Biodiesel production methods of rubber seed oil: a review

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Abstract. The utilization of rubber seed as raw material of biodiesel production is seen highly potential in Indonesia. The availability of rubber seeds in Indonesia is estimated about 5 million tons per annum, which can yield rubber seed oil about 2 million tons per year. Due to the demand of edible oils as a food source is tremendous and the edible oil feedstock costs are far expensive to be used as fuel, production of biodiesel from non-edible oils such as rubber seed is an effective way to overcome all the associated problems with edible oils. Various methods for producing biodiesel from rubber seed oil have been reported. This paper introduces an optimum condition of biodiesel production methods from rubber seed oil. This article was written to be a reference in the selection of methods and the further development of biodiesel production from rubber seed oil. Biodiesel production methods for rubber seed oils has been developed by means of homogeneous catalysts, heterogeneous catalysts, supercritical method, ultrasound, in-situ and enzymatic processes. Production of biodiesel from rubber seed oil using clinker loaded sodium methoxide as catalyst is very interesting to be studied and developed further.

1. Introduction

Recently, production costs between biodiesel and diesel indicate that diesel fuel from fossil sources is lower than biodiesel. An effective way to reduce the cost of biodiesel is to use raw materials that have high free fatty acids (FFAs) or non-edible oils [1] [2]. The price of non-edible oil is much lower than edible oil whose demand continues to increase, so the use of non-edible oil such as rubber seed oil as a feedstock of biodiesel production is very promising.

Biodiesel from rubber seed oil had tested as a fuel in diesel engines. Rubber seed biodiesel can be used as a partial substitute for diesel fuel. The blending of the biodiesel with diesel fuel can be used to fuel diesel engines providing comparable performance, reduced emissions, and wear reduction of engine components and neutral effects of lubricating oil. Engine diesel modifications are not required [2], [3], [4], [5]. The utilization of rubber seed as raw material of biodiesel production is highly potential in Indonesia. The availability of rubber seed in Indonesia is estimated about 5 million tons per year [6]. The yield of brown colored oil extracted from the rubber seed kernel is about 40-50% [7]. Therefore, Indonesia can yield rubber seed oil about 2 million tons per year. It can be utilized as the main feedstock for biodiesel production. The usage of rubber seed oil as an alternative fuel has been investigated extensively due to the objective of ensuring energy security and reducing the environmental impact of diesel emissions. This article introduces the biodiesel production methods of

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rubber seed oil. Aspects written on the method include the ratio of methanol to oil, the amount of catalyst, the type of catalyst, reaction time and reaction temperature. The purpose of this article is to find out the methods that have been developed in the production of biodiesel from rubber seed oil and to choose the method for further development so that the method can be applied on a commercial scale. The structure of the paper as follows: section 2 describes the fatty acid composition of rubber seed oil, section 3 deals with alternative transesterification methods for biodiesel from RSO and, section 4 for the conclusion.

2. Fatty acid composition of rubber seed oil (RSO)

Normally, the rubber seed oil is acquired by disposing of seed. The colour of the oil depends on the pre-extraction of the history of the kernels. It ranges from white to pale yellow for low FFA content of approximately 5% to dark for high FFA content of 10-40% [7]. The composition of fatty acid in the rubber seed oil described in table 1.

| Palmitic acid C16:0 | Stearic acid C18:0 | Oleic acid C18:1 | Linoleic acid C18:2 | Linoleic acid C18:3 | Ref. |
|---------------------|-------------------|------------------|--------------------|--------------------|------|
| 10.2                | 8.7               | 24.6             | 39.6               | 16.3               | [8]  |
| 0.23                | 35.85             | 12.7             | 52.85              | -                  | [9]  |
| 10.102              | 10.704            | 25.605           | 37.054             | 15.099             | [10] |
| 13.11               | 12.66             | 39.45            | 33.12              | -                  | [11] |
| 19.3                | 3.9               | 23.7             | 37.9               | 15.1               | [12] |
| 9.1                 | 5.6               | 24.0             | 46.2               | 14.2               | [13] |

It is obvious in the table that the rubber seed oil consists of mainly fatty acid with 18 carbon atoms. Meanwhile, petroleum diesel composes of mainly hydrocarbon with carbon chain length of 8 to 10 atoms. Cetane number, which refers to indicator to fuel diesel engine quality, increases along with the increases in carbon number. Branched chains and double bonds improve low temperature, flow properties. So, biodiesel produced by rubber seed oil will have a higher cetane number as its fatty acid contains of 18 carbon atoms [9].

3. Alternative transesterification methods for biodiesel from RSO

There are many methods that have been used recently to produce biodiesel from various non-edible feedstock. These methods are pyrolysis, micro-emulsification, dilution, and transesterification [1]. The most common way to produce biodiesel is transesterification. Transesterification is the chemical reaction between one mol triglycerides and three mol alcohol to produce methyl ester and glycerine in the presence or no of catalyst. Alcohols used in transesterification include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are used most frequently in both laboratory scale and the biodiesel industry scale. Methanol becomes the first choice for transesterification reaction as its low cost [2].

A literature survey reveals that some transesterification methods available to produce biodiesel from rubber seed oil such as: conventional transesterification (homogeneous catalyst), heterogeneous catalyst, supercritical method (SCM), in-situ process, ultrasound assisted process, and enzymatic process.
3.1. Conventional transesterification methods (homogeneous catalyst)
Rubber seed oil contains high amount of Free Fatty Acid (FFA), in the range 5-40 % [7]. An effective way to produce biodiesel from raw materials of non-edible oil is through two stages [2]. The first step is esterification to reduce the FFA content of the oil. The second step is converting the triglyceride portion of the oils to mono-alkyl ester and glycerol by transesterification [2].

The FFA emerges serious problem on transesterification reaction catalyzed by base catalyst. FFA is able to react with the base catalyst to produce soap. It certainly leads to a loss of catalyst, while the soap produced deactivates the catalyst. Therefore, the FFA content has to be removed or converted to alkyl esters via acid esterification. Conventionally, sulfuric acid catalyst is used in acid esterification and alkali metal hydroxides and alkoxydes used as catalyst for transesterification reaction [14]. Condition operation of biodiesel production from rubber seed oil by conventional methods as shown in table 2.

| Table 2. Operating condition of biodiesel production from RSO by homogeneous catalyst. |
|---------------------------------------------------------------|
| Optimum operating condition | Initial FFA, % | Conversion efficiency, % | Ref |
| Esterification: 0.5 % (v/w) H₂SO₄ catalyst, 6:1 molar ratio of methanol to RSO, 45 ± 5°C and 30 min. | 17 | 99<sup>a</sup> | [15] |
| Transesterification: 0.5 % (w/w) NaOH catalyst, 6:1 molar ratio of methanol to RSO, 45 ± 5°C and 30 min. | | 99<sup>b</sup> | |
| Esterification: 1 % (v/v) H₂SO₄ catalyst, 0.75 v/v methanol-RSO ratio, 63 ± 2°C and 60 min. | 24 | 96<sup>a</sup> | [16] |
| Transesterification: 0.5% w/v KOH catalyst, methanol–RSO ratio of 0.30 v/v, 55±2°C and 40 min. | | 98-99<sup>b</sup> | |
| Esterification: 10 % (w/w) H₂SO₄ catalyst, 15:1 molar ratio of methanol to RSO, 45°C and 90 min. | 42 | 98<sup>a</sup> | [17] |
| Transesterification: 1 % (w/w) KOH catalyst, 6:1 molar ratio of methanol to RSO, 55°C and 67.5 min. | | 81.8<sup>b</sup> | |
| Esterification: 2.5 % (w/w) H₂SO₄ catalyst, 6:1 molar ratio of methanol to RSO, 60°C and 30 min. | 20 | 85<sup>a</sup> | [18] |
| Transesterification: 1.5 % w/w KOH catalyst, 4.5:1 molar ratio of methanol to RSO, 60°C and 30 min. | | 90<sup>b</sup> | |
| Esterification: Para-toluene sulphonic acid catalyst. | 16.58 | * | [19] |
| Transesterification: 1 % (w/w) KOH catalyst, 9:1 molar ratio of methanol to RSO, 65°C and 100 min. | | 92.8<sup>b</sup> | |

<sup>a</sup>FFA conversion  
<sup>b</sup>FAME yield  
<sup>c</sup>FAME conversion

In an aspect of the yield of FAME, the homogeneous catalyst method is superior to the other five transesterification methods [15], [16] but using sulfuric acid catalysts provides high biodiesel production costs [14].

3.2. Heterogeneous catalyst
The weakness of homogeneous acid catalysts is difficult to recycle and they also impact to serious corrosion and environmental problems. Meanwhile, homogeneous base-catalysts are reactive on free fatty acids to form unwanted soap as by-products that need expensive separation cost. Thus, the biodiesel production using solid catalysts is preferred. Moreover, the main advantages of heterogeneous reaction come from compatibility with the environment and reduction of manufacturing cost by elimination of the expensive process steps such as separation and purification of biodiesel [20-
Different heterogeneous catalytic transesterification for producing biodiesel from rubber seed oil are summarized in Table 3.

Table 3. Optimum parameter condition and conversion efficiency via heterogeneous catalytic.

| Optimum operating condition                                                                 | Initial FFA, % | Conversion efficiency, % | Ref |
|--------------------------------------------------------------------------------------------|----------------|--------------------------|-----|
| 5 wt.% of clinker loaded with methanol as catalyst; methanol to RSO molar ratio of 4:1, 65°C and 4 hours. | 17.75          | 96.9<sup>a</sup>         | [20]|
| 0.6 wt% of clinker loaded with 0.5 wt% of sodium methoxide as catalyst; methanol to RSO molar ratio of 7:1, 60°C and 4 hours | 17.75          | 100<sup>a</sup>          | [21]|
| 14.5 wt.% SO₃H-MCM-41 catalyst; methanol to RSO molar ratio of 16:1, 129.6°C and 48 hours | -              | 83<sup>b</sup>          | [22]|
| 9 wt.% sodium metasilicate catalyst; methanol to RSO molar ratio of 9:1, 65°C and 40 minute | 5.2            | 98<sup>b</sup>          | [13]|
| 9 wt.% CaO-AR grade catalyst; methanol to RSO molar ratio of 15:1, 65°C and 180 minute |                  | 97<sup>b</sup>          |     |
| 100 wt.% CaO-based coral fragment catalyst; methanol to RSO molar ratio of 15:1, 65°C and 210 minute |                  | 98<sup>b</sup>          |     |
| 3 wt.% poly (sodium acrylate) supporting NaOH (NaOH/NaPAA) catalyst, methanol to RSO molar ratio of 6:1, 60°C and 120 minute | 0.6            | 96<sup>b</sup>          | [23]|

<sup>a</sup>FFA conversion  
<sup>b</sup>FAME yield

Biodiesel from rubber seed oil has been able to be produced through one step transesterification even though the rubber seed oil contains high free fatty acids. Transesterification of rubber seed oil using clinker loaded with sodium methoxide as catalyst doesn't take place under extreme conditions; total mole ratio of methanol to oil, the amount of catalyst and reaction temperature is low. The reaction time of transesterification of rubber seed oil using clinker loaded methoxide catalyst is long, but total biodiesel production time is relatively shorter than via homogeneous catalyst process [21]. The ability reuse of clinker loaded methoxide catalysts in the rubber seeds transesterification reaction has not been reported by Muhammad S A W [21] and yield FAME from the reaction results only reached 88%, so the development of the solid catalyst needs to be studied further.

3.3. Supercritical methanol method (SCM)

The content of water in rubber seed oil is about 3.71% [21]. The water existed in conventional base catalyst transesterification reaction of biodiesel causes the formation of free fatty acids. The FFA formed, then reacts with the base catalyst to form saponification materials in the final product that is normally avoided or limited. After the transesterification reaction takes place, separation between saponification materials emulsify the biodiesel product and other materials turn to be very difficult. Meanwhile the oil contains amount water, when the non-catalyzed supercritical methanol treatment is applied, the yield of biodiesel has no less significant [21-23]. By this process, the transesterification of feedstock oil with methanol is done under temperature and pressure, which exceeding the critical properties of methanol. Table 4 summarizes the works have been done in the area of biodiesel production from rubber seed-oils by using non-catalyzed supercritical methanol method.
Table 4. Operating condition by SCM methods.

| Optimum operating condition | Initial FFA, % | FAME yield, % | Ref |
|-----------------------------|----------------|---------------|-----|
| methanol to RSO molar ratio of 42:1, 350°C, 43 MPa, 9 min | 17 | 90.86 | [21] |
| methanol to RSO molar ratio of 40:1, 260°C, 160 bar, 10 min | 12 | 87.54 | [22] |
| methanol to RSO molar ratio of 40:1, 250°C, 100 bar, 5 min | 16.58 | 87.1 | [16] |
| methanol to RSO molar ratio of 42:1, 280°C, 85 bar, 20 min | 21.35 | 92.7 | [7] |
| 1:40 (w/v) seeds-to-methanol ratio, 280°C, 12 Mpa, 30 min | - | 97.9 | [23] |

The consequence of transesterification reactions that use supercritical conditions is an expensive investment in process equipment.

3.4. In situ-transesterification

Another alternative method of producing ester transport fuels is in-situ transesterification, in which the oil-bearing material contacts with acidified or alkalized alcohol directly. A catalyst is needed to activate the reaction. Acid or alkali catalyst also helps to hit the cell wall of the seed and improve the ability of the solvent to access the oil. The operating conditions of biodiesel production from rubber seed oil using in-situ method are presented in Table 5.

Table 5. Operating condition by in situ transesterification methods.

| Optimum operating condition | FAME yield, % | Ref |
|-----------------------------|---------------|-----|
| 0.25 % (w/v) H₂SO₄ catalyst, methanol to rubber seed weight ratio of 3:1, 60°C, 1 atm, 120 min | 91.5 | [29] |
| 3 % (w/w) KOH catalyst, methanol to oil weight ratio of 6:1, 60°C, 1 atm, 120 min | 96 | [30] |
| 0.75 % (w/v) KOH catalyst, methanol to rubber seed weight ratio of 3:1, 60°C, 1 atm, 120 min | 52.86 | [31] |

The problem arising from this in-situ method is relatively similar to that of a homogeneous catalyst process; difficult to recycle and impact of serious corrosion and environmental problems.

3.5. Ultrasound assisted process

The interactions between alcohols and vegetable oils are weak because of their difficult mixed properties and different reactant densities lead to low reaction rates and increased reaction time. One of the most effective and interesting procedures to overcome this problem is by using ultrasonication (ultrasound) that produces sound waves. The ultrasound phenomenon has its own physical and chemical effects. The chemical effect comes from radicals such as H⁺ and OH⁻ produced during a transient implosive collapse of bubbles (in a liquid irradiated with ultrasound), accelerate chemical reaction in the bulk medium. Meanwhile, the physical effect comes from emulsification, in which the microturbulence generated due to radial motion of bubbles leads to intimate mixing (homogenize the mixture) of the immiscible reactants. Considering all these principles, increases intensively the interfacial region between the oil and alcohol, resulting in faster reaction kinetics and higher conversion of oil and product yield [24]. Reaction parameters and results of some studies that are focused on the use ultrasonic irradiation on biodiesel production from rubber seed oil are summarized in table 6.
Table 6. Performance of ultrasonic assisted transesterification for biodiesel production from RSO.

| Optimum operating condition | Initial FFA, % | Conversion efficiency, % | Ref |
|-----------------------------|---------------|--------------------------|-----|
| Esterification: 1 % (v/v) H₂SO₄ catalyst, ratio of rubber seed to methanol was 1:2 (wt/v), 60°C, 1 atm, 30 min and 42 kHz frequency. | 16.48 | 97a | [25] |
| Transesterification: 0.1% (w/v) KOH catalyst, rubber seed to methanol was 1:1.72 (wt/v), 60°C, 1 atm, 30 min and 42 kHz frequency. | | 92.5b | |
| Esterification: 1 % w/w H₂SO₄ catalyst, methanol to RSO molar ratio of 9:1, 50±2°C, 20 min and amplitudo 30%. | 42 | 99.52a | [26] |
| Transesterification: 0.3-0.7% (w/w) KOH/EFB (empty fruit bunch) catalyst, methanol to RSO molar ratio of 3:1, 50±2°C, 20 min and amplitudo 30%. | | | |
| Esterification: 1 % (w/w) HCl catalyst, methanol to RSO molar ratio of 20:1, 45°C, 1 atm, 30 min and amplitudo 40%. | 14.42 | 79.14a | [27] |
| Transesterification: 0.5 % (w/w) NaOH catalyst, methanol to RSO molar ratio of 6:1, 45°C, 1 atm, 15 min and amplitudo 40%. | | 78.84b | |
| Esterification: 2 % w/w HCl catalyst, methanol to RSO molar ratio of 15:1, 95°C and 60 min. | 23.21 | 97.84a | [20] |
| Transesterification: 0.8 % (w/w) KOH catalyst, methanol to RSO molar ratio of 6:1, 65°C, 15 min and frequency of 33±3 kHz. | | 95b | |

aFFA conversion  
bFAME yield

Table 6 shows that the type of catalyst used in the esterification and transesterification of the ultrasonic method is a homogeneous catalyst so that the cost of producing biodiesel from this method is not much different from the homogeneous method. The ultrasonic method can be considered for transesterification of rubber seed oil using clinker loaded methoxide to shorten reaction time.

3.6. Enzymatic transesterification

Many investigations have been conducted for the synthesis of biodiesel mediated by lipases. The enzymatic approach for the modification of oils and fats takes advantage of the specificity of some lipases, leading to high purity products, therefore reducing post processing operations and costs. Due to the mild conditions under which the enzymatic reaction occurs, oil oxidation becomes a negligible problem and less energy is required. Moreover, wastes are minimized and by-products are more easily purified [32].

*Thermomysis Lanugonosus Lipase* was found to be the most suitable for the transesterification of rubber seed oil with a biodiesel conversion of 92.83% at a molar ratio of 4 and 5% (w/v) enzyme concentration in solvent free reaction medium [33]. Biodiesel conversion with rubber seed oil as a feedstock of more than 90% was attained for chemical-catalysed transesterification, whereas the conversion rate was 85% for enzyme-catalysed method [34].

4. Conclusion

This review aims to develop further biodiesel production method from the rubber seed oil, which is potential as a raw material. The literature search results show that the biodiesel production methods of the rubber seed oil include homogeneous catalyst processes, heterogeneous catalysts, supercritical methods, in-situ processes, ultrasound processes and enzymatic processes. The method of producing biodiesel from the rubber seed oil, which is considered to be efficient is to use a clinker loaded methoxide solid catalyst. Using this method, the transesterification of rubber seed oil...
containing 17.75% free fatty acids can be carried out in one step, the mole ratio of methanol to oil is not high, the reaction temperature is low and the amount of catalyst use is small. The correlation between the characteristic of clinker loaded methoxide catalyst with free fatty acid conversion up to 100% and the low FAME yield (88 %) of the method compared to the homogenous catalyst method (99 %) has not been studied.

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