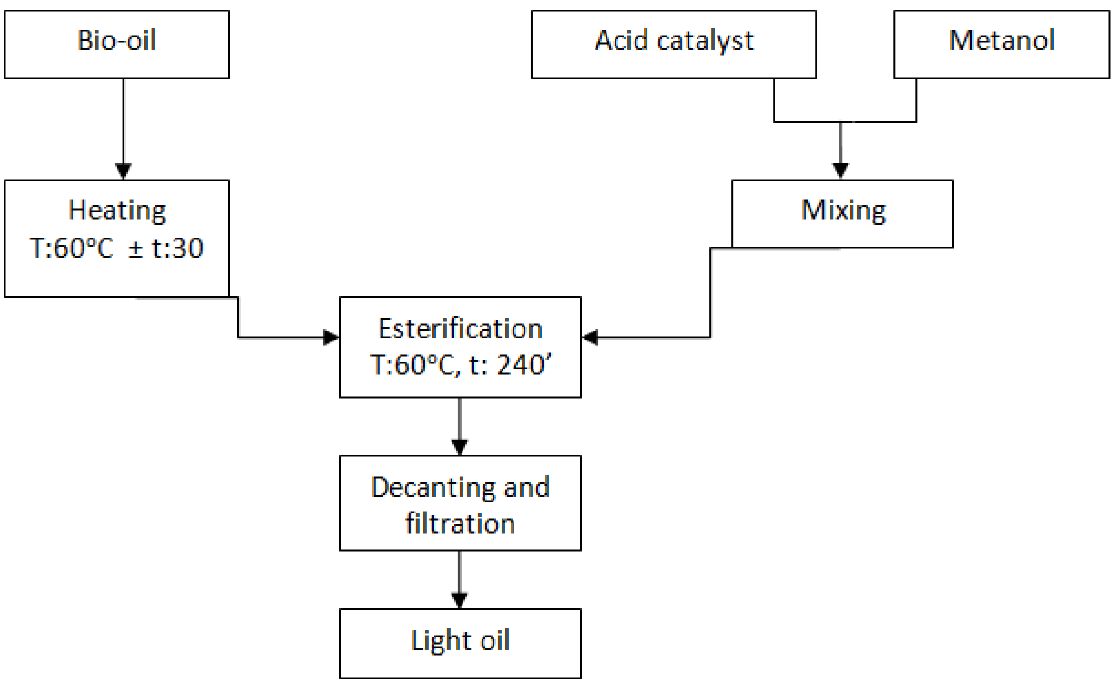

Figure1. Steps of research

Characteristics bio-oil

Analysis performed after esterification is an analysis of bio-oil chemical properties and analysis physical properties of bio-oil. Characteristics bio-oil refers to standard specification for pyrolysis liquid bio-oil by American Standard Testing and Material (ASTM D7544) can be seen at Table I. In this research some characteristics were determined using test method such as density (density meter DMA 4500 M Anton Paar), kinematic viscosity (Rheometer Brookfield DV III Ultra), pH (pH Meter Schoot HandyLab), ash (Tanur), acid number (FBI-A01-03 Titration).

Table 1. Standard specification for pyrolysis liquid bio-fuel (ASTM D7544)

Characteristics	value	Test method
pH	Report	ASTM E70
Kinematic viscosity cSt @40^{o}C	125 max	ASTM 445
Density kg/dm^3 @20^{o}C	1.1-1.3	ASTM D4052
Ash content wt%	0.25 max	ASTM 482
Acid Number mg-KOH/g	0.8 max	FBI-A01-03

III. RESULTS AND DISCUSSION

Esterification of varies acid catalyst with ethanol was chosen as a model reaction. Experiments showed the following improvements for bio-oil condensed with 50% ethanol (w/w) relative to the control viscosity, density and others. In order to optimize the process, the free fatty acid was first investigated. Free fatty acid was found before esterification 5.90 mgKOH/g and after esterification the free fatty acid was below 2 mgKOH/g. The reaction was carried out at catalyst concentration according to amount FFA of sample weight and catalyst was used H_2SO_4, HCl, and citric acid. Table 2, shows all the treatment in process esterification and values every analysis of characteristics.

Table 2. Treatments in esterification process

Acid catalyst	pH	Density	Viscosity kinematic	Acid number	Ash
H_2SO_4	2.05	1.11	11.61	0.64	0.0003
HCl	2.33	1.12	11.83	1.02	0
citric acid	3.06	1.21	13.64	3.39	0.04

Effect on viscosity

Viscosity is the resistance possessed by the fluid that flows in the capillary tube to the force of gravity, if the viscosity is higher and then the resistance to flow will be higher. This means lower viscosity values will be better. Research found best viscosity for catalysts H_2SO_4, HCl, and Citric acid are 11.61, 11.83 and 13.64 cSt @40^{o}C. it seem H_2SO_4 has better quality lower viscosity than others. Figure 2 shows concentration catalyst according to FFA has good effect on viscosity.

Effect on density

Density or specific gravity is the ratio weight of the material to the water weight which has the same volume as the material. Specific gravity shows the mass density that is affected by gravity. The higher the specific gravity contained in the fuel the more impurities and water content in the fuel. Density was decreased at FFA concentration catalyst. FFA concentration catalyst shows better value but H_2SO_4 has the lowest density, it shows in figure 3.

Effect on Ash

The presence of ash in bio-oil can cause erosion, corrosion and kicking problems in the engines and the valves and even deterioration when the ash content is higher than 0.25 wt%. However, alkali metals are problematic components of the ash. More specifically, sodium, potassium and vanadium are responsible for high temperature corrosion and deposition, while calcium is responsible for hard deposits. The research showed that best reducing ashes is by FFA concentration for all catalysts. HCl shows more aggressive changing 0 wt% which means there no ashes in bio-oil can be seen at figure 4.

Effect on Acidity (pH)

Acidity makes bio-oil very corrosive and extremely severe at elevated temperature, which imposes more requirements on construction materials of the vessels and the upgrading process before using bio-oil in transport fuels. This research found that bio-oil after esterification for all of treatments have pH value around 2-3, which high acidity. Citric acid showed better quality because it include weak acid. Figure 5, Show pH value for all treatments

Effect on acid number

In comparison to original bio-oil, acid numbers of upgraded bio-oil on H_2SO_4, HCl, and citric acid were lowered. Respectively, which is represents the conversion of organic acids to neutral esters, Acid numbers of bio-oil determined with 0.1 mol/L KOH. All catalysts showed some critical changes were shown in figure 6.

IV. CONCLUSION

The best catalyst was H_2SO_4 at FFA concentration catalyst of sample bio-oil which can reduces viscosity kinematic 11.61 cSt @40^{o}C, density 1.11 kg/dm^3 @20^{o}C, ash 0.0003 wt%, and acid number 0.64 mg-KOH/g. Organic acids can be converted to esters over H_2SO_4, HCl, and citric acid catalyst. H_2SO_4 shows good quality and according to standards.

ACKNOWLEDGMENTS

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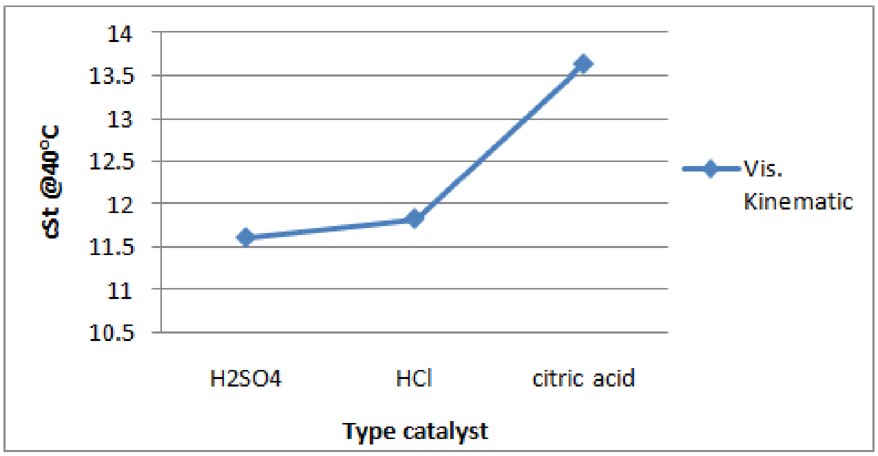

Figure 2. Viscosity by different type catalysts

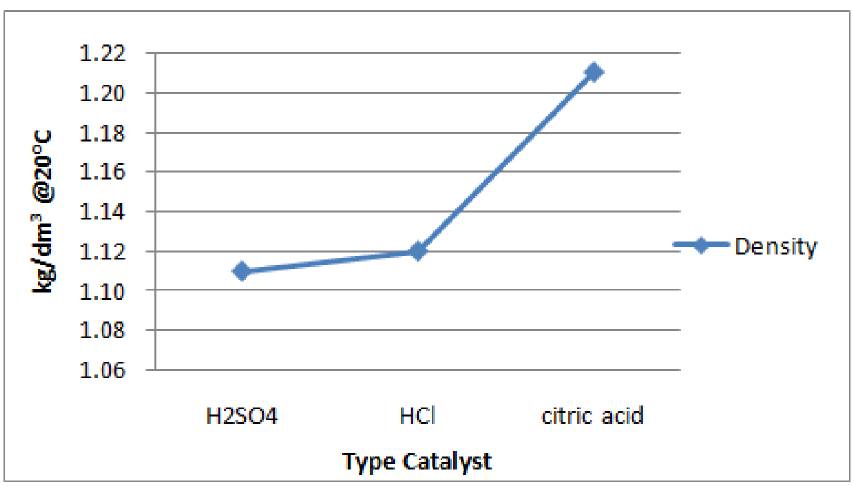

Figure 3. Density by different type catalysts

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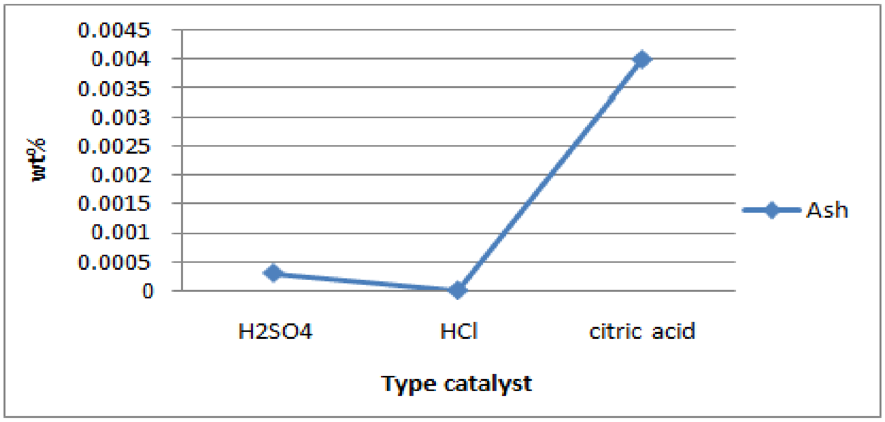

Figure 4. Ash by different type catalyst

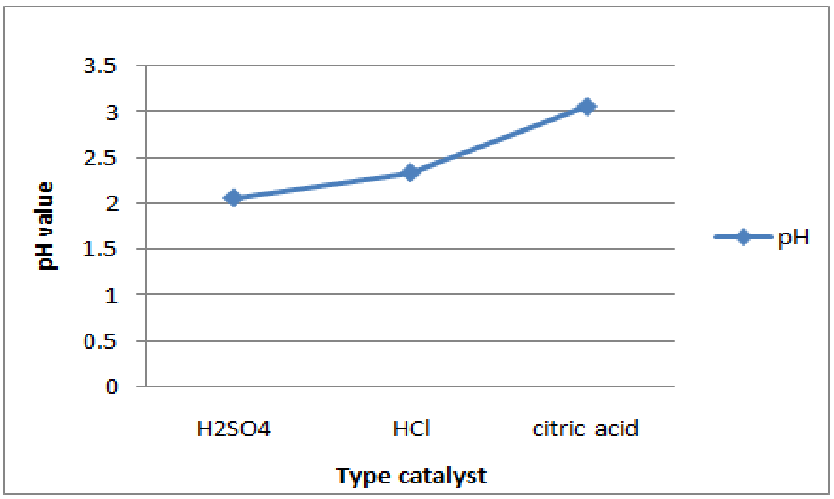

Figure 5. pH value by different type catalyst

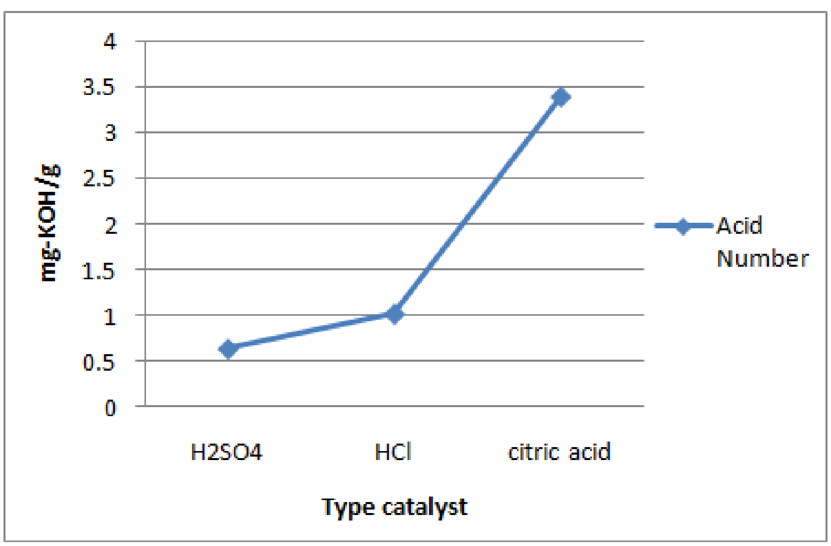

Figure 6. Acid number by different type catalyst