PROCEEDINGS

2015 3rd International Conference on Adaptive and Intelligent Agroindustry (ICAIA)

ICAIA 2015

August 3rd - 4th, 2015
IPB International Convention Center
Bogor, Indonesia

ISBN : 978-1-4673-7405-7
IEEE Catalog Number : CFP15C67-ART

IEEE INDONESIA SECTION

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Frontier Approaches in Process and Bioprocess Engineering

 ISBN : 978-1-4673-7405-7

The Effects of Molar Ratio of Glycerol 80% and Palm Oleic Acid on the Synthesis Process of Ester Glycerol

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***Abstract*—Glycerol ester was synthesized by esterification of glycerol and palm oleic acid using methyl ester sulfonic acid (MESA) as catalyst. The purpose of this study was to obtain the best molar ratio in the esterification of 80% glycerol with palm oleic acid using 0.5% MESA catalyst. Glycerol 80% was esterified by using a nitrogen stream at 180°C and a stirring speed of 400 rpm for 90 minutes. Results showed that the best molar ratio was 0.8:1 (glycerol: oleic acid) which produced glycerol ester with the yield of 75.33%, density of 0938 g/cm^3, acid number of 39 ml KOH/g sample, viscosity value of 92 cP (30°C), kinematic viscosity of 53 cSt (40°C), flash point at 204°C, pour point at 0°C, and boiling point at 105°C.**

I. Introduction

GLYCEROL ester can be synthesized through an esterification process by reacting glycerol with carboxylic acid and catalyst. This process produces water as a by-product. Esterification is a reversible process so that one of the reactants needs to be priorly fed in order to push the reaction to the right side or to product formation. A catalyst is used to avoid the need of high temperature, longer reaction time, and the formation of dark-colored product [18].

Manuscript received April 29, 2015. This work was supported in part of facilities from Surfactant and Bioenergy Research Center-Bogor Agricultural University (SBRC IPB) and finance from Lembaga Pengelola Dana Pendidikan (LPDP) were acknowledged. The Effects of Molar Ratio of Glycerol 80% and Palm Oleic Acid on the Synthesis Process of Ester Glycerol.

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Handayani *et al.* [5] stated that reactant-catalyst ratio was one of the factors affecting reaction effectiveness. In the esterification of glycerol with oleic acid, the molar ratio of glycerol to oleic acid reactant is an important factor to observe. In this study, the esterification was done with glycerol 80%: oleic acid reactant ratios of 0.8:1; 1.7:1; and 2.6:1. Methyl ester sulfonic acid 0.5% was used as a catalyst.

II. Procedure

A. Purification of Glycerol as a By-product of Biodiesel Production

Glycerol purification was done by using a purification reactor of 25 L scale. The purification device is shown in Figure 1.

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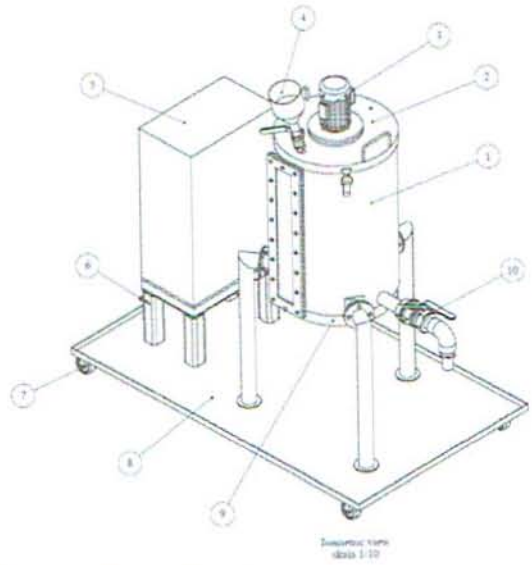

Component of purification rector

1. Purification tank
2. Cap tank
3. Electric motor
4. Entry funnel
5. Control panel
6. Framework of panel
7. Wheel
8. Unit holder
9. Cooker unit
10. Output

Figure 1. Design of purification reactor of 25 L scale

Glycerol purification process was done under a condition process used by [15] with some modifications. First, crude glycerol, a by-product of biodiesel industry, was placed in a purification tank and heated until the temperature reached 50°C. Then, 85% technical grade phosphoric acid was added in by 5% (v/v), the temperature was raised to 80°C. The mixture was heated and stirred for 4 hours before it was left for 30 minutes until three layers were formed. From top to bottom, the three layers consisted of free fatty acid, glycerol (product of purification), and salt. Glycerol and salt were taken out from the purification tank before they were separated by using a filtration device.

B. *Esterification of Purified Glycerol*

In this synthesis of glycerol done through esterification, glycerol resulted from the purification was reacted with oleic acid in molar ratios (glycerol:oleic acid) of 0.8:1, 1.7:1, and 2.6:1 with an addition of MESA catalyst (w/w) by 0.3%. The esterification was conducted in triple neck flasks put on hot plates at 180°C for 90 minutes. During the esterification process, nitrogen was flown into the flasks at the rate of 100 mL/minutes to avoid the existence of oxygen and push the formed water vapor out to the condenser.

C. *Analyses of Glycerol, MESA Catalyst, and Glycerol Ester*

Analysis of glycerol, MESA catalyst, and glycerol ester were done to measure glycerol content, density (DMA 4500M Anton Paar), viscosity (Brookfield DV-III ultra), pH, acid number, kinematic viscosity (ASTM D 445), boiling point (ASTM D 86), flash point (ASTM D 92), and pour point (ASTM D 97).

D. *Data Analysis*

A factorial completely randomized design with two replicates was used. The factor was MESA catalyst concentration (A). The experimental design model was:

$$Y_{ij} = \mu + A_i + \varepsilon_{ij} \quad (1)$$

where:

Y_{ijk} = Observation value as affected by factor A at i-level

μ = Mean value

A_i = Effect of molar ratio at j-level (j=0.8:1; 1.7:1; 2.6:1)

ε_{ij} = Error of experimental unit at i-level of factor A and j-level of replicate (j=1,2)

Data were subjected to analysis of variance by using SPSS 16.0 program and a Duncan test at α = 5%. The test was done to measure inter-level differences in a factor.

III. Result and Discussion

A. *Physicochemical Properties of Purified Glycerol*

Crude glycerol was purified by the addition of 85% phosphoric acid by 5% (v/v). The acid reacted with the remains of potassium hydrochloride catalyst to form a potassium phosphate salt and at the same time separate free fatty acids. The remaining methanol, which did not react, evaporated when glycerol was heated at 65°C. The result was 80% pure glycerol having different physicochemical properties from those of crude glycerol. These differences are shown in Table 1. Purification process increased glycerol level, lowered viscosity and density levels, and brightened the color.

TABLE I
PHYSICOCHEMICAL PROPERTIES OF CRUDE AND PURIFIED GLYCEROL

Parameter	Unit	Crude glycerol	Purified glycerol	Pure glycerol*
Level of glycerol	%	45 ± 2.05	84 ± 2.00	100%
Viscosity at 30°C	cP	625 ± 1.07	189 ± 0.70	1499
Density at 25°C	g/cm^3	1.0745 ± 0.0001	1.2576 ± 00001	1.261
Color		Blackish brown	Brownish yellow	No color
Boiling point	°C	80 ± 3.25	82 ± 2.05	290

* [7], [13]

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B. *Physicochemical Properties of MESA Catalyst*

MESA (*methyl ester sulfonic acid*) is an intermediate compound resulted from the sulphonation reaction of methyl ester. It is dark colored and acidic. The properties of MESA in this study are shown in Table 2. Based on its pH value, MESA is strongly acidic. This specific property of MESA has been the basis of its use as catalyst in esterification. As in other acidic catalysts, the acidity of MESA is suspected to result in the protonation of oleic acid which is the initiation of ester formation process.

TABLE 2.
PHYSICOCHEMICAL PROPERTIES OF MESA CATALYST

Parameter	Unit	Value
pH (1% in distilled water)		2.2 ± 0.20
Density at 25°C	g/cm^3	0.9173 ± 0.0001
Color		Black

C. *Physicochemical Properties of Glycerol Ester*

Esterification is the formation of ester by reacting fatty acid with alcohol. Glycerol ester is an ester whose alcohol molecule is glycerol. As the esterification result, two layers are formed. The top layer is glycerol ester and the bottom layer is the remaining glycerol which does not react. In this study, the resulted glycerol ester was a mixture of monooleic, dioleic, and trioleic glycerols and the remaining fatty acids which did not react.

According to [16], in order to get optimum product, the reaction balance of esterification should be pushed to the right position or product formation by supplying energy to the reaction, overfeeding the reactants, and continuous removal of product during the process. Esterification process is a reversible reaction so that it is necessary to maintain the direction of the process to the production side. In this study, this was done by overfeeding glycerol reactant to the reaction. The formation of two layers in the esterification product was caused by the finding that in the end of the reaction there was some glycerol which did not get reacted. During the esterification process, nitrogen gas was continuously flown into the flask to push the water vapor out of the flask. As water vapor was a by-product of esterification, the removal of it would lead to an optimal glycerol ester production. If it was not removed out from the reactor, the formed water vapor might hydrolyze glycerol ester back to glycerol and oleic acid. The yield and the physicochemical properties including acid number, density, viscosity, kinematic viscosity, flash point, pour point, and boiling point of glycerol ester produced were measured.

1) Yield

In this study, yield was the amount of glycerol reacted with oleic acid to result in glycerol ester. It is shown in Figure 2 that wider molar ratios resulted in fewer yields. This indicated that overfeeding of glycerol, under the esterification condition used in this study, did not result in higher glycerol ester yield. This might be caused by the fact that the purity level of glycerol was only 84% so that when it was overfed to the esterification process, more filth was found in the esterification material. These filths inhibited the formation process of glycerol ester.

Esterification done with higher amount of oleic acid (molar ratio of 0.8:1) resulted in high yield. This indicated that higher amount of oleic acid fed in the esterification process increased the possibility of the formation of ester bonds between glycerol and oleic acid.

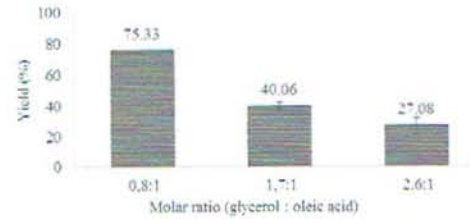

Figure 2. Effects of molar ratio on glycerol ester yield

It was also shown that molar ratio factor did not give significant effect ($P>0.05$) on yield. It was suggested therefore that a molar ratio of 0.8:1 be used to get high yield of glycerol ester.

2) pH

The glycerol ester sample taken from the esterification was a mixture of monooleic, dioleic, trioleic glycerols, remaining oleic acid which did not react, and MESA catalyst. pH measurement was done by dissolving glycerol ester in 30% distilled water. It was found that glycerol ester sample did not dissolve in the water but MESA catalyst did. pH measurement was taken to assess the amount of MESA catalyst found in the esterification product. Higher pH level indicated higher amount of MESA catalyst found in glycerol ester. Results of pH measurement are depicted in Figure 3.

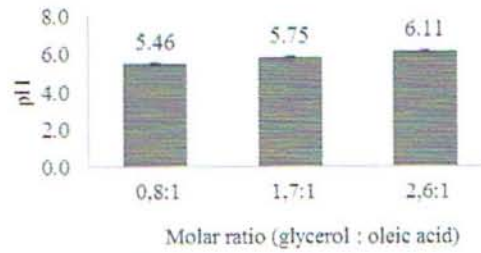

Figure 3. Effects of molar ratio on pH

It is shown in Figure 3 that a wider molar ratio or higher amount of glycerol fed into esterification led to lower pH levels. This was caused by the finding that the pH level of glycerol ester formed was in line with

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the pH level of glycerol. In this study, purified glycerol had a pH level of 6.24.

3) Density

Density or specific gravity is a weight of a liquid per unit volume. Density measurement was taken to assess the inter-molecule denseness in glycerol ester yielded. It is shown in Figure 4 that glycerol ester with high density was yielded in wider molar ratios. According to [9], the density level of ester of carboxylic fatty acid was affected by molecular weight and temperature. Higher molecular weight meant higher density level.

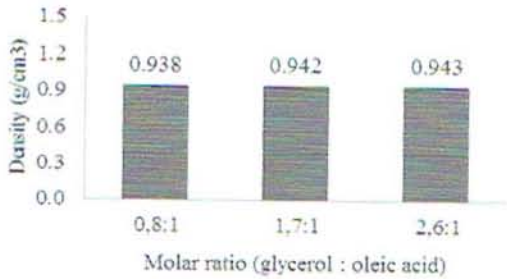

Figure 4. Effects of molar ratio on density level of glycerol ester

It was found that molar ratio factor did not give significant effect on density levels. This might be caused by the fact that each sample of esterification product contained similar main components, namely monooleic, dioleic, and trioleic glycerols. Therefore, the density level of each sample was not too different.

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4) Acid Number

Acid number is used to assess the amount of fatty acids per gram of sample. Higher acidic number indicates higher amount of fatty acid content. Acid number shows how much (ml) KOH is needed to neutralize 1 gram of fat/oil. It is shown in Figure 5 that, in general, an increase in molar ratio led to an increase in acid number. This meant that wider molar ratio was not followed by higher yield conversion to glycerol ester leaving more fatty acid which did not react in the esterification process. As oleic acid has an acid number of 200 mg KOH/g sample, high amount of oleic acid remains which did not react in the process would lead to the production of glycerol ester with high acid number.

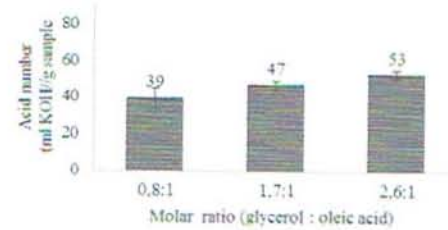

Figure 5. Effects of molar ratio on acid number of glycerol ester

It was found that molar ratio factor gave significant effects on acid number of glycerol ester.

5) Viscosity

Viscosity is a physicochemical property showing the level of thickness of a fluid. An increase in viscosity is a result of increased molecule concentration [10]. Increased viscosity of a material may also caused by increased chain length and molecular weight. Viscosity affects the flowing characteristic of a fluid; higher viscosity means lower capacity of the fluid to flow. As can be seen in Figure 6, higher amount of glycerol fed into the process led to wider molar ratio and higher viscosity level. This was attributed to the fact that the viscosity of glycerol ester yielded was always in line with the viscosity of glycerol used. In addition, as discussed above, wider molar ratio did not yield in higher amount of glycerol ester leaving more oleic acid which did not involve in the reaction. This, in turn, led to a higher viscosity level of glycerol ester.

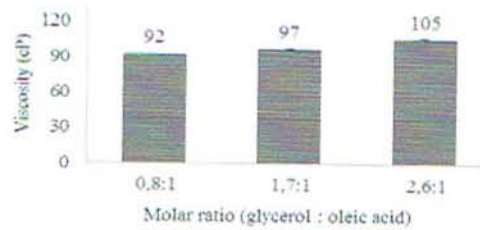

Figure 6. Effects of molar ratio on viscosity levels of glycerol ester.

It was revealed that, in general, glycerol ester yielded from the molar ratio of 0.8:1 the lowest viscosity level. This indicated that most glycerol ester was produced in the esterification process done with a molar ratio of 0.8:1. This was supported by the finding that molar ratio factor gave significant effect on the viscosity levels of glycerol ester.

6) Kinematic Viscosity

Kinematic viscosity is the measure of the resistance of glycerol ester to flow. Higher kinematic viscosity level means that it is more difficult for the substance to flow. According to [11], the value of kinematic viscosity is affected by the length of carbon chain and the position and number of double bonds of fatty acid or alcohol used in an ester synthesis. Longer carbon chain means higher kinematic viscosity level while

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number of double bonds has a negative relation with kinematic viscosity level. Kinematic viscosity is a function of dynamic viscosity and density; increased kinematic viscosity is resulted from higher dynamic viscosity and lower density level [8]. In this study, it was revealed that wider molar ratios gave higher kinematic viscosity level which was in line with viscosity level (Figure 7).

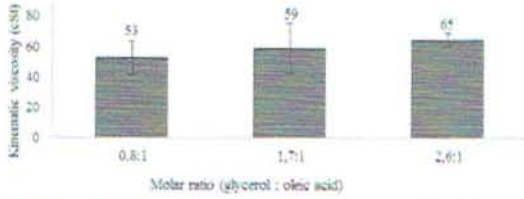

Figure 7. Effects of molar ratio on kinematic viscosity of glycerol ester

Molar ratio was found to give no significant effects on kinematic viscosity levels of yielded glycerol ester. As discussed above, esterification of glycerol and oleic acid resulted in glycerol ester in the forms of monoolein, diolein, or triolein. One of them was found to be dominant and affect their general physicochemical properties. This non-significant difference suggested that all samples share common main components in relatively similar concentration.

7) Flash Point

Flash point is the lowest temperature at which a substance starts to ignite and burn itself [1]. It is a parameter affected by the content of volatile fractions (alcohol residue). According to [12], higher content of volatile fractions in an ester makes it need only low temperature to ignite. A material with low flash point is easier to get burnt and therefore needs special handling and storing. In esterification, as an alcohol, glycerol releases its hydroxyl groups and binds oleic acid to form ester. This makes the flash point of glycerol ester higher. Purified glycerol and oleic acid have flash points of 120°C and 204°C, respectively. Relatively similar component compositions found in samples make their flash points relatively the same.

8) Pour Point

According to [4], pour point is the lowest temperature at which a sample is still able to flow. Lower pour point of a material indicates that the material is able to flow at low temperatures. According to [14], the chain length and unsaturation of a molecule affect its pour point. Longer chain length increases pour point while double bonds indicating unsaturation lowers it. In this study, the pour points of all glycerol ester samples were found to be the same, namely 0°C. This showed that at temperatures below 0°C, there would be white crystals formed in the glycerol ester and it would no longer be able to flow. A fluid with low pour point is better to be used in areas with low temperature.

9) Boiling Point

Boiling point is a physicochemical property showing a temperature at which a material starts to boil. Boiling point shows intermolecular force in a fluid; stronger force means higher boiling point. According to [6], boiling point is affected by molecular weight and the existence of hydrogen bonds. In this study, as shown in Figure 8, boiling points of glycerol ester were slightly fluctuating. The highest boiling point was shown by glycerol ester yielded from the molar ratio of 1.7:1.

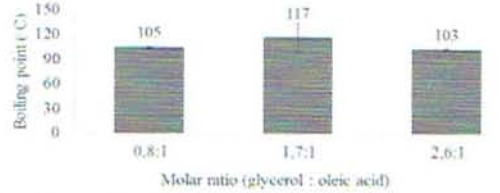

Figure 8. Effects of molar ratio on boiling point of glycerol ester

It was shown that molar ratio gave significant effects (α = 5%) on the boiling points of glycerol ester yielded. The boiling points in molar ratios of 0.8:1 and 2.6:1 were not different but they were significantly different from the boiling point of glycerol ester in molar ratio of 1.7:1. This was an indication that glycerol ester yielded in the molar ratio of 1.7:1 had the highest concentration.

After the properties of glycerol ester were analyzed, the best esterification condition was determined based on the parameters of the analysis done. First, based on the yield, the highest yield of glycerol ester was obtained from molar ratio of 0.8:1. Density level was not included in the consideration as no significant effect of molar ratio was found on it. In addition, the difference in the density levels of glycerol ester yielded in different molar ratios was negligible. The lowest acid number was found in glycerol ester yielded in molar ratio of 0.8:1. Further, glycerol ester in this molar ratio also had the smallest viscosity and kinematic levels. Low viscosity and kinematic viscosity levels indicated most preferred glycerol ester as it would be the easiest one to flow. The next parameter was flash point and the preferred glycerol ester was the one with highest flash point. A substance with high flash point is not easy to get burned making it easier to handle. As no significant difference was found flash points, glycerol ester yielded in molar ratio of 0.8:1 was then selected as the best. Similar consideration was given to pour points which were not significantly different making glycerol ester yielded in molar ratio of 0.8:1 as the best. Finally, based on the boiling point, the best glycerol ester was the one yielded in molar ratio of 1.7:1 as it had the highest boiling point. Overall, it was decided that the best

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esterification condition was the one done in molar ratio of 0.8:1.

IV. Conclusion

The best esterification process was obtained in molar ratio of 0.8:1. Glycerol ester produced in this condition had a yield of 75.33%, density level of 0.938 g/cm^3, acid number of 39 ml KOH/g sample, viscosity of 92 cP (30°C), kinematic viscosity of 53 cSt (40°C), flash point of 204°C, pour point of 0°C, and boiling point of 105°C.

Recomendation

It was suggested that esterification of glycerol 80% with palm oleic acid be done in molar ratios wider than 0.8:1.

Acknowledgment

Supports of facilities from Surfactant and Bioenergy Research Center (SBRC IPB) and finance from *Lembaga Pengelola Dana Pendidikan* (*LPDP*) were acknowledged.

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