EFFECT OF GLYCEROL SEPARATION ON PALM OIL TRANSESTERIFICATION

Budy Rahmat[1,*], Imas Siti Setiasih[2], and Roni Kastaman[2]

[1]*Department of Agrotechnology, University of Siliwangi, Jl. Siliwangi No. 24 Tasikmalaya, West Java Indonesia*

[2]*Department of Agroindustry, University of Padjadjaran, Jl. Dipatiukur No. 35 Bandung, West Java Indonesia*

ABSTRACT

This research was aimed to study the effect of glycerol separation on palm oil transesterification. Objectives of this study were to suppress the use of excess methanol and shorten the processing time. This research consisted of: design-build reactor, the effect of the glycerol separation on the transesterification reaction, characterization of biodiesel, and mass balance analysis. The reactor was designed by integrating circulate stirrer pump, static mixer, and sprayer that will bring out the intense reaction in the outer tank reactor. The experiment in this research was the treatment of decreasing the quantity of methanol to 5:1 molar ratio and reducing of processing time to 20 min, which was arranged in a completely randomized factorial design. The result showed that, (i) the stirring system was effectively worked outside the reactor tank, and in its reactor tank occurred glycerol separation during the process; (ii) the rate of glycerol during the process followed the inverse regression equation of $\hat{Y} = 66.44-351.17\ X^{-1}$; (iii) the decrease in the level of methanol to 5:1 molar ratio and the reduction of processing time to 20 min in this engineering did not influence the biodiesel yield and quality that met the SNI 04-7182-2006 standard.

Keywords: *glycerol separation; biodiesel; palm oil; transesterification*

ABSTRAK

Penelitian ini bermaksud untuk mengetahui pengaruh pemisahan gliserol pada transesterifikasi minyak sawit. Tujuan dari penelitian ini adalah untuk menekan penggunaan metanol berlebih dan mempersingkat waktu proses. Penelitian ini terdiri dari: rancang-bangun reaktor, efek pemisahan gliserol pada reaksi transesterifikasi, karakterisasi biodiesel, dan analisis neraca massa. Reaktor didesain dengan mengintegrasikan pompa pengaduk sirkulasi, mixer statis, dan sprayer yang akan membawa keluar reaksi intens dalam reaktor tangki luar. Percobaan dalam penelitian ini adalah perlakuan penurunan jumlah metanol sampai rasio molar 5:1 dan mengurangi waktu pengolahan untuk 20 menit, yang disusun dalam rancangan acak lengkap faktorial. Hasil penelitian menunjukkan bahwa, (i) sistem pengadukan itu bekerja efektif di luar tangki reaktor, sedangkan di dalam tangki reaktor terjadi pemisahan gliserol selama proses; (ii) tingkat gliserol selama proses mengikuti persamaan regresi invers $\hat{Y} = 66,44-351,17\ X^{-1}$, (iii) penurunan tingkat metanol sampai 5:1 rasio molar dan pengurangan waktu proses sampai 20 menit dalam rekayasa ini tidak mempengaruhi hasil biodiesel dan kualitas yang memenuhi persyaratan SNI 04-7182-2006.

Kata Kunci: *pemisahan gliserol; biodiesel; minyak sawit; transesterifikasi*

INTRODUCTION

Biodiesel could be synthesized from oil and methanol via transesterification reaction. Catalytic preparation of biodiesel has the problem on the production cost, which is particularly related on the properties of methanol and vegetable oil that are not miscible, thus the reaction need the strong and long stirring. Besides, the reaction is reversible and the yield is determined by the quantity of methanol as reactant [1].

Development on biodiesel production is aimed to give maximum conversion. The optimization of transesterification could be done by applying the open system [2-3] with two options of (1) employing the excess methanol and the cost will increase as the consequence and (2) immediately removing one of the products.
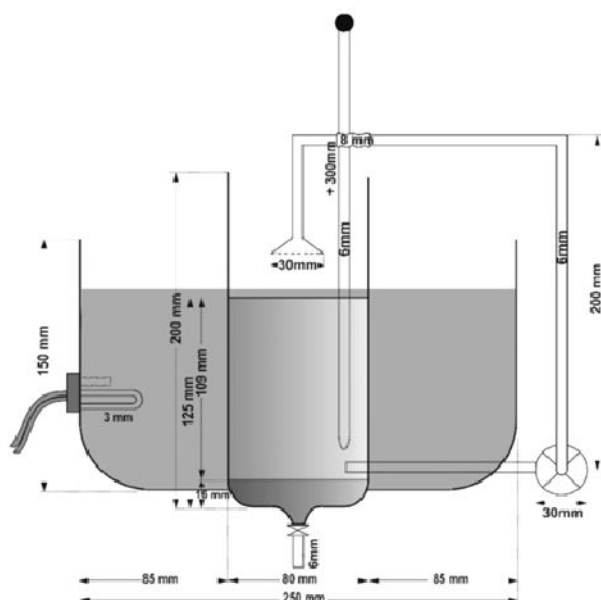
Glycerol as the by product is usually separated after the reaction complete, event decanted at few hours before separation [4]. This action is conducted as the glycerol could be a reactant on the back reaction if the methanol is not employed in excess amount.

In this research, the strategy to optimize the transesterification reaction was to gradually separate glycerol during the process. According to Law of Mass Action, removing of glycerol from the reaction system could compensate the excess methanol and increase the reaction rate. The aim of the research was to study

* Corresponding author. Tel/Fax : +62- 265 323531/325812
Email address : budy_unsil@yahoo.com

Table 1. Properties of palm oil

Parameter	Results	Unit
Relative molecular mass (M_r)	856.1*	g/mole
Density (ρ) at 40 °C	902.1	kg/m^3
Kinematic viscosity (υ) at 40 °C	47.9769	mm^2/sec
Flash point	286	°C
Acid number	0.267	mg KOH/g

Fig 1. Design of biodiesel reactor, capacity of 500 mL

the effect of glycerol separation on the efficiency of methanol utilization and to increase the conversion rate of vegetable oil into biodiesel. This research could give benefit to increase the efficiency of biodiesel production.

Transesterification is a reversible reaction. Thus biodiesel could be obtained in 100% yield as the formation of product will be followed by the back reaction (formation of reactant) until the equilibrium is reached. Such condition could be considered as dynamic equilibrium law [2-3].

Methanol and vegetable oil are not miscible; therefore, strong and long stirring are required. Transesterification reaction could occur on few hours at room temperature, where the conversion is not maximum. In the case of stirring using blade agitator, the slow stirring could not give the optimal mixing thus the reaction would need long time and high energy consumption. By using blade agitator, conversion of methyl ester could reach the maximum conversion (>96.5%) in 1 h [5].

Reactor equipped with circulation pump integrated with static mixer and sprayer is proved to give effective conversion. Besides, the stirring is only integrated on the circulation flow, the condition of the reactor tank would be quieter as the mixture was gradually and continuously dropped into the surface of liquid and transferred into

circulation pump [6-7]. When the liquid is on the reaction tank, there is some time for the formation and separation of glycerol from the reaction system. Such condition should be used and considered to build certain reaction, at which the glycerol could be accumulated on the bottom of reactor or gradually removed so glycerol is not involved in the back reaction. It could also control the reaction to the formation of product and optimize the formation of biodiesel.

In this research, several aspects were studied including (1) the pattern of glycerol formation during the transesterification reaction, thus equation model could be determined and (2) effect of glycerol separation on the transesterification reaction in order to reduce the amount of methanol used and to shorten the reaction time.

EXPERIMENTAL SECTION

Materials

The reagents employed in this research were palm oil, methanol, potassium hydroxide and aquadest.

Instrumentation

The tools in this research included self-assembled biodiesel reactor (capacity of 500 mL), analytical mass balance, technical balance, stopwatch and laboratory glassware.

Procedure

Preparation of biodiesel process

As much as 500 mL (0.527 mol, 451.4 g) of palm oil was transesterified using methanol (3.16 mol, 128 mL, 101.12 g) in the presence of 1% basic catalyst (4.5 g). The Properties of the oil were tabulated on Table 1.

Assembly of reactor

This section employed the design-build method, i.e. study to give the design of machine including structural and functional design.

Determination of reaction capacity

Determination of reaction capacity included the determination of circulation flow rate, time of glycerol formation and curve of glycerol formation during the process.

Effects of decrease of methanol concentration and time on transesterification

Two variations were conducted to evaluate the preparation of biodiesel. They were time (60, 50, 40, 30
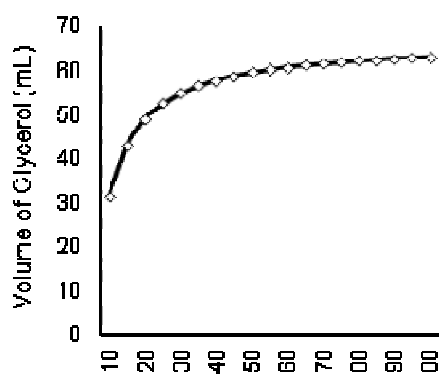
Figure 2. Increase of the produced glycerol

and 20 min) and methanol concentration 128 (ratio of 6:1), 117.3 (5.5:1) and 106.7 (5:1). The variations were then applied factorial complete randomized design using three repetitions.

The observed responses were volume of crude biodiesel (biodiesel produced after separation of glycerol at the end of process), volume of biodiesel after washing (biodiesel produced after 2 times washing using warm water at 60 °C) and volume of biodiesel after drying biodiesel produced after heating in oven at 60 °C for 1 h.

Characterization of biodiesel

Having obtained the optimum condition of transesterification, the biodiesel was then synthesized. The produced biodiesel was characterized based on procedures of *Forum Biodiesel Indonesia*.

Analysis of mass balance

Mass balance is molar equation of substance before (oil, methanol and KOH) and after (biodiesel and glycerol) reaction, which was calculated.

RESULT AND DISCUSSION

Design of Reactor

Biodiesel reactor components were (1) reactor tank, (2) circulation pump, (3) heating element, (4) static mixer and (5) sprayer.

In the reactor tank, the condition was quieter since there was no pounding wave or turbulence as in the blade stirring mechanism. On the calm condition, there was gradual time to separate glycerol from the reaction mixture. The time was utilized optimally; therefore glycerol would not be the reactant on the back reaction. Besides, the position of output pipeline was set into circulation pump from the bottom of reactant tank.

Structural design of transesterification tank consisted of (1) glass column with diameter of 8 cm and height of 20 cm as reaction tank; (2) circulation stirrer (Denso pump No. 06021-1480 windshield washer,

voltage: 12 V; current: 3.5-3.9 A; debit: 36 cm^3/sec); (3) static mixer with diameter of 8 mm, equipped with spiral plat on breaking and splitting position; (4) sprayer with hole (1 mm); (5) electrical heating element SG 1103 20 W; (6) thermostat EGO 0913 limit 110 °C; (7) hand thermometer; (8) input pipeline of oil; (9) input pipeline of methanol and catalyst; (10) output tap of glycerol and biodiesel; (11) distributing pipeline SMC TY 0805 polyurethane 8x5; (12) regulated DC power supply Montana SPS 7A and (13) static (Fig. 1).

Design of Reactor Capacity

Determination of stirring circulation rate

Stirring circulation with the flow rate of 20.11 mL/sec with the process time of 20, 40 and 60 min would need the volume of reaction mixture of 620 mL (500 mL of oil + 120 mL of methanol) and circulation occurred effectively for 39, 78 and 117 times since it had three stirring phases. There were stirring agitation by propeller pump and sprayer to the mixture surface by nozzle. Thompson and He [6] stated that the application of circulation pump and static mixed were more effective than the blade mixer. The blade mixer has limitation on higher energy consumption and requirement of strong construction of reaction to support all the reaction components.

Time of glycerol formation

The formation of glycerol was indicated by phase, color and weight, which were different with ester. The formation could be observed by the occurrence of brownish red phase on the bottom of reactor, which was contrast with the light yellow phase of ester.

The average time of glycerol formation was 4.8 min after the transesterification began. Although, the observation was visually obtained, the information was important for the next step particularly on the determination of initial time to determine of the volume of produced glycerol.

Increase of the produced glycerol

Curve of relation between process time (axis) and the increase of the produced glycerol (ordinate) tended to follow inverse model, either by using direct scatting plot or regression analyses (Fig. 2). The curve was considered as inverse or reciprocal model with the equation of:

$$\hat{Y} = 66.44 - 351.17\ X^{-1}$$

The equation was tested for the significance using T-test. The calculated t was 4.91, which was higher than t-table of 2.101 (db18; α 0.05).

In inverse model, if the variable of X increases unlimitedly, therefore the $b_1 X^{-1}$ will reach 0 and Y will approach the limit of b_o value (intercept) [10]. The

Table 2. The effects of decrease of methanol concentration and process time on the produced glycerol.

Treatment	Glycerol Volume (mL)	
m_1 (ratio 6:1)	85.50	c
m_2 (ratio 5.5:1)	80.93	b
m_3 (ratio 5:1)	75.50	a
w_1 (60 min)	82.56	a
w_2 (50 min)	81.56	a
w_3 (40 min)	80.22	a
w_4 (30 min)	80.22	a
w_5 (20 min)	78.67	a

Information: Number followed with the same letter showed no significant difference based on Duncan double distance test 5%.

Table 3. Effect of decrease of methanol concentration and process time on the produced crude methyl ester

Treatment	Volume of crude methyl ester (mL)	
m_1 (ratio 6:1)	536.02	c
m_2 (ratio 5.5:1)	532.13	b
m_3 (ratio 5:1)	528.50	a
w_1 (60 min)	531.59	a
w_2 (50 min)	529.94	a
w_3 (40 min)	531.61	a
w_4 (30 min)	533.06	ab
w_5 (20 min)	534.89	b

Information: Number followed with the same letter showed no significant difference based on Duncan double distance test 5%.

Table 4. Effect of decrease of methanol concentration and process time on volume of methyl ester after washing and drying

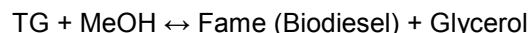| Treatment	Volume of ME after drying (mL)		Volume of ME after washing (mL)		Yield (%)
m_1 (ratio 6:1)	502.67	a	496.97	a	99.394
m_2 (ratio 5.5:1)	501.17	a	495.92	a	99.184
m_3 (ratio 5:1)	501.93	a	497.00	a	99.400
w_1 (60 min)	500.89	a	495.06	a	99.012
w_2 (50 min)	501.11	a	496.26	a	99.252
w_3 (40 min)	502.33	a	496.78	a	99.356
w_4 (30 min)	503.50	a	498.22	a	99.644
w_5 (20 min)	501.78	a	496.83	a	99.366

Information: Number followed with the same letter showed no significant difference based on Duncan double distance test 5%.

equation of experimental results have b_1 value (regression coefficient) of -351.17, therefore the increase of glycerol volume will be reach the limit intercept value of 66.44.

Effects of methanol concentration and process time on transesterification

Effects on the produced glycerol. The results showed that there was no interaction between the effects of methanol concentration and process time on the volume of crude methyl ester. The variation of time did not significantly affect the reaction. On the contrary, the concentration of methanol significantly affected the obtained glycerol.

As showed in Table 2, the decrease of methanol concentration gave significant decrease on volume of glycerol. Therefore, the glycerol would be more viscous. In addition, the variation of time did not significantly affect the volume of glycerol. The process time could be reduced by integrating three kinds of stirring as these stirrings were more effective than the conventional one. This phenomenon was in line with the results of Thompson and He [6], which stated that the utilization of circulation pump and static mixture could reduce the usage of methanol and time. The positive of this research was on the application of separation of glycerol from the reaction system which could shift the equilibrium into the formation of product.

TG + MeOH ↔ Fame (Biodiesel) + Glycerol

According to Mass Action Law, the equilibrium of transesterification reaction could be shifted into the formation of biodiesel in two ways. There was (1) application of excess reactant (methanol) or (2) separation of the product (glycerol). The later was more preferred as it was more effective and simple. Glycerol would separate based on its density. This could be conducted by placing input pipeline of circulation pump 5 cm on the top of cone tank. Volume of cone on the bottom side of pipeline was 50 mL. The structure would accommodate and decantate the formed glycerol and would not let the glycerol to go back to the circulation pump.

Effect on the produced crude methyl ester. The difference of volume of crude biodiesel was not necessary to be considered since the product was mixed with the other component such as methanol, KOH, glycerol and soap. In the uncompleted transesterification would give mono or diglyceride, soap and methyl ester to produce emulsion. As consequence, volume of biodiesel will reduce as some of it was disposed on the washing process. On the failed transesterification, emulsion was also formed and difficult to separate after the washing [3-4].

Effect on volume of methyl ester after washing and drying. The results showed that the effect of methanol concentration and process time did not affect the volume

Table 5. Characterization of biodiesel

Parameter	Unit	Biodiesel quality standard SNI 04-7182-2006	Results	Petrodiesel **
Density (on 40 °C)	kg/m^3	850 – 890	858,39	870
Viscosity (on 40 °C)	mm^2/s	2.3 – 6.0	4.75	1.6-5.8
Cetane number		> 51	62 *	48
Flame point	°C	≥ 100	175	176
Acid number	mg KOH/g	< 0.8	0.09	0.6
Total glycerol	%-b	< 0.24	0.21	-
Methyl ester concentration	%-b	> 96.5	98.98	-

Information: * Puslit Kelapa Sawit [10] ; ** Ditjen Migas *dalam* UPPDN V [11]

of methyl ester after washing and drying. Therefore, there was no interaction between the two factors. It indicated that separation of glycerol could compensate the decrease on methanol. Based on Law of Action, equilibrium of transesterification could be shifted to the formation of biodiesel by separating one of the products. The separation of glycerol was conducted as it would be separated easily based on the density.

Process time could be reduced to be 20 min (m_5) by employing the reactor equipped circulation pump and static mixer as well as sprayer, which was more effective comparing to continued flow reactor. Transesterification could occur by conducting the effective stirring to overcome the mass transfer between vegetable oil and methanol.

Characterization of Biodiesel

The determination of biodiesel quality was conducted to know the qualification of the produced biodiesel to be applied as diesel fuel. The parameters tested were (1) viscosity as indication of the ease of injector component to atomize the fuel on the diesel machine; (2) density as the completeness of burning process on diesel machine; (3) acid number as indication of the presence of free fatty acid and mineral acid; (4) concentration of total glycerol to describe the amount of glycerol on biodiesel after washing and drying and (5) concentration of methyl ester to know the completeness of transesterification reaction [4].

The parameters did not describe the yield of conversion of vegetable oil into biodiesel. They describe the quality assurance of the biodiesel to be applied on diesel machine. Biodiesel with high acid number would stimulate the corrosion on the all components of machine. Parameters of viscosity, density and total glycerol which exceeded the quality standard would lead non-complete burning process and give crust on the burning chamber. The crust was abrasive and could damage the machine.

Sample used in the characterization of biodiesel was product of transesterification with the ratio of methanol 5:1 for 20 min. Properties of biodiesel were presented on Table 5. Transesterification could optimize

the properties of vegetable oil. For instance, viscosity could be reduced from 47.98 (Table 1) into 4.75 (Table 5) mm^2/sec. Properties of biodiesel met the quality standard of SNI 04-7182-2006 [12] and ASTM [13].

Analysis of Mass Balance

Transesterification by applying the glycerol separation could compensate the decrease on the usage of methanol from the molar ratio of 6:1 (m_1) into 5:1 (m_3), which lead the change on mass balance, (1) increase the yield of biodiesel from 42.73 (on m_1) into 49.34% (on m_3) and (2) reduced the disposed methanol from 42.37 (on m_1) into 32.89% (on m_3). The calculation showed that the efficiency of biodiesel production could be enhanced by separating the glycerol.

CONCLUSION

Reactor of biodiesel could intensively mediate the reaction outside the reaction tank. In the same time, separation of glycerol occurred on the reaction tank based on precipitation mechanism. The relationship between the increase of produced glycerol and transesterification time could be described using inverse regression equation of $\hat{Y} = 66.44 - 351.17 X^{-1}$. Technology of glycerol separation on the biodiesel reactor could: (i) Decrease the usage of methanol into molar ratio of 5:1 and process time of 20 min, without affecting the quality and yield of biodiesel. The properties of biodiesel met the quality standard of SNI 04-7182-2006; and (ii) Decrease of the usage of methanol from the molar ratio of 6:1 into 5:1. However, there was change on mass balance, (1) increase the yield of biodiesel from 42.73 into 49.34% and (2) reduced the disposed methanol from 42.37 into 32.89%.

REFERENCES

1. Dubé, M.A.,Tremblay, A.Y, and Liu, J., 2007, *Bioresour. Technol.*, 98, 3, 639–647.

2. Yusuf, N., Salaudeen, N., and Muhammad, F., 2011, *Aust. J. Basic Appl. Sci.*, 5, 6, 912–919.
3. Wenzel, B., Tait, M., Módenes, A., and Kroumov, A., 2006, *Bioautomation*, 5, 13–22.
4. Demirbas, A., 2008, *Energy Convers. Manage.,* 49, 125–130.
5. Alamsyah, R., Tambunan, A.H., Purwanto, Y.A., and Kusdiana, D., 2010, *Agric. Eng. Int.*, 12, 1, 99–106.
6. Thompson, J.C., and He, B.B., 2007, *Am. Soc. Agric. Biol. Eng.,* 50, 1, 161−165.
7. Math, M.C., Kumar, S.P., and Chetty, S.V., 2010, *Indian J. Sci. Technol.,* 3, 3, 318–321.

8. Yoeswono, Triyono, and Tahir, I., 2008, *Indo. J. Chem.*, 8, 2, 219–225.
9. Ahmad, M., Rashid, S., Khan, M.A., Zafar, M., Sultana, S., and Gulzar, S., 2009, *Afr. J. Biotechnol.,* 8, 3, 441–446.
10. Puslit   Kelapa   Sawit,   2007, http://pustaka.litbang.deptan.go.id/
11. UPPDN   V   Surabaya,   2001, http://www.mesran.co.id/
12. Badan   Standarisasi   Nasional,   2006, http://www.bsn.go.id/
13. Knothe, G., 2006, *J. Am. Oil Chem. S*oc., 83, 10, 823–833.