



Contribution of the Reactive Separation Process to Methanol Recovery and Biodiesel Characteristics

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Authors' contributions

This work was carried out in collaboration among all authors. Author YP designs studies, analyzes data, wrote the protocol, wrote the first draft of the manuscript and completes final manuscripts. Author LB conducted data collection in the laboratory. Author ELA analyzed physical and chemical properties. All authors have agreed the final manuscript.

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ABSTRACT

The chemical reaction that occurs in the biodiesel processing is a type of reversible reaction between oil and methanol. Therefore, to increase the conversion of the reaction, the amount of methanol used is more than the stoichiometric equilibrium. The excess methanol is often difficult to recover after washing biodiesel. Determine of the contribution of the reactive separation process to methanol recovery and biodiesel characteristics are the focus of this study. The transesterification reaction process is carried out in reactive separation equipment, using palm oil as raw material, NaOH, and super base CaO as the catalyst. The results showed that the reactive separation process could recover methanol as much as 55.88% for the reaction process using a NaOH catalyst, and 52.94% for the reaction process using a super base CaO catalyst. The biodiesel characteristics produced to meet the criteria set out in the Indonesian National Standard.

Keywords: Biodiesel; reactive separation; methanol recovery; palm oil; transesterification.

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1. INTRODUCTION

Biodiesel is a biofuel that has similar properties to diesel fuel. Biodiesel as a potential energy source has been developed in several countries in recent years. The raw materials for biodiesel industry in the form of vegetable oils and animal fats are abundant in nature and can be cultivated. The use of biodiesel in engine combustion can be mixed with diesel or used directly [1]. The use of biodiesel as fuel provides many advantages, including being very easy to use and biodegradable in the environment. Another advantage is that biodiesel does not contain toxic substances, sulfur and various aromatic compounds [2]. The quality of biodiesel is determined by its physical and chemical properties. These physical and chemical properties are strongly influenced by the type of vegetable oil used as raw material [3], and the success of the transesterification reaction process and the purification process carried out. If the process is incomplete, biodiesel can be contaminated with free glycerol, triglycerides, and methanol which will have an impact on engine combustion performance and emissions [4].

The challenge for biodiesel research today is how to produce biodiesel with low factory investment and production costs, save energy, and be environmentally friendly. It is also hoped that the available biodiesel will be of high quality and meet national and international standards. In previous studies [5,6,7,8,9,10] has been carried out on the use of various non-food oil raw materials, improvement of the biodiesel washing process, making biodiesel additives, extractive reaction processes, utilization natural zeolite catalysts, and research into biodiesel production which has high cetane numbers. These studies have been able to improve the quality of biodiesel, especially cetane numbers, pour points, and emission, but the production costs have not been able to reduce significantly. Of the various components that require costs in the biodiesel industry, one component that requires high costs is the cost of supplying alcohol. In every transesterification reaction carried out to produce biodiesel, the use of methanol is generally greater than the stoichiometric requirements of the reaction. This is the effect of the reaction which can be reversed, so it takes more methanol reactant than stoichiometry to increase the yield on the product side [11]. The excess unreacted methanol should be recovered for reuse, but in practice, a lot of methanol is

wasted in the process of separating, washing, and refining biodiesel. In the process of separating biodiesel from glycerin, methanol can be in both phases. So that when the process of washing biodiesel, methanol will dissolve in washing water and then wasted into the environment. Likewise, methanol that is in the glycerin phase will be wasted in the glycerin further processing process. For this reason, innovation is needed to recover the unreacted methanol before proceeding to the separation, washing, or refining stages of biodiesel.

In this research, the biodiesel production process is carried out using reactive separation process technology. The reactive separation process is a process that combines two processes at once occurring in one process unit, namely the reaction and separation process [12]. The triglycerides in vegetable oil are converted into biodiesel products in the reaction unit by adding alcohol and a catalyst, then purified and separated. With the use of reactive separation technology, the methanol used can also be recycled back into reactants so that it is more economical [7]. The use of reactive separation technology in a reaction will accelerate the reaction to reach equilibrium [13]. For some chemical processes, reactive separation provides several advantages, namely: reactive separation is a combination of reactions and separation in one process unit so that the product produced from reactive separation has a high conversion price, high purity price, high selectivity and with the use of reactive separation it can reduce production costs so that they are more economical [14].

The focus of this research is the integration of the reaction process unit with the methanol recovery process unit by applying a reactive separation technology with a capacity of 5 liters/batch to produce biodiesel from Palm oil, using NaOH and super base CaO as catalysts.

2. MATERIALS AND METHODS

Palm oil as main reactant obtained from Luwu Utara-Indonesia, NaOH, CaO, and methanol, obtained from chemical stores in Makassar.

2.1 Preparation of Catalyst

The preparation of the super base CaO catalyst was carried out by referring to the procedure performed by Kouzu M, et al. [15]. CaO (12 g) was dissolved in ammonium carbonate 0.12 g/ml

(171.5 ml). The solution is stirred for 30 minutes, then filtered. The solid obtained was heated at 110°C, then calcined at 700°C for 1.5 hours. When the calcination time has been reached, the furnace temperature is lowered to 250°C. The resulting solid from the furnace is then stored in the desiccator. The preparation of NaOH as a catalyst was carried out by referring to the procedure performed by G. Arzamendi, et al. [16]. NaOH (40 g) is dissolved in methanol until it reaches a solution volume of 400 ml. The solution is stirred until a homogeneous solution is formed.

2.2 Biodiesel Production Process using Reactive Separation

3478 ml of palm oil, 1000 ml of methanol, and the dissolved catalyst were filled into the reactor. The reaction process was carried out in the reactor at 65°C, 2 hours and stirring 200 rpm. After the reaction process reaches 2 hours, the reactor temperature is increased to 75°C to carry out the methanol recovery process for 30 minutes. Subsequently, the reactor temperature was lowered to 50°C, then continued with the separation of the reaction products. The crude biodiesel obtained is washed with water at 50°C. After the washing process, it is followed by an evaporation process to remove water in the final product.

2.3 Biodiesel Characteristics Test

Analysis of biodiesel characteristics refers to SNI 04-7182-2015 (Indonesian National Standard). The parameters tested were density, viscosity, saponation number, acid number, iodine number.

3. RESULTS AND DISCUSSION

Research on the biodiesel production process carried out in this study uses a separation reactive equipment, which is a reactor connected to a condenser. The condenser has a dual function, namely to reflux methanol during the reaction and to recover methanol after the reaction time has been reached. 3478 ml of palm oil, 1000 ml of methanol, and 0.05%-b catalyst were put together into the reactor equipped with a mixer and condenser. The transesterification process was carried out in duplicate for each type of catalyst (NaOH and super base CaO), for 2 hours at a temperature of 65°C. After the reaction time is reached, the

methanol recovery process is then carried out by increasing the temperature to 75°C. The methanol recovery process was carried out for 30 minutes using a condenser. Furthermore, the temperature of the reactor is gradually lowered until it reaches a temperature of 50°C. The reactor product consisting of a mixture of methyl ester and glycerol is flowed to a separator column to separate the crude biodiesel and glycerol.

After being separated from the by-product, the formed methyl ester is gently washed with water at 50°C. The purpose of this washing is to remove the remaining catalyst that is still in the product. After washing, the next processing process is to remove the water content in the methyl ester product which is formed by heating until the water bubbles in the methyl ester disappear and appear clear. The process of removing water content is intended to prevent sustainable saponification reactions from occurring [17]. Table 1 shows the yield of biodiesel as the main product and glycerol as a byproduct, from the processes and catalysts, respectively. The yield (average) of the reactive separation process using NaOH catalyst was 56.75%, and glycerol 73,5 ml. While the yield for the active separation process using a super base CaO catalyst was 95.68%, and glycerol 41,5 ml.

In Table 2, the results show that methanol is obtained from two types of processes carried out. The initial amount of feed methanol is 1000 ml, the methanol requirement according to stoichiometry is 966 ml and excess methanol is 34 ml. For methanol recovery measurement results using NaOH catalyst on run, I and II were 19 and 15 ml respectively, so that the % recovery methanol obtained was 55.88% and 44.12% respectively, while those using super alkaline CaO catalyst on run I and II were 18 and 14 ml, so that the% recovered methanol obtained was 52.94% and 41.18%, respectively.

From these results it is known that the use of a super alkaline CaO catalyst in the reactive separation process can produce a higher yield compared to the use of a NaOH catalyst. This can be due to the process using a NaOH catalyst which can trigger a saponification reaction so that some of the raw material is consumed in the saponification reaction and is in the form of soap [18].

Table 1. Yield of reactive separation process

Run	Palm Oil (ml)	Methanol (ml)	CaO super basa (g)	NaOH (g)	Biodiesel (ml)	Yield (%)	Glycerol (ml)
I	3478	1000	-	3.48	1973	56.72	67
II	3478	1000	-	3.48	1975	56.78	80
I	3478	1000	3.48	-	3321	95.48	39
II	3478	1000	3.48	-	3335	95.88	44

Table 2. Recovery of Methanol

Run	Methanol Feed (ml)	Methanol Stoichiometry (ml)	Methanol Excess (ml)	Methanol Recovery (ml)	Methanol Recovery (%)
I	1000	966	34	19	55.88
II	1000	966	34	15	44.12
I	1000	966	34	18	52.94
II	1000	966	34	14	41,18

Table 3. Comparison of the results of the biodiesel characteristic test with the SNI standard characteristics

Catalyst	Average Density (kg/m ³)	Average Viscosity (mm ² /s)	Average Acid Number (mg-NaOH/g)	Average Saponification Number (mg-KOH/g)	Average Iodine Number (I ₂ /100 g)
NaOH	880	11.16	0.28	134.64	17.02
Super base CaO	889	14.26	0.89	100.98	12.95
	SNI:850-890	SNI:2,3-6,0	SNI: Max 0.8	SNI: 179-191	SNI: Max 115

SNI: National Standard of Indonesia

Table 3 shows the comparison of the results of the biodiesel characteristics test with the SNI standard characteristics. The density of biodiesel produced from the reactive separation process using a NaOH catalyst is 880 kg/m³ while the process using super base CaO is 889 kg/m³. This value range is still in the standard range for biodiesel SNI 04-7182-2006 [19].

The viscosity of biodiesel from the reactive separation process using a NaOH catalyst is 11.16 mm²/s (cSt), while biodiesel using a super base CaO catalyst is 14.26 mm²/s (cSt). The viscosity value of these two types of catalysts is still relatively high when compared to the SNI for biodiesel, which is around 2.3-6.0 mm²/s (sSt). However, when compared with the raw material viscosity value of 35.15 mm²/s, the viscosity of the two catalysts has decreased.

The acid number of biodiesel produced from the reactive separation process using a NaOH catalyst is 0.28 mg-NaOH/g while using a super base CaO catalyst is 0.89 mg-NaOH/g. If this value is compared with the value specified in SNI, it is clear that the acid number of biodiesel

produced from processes using NaOH catalysts is better than the acid numbers of biodiesel produced from processes using super base CaO as a catalyst. A high acid number is an indicator that biodiesel still contains free fatty acids. This means that biodiesel is corrosive and can cause scale in diesel engine injectors [20].

The iodine number biodiesel produced from the reactive separation process using a NaOH catalyst is 17.02 I₂/100g while using a super base CaO catalyst is 12.95 I₂/100g. The use of these two catalysts is still within the SNI biodiesel range, which is a maximum of 115 I₂/100g (BPPT 2015). However, the use of a super base CaO catalyst is better because its value is greater than the use of a NaOH catalyst.

The saponification number of biodiesel obtained from the process using NaOH catalyst was 134.64 mg-KOH/g while using a super base CaO catalyst was 100.98 mg-KOH/g. The use of the two catalysts is classified as low when compared to the SNI range for biodiesel. However, the use of NaOH catalyst is better because the value is closer to the range of SNI values compared to the use of a super base CaO catalyst.

4. CONCLUSION

The conclusions of this research are:

1. The contribution of the reactive separation process to the methanol recovery process carried out in this study is effective for obtaining unreacted methanol
2. Methanol obtained from the process using NaOH and super base CaO catalysts respectively 55.88% and 52.94%. The yield of the process using a super base CaO catalyst (95.88%) was greater than the yield of the process using a NaOH catalyst 56.78%.
3. The characteristics of biodiesel from the production process using reactive separation meet the characteristics of the Indonesian National Standard (SNI).

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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