

Enhancing Biodiesel from Kemiri Sunan Oil Manufacturing using Ultrasonics

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Abstract. Kemiri Sunan (*Reutalis trisperma* (Blanco) Airy Shaw) is a potential plant to be developed as biodiesel feedstock. The advantage of Kemiri Sunan seeds when compared to other biodiesel raw materials is their high oil content. This plant is also very good for land conservation. Due the increasingly demand for biodiesel, research and new methods to increase its biodiesel production continue to be undertaken. The weakness of conventional biodiesel manufacturing process is in the mixing process in which mechanical stirring and heating in the trans-esterification process require more energy and a longer time. A higher and stronger mixing process is required to increase the contact area between the two phases of the mixed substance to produce the emulsion. Ultrasonic is a tool that can be useful for a liquid mixing process that tends to be separated. Ultrasonic waves can cause mixing intensity at the micro level and increase mass transfer, so the reaction can be performed at a much faster rate. This study is to figure out the effect of ultrasonic irradiation on the transesterification process of biodiesel from Kemiri Sunan Oil.

1 Introduction

Indonesia, which is currently a net importer of fossil fuels, should make biofuels the backbone of fuel provision as a substitute for fossil fuels whose reserves are depleted. Sources of biofuels in Indonesia are abundant where more than 30 species of plants can be a source of biofuels. One of the potential plants to be developed as biodiesel feedstock is Kemiri Sunan (*Reutealis trisperma* (Blanco) Airy Shaw). In addition to its high oil content, Kemiri Sunan also has specific oil characteristics, relatively rapid growth, wide area development (from lowlands up to 1,000 m above sea level), high productivity, and very suitable for land conservation [1, 2].

Biodiesel is a fuel consisting of a mixture of mono-alkyl esters of long chain fatty acids, obtained from vegetable / vegetable oils or animal fats. As a fuel, biodiesel has several advantages: renewable energy, low CO₂ and SO_x emissions, biodegradable, non-toxic, high Cetane number and does not require engine modification [3,4]. However, if biodiesel is made with raw materials derived from edible sources, it will compete with food requirements and is still not competitive compared to fossil fuel oil [5]. Therefore, non-food raw materials are more likely to be developed. Kemiri Sunan (*Reutalis trisperma* (Blanco) Airy Shaw) is a potential crop to be developed as biodiesel feedstock in Indonesia, whose seeds contain 52% of the oil content [2]. The

productivity of Kemiri Sunan trees is 4-5 times greater than *Jatropha* and 2 times higher than Palm Oil [6,7,8]. The process of making biodiesel includes esterification, transesterification and leaching which requires a strong mixing to make sufficient contact between vegetable oils with catalysts or alcohols. The mixing and stirring process between the biodiesel feedstock is carried out at the reactor, where the main raw material and the catalyst undergo a transformation. Reactor performance is very important in the operation of biodiesel production, because it will affect the efficiency and productivity of production process.

Conventional processing of biodiesel is performed manually in reactors by mechanically mixing and heating in the transesterification process which requires considerable energy, labor and a longer processing time [9,10]. Therefore, the design of the reactor which is in accordance with the type of biodiesel feedstocks becomes important. Ultrasonic waves can be an alternative to be applied to biodiesel production processes to replace stirring and heating functions in transesterification. The waves can serve to increase mixing intensity at the micro level and increase mass transfer, so that the reaction process can be done at a much faster rate [11,12]. Since the transesterification process with the use of ultrasonic waves has not been done in processing of Kemiri Sunan for biodiesel, this paper will discuss the effectiveness of ultrasonic wave in processing biodiesel from Kemiri Sunan.

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2 The Potential of Kemiri Sunan (*Reutealis trisperma* (Blanco) Airy Shaw) in Indonesia

Kemiri Sunan originally from the Philippines, has grown widely in Indonesia. The population of Kemiri Sunan crop is concentrated in Garut and Majalengka regency, West Java and in 2008 started to spread to various places that have various agro-ecosystem such as Central Java, East Java, East Nusa Tenggara, West Nusa Tenggara, Riau, Jambi, Bangka, And East Kalimantan. The data of Kemiri Sunan tree distribution in Jakarta are 3,500 trees, Bekasi as many as 30,000 trees, Kuningan as many as 10,000 trees, Majalengka as many as 10,000 trees, Jati Gede as many as 10,000 trees, Bandung as many as 3,000 trees, Ngawi as many as 40,000 trees, Lamongan as many as 13,000 trees, Nusa Penida -Bali as many as 15,000 trees, Lombok as many as 14,500 trees and Timor as many as 20,000 trees.

Bogor Agricultural University has prepared a land area of 200 hectares belonging to the University to be a pilot development project of Kemiri Sunan crops. Head of Department of Energy and Mineral Resources of West Java Province has data of land groups that are potential for planting of kemiri Sunan in West Java province: 591,000 hectares of critical land, 268,000 hectares of mine reclamation, 810,000 hectares of CSR from geothermal developers, 224,000 hectares Non- Active land, 16,000 km border of the main river in West Java, 2,000 km of roads along the province of West Java.

Currently, it is planned that around 5,000 hectares of area in Production Forest that belongs to Landak, Mempawah and Kubu Raya districts, will be planted with Kemiri Sunan plant. This area will be made forest area with special purpose which is managed by Tanjungpura University.

Chemical and Physical properties of Crude Oil from Kemiri Sunan seeds are: Acid Numbers, 13,26 mg KOH/g; Fat Free Acid Content, 6,63%; Water content 9,6%; Density 985,49 kg / m; Kinematic Viscosity 26,57mm² / s (c St), rendement 43,33% [8]. Furthermore, the oil composition consists of 10% palmitic acid, 9% stearic acid, 12% oleic acid, 19% linoleic acid, and 51% a-elaostearic acid. Acid content a-elaostearic explains the presence of toxins in oil [13]

Development of Kemiri Sunan in post mining reas is expected to be made as:

1. Land conservation facilities to reforest critical lands to improve the quality of the environment;
2. The source of diversified supply of raw materials to produce environmentally friendly biodiesel oil (one hectare of land with 100-150 Kemiri Sunan trees can produce 6-8 tons of biodiesel per year) instead of fuel oil and reduce dependence on imports of fuel oil;
3. Increasing the economy of the community by creating employment and business development, investment in the country, the development of downstream agricultural sector, as well as increased value-added products in the country.
4. Improving environmental quality by reducing greenhouse gas emissions, reducing air pollution

levels, and improving air quality, public health, and community welfare.

5. Increasing national energy security through the provision of biodiesel from plants that do not compete with food and industrial raw materials.

3 Biodiesel Processing

The basic process of making biodiesel is the transesterification process. Transesterification is a chemical reaction of vegetable/animal fats with alcohols with the aid of a catalyst to produce methyl methyl ester (biodiesel) and glycerin. The transesterification process includes three stages: (1) mass transfer between oil and alcohol; (2) transesterification reaction; And (3) equilibrium formation [14]. Methanol is used as an alcohol in the reaction process because it is cheaper and easily available on the market. Several parameters affect biodiesel yields, among others the amount of catalyst, reaction temperature, alcohol to oil ratio and mixing intensity [10,14, 15]

A study on the effect of the amount of alcohol (methanol) on the production of biodiesel from Kemiri Sunan oil was conducted. The results concluded that the mixed alcohol was about 1.6 times the theoretical amount, while more than 1.75 the theoretical amount did not speed up the reaction, even complicating the separation of glycerin from biodiesel [15].

A two-stage transesterification method using oil extracted from Kemiri Sunan seed (50 l), methanol (11.5 l), KOH (96 g), water (10 l), chloroform and phenolphthalein indicator was conducted. The results showed that 44 liters of Kemiri Sunan biodiesel and 6 liters of glycerol were obtained. Using this method, yields of biodiesel from the Kemiri Sunan crude oil was about 88% [7].

The catalyst used in the production of biodiesel serves to decrease the activation energy of the reaction, so that the reaction can take place more quickly. Two commonly used catalysts are transesterification with alkaline catalyst and transesterification with acid catalyst. However, alkaline catalysts can provide better performance than acid catalysts, ie faster reaction, lower reaction temperature (at room temperature) and greater oil conversion [7, 10,15, 16] If not using a catalyst, high temperatures, long pressures and reaction times are required, with the consequence of which is a relatively large cost.

The most commonly used basic catalysts are Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH), Sodium Methoxide (NaOCH₃) and Potassium Methoxide (CH₃OK). The use of lipase (enzyme) as a catalyst in the biodiesel production process which requires more complex processes and tools, has begun to be developed and aiming to overcome the problem of by-products at the end of the process. However, the constraint faced in the use of enzyme catalysts is expensive lipase prices.

The production of biodiesel from Kemiri Sunan oil, with 2 stages of reaction was examined, ie esterification with H₂SO₄ catalyst and transestrification using NaOH

catalyst. In this study, the effect of catalyst concentration on biodiesel products and their characteristics was observed. The results showed that the yield of biodiesel increased with the increase of catalyst concentration from 0.5-1.0 wt%, then with the increase of catalyst concentration from 1.5-2.0 wt% made the yield decrease. The optimum yield was achieved at 84.7%, with a catalyst concentration of 1 wt% under reaction conditions of 65 ° C., a reaction time of 1 hour and a methanol / oil ratio of 1: 2 (wt / wt) [17].

The effect of catalyst concentration of NaOH on reaction time with at temperature 50 and 60°C with raw material of sunflower oil was examined by Meka et al. [18]. The molar ratio of methanol / oil is maintained at 6: 1. The study concluded that the reaction time decreased proportionally with increasing catalyst concentration from 1% to 2%. However, soap was formed when the catalyst concentration was more than 2%. Ataya et al. [19] conducted a transesterification study of Canola oil with results showing that the conversion of oil to biodiesel increased when the concentration of NaOH catalyst increased from 1-3%. The findings of Rashid and Anwar [20] showed that the production of biodiesel from rapeseed, increased at a KOH catalyst concentration between 0.25-1.5 %, with an optimum value at 1% concentration. Results are consistent with the results of the research by Meher et al. [21].

In biodiesel production, adequate mixing is required to create sufficient contact between oils with alcohol and catalysts. The use of mechanical stirring (mechanical stirring) is not yet maximized to produce the mixing process between the reactants, therefore ultrasonic gets attention in the production of biodiesel.

Ultrasonic energy transfers to the liquid and create a great vibration, which forms a cavitation bubble. As the bubble bursts, a sudden contraction in the liquid occurs, causing mixing in the bubble area. Ultrasonic waves cause intense mixing so that the reaction can continue at a much faster rate without involving high temperatures.

The ultrasonic irradiation method proved to be efficient, time-saving and economically functional to produce biodiesel fuel. Colucci et al. investigated the feasibility of ultrasonic use in mixing to produce biodiesel from soybean oil. The results showed that the reaction rate constants were three to five times higher than those reported in the literature for mechanical stirring. This was explained by the fact that the interface and microscopic and macroscopic areas of the bubble increased when the 20 kHz ultrasonic wave was applied to a two-stage system reaction [22,23].

The effect of ultrasonification on the droplet size of biodiesel blends was investigated. The result showed that ultrasonic mixing resulted in dispersion with an average droplet size 42% smaller than that produced using standard mechanical stirring implants [24]. Stavarache et al. [25] also conducted extensive studies on the application of ultrasonic energy in transesterification of commercial edible oil. The researchers concluded that by using ultrasonic, reaction time is much shorter than with mechanical stirring. Thus it can be concluded that using ultrasonic irradiation for transesterification of vegetable

oils in biodiesel production is more efficient than using conventional methods.

Topare et al [26]. synthesized biodiesel from soybeans by using ultrasonic waves. The results showed that the amount of catalyst and alcohol required could decrease substantially compared to conventional processes. The ultrasonic technique resulted in short reaction time, shorter glycerin phase separation time (1-2 hours), and the glycerine obtained had a better purity level than that obtained in conventional process. Likewise the process was more energy efficient than heating and stirring in conventional processes [26].

Cancela et al.[27] conducted research on the effect of ultrasonic conversion of used cooking oil into biodiesel. In this study, with different process parameters such as reaction time (30-90 min), the amount of catalyst (0.5 - 1% NaOH weight) and temperature (20-40 °C) were also analyzed to obtain higher conversion. The ratio of methanol to 6: 1 molar oil, 0.5% of the amount of catalyst and 30 °C was sufficient to complete the process in 60 minutes. The results obtained in this study confirmed that ultrasonic assisted transesterification is a fast and efficient method of producing biodiesel from waste cooking oil despite low reaction temperatures [27].

4 Comparison between ultrasonic technique and mechanical stirring on Kemiri Sunan oil processing

The process of making biodiesel was carried out in Laboratory to establish optimum conditions. The transesterification treatment of mechanical stirring used mixture of methanol-catalyst by 10%, 15%, 20% (v/v), with KOH and NaOH 0.4%, 0.6% (w/v). The process of transesterification was conducted in a way by heating until the temperature reaching 60° C and stirring for 1hour. The next process is the emulsion was keeping in a separation tank for a minimum of 3 hours, Further step was separating between biodiesel and glycerol. The ultrasonic experiment was carried out using the same amount of catalyst, reactant and molar ratio between methanol and crude oil as performed on transesterification using a mechanical stirrer. The frequency ultrasonic was 20 kHz [26] and reaction times were conducted at, 10 and 15 minutes. After completion of the reaction, the emulsion was transferred into a separation tank for phase separation.

The physical and chemical properties of biodiesel from the raw material of Kemiri sunan seed oil which was observed in this research were: water content, density, kinematic viscosity, cetane number. Biodiesel Standard according to Standar Nasional Indonesia (SNI) 2015 was used.

Density denotes the weight ratio of unit volume of a liquid at a certain temperature. Biodiesel with density value exceeding provisions standard requirements of biodiesel will improve engine wear, have high emission values, and damage engine components, otherwise this density value can be used to determine cetane number.

Viscosity is the most important biodiesel property because it affects the system of pressurized burning.

Lower biodiesel viscosity produces easier pumping and better spray pattern. The viscosity of biodiesel is affected by the amount of trigeliserides does not react with Methanol, the fatty acid composition of methyl constituents esters, as well as compounds between monoglycerides and Diglycerides having quite high polarity and the molecule weight is quite high

The value of cetane number is a measure of quality burning quality or burning waiting time. This is related to the time required for liquid fuel to burn after pumping to the combustion engine. The higher the Cetane number, the faster the burning time. This leads to burning More effective and efficient, smoke, CO and HC emission [28]. This number will be increasing with the increase of long carbon chain fatty acids and degrees of saturation.

Water content in vegetable oil will cause the occurrence of hydrolysis which raise the levels of free fatty acids in vegetable oil. The presence of excess water can cause some of the reaction to change into Saponification reaction between free fatty acid resulting from Hydrolysis of oil with the base catalyst to produce soap. Soap will reduce efficiency of the catalyst thereby increasing the viscosity, forming gel, and complicating the separation of glycerol with methyl esters.

Table 1 represents the result obtained on the conversion of Kemiri sunan oil, with mechanical stirring and untrasonic methods Yield of biodiesel for mechanical stirring method was ranged from 78.44 to 85.5%. while for ultrasonic method was ranged from 90.2 to 98.5 %. The yield of biodiesel produced was affected by raw materials on crude oil manufacture, origin of raw material (where to grow), timeliness of harvest,, seed storage, genetic factors, and moisture content [8]. Besides, it was also strongly influenced by the reaction between the oils with a mixture of methanol and base catalysts [23].

The high conversion obtained on the ultrasonic method can be caused by the acceleration and high mass transfer between methanol and oil, as well as the formation of micro-emulsions resulting from the ultrasonic cavitation phenomenon [23]. The ultrasonic method yielded 98.5% at 10 minutes while the mechanical stirring resulted in a much lower conversion extension of 85.5% at 60 minutes. The indication showed that the reaction under the ultrasonic reactor was much faster than the mechanical stirring process.

The transesterification process either by mechanical stirring or ultrasonic irradiation showed that it was capable of changing the saturated Kemiri Sunan oil into a diesel fuel as can be seen oin Table 2. The transesterification process is aimed to transforming [tri, di, mono] glycerides with high molecular weight and viscosity dominating the composition of vegetable oils into Fatty acid methyl ester (FAME) having lower molecule and viscosity.

Table 2 shows that properties of biodiesel from Kemiri sunan oil fulfilled the biodiesel requirement standard (SNI-2015). Density of biodiesel 867 kg/m³ (mechanical Stirring) and 856 kg/m³ (ultrasonics) have fulfilled the requirements set of 850-890 kg/m³.

Table 1. Biodiesel yield from Kemiri Sunan (*Aleurites trisperma*) seed oil

Treatment	Biodiesel Yield (%)	
	Mechanical Stirring	Ultrasonic
Methanol 10%-KOH 0.4%	82.7	97.4
Methanol 15%-KOH 0.4%	85.3	98.5
Methanol 20%-KOH 0.4%	85,5	98.4
Methanol 10%-KOH 0.6%	83.1	96.3
Methanol 15%-KOH 0.6%	84.1	97.4
Methanol 20%-KOH 0.6%	85.2	97.9
Methanol 10%-NaOH 0.4%	79.4	91.5
Methanol 15%-NaOH 0.4%	78.4	90.2
Methanol 20%-NaOH 0.4%	80.2	92.5
Methanol 10%-NaOH 0.6%	78.4	96.5
Methanol 15%-NaOH 0.6%	79.3	97.4
Methanol 20%-NaOH 0.6%	80.3	96.2

Kinematic Viscosity of biodiesel produced of 5.42 mm² / s (cSt) (Mechanical Stirring) and 4.82 mm² / s (cSt) (ultrasonics) indicated that the value of this viscosity already meet the requirements of biodiesel standards ie.

ranging from 2.3-6.0 mm² / s (cSt). The high of biodiesel oil viscosity is due to the bond of intermolecular hydrogen in the outer acid of the carboxyl group. The viscosity value is proportional to density, the higher the viscosity then the density will be higher [3].

Table 2. Properties of biodiesel from Kemiri Sunan (*Aleurites trisperma*) seed oil

Parameter	Methods	
	Mechanical Stirring	Ultrasonics
Kinematic viscosity mm ² /s (cSt)	5.42	4.82
Density (kg/m ³)	867	856
Cetane number	56.3	59.8
Moisture content (%)	0.05	0.05

The biodiesel production results show that Cetane numbers of biodiesel has been fulfilled the minimum requirement of biodiesel which is 51.

5 Conclusion

The ultrasonic technique proved to be much better than mechanical stirring in producing biodiesel from Kemiri Sunan. The Kemiri Sunan crude oil conversion was 98.5% compared to mechanical stirring 85.3%, with the methanol to oil molar ratio of Methanol 15%v/v/-KOH 0.4% w/v. The reaction time of ultrasonic irradiation required only 15% compared to reaction time required by mechanical stirring method. Properties of biodiesel meet the requirements of biodiesel standards. It can be concluded that ultrasonic is a more valuable tool for the transesterification of Kemiri Sunan oil to biodiesel compared to the mechanical stirring process.

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