Production of Biodiesel from Waste Cooking Oil with Ultrasonic Irradiation Method as Renewable Energy Source

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Abstract. Biodiesel is an alternative product, as a substitute fuel from fossil sources. Biodiesel is produced from the transesterification reaction between alcohol (methanol and ethanol) and triglycerides, the byproduct produced is glycerol. The advantages of biodiesel compared to fossil fuels are low emission levels, non-toxic, renewable and biodegradable. By conventional methods, to produce biodiesel that uses mechanical stirrings that cost a lot with electric bills because the transesterification reaction takes more than an hour to complete the reaction. An alternative method for producing biodiesel by saving the use of power and time resources with ultrasonic irradiation. The ultrasonic irradiation method has been widely used in the transesterification process of making biodiesel which increases mass transfer between alcohol and triglycerides. The use of a catalyst is required in the transesterification reaction because it will accelerate the reaction and the product eligible from Indonesian National Standar Agency 04-7182-2006.

1. Introduction

Along with the increasing number of population, the increase of economic growth, the development of the industrial world, especially the automotive industry in the country, the demand for fuel, especially fossil fuels is increasing. The increasing demand was not accompanied by the availability of fossil fuels domestically and in 2004 Indonesia officially perceived as a net importer of world oil. Indonesia must import 350,000 barrels per day to meet its domestic needs, mostly imported from Arab countries, Africa and Russia.
Figure 1. National Fuel Consumption from 2006 to 2017 [1]

Provision of energy sources that can support national energy security continues to be sought, especially new and renewable energy sources. According to the [1], by 2017 Indonesia has new and renewable energy potentials of more than 441 GW but only realized 8.89 GW. The Government of Indonesia is committed to targeting renewable energy contribution of 23% of overall national energy needs by 2025 and intensifying its energy savings program by reducing 17% of fossil fuel consumption.

A number of measures taken by the government to curb fossil fuel use include electricity savings in government buildings, restrictions on the use of official vehicles, the conversion of kerosene to LPG, the conversion of fuel from gasoline to gas, the development of nuclear technology, restrictions on the number of passengers for the vehicle (3 in 1), the use of solar cells for traffic regulators until the development of new and renewable energy such as the utilization of geothermal energy, wind energy, solar energy, water energy, sea tidal energy, energy from plants such as biomass and biodiesel. Biodiesel is increasingly ogled by the government and the private sector as Indonesia as one of the largest palm oil producers in the world has huge potential to develop this type of fuel. Pertamina as an agency authorized to produce and distribute fuel in Indonesia has been mass producing B5 type which means 5% fuel oil vegetable and 95% fossil fuel.

| No | Parameter | Unit | Value | Method |
|----|-----------|------|-------|--------|
| 1  | Densitas (40 °C) | Kg/m3 | 850-890 | ASTM D 1298 |
| 2  | Viscositas (40 °C) | Mm2/s (cSt) | 2,3 – 6,0 | ASTM D 445 |
| 3  | Cetane Number | Min. 51 | ASTM D 613 |
| 4  | Flash Point (close cup) | °C | | |
| 5  | Cloud Point | °C | | |
| 6  | Copper Strip Corrosion (3 jam, 50 °C) | Max. No. 3 | ASTM D 130 |
| 7  | Carbon Residu | % mass | Max 0,05 | ASTM D 4530 |
|    | - Sample | - Max 0,3 | | |
|    | -10 dist. Residu | | | |
| 8  | Air dan sedimen | % vol | Max 0,05 | ASTM D 2709 atau ASTM D1160 |
| 9  | Temperatur Destilasi, 90% recovered | °C | Max 360 | ASTM D1160 |
| 10 | Sulfated Ash | % mass | Max 0,02 | ASTM D 874 |
| 11 | Sulfur | ppm (mg/kg) | Max 100 | ASTM D 5453 atau ASTM D 1266 |
| 12 | Phosphorous Content | ppm (mg/kg) | Max 10 | AOCs Ca 12-55 |
| 13 | Bilangan Asam (Nₐ) | Mg-KOH/g | Max 0,8 | AOCs Cd 3-36 atau ASTM D 664 |
| 14 | Free Gliserin | % mass | Max 0,02 | AOCs Ca 14-56 atau ASTM D 6584 |
| 15 | Total Gliserin (Gₗₐ) | % mass | Max 0,24 | AOCs Ca 14-56 atau ASTM D 6584 |
| 16 | Kandungan Ester | % mass | Min 96,5 | |
| 17 | Bilangan Iod | % mass (gr I2/100 gr) | Max 115 | AOCs Cd 1-25 |
| 18 | Halphen Test | | Negative | AOCs Cd 1-25 |

Biodiesel is defined as monoalkyl ester of long chain fatty acids contained in vegetable or animal oils for use as diesel fuel engines. Generally in Southeast Asia such as Indonesia, Thailand, and Malaysia use palm oil as raw material for biodiesel production. However, the use of palm oil as a raw material for
the manufacture of biodiesel collided with the interests of food for human basic needs. In this research used waste cooking oil to produce biodiesel by reacting with methanol and catalyst. The type of catalyst used is an alkali catalyst that is KOH because it is cheap and widely available [2] [3].

**Table 2. Characterization of waste cooking oil [4]**

| Properties                              | Values          |
|-----------------------------------------|-----------------|
| Density @ 15 (°C)                       | 934 (kg/m³)     |
| Spesific gravity @ 15 (°C)              | 0.9232          |
| Kinematic viscosity @ 49 (°C) in catalyst| 24.9            |
| Flash point (°C)                        | 207             |
| Acid value (mg KOH/gr oil)              | 1.8             |
| Saponification value                    | 192.3           |
| Iodine value (mg KOH/gr oil)            | 69.7            |
| Density                                 | 930 (kg/m³)     |
| Molecular weight                        | 883 (gr/mol)    |

The ultrasonication increases the chemical reaction speed of the transesterification and also facilities the change of production method from batch processing to continuous flow processing. The principle of ultrasound action in biodiesel production is primarily based on the emulsification of the immiscible liquid reactants by microturbulence generated by radial motion of cavitation bubbles. It allows a short reaction time and high yield because of emulsification and cavitation of the liquid–liquid immiscible system [5]. The ultrasonic irradiation biodiesel process reduces the reaction time by 30 min or more as compared to the conventional method. The highest biodiesel yield and methyl ester content were observed at an ultrasonic power of more than 450 W [6].

Do Van Manh et al. [7] studied the effects of ultrasonic irradiation time (t) on the biodiesel yield (Y) of biodiesel produced from blended oil consisted of 20, 50 and 30% of tung, canola and palm oils, respectively and CH₃OH and KOH. Their results showed that biodiesel yield reaches high value of 87–91% for tung oil as t ≥ 5 min, while of about 92–94% for blended oil as t ≥ 1 min. The researchers suggested that the tung oil should be blended with other oils in order to produce biodiesel satisfying the biodiesel standards. Table 2 shows the optimum condition required for biodiesel production from various oils. The properties of biodiesel obtained by this method are in agreement with the standard biodiesel [8].

**Table 3. Biodiesel Production using Ultrasonic Technology**

| Type of oil  | Optimum Condition                                                                 | Reference |
|--------------|-----------------------------------------------------------------------------------|-----------|
| Waste cooking oil | Molar ratio of alcohol to oil of 6:1, 1 wt.% KOH, temperature of 45°C, ultrasound power of 200 W, irradiation time of 40 min | 9         |
| Coconut oil  | Molar ratio of oil to ethanol of 1:6, 0.75 wt.% KOH, 7 min reaction time.         | 10        |
| Canola oil   | Methanol/oil molar ratio of 5:1, 0.7 wt.% KOH, reaction time of 50 min, ultrasonic irradiation of 20 kHz with an input capacity of 1 kW. | 11        |
| Coconut oil  | Molar ratio oil to ethanol of 1:6, 0.75 wt.% KOH of of oil, 7 min reaction time.   | 12        |
| Jatropha Oil | Molar ratio oil to methanol of 1:4, catalyst of 5 wt.% of oil, reaction time 30 min, ultrasonic amplitude 50% (100 W/m²) and cycle 0.7 s. | 13        |
| Crude Cottonseed Oil | Methanol/oil molar ratio of 6.2:1, 1 wt% NaOH, reaction time of 8 min. | 14        |
Ultrasonic technology has been recognized as an effective method to enhance mass transfer rate between immiscible liquid-liquid phases within a heterogeneous system [15]. When a liquid is irradiated by a strong ultrasonic wave, large quantity of tiny gas bubbles appear and collapse violently, which is a phenomenon known as acoustic cavitation [16]. The tiny bubbles repeatedly expand and contract according to the pressure oscillation of an ultrasonic wave [17].

The speed of the bubble collapse sometimes increases up to the sound velocity of the liquid and the temperature and pressure inside a bubble increase dramatically because a strong collapse is nearly adiabatic [18,19]. As a result, ultrasonic in transesterification has proven to be an efficient activation energy to initiate the reaction [20]. Ultrasonic assisted transesterification does not only shorten reaction time but also minimize the molar ratio of alcohol to oil and reduce energy consumption compared to conventional mechanical stirring method.

2. Materials, Equipment and Experimental Procedure
2.1 Materials
Waste cooking oil was collected from residual usage of household. Methanol and KOH (Merck KGaA Germany) were purchased from Dira Sonita supplies, Palembang.

2.2 Equipment
Ultrasonic cleaner type GT Sonic P3 is used to perform transesterification reaction between methanol and waste cooking oil. The specification GT Sonic P3 have 12 cm x 25 cm x 22 cm (W x L x H) with adjustable ultrasonic power from 30% to 100% (maximum power 100 W and 40 KHz) and adjustable heater from 30 °C to 80 °C.

2.3 Experimental Procedure
The experiment was carried out by reacting the waste cooking oil with methanol with 6:1 molar ratio and adding a catalyst of 1% of the waste cooking oil weight. The pellet of KOH was first added to methanol and make sure that the KOH dissolved completely in methanol. As soon as, this mixture was added to waste cooking oil and the time is set for 10 minutes. The product consists of two layers, upper layer is biodiesel and lower layer is glycerol. This layer can separate by using separator funnel. The catalyst present in biodiesel is removed by mixing it with hot water at a ratio of 1:1. This mixture also separate by using separator funnel. Biodiesel is boiled until 100 °C to remove the water content and analyzed. This experiment was conducted by varying the time, ultrasonic power and temperature of the heater. Variation of time at 30, 35, 40, 45 and 50 minute, ultrasonic power were set to constant at 100% simultaneously the heating temperature is turn on at 50 °C.

![Figure 2. Effect of time reaction on density of biodiesel](image)

3. Result and Discussion
The obtained biodiesel is then analyzed to refer to Indonesian National Standard Agency (INSA) 04-7182-2006. The results of biodiesel analysis can be seen in figure 2-5.
Based on figure 2 and 3, biodiesel characteristics (density and viscosity) are inversely proportional, maksimum density is obtained by 50 minute transesterification reaction time ie 931 kg/m³, while for maksimum viscosity is obtained by 30 minute transesterification reaction time ie 5.86 cSt.

Based on figure 4 and 5, when the transesterification reaction time got longer than before, the flash point and water content are decrease, maksimum flash point is obtained by 30 minute transesterification reaction time ie 172 °C, while for maksimum water content is obtained by 30 minute transesterification reaction time ie 0.0126 % volume.
4. Conclusion
The research has explored the ultrasonic irradiation method to produce biodiesel from waste cooking oil. Transesterification product (biodiesel) has been analyzed at laboratory indicates that mets the requirement from Indonesian National Standar Agency (INSA) 04-7182-2006.

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Figure 5. Effect of time reaction on water content of biodiesel
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