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SPEECH OF CHAIRMAN OF INTERNATIONAL CONFERENCE ON GREEN WORLD IN BUSSINESS AND TECHNOLOGY 2012

With all my respect, Rector of Ahmad Dahlan University, keynotes speakers, authors, participants, and other guests of International Conference on Green World in Business and Technology 2012.

The issue of global warming, increased CO_2 emissions in the air, high air temperature, climate change, deforestation, flooding, energy crisis, food crisis is causing human life to be uncomfortable and crime increases. These problems are global problems require solutions that are found and solutions through a conference.

International Conference on Green World in Business and Technology 2012 designed to invite and bring together practitioners, scientists and environmentalists from various disciplines who are expected to contribute to the government of Indonesia and the world in preventing, overcoming all the consequences of environmental damage. The theme *"Technopreneurship based on Green Business and Technology"* has been chosen to support celebration of 51th Ahmad Dahlan University anniversary.

This conference is the result of dedication and commitment of many people. We are grateful to the authors who have submitted papers, to the reviewers, to the conference committee member who have been untiring in their efforts to make this conference a success. We also would like to thank our sponsors and cooperating societies who have been generous in their contributions to the conference.

Finally, I would like to extend my welcome to participants of the International Conference on Green World in Business and Technology 2012. We hope this will be an exciting meeting for everyone. We apologize if there are some unpleasant things about organizing and holding this conference.

Thank you.

Yogyakarta, March 2012
Chairman of International Conference on Green World
in Business and Technology 2012

Dr. Abdul Fadlil, M.T.

Table of Contents

Characterization of rubber seed oil and the decreased in the value of FFA (Free Fatty Acid) as a introduction to produce of alternative fuels biodiesel

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Abstract

The alternative fuel for diesel engines was increasingly important because of decrease oil reserves and the environmental consequences of exhaust gases from petroleum-fueled engines. Air pollution was serious environmental problem around the world from CO_2 pollution and other particles. Because it was a clean alternative fuel a growing number of requests. Sources of biodiesel fuel derived from vegetable oils is the potential as a replacement for conventional diesel fuel. Biodiesel was an alternative fuel from renewable resources and environmentally benefits. One was to process the rubber seed oil into biodiesel. Rubber seeds to be very potential biodiesel feedstock because of rubber seed oil contains 40-50% fat of dry matter and the availability of rubber seeds are very high in Indonesia.The research was prepared characterization of rubber seed oil determining chemical properties and the FFA decreased. The rubber seed shell was opened to be taken and pressed to take the oil. Rubber seed oil tested its chemical and physical properties. When FFA was obtained over 2% reduction was carried out by esterification with H_2SO_4 catalyst. Esterification was prepared by with variable time and H_2SO_4 concentration. The ratio of oil and methanol used 1 : 6. The results showed that chemical properties involve Saponification Value, Iodine Value, Acid Value) of rubber seed oil was a non edible fat so making it feasible for used as raw material for biodiesel with a value of 23.1 % FFA. To decreased the FFA value of the increase concentrations of H_2SO_4 that FFA value was decreased, the optimum concentrations of H_2SO_4 was 4 N with a value of FFA = 4.6%.

Keywords: *Characterization, FFA (Free Fatty acid), Biodiesel*

1. Introduction

Road map in the National Energy Mix showing things that were not much different. The need for fuel oil (BBM) in 2008 reached 215 million liters /day, while production reached 178 million liters per day was imported from other countries. Through Presidential Decree number 5 of 2006 on national energy policy and the President of Instruction No. 1 of 2006 on the supply and use of biofuels as other fuels [2]. ROAD MAP according to the development of biofuels, the government plans a 20% biodiesel used consumption 10.22 million kilo liters of diesel fuel [3]. Therefore this research on biodiesel was prospective. Biodiesel was an alternative fuel from renewable raw materials in addition to diesel fuel from petroleum. Biodiesel was compose of various fatty acid esters that can be produced from plant oils such as palm oil, coconut oil, castor oil, rubber seed oil [4]. According [5], rubber seed so potential raw material for biodiesel rubber seed oil contains 40 -50% fat of dry matter.

One source of vegetables that is highly prospective for use as raw material for biodiesel is the rubber seed [4]. The results from the sap of the rubber plantations and fruit. Until now only the rubber is widely used. In addition to seeds, can be taken rubber seed and its meal oil [6]. Availability of rubber seeds are very high in

Indonesia, because Indonesia is the largest rubber producing countries in the World. Based on statistical data, extensive rubber plantations in Indonesia reached an estimated 3,318,105 ha and is capable of producing rubber seed oil for 25,622,406.8 L / year to date, has not been widely used rubber seeds [8].

Rubber seed oil contains saturated fatty acids and unsaturated fatty acids include palmitic acid 25%, 12% stearic acid, 1% arakhidonat acid, linolenic acid 25%, 35% linolenic acid and oleic acid 17%. The content that can be made of rubber seed oil this edebel fat but the content is high enough content cyanide in rubber seeds to this is just wasted as waste. Toxin contained in the rubber seed oil is a cyanide with an average level of 330 mg/100 g of rubber seeds. These compounds are toxic to humans known as "Linamasin". Cyanide boiling point of about 260 ^{o}C so that the volatile and soluble in water. The preparation of rubber seeds as biodiesel can be cope with the waste material that had been there in the jungle rubber [7].

The results rubber seed oil can not be directly used as biodiesel, because the rubber seed oil contains free FFA (Free Fatty Acid). The FFA contained in the rubber seed should not exceed 2% to production of biodiesel. Transesterification process will not occur if the FFA in the oil about 3%. Process carried out in order to decrease FFA. The FFA levels in rubber seeds to fall to 2% so it can be processed into biodiesel [6]. The Free fatty acid (FFA) is a fatty acid which is free, no longer bound to the glycerol group and triglycerides. In general, vegetable oils contain free fatty acids and water, although in small amounts allowing saponification reaction [12]. In the process of conversion of triglycerides into alkyl esters through a transesterification reaction with the base catalyst, free fatty acids to be separated or converted into an alkyl ester first because the free fatty acid will consume the catalyst. Free fatty acid content in biodiesel will result in the formation of acidic conditions that can lead to corrosion of the fuel injection equipment, make a clogged filter and sedimentation occurred in the injector [6]. Free fatty acid can be converted into alkyl ester compounds that are the basis of the biodiesel itself. The process of conversion of free fatty acids into alkyl ester is called esterification.

Biodiesel or FAME (fatty acid methyl ester) is a vegetable oil or animal fat, which is converted through a transesterification process that basically reacting oils with methanol or ethanol and a catalyst KOH or NaOH [6]. Vegetable oil is first converted into methyl ester is intended to reduce the viscosity or viscosity of the oil that reached 20-fold higher than the viscosity of fossil fuels [11].The process of making biodiesel from vegetable oil is called transesterification. Transesterification is a change in the shape of one type of ester into another ester form. The process of transesterification reaction of triglycerides into alkyl esters with acid or base catalyst produces methyl esters and glycerol. Most of the process of making biodiesel in the world using the transesterification method. Free Fatty acid (FFA) or free fatty acid is the acid groups in the triglycerides in mind that regardless of this bonding. The FFA contained vegetable oil has a high (0.5 - 5%). The high FFA content will affect the biodiesel reaction process, therefore, be appropriate to reduce the FFA content in raw materials [6].

The transesterification process can be prepared if the low water content and free fatty acid levels are only about 2%. When high levels of free fatty acids, acid esterification is carried out to reduce levels of free fatty acids as a preliminary process with acid catalysts, e.g. H_2SO_4 [6].

$$\text{Oil /fatty} + \text{Methanol/Ethanol} \xrightleftharpoons{\text{catalys}} \underset{\text{(Biodiesel)}}{\text{Methyl ester/ Ethyl ester}} + \text{Gliserol}$$

Several researched on rubber seed, among others, performed by Septiningsih, Santi, and Salamah [8] was extract of rubber seed oil with hexane solvent and hydraulic pressure Ramadhan [6] was performance and emissions evaluation of biodiesel from rubber seed. Optimization of the extraction of rubber seed with Oven rubber seeds for tanning leather by Suparno [9]. Demibras [4] studies on cottonseed oil biodiesel prepared in non–catalytic SCF conditions. Salimon and Kadir [10] research about of fatty acid composition and physicochemical properties in kekabu seed oil with extraction.

In this research will be carried out characterization of rubber seed oil to determine the chemical properties (Acid value, Iodine value, Saponification value, FFA), physical properties and decrease FFA in rubber seed oil early stages for the introduction to production of biodiesel, with the production of rubber seed into biodiesel could increase the value of rubber seed which has been just a waste.

2. Experimental

2.1. Analysis of fatty acid content of rubber seed oil

The rubber seed oil produced from pressing seed gum, the oil was analyzed using GC-MS (Gas Chromatography - Mass Pec) in the laboratory of Organic Chemistry, Faculty of Mathematics and Natural Sciences, University of Gadjah Mada. The result of analysis was use to determine the FFA content of oil.

Determination of Acid value

The Acid value was calculated using the formula:

$$\text{Acid value} = \frac{A \times N \times 56.1}{G}$$

A : amount of ml KOH for titration
N : normality of KOH
G : weight of sampel (gram)
56.1 : weight of KOH molecule

2.2. Determination of Iodine Value

The oil weight accurate about 0.1 to 0.5 gram of oil dissolved in 10 ml of chloroform or carbon tetra chloride was then added 25 ml of iodine bromide in glacial acetic acid. Left for one hour there will be oil on the binding of iodine by the double bond had been left in the dark. Residual iodine titrated with sodium thiosulfate 0.1 N using a starch indicator, the end of the titration was characterized by the loss of blue color. Titration of the sample e.g. (= ts) ml. To find out early in the iodine reagent blank treatment was carried out with the same path. Blank titration i.e. (= tb) ml.

$$\text{Iodine value :} = \frac{(tb-ts) \times N.\ Na_2S_2O_3 \times 12.69}{\text{Weight sampel (gram)}}$$

2.3.Determination of Saponification Value

Procedure

The Oil weight approximately 5 grams of the erlenmeyer was then added by 50 ml of 0.5 N alcoholic KOH. After close to the cooler then simmer until perfectly shaponificated with characterized by no visible grains of fat or oil in the solution. Once cooled and then titrated with 0.5 N HCl using phenolphthalein indicator. The titration end point was marked with the appropriate loss of red color. For example, requires titration (ts) ml.

The solution blank that is treated as made above treatment only without the sample. This blank titration showed that KOH initially used in the saponification reaction, for example requiring blank titration (tb) ml. Alcohol present in KOH serves to dissolve the fatty acids in order to facilitate the hydrolysis reaction with alkali to form soap.

$$\text{Saponification Value} = \frac{(tb-ts) \times N\ HCl \times BM\ KOH}{\text{weight sampel in gram}}$$

2.4.Determination of FFA

The rubber seed oil weight 10-20 grams. Neutral alcohol 96% was added and then heated in a water bath 10 minutes while stirring and cooling with a closed back cooling. After cooled and then titrated with 0.1 N KOH used the indicator was red phenolphtalein until the proper the solution guava red cooler. FFA is determined by the formula:

$$\%\ FFA = \frac{mlKOH \times N\ KOH \times Mr}{\text{Weight sample in gram} \times 10}$$

2.5 Esterification process to decrease levels of FFA from the oil:

Setting up of rubber seed oil and methanol with mole ratio 1:6 and 1.5 N H_2SO_4, 1.5% from of rubber seed oil. Reacting the rubber seed oil, methanol and H_2SO_4, in three neck flask equipped with a cooling loop, stirrer, thermometer and water bath as heated. Reaction at 60 ^{0}C and stirring at 300 rpm for 30 minutes. Heating the reaction to remove methanol and water. The result FFA levels of esterifiksai results obtained. If the FFA content of <2 then continue with the process of make biodiesel. If FFA levels> 2 the experimental 6 is done by varying the concentration of H_2SO_4 with variable concentrations used 2 N; 2.5 N; 3 N; 3.5 N; 4 N. The oil then determined by FFA esterified.

2.6 Determination of FFA

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$$\%\ FFA = \frac{Ml\ KOH \times N\ KOH \times Mr}{\text{Weight sample in gram} \times 10}$$

2.7.Esterification process to decrease levels of FFA from the oil:
Setting up of rubber seed oil and methanol with mole ratio 1:6 and 1.5 N H_2SO_4, 1.5% from of rubber seed oil. Reacting the rubber seed oil, methanol and H_2SO_4, in three neck flask equipped with a cooling loop, stirrer, thermometer and water bath as heated. Reaction at 60 ^{0}C and stirring at 300 rpm for 30 minutes. Heating the reaction to remove methanol and water. The result FFA levels of esterifiksai results obtained. If the FFA content of < 2 then continue with the process of make biodiesel. If FFA levels > 2 the experimental 6 was done by varying the concentration of H_2SO_4 with variable concentrations used 2 N; 2.5 N; 3 N; 3.5 N; 4 N. The oil was then determined of FFA esterified

3.Result and discussion

3.1.Characteristics of rubber seed oil

The rubber seed oil pressing the test results brownish yellow coller . The rubber seed oil quality listed in Table 1 below.

Table 1. Physical properties of rubber seed oil by the method of pressing

No	Property	Result experiment	Experiment method
1	Viscosity Kinematic at 40^{o}C, mm2/s	31.55	ASTM D 445-07
2	Density at 15^{o}C, gr/ml	0.9485	ASTM D 1298-07
3	Flash Point P.M.C.C., ^{o}C	238.5	ASTM D 93-07
4	Cloud Point, ^{o}C	30	ASTM D 97-07
5	Water Content, % vol	0.24	ASTM D 95-07

Table 1 show the research results obtained by rubber seed oil water content 0.24%. The water content contained in the rubber seed is still normal. According to ISO quality standards of cooking oil a maximum of 0.3% water content, and from these results physical properties showed that the rubber seed oil has properties that could feasibly be used for the production of biodiesel feedstock.For the characteristic chemical properties include saponification value, iodine value, acid value were listed in the Table 2.

Table 2. Chemical properties of rubber seed oil

No	**Property**	**Result**
1	Saponification value	85.57 mg KOH/g minyak
2	Iodine value	20.68 cgl/g minyak
3	Acid value	12.63 mgKOH/gminyak

Table 2 shows that from the saponification value of 100 were taken; according to ISO standard cooking oil have a value of 196-206. For the iodine acid value the result was also relatively small, according to ISO standard cooking oil has value 45 -46. Acid value of rubber seed oil obtained in 12.63, the result was relatively high, the contrast used walnut oil (edebel fat) had a 6.3 to 8. Acid value in the rubber seed oil was high indicates the large number of free fatty acids contained in oils. From the data of chemical properties of rubber seed oil is not suitable as food oil (edebel fat) so that the rubber seed oil can be used as raw material for biodiesel.

The results of the analysis of their fatty acid content in the analysis by means of Gas Chromatography Maspecc (GC-MS) data showed that the samples contained 12 fatty acid compounds, such as palmitic acid, linoleic acid, arachidonic acid, oleic acid and stearic acid. Among the most dominant acid is linoleic acid which has a percentage of about 41.25% with a molecular weight of 294 g / mol. For the determination of FFA then used the fatty acid was linoleic acid base calculations. From the analysis of the content of FFA rubber seed oil has an FFA value is high at above 20% so it is necessary to decrease the value of esterified free fatty acid content was. In this researched the use of methanol as an ingredient reagent alcohol because alcohol was methanol which has a shorter carbon chains and polar thus could react more quickly to the fatty acid, could dissolve more of a catalyst (acid and alkaline) and more economical.

3.2.Effect of the concentration of acid catalyst to the decrease in FFA esterification reaction

The esterification used H_2SO_4 acid catalyst with variable concentrations used were 2 N; 2.5 N; 3 N; 3.5 N; 4 N. Esterification reaction using a temperature of 60 °C, rotation speed of 300 rpm and the time used was 120 minutes. Results of the study decreased % FFA by using variable concentrations of the catalyst shown in Figure 1 as follows:

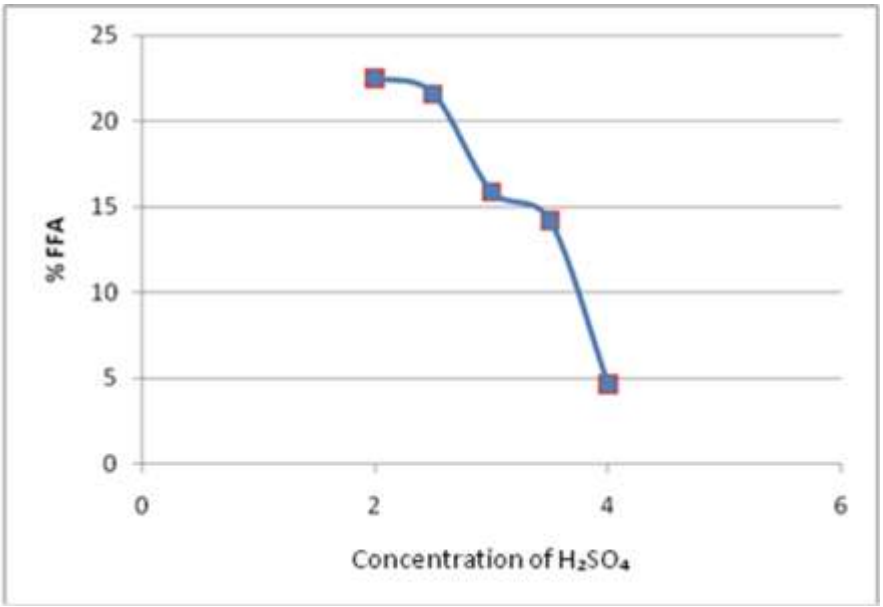

Figure 1. Graph of the relationship between the concentration of H_2SO_4 and % FFA

Figure 1 show that the higher concentration of catalyst is used then the value that the lower of % FFA. At a concentration of 4 N H_2SO_4 decreased % FFA can provide a very significant at 4.62%, that means in this study the use of a catalyst with a concentration of 4 N will give good results in the decrease in% FFA with time spent of 60 minutes. This was because the catalyst concentration effect on the esterification reaction rate constants, where the increase concentration of the catalyst the reaction rate constants will also be increase. The catalyst can decreased the activation energy thus increasing the number of activated molecules react to form esters and other than that the increase the concentration of the molecule to be will collide more and more so the reaction rate will increase.

4.Conclusion

From this the researched can be concluded as follows:

1. Based on the chemical properties of rubber seed oil was non edebel fat. Based on the results physical properties showed that the rubber seed oil has properties that oil could feasibly be used as raw material for the production of biodiesel feedstock.
2. The value of FFA (Free Fatty Acid) samples of rubber seed oil was 23.1 %
3. The higher concentrations of H_2SO_4 to decrease FFA esterification of rubber seed oil, the lower the value of FFA, the optimum H_2SO_4 Concentration was 4 N with a value of 4.6% FFA.

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