Investigation of the Catalyst Type Effect on Biodiesel Production from Nyamplung Seed Oil and Ethanol

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***Abstract* — Indonesia's oil production in 2004 amounted to 400,486 barrels, while the produced oil in 2012 only reaches 163,633 barrels. The decline of production is so significant, while consumption level increased. All Indonesian people should be aware to this condition, and play an active role to reduce dependence on petroleum. Biodiesel is an environmentally alternative fuel, which can be an interesting solution. Based on the previous description, it needs a real effort to develop biodiesel from plants (vegetable raw materials) which have a good quality. One of the plants were able to answer the problem is the nyamplung seed that contains very high oil, around 40% to73% [1]. This research will study the effect of the catalyst type in the manufacture of biodiesel from the nyamplung seed oil.**

Esterification –transesterification process takes place for high acid number oil. So it needs the special treatment to reduce the sap, which is the degumming process. In degumming, 2% (w) phosphate acid is added into 100 gram of nyamplung seed oil. Then, estherification process is done by adding ethanol and H_2SO_4 at 60 – 70^{o}C. This process use constant mixing. The resulting solution of esterification is separated by a separator funnel for 2 hours. Weight the resulted oil and enter the oil into a three-neck flask with a varied of reaction time and catalyst type. Separating the transesterification results by a separator funnel for 2 hours. Oil is washed with warm water (50°C) for twice, and separated again with a separator funnel for 1 hour. Then, the separated oil is heated in the oven with the temperature of 90-95^{o}C. Analysis of the results is done by measuring the density, viscosity, volume, and mass of biodiesel.

The result showed that the viscosity of biodiesel is fluctuated to the ratio of reactants and catalyst type. Maximum volume and mass produced biodiesel were 98.15 mL and 90.26 gram, respectively, which they are obtained at 90 min reaction time and K_2CO_3 as catalyst.

Keywords: biodiesel, degumming, esterification, nyamplung oil, transesterification.

I. INTRODUCTION

Petroleum is an undeniable natural resource. Efforts are conducted to overcome these problems, such as coal liquefaction processes or converting natural gas into liquid fuel. These activities are still less commercial value because the production cost is very expensive. Renewable fuel can be an attractiveness problem solving. However, contribution of renewable energy to total energy consumption is still below 1%.

The Indonesian government has implemented various other energy sources application that can be used as an alternative fuel. In this case, the application of vegetable oils owning huge potential for alternative fuel diesel engines. Several vegetable oils in Indonesia are sunflower oil, peanut oil, soybean, coconut, palm oil, castor seeds, and nyamplung seeds. Advantages of biodiesel as a fuel alternative solar successor them is a high cetane number, the eco-friendly because they contain little gas SOx, it's a good grease, exhaust emissions and some characters that are relatively clean burning. In addition to these advantages, the use of biodiesel has also benefited the vehicle engine maintenance. Processing biodiesel from renewable raw materials (renewable) have done in various countries among European countries using rapeseed, USA using soy, coconut oil (coconut oil) in the Philippines and Malaysia using CPO (Crude Palm Oil). Indonesia use CPO and castor oil (Jatropha) [2].

Nyamplung (Calophyllum inophyllum L.) is one of the types of crops that can be processed into fuel vegetable [3]. Benefit of nyamplung as fuel is vegetable seeds have a higher yield than other crops (Jatropha from 40% to 60%, CPO from 46% to 54%, and nyamplung from 40% to 74%), and it is not compete with food interests. Besides it, nyamplung seed productivity (20 tons/ha) is higher than a jatropha (5 ton/ha), CPO (6 tons/ha) and other vegetable crops [4]. Nyamplung oil is one of the potential crops as the hydrocarbon or energy source in Indonesia. Nyamplung oil has a higher viscosity than paraffin or kerosene.

Biodiesel is produced from the transesterification reaction of triglycerides with alcohol and added catalyst to accelerate the reaction. Biodiesel production with homogeneous catalysts produces high yield and faster reaction time. However, problems arise requires more complicated technology to support the separation process of the product from the catalyst mixture. While with heterogeneous catalysis, separation processes can take place more quickly and catalyst can be regenerated.

II. THEORY

A. Nyamplung

Nyamplung (Calophyllum inophyllum L.) is a tropical tree originating from Madagascar, East Africa, South and Southeast Asia, the Pacific Islands, West Indies, and South America. Nyamplung plants have different names in each region, such as "Camplong" in Madura, Bali, and Timor, "Mantan" in Bima, "Dingkalreng" in Sangir, "Dongkalan" in Mongondow, "Dungala" in Gorontalo, "Pude" in Bugis. Nyamplung grows in the mountains' forest and the swamp area of tropical climate. Plant height is around 30 m and trunk diameter appoximately 0.8 m. The leaves are shiny, and trunk colours are brown, gray, and white. Fruit is round shape, with 2.5-3.5 cm in diameter and brown colour. Nyamplung can be found in several areas in Indonesia, so it is very potential source.

Nyamplung seed production per year reach 20 tons / ha. Nyamplung seeds have a high oil content is 55% in fresh seeds and 70.5% in the seeds of dry beans [5]. "Reference [6]" one nyamplung tree can produce 100 kg of fruit / year and the oil yield is as much as 5 kg. If the spacing is 3 x 3.5 m^2, each tree produces 30 kg of seed or 5.1 kg of oil. Therefore 26,973 kg of seed or 4,585 kg of seeds oil of nyamplung is produced in 1 hectare.

Other benefits of the plant nyamplung are:

- The wood can be used for the manufacture of boards on residential buildings and light construction materials.
- Sap can be used to treat swelling and cancer disease.
- Leaves contain compounds costatolide-A, saponins and acid hydrocyanic is efficacious as a wash in eye inflammation and Cambodia nyamplung leaf extract is used to treat vertigo and migraine.
- The flowers can be used as a mixture for scent hair oil.
- The seeds after are processed into useful oil can be used to polish, hair oil and massage oil, also efficacious for rheumatism.
- Skin stem is used to treat swollen glands and facilitate urination (diuretics).

Fig. 1 Nyamplung Seeds

Nyamplung Seed Processing

Nyamplung seed oil contains 40% - 55% of the current condition of green beans, and 70-75% when conditions are dry beans. Moisture content of nyamplung fresh seed is 37-45%. The processing stages of nyamplung seeds oil are:

a) Seeds Storage
Nyamplung seeds that have been harvested are dried to achieve a moisture content of approximately 12%. Drying can be done using sun drying or drying machine. If the sun is quite hot, then drying for 2-3 days. Dried seeds separated from the shell. Nyamplung shell or beans shell reach 30% of total weight. Peeling the shells obtained seed yield by 70%. Seeds inserted into burlap sacks and sealed in the store with a temperature of 26-27 ° C and humidity around 60-70%. Storage is done when there is a long enough time span between harvesting and seed processing nyamplung.

b) Seeds Drying
At the time of storage, nyamplung seeds absorb moisture so water content increases. Drying before extracting the oil needs to be done because the presence of water can inhibit the extraction of oil from nyamplung seeds. Drying of seeds without shell can be done by various ways, namely:
- Dried under the sun
- Fry the sand
- Drying machine

Drying is done until the beans nyamplung reddish brown. Drying the right to determine the yield of oil produced.

c) Seeds Pressing
Pressing can be done with two kinds of pressing machines, namely: manual hydraulic press machine and pressing machine extruder (screw system). Hydraulic pressing machine requires less energy but in a day of oil production is also small. While pressing machine extruder requires greater energy to the production of more oil. The yield of oil produced from the press is 20-30%. Pressing process residues such as residues / seed meal can be used as raw material for making briquettes. The oil that came out of the pressing machine black / dark because it contains impurities from the skin and chemical compounds such as: alkaloid, phosphatises, carotenoids, chlorophyll, etc.

d) Degumming
Degumming aim is to separate the oil from the sap / mucus consisting of fostatide, proteins, carbohydrates, residue, water and resin. Degumming process carried out by the addition of 20% phosphoric acid of 0.3-0.5% (w/w) of oil, so it will form the fosfaside compounds that are easy to be separated from the oil. Results from degumming process will show a clear difference in colour compare to raw oil, which is reddish. Degumming performed at 60°C for 30 minutes, until the precipitate is formed. The precipitate was separated, and then the oil is settled for 1 hour in a separator funnel.

Nyamplung Oil

Nyamplung greenish-black oil is like lubricating oil. Nyamplung oil is an important source of vegetable oil in addition to coconut oil, castor oil, and so on. Some types of plants that can be developed as a raw material to produce alternative energy (biodiesel). One of them is Nyamplung as a substitute for diesel fuel.

Petroleum oils classified nyamplung with unsaturated fatty acids of carbon chain length, with a main content of 37.5% oleic acid, linoleic acid 26.33%, and 19.96% stearic acid. Other contents are palmic acid form, arechidic acid, acid and acid linolinic [7].

TABLE 1
COMPOSITION OF OIL NYAMPLUNG

Component	Content (%)
Myristic acid (C14)	0.09
Palmitic acid (C16)	14.6
Stearic acid (C18)	19.96
Oleic acid (C18:1)	37.57
Linoleic (C 18:2)	26.33
Linolenic acid (C18:3)	0.27
Arachidic acid (C20)	0.94
Erukat acid (C20:1)	0.72
Gadoleic acid (C19 :1)	0.5

To obtain 1 liter of oil nyamplung requires 2.5 kg of dry nyamplung, while for 1 liter of castor oil requires 4 kg range. Nyamplung kernel oil contains very high at 75% [8]; 71.4% on a dry core with water content of 3.3% [5]; 40-73% [1]; 55.5% on fresh core and 70.5% on a dry core. Nyamplung seed production can reach 100 kg per tree [6,8]. In the pressing process 100 kg of fruit produced 17.5 kg of oil, or approximately 17.5% of the seed weight, or 48.6% of the weight of the dry core [9].

B. Biodiesel

Biodiesel is a fuel derived from the esterification or transesterification process of fatty acids with an alcohol and a catalyst support. The viscosity of fatty acids derived from plants or animals is similar to diesel fuel. Biodiesel is obtained through esterification of free fatty acids or transesterification of triglycerides with ethanol, will produce ethyl esters of fatty acids and glycerides. Biodiesel emit a very low pollutant, which the emissions of biodiesel fuel are non-toxic. It helps reducing the effects of global warming that are very dangerous to human life.

Biodiesel has a very high lubricating effect, thus making diesel engines more durable. Biodiesel also has a relatively high cetane numbers, reduce knock in the engine so the engine works more smoothly. Numbers higher flash point than diesel does not cause harmful odors making it easier and safer to handle. Other advantages of biodiesel as a renewable can be decomposed by microorganisms, it contains no sulphur and benzene is a carcinogen that has character. Can easily be blended with diesel fuel in various compositions and do not require any engine modifications. Reduce black smoke from the exhaust gases of diesel engines significantly, although the addition of only 5% -10% volume biodiesel into diesel fuel, providing added value to the agribusiness sector to encourage the use of biodiesel began to get the attention of the world as an alternative diesel fuel substitute.

The biodiesel product quality requires to the National Standardization Agency of Indonesia in 2006.

TABLE 2
QUALITY OF BIODIESEL [10]

No.	Parameter	Unit	Value
1	Density at 40°C	kg/m3	850 – 890
2	Cinematic viscosity 40°C	mm2/s (cSt)	2.3 – 6.0
3	Cetane number	-	min. 51
4	Flash point	°C	min. 100
5	Cloud point	°C	max. 18
6	Corrosion of copper plate (3 hours at 50°C)	-	max. no 3
7	Carbon residue In the original sample In the 10% distillation residue	%-mass	 max 0.05 max. 0.30
8	Water and sediment	%-vol.	max. 0.05*
9	Temperature of 90% distillation	°C	max. 360
10	Sulphated ash	%-mass	max 0.02
11	Sulphur	ppm-m (mg/kg)	max. 100
12	Phosphor	ppm-m (mg/kg)	max. 10
13	Acid number	mg-KOH/g	max.0.8
14	Free glycerol	%-mass	max. 0.02
15	Total glycerol	%-mass	max. 0.24
16	Alkyl ester level	%-mass	min. 96.5
17	Iodium number	%-mass (g-I2/100 g)	max. 115
18	Halphen test	-	Negative

C. Esterification

Esterification is the reaction between methanols with free fatty acids forming ethyl esters using acid catalysts. Acid catalysts are often used is a strong acid such as sulphuric acid (H_2SO_4) and chloride acid (HCl).

$$\underset{\text{Fatty acid}}{RCOOH} + \underset{\text{methanol}}{CH_3OH} + \underset{\text{water}}{H_2O} \leftrightarrow \underset{\text{methyl esters}}{RCOOCH_3}$$

Esterification reaction is not only converting free fatty acids into ethyl esters but also into triglycerides, although with a lower speed than the base catalyst [11].

D. Transesterification

Transesterification is the process of converting vegetable oil into biodiesel, which is the process of triglycerides as a component of vegetable oil with alcohol, using acid or base catalyst. Transesterification reaction products are ethyl esters (known as biodiesel) and glycerol. Conversion reaction is strongly influenced by the catalyst, reaction time, temperature, flow rate, water content in the alcohol, and the amount of alcohol excess and free fatty acids in raw materials [11].

The raw materials are the oil and alcohol. Conversion can be increased by stirring the raw material before it is treated. Homogenization process is very important at the beginning of the process. This phase of the state, will not lead to lower conversion due to the lack of turbulence in the fluid flow fixed bed catalytic reactor.

The water content in the alcohol will lead to soap formation by consuming the catalyst and this will reduce the efficiency of catalyst. Moreover, the transesterification reaction is reversible. Thus, excess alcohol consumption will shift the reaction equilibrium to the right and ethyl esters production increases.

III. METHODOLOGY

Nyamplung oil obtained from the district of Bantul, Yogyakarta. Initially, degumming process is conducted in order to separate the rubber or dirt in the oil. The process is by adding a solution of phosphoric acid (2% of the oil nyamplung weight) into a measurement glass containing the 100 grams oil. Then heat the oil to a temperature of 60-70°C and use magnetic stirrer to support the mixing during 30 minutes. Enter the degumming results oil into the funnel separator to separate the oil from dirt or gum.

Esterification is the process of biodiesel formation by adding ethanol or alcohol in order to reduce the FFA (Free Fatty Acid) and convert triglycerides into ethyl esters. The first step, enter degumming result oil into three-neck flask. Then the mixture of alcohol (20% by weight of oil) and catalyst (2% by weight of oil) is added into the flask. Then reflux for two hours with stirring speed of 600 rpm and a temperature of 60-70 ° C. Then do the separation between biodiesel and ether by precipitation for around 1 hour. Repeat the reflux process.

Transesterification then carried further by adding alcohol and a catalyst in the process, the type of catalyst are KOH, NaOH, K_2CO_3, and without a catalyst. Reactions are conducted with a temperature of 60-70°C for 30; 60; 90; 120; and 150 minutes. The results are separated to separate biodiesel and glycerol.

Biodiesel is washed with aquadest by adding 50% warm aquadest and stirring is done. Then separate the water from biodiesel by precipitation for 1 hour. Do washing process 2-3 times. Then enter products into the oven to remove the remaining water content in biodiesel at temperatures of 90-95°C.

IV. RESULTS AND DISCUSSIONS

A. Research Results

The values of the density, viscosity and yield of biodiesel is shown in Table 3

TABLE 3
DATA OF RESEARCH RESULTS

No	Time	Catalyst type	Density	Viscosity	Yield
1.	30 minutes	KOH	0.9071	0.3748	0.7559
		NaOH	0.9111	0.1882	0.4824
		K_2CO_3	0.9175	0.1900	0.8517
		Without catalyst	0.9135	0.2521	0.3626
2.	60 minutes	KOH	0.9092	0.2505	0.8629
		NaOH	0.9063	0.1872	0.5418
		K_2CO_3	0.9222	0.1910	0.8869
		Without catalyst	0.9098	0.1255	0.4826
3.	90 minutes	KOH	0.9157	0.0630	0.8912
		NaOH	0.9150	0.2524	0.6221
		K_2CO_3	0.9196	0.2538	0.9026
		Without catalyst	0.9064	0.3123	0.7672
4.	120 minutes	KOH	0.9167	0.1897	0.8447
		NaOH	0.9004	0.1862	0.8261
		K2CO3	0.9192	0.1899	0.9013
		Without catalyst	0.9061	0.0625	0.6440
5.	150 minutes	KOH	0.9107	0.2513	0.8260
		NaOH	0.9080	0.1877	0.6467
		K2CO3	0.9248	0.1914	0.8703
		Without catalyst	0.9133	0.0634	0.6354

B. Discussions

Nyamplung oil is a vegetable oil which has a blackish green colour and has a rancid odor. Nyamplung oil contains Free Fatty Acid (FFA), which can make a metal corrosion. FFA value is obtained by FFA test. FFA testing process is done by taking 10 grams of oil nyamplung and adds 25 mL of ethanol. Mix that solution to be homogeny, continued by heating process with a temperature of 60°C and stirring for 10 minutes. Then add three drops of indicator PP and titrate with KOH. Nyamplung oil FFA value is 0.763.

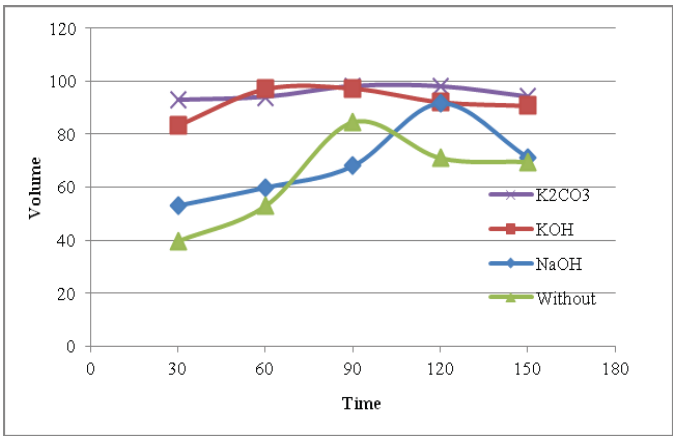

Fig. 2 Volume of Biodiesel as a Function of Time and Catalyst Type

From the fig 2 can be seen the relationship between reaction time and the type of catalyst to the volume of biodiesel. The highest volume of biodiesel is obtained at the time of 90 minutes with K_2CO_3 as catalyst was 98.15 ml. Generally, for all reaction time, the esterification-transesterification without catalyst gains the lowest result (except at 90 minutes, NaOH reaches the lowest). This indicates that the catalyst give big effect to increase the reaction rate, because it can reduce the activation energy. Besides that, fig 2 also shows that the type of catalysts affect the volume of biodiesel. It can be explained that the catalyst properties (solubility) depends on the nature and concentration of other substances, especially in the solution.

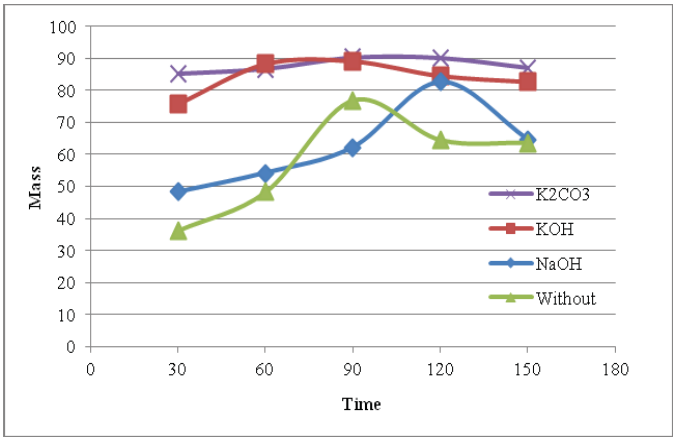

Fig. 3 Mass of Biodiesel as a Function of Time and Catalyst Type

The Fig. 3 shows the highest mass of biodiesel at 90 min reaction time for each catalyst K_2CO_3, in the amount of 90.26 g to 89.12 g KOH catalyst to 62.21 g NaOH catalyst without catalyst 76.22 g. It also suggests that from 30 to 90 minutes the longer reaction time the volume of biodiesel formed increases. This is due to the increasing number of triglycerides are formed due to the longer time contacting. This causes the increasing of formed biodiesel mass. However, after 90 minutes there is tendency that the mass decrease. It's happen because the presence of oil and stirring causes the catalyst to form an emulsion, the greater the mass of the catalyst with the same mass of oil, causing the emulsion to form more viscous (viscosity increases) and ethanol led to contact with oil getting harder so produced mass is decline.

Refer to SNI No. 04-7182-2006 the density of biodiesel was 0.85 to 0.89 g/ml. Density of this research is 0.9004 g/ml to 0.9248 g/ml. The difference of density associated with the fatty acids composition of biodiesel and the degree of purity of biodiesel, which shows the transesterification reaction is not perfect and still contains many impurities. Increased density also show a decrease in the carbon chain length and increased double bond.

Kinematic viscosity is the friction or resistance measurement of liquid flow rate at a given temperature. Biodiesel viscosity at 40°C in the SNI No. 04-7182-2006 was 2.3 to 6.0 cSt. Viscosity values in the transesterification process are 0.189 to 0.191 g/cm.s (K_2CO_3 catalyst), 0.063 to 0.37 g/cm.s (KOH), 0.186 to 0.25 g/cm.s (NaOH)., and 0.062 to 0.31 g/cm.s (without catalyst). The biodiesel viscosity is affected by the un-reacted triglyceride content and composition of the fatty acids constituent. The too low or too high viscosity will reduce the fuel burning and can lead to increase fuel consumption

The results obtained biodiesel not meet the quality standard ISO No. 04-7182-2006 so it should not be used on the vehicle. For that we need more research to meet the standards that have been defined.

V. Conclusions

1. Yield of produced biodiesel maximum obtained at 90 min reaction time K_2CO_3 catalyst is 0.9026
2. Density of nyamplung oil biodiesel has a value range of 0.9004 to 0.924 (g/ml)
3. The viscosity of biodiesel is from 0.062 g/cm.s to 0.37 g/cm.s
4. Volume and mass produced maximum biodiesel obtained at 90 minutes and K_2CO_3 as catalyst

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