



PERFORMANCE OF REACTIVE SEPARATION PROCESS ON BIODIESEL PRODUCTION

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ABSTRACT

The reactive separation process in the biodiesel industry is important to reduce the number of process steps so that the process becomes more economical. In this research, the Reactive Separation Process has been applied to carry out the process of transesterification reaction between vegetable oil and methanol which is excessively stoichiometric, while also carrying out the process of recovery of excess methanol from the reaction product. The parameter of the success of the Reactive Separation Process is in terms of the effectiveness of the process and the quality of waste cooking oil biodiesel produced using several types of catalysts. The stages of the process carried out consisted of refining used cooking oil, catalyst preparation, transesterification reaction, recovery of excess methanol, refining biodiesel, and testing the characteristics of biodiesel. Based on the acquisition of biodiesel and recovery of methanol produced from this research, it shows that the effective reactive separation process is used for biodiesel production; however some of the characteristics of biodiesel produced still need to be increased until all of them meet the standards set in the Indonesian National Standard.

Keywords: reactive separation, biodiesel, recovery methanol.

INTRODUCTION

The challenge in developing biodiesel production now is how to produce biodiesel with low cost, both plant investment costs and production costs, saving energy and being environmentally friendly. It is also hoped that biodiesel is available in high quality and meets national and international standards. Several studies have been carried out to develop production process technologies such as the utilization of various non-food oil raw materials, improvement of the biodiesel washing process, making biodiesel additives, extractive reaction processes (Pasae, *et al.* 2016), utilization of natural zeolite catalysts, and research on biodiesel production that has high cetane rates (Pasae, 2017). These studies have been able to improve the quality of biodiesel, especially the cetane number and pour point, but the production costs have not been significantly reduced.

In general, biodiesel plants that are already operating are designed with high production capacity, thus requiring high investment costs. This resulted in the number of biodiesel plants in Indonesia is still very limited, even though the potential of raw materials is very large. The potential of raw materials available in various regions can be an opportunity to develop a small-medium capacity biodiesel plant that can be set up and operated by productive groups in the community, such as fishing groups to meet their fuel needs.

The process of biodiesel production is largely determined by the transesterification reaction between vegetable oils and alcohol. Transesterification reactions are series and reversible reactions. To achieve a perfect reaction, the ratio of methanol to oil is 3: 1. But because the reaction is reversible, to obtain a high conversion, excess methanol is added. For this reason, methanol

recovery method is needed. The recovery process of methanol in the biodiesel industry is generally carried out twice in different processes, namely the recovery of methanol from the biodiesel phase and the recovery of methanol from the glycerol phase. In this research a Reactive Separation Process has been carried out to carry out the process of methanol recovery simultaneously in the same process equipment as the reaction process.

Reactive separation process is a process where reaction and separation occur in the same unit of equipment. Triglycerides in vegetable oils are converted into biodiesel products in the reaction unit by the addition of alcohol and catalyst, then purified and separated. With the use of reactive separation technology, the methanol used can also be recycled back into a reactant so it is more economical. The use of reactive separation technology in a reaction will accelerate the reaction to reach equilibrium. For some chemical processes, reactive separation provides several advantages, namely: reactive separation is a combination of reaction and separation in one process unit so that the products produced from reactive separation have high conversion prices, high purity prices, high selectivity and with the use of reactive separation can reduce production costs so that it is more economical.

To find out the performance of the reactive separation process applied in this research, the reaction process uses used cooking oil which has been refined as raw material with the help of 2 different catalysts, namely super base CaO catalyst and NaOH catalyst.



METHODS

Materials

Used cooking oil used in this study was obtained from culinary waste in Mamuju City, West Sulawesi Province. Chemicals for catalysts namely NaOH and CaO were obtained from chemical stores in Makassar City, South Sulawesi Province.

Preparation of catalyst

The preparation of super base CaO catalysts and NaOH refers to the results of the research of Pasae, Y et al (2019). To obtain a superbase CaO catalyst, 12 grams of CaO was dipped in a solution of ammonium carbonate 0.12 g/mL, as much as 171.5 mL, stirred for 30 minutes and filtered. The collected solids are heated at 110 °C, and calcined at 700 °C for 15 hours. After calcining, CaO solids are allowed to reach temperatures of 250 °C and put into a desiccator to prevent contact between the surface of the catalyst and water vapor which results in decreased catalyst base strength. As for the preparation of the NaOH catalyst, 40 g of NaOH was dissolved in methanol. The methanol used to dissolve is calculated and then reduced from the methanol requirement that will be used in the reaction.

Pretreatment of waste cooking oil

The process of refining used cooking oil refers to Pasae, *et al* (2019). Purification using wood charcoal: wood charcoal is ground until smooth. Wood charcoal powder as much as 5 grams mixed into 500 mL cooking oil waste and allowed to stand for about 5 minutes later. Then filtering is done to separate the sediment from oil.

Biodiesel production process

Purified used cooking oil is put into the reactor as much as 3500 mL. Furthermore, a catalyst with a concentration of 0.05% was also put into the reactor, and 750 ml of methanol. The reaction was carried out for 2 hours at 65°C. After the reaction time was reached, a methanol recovery process was carried out by raising the reactor temperature to 75°C. The recovered methanol is collected, and then the reaction results are put into a separation column to separate the glycerol phase from the crude biodiesel. Crude biodiesel is then washed with distilled water at 50°C twice as much washing. The final stage of the biodiesel production process is heating to evaporate water. Warming is done until the biodiesel product looks clear.

Analysis of biodiesel characteristic

Quantitative analysis of biodiesel characteristics including density, viscosity, acid number, saponification rate, and iodine number were carried out based on SNI 04-7182-2015.

RESULTS AND DISCUSSIONS

Table-1 shows the product of the transesterification reaction using two types of catalysts, NaOH and CaO super base. Biodiesel products obtained from the reaction process using NaOH catalyst obtained a yield of 87.14 % and glycerol as much as 170-190 mL. While the reaction process using super alkaline CaO catalyst obtained yield of 88.57 %, and glycerol 100-110 ml. The amount of methanol that can be recovered is shown in Table-2. The initial volume of methanol used was 1000 ml. For the needs of the reaction based on stoichiometry 966 ml of methanol is needed. Thus it is known that excess methanol from stoichiometry needs is 34 ml. For the measurement of methanol recovery results using NaOH catalysts in run I and II were 13 and 15 ml, respectively, so that the % methanol recovery obtained was 38.23 % and 44.12 %, while those using super alkaline CaO catalysts in run I and II are 18 and 14 ml, respectively, so the % methanol recovery obtained is 52.94 % and 41.18 %.

The use of super base CaO catalysts produces higher yields compared to NaOH catalysts, this is because in the transesterification process where fatty acids react with NaOH catalysts and form a lot of soap, so the glycerol produced in the use of NaOH catalysts is higher than the super alkaline CaO catalysts and the yield of methanol recovery using a NaOH catalyst is lower than using a super alkaline CaO catalyst.

The biodiesel characteristic test results are presented in Table-3 including density, viscosity, acid number, saponification number and iodine number. Density of biodiesel produced from processes using NaOH catalyst is 876-884 kg/m³ while biodiesel from processes using super base CaO is 888-904 kg/m³. Density of biodiesel produced from the process using NaOH catalyst is still within the range of SNI biodiesel standard which is 850-890 kg/m³. Thus, in terms of density, the use of NaOH catalyst is better than the use of super base CaO catalyst. The viscosity of biodiesel using NaOH catalyst is 22.42-29.54 mm²/s while biodiesel using super base CaO catalyst is 26.80-29.29 mm²/s. The value of viscosity in the two uses of this type of catalyst is still relatively high when compared to the range of biodiesel SNI which is around 2.3-6.0 mm²/s. However, when compared with the viscosity value of raw materials which is 35.15 mm²/s, the viscosity using both catalysts has decreased. High viscosity or thicker fluid will cause the flow velocity to be slower so that the degree of fuel atomization will be too late in the combustion chamber. If the viscosity is higher, the resistance to flow will be higher. This characteristic is very important because it affects the performance of the injector on a diesel engine. Fuel atomization is very dependent on the viscosity, injection pressure and injector hole size. In general, fuel must have a relatively low viscosity so that it can flow easily and is atomized; this is because a fast engine speed requires a fast fuel injection as well. However, there is still a minimum limit because lubrication properties that are good enough to prevent



wear due to rapid piston movement are needed. With the transesterification process in making biodiesel, it will reduce the viscosity value of the edible oil until it is included in the range of viscosity figures of the Indonesian National Standard (SNI).

The acid number of biodiesel using NaOH catalyst is 0.88-1.52 mg-NaOH while using super base CaO catalyst is 1.04-1.36 mg-NaOH. When compared to the SNI range for biodiesel which is a maximum of 0.8 mg-KOH, it can be seen that biodiesel using NaOH catalyst is better because it is closer to the SNI range than the super base CaO catalyst. This acidity level is related to the fuel's resistance to storage and its level of corrosiveness. The high acid number is an indicator of

biodiesel still containing free fatty acids. Means, biodiesel is corrosive and can cause crust on the diesel engine injector.

The biodiesel iodine number using the NaOH catalyst produced was 1.06 - 6.13 I₂/100 g while using the super base CaO catalyst was 4.74 - 6.32 I₂/100 g. The use of these two catalysts is still in the range of SNI biodiesel, which is a maximum of 115 I₂/100 g. However, the use of super base CaO catalyst is better because the value is greater than the use of NaOH catalyst. The low value of the iodine number is due to used cooking oil is used oil which is the result of repeated use, and can be done continuously resulting in a level of saturation.

Table-1. Composition of raw materials and result of biodiesel production.

Run	Used Cooking Oil (ml)	Methanol (ml)	CaO Super Base (g)	NaOH (g)	Biodiesel (ml)	Yield (%)	Glycerol (ml)
I	3500	1000	-	1.75	3050	87.14	170
II	3500	1000	-	1.75	3050	87.14	190
I	3500	1000	1.75	-	3100	88.57	110
II	3500	1000	1.75	-	3100	88.57	100

Table-2. Recovery Methanol.

Run	Feed Methanol (ml)	stoichiometry Methanol (ml)	excess methanol (ml)	Recovery Methanol	
				(ml)	(%)
I	1000	966	34	13	38.23
II	1000	966	34	15	44.12
I	1000	966	34	18	52.94
II	1000	966	34	14	41.18

Table-3. Biodiesel characteristic.

Catalysts	Density(kg/m ³)	Viscosity (mm ² /s)	Acid Value(mg-NaOH)	Saponification number(mg-KOH)	Iodin number (I ₂ /100g)
NaOH	884-876	22.42-29.54	0.88-1.52	61.71-134.64	1.06-6.13
CaO super base	888-904	26.80-29.29	1.04-1.36	85.55-100.98	4.74-6.32
SNI	850-890	2,3-6,0	Max 0.8	179-191	Max 115

CONCLUSIONS

Based on the research that has been done, it can be concluded that the effective reactive separation process is used for the biodiesel production process, where the acquisition rate of biodiesel is quite high, which is 88.57% for processes with super alkaline CaO catalyst and 87.14% value for processes with NaOH catalyst. Likewise, the recovery rate of methanol was 41.18-52.94 % (super base CaO catalyst) and 38.23-44.12 % (NaOH catalyst). However, the characteristics of biodiesel produced have

not fully met the standards set in the Indonesian National Standard.

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