

Esterification Reaction of Glycerol and Palm Oil Oleic Acid Using Methyl Ester Sulfonate Acid Catalyst as Drilling Fluid Formulation

V I Sari¹⁾, E Hambali^{2,3)}, A Suryani,^{2,3)} and P Permadi⁴⁾

¹⁾ Program Study of Agriculture Industrial Technology, Postgraduate School, IPB Darmaga St, Campus IPB, Bogor 16680

²⁾ Surfactant and Bioenergy Research Center, LPPM, IPB Pajajaran St, Campus IPB Baranangsiang, Bogor 16153

³⁾ Department of Agroindustrial Technology, Faculty of Agricultural Technology, Bogor Agricultural University

⁴⁾ Program Study of Petroleum Engineering, ITB

E-mail: vondi.2297@gmail.com

Abstract. Esterification reaction between glycerol with palm oil oleic acid to produce glycerol ester and one of the utilization of glycerol esters is as ingredients of drilling fluids formula for oil drilling needs. The purpose of this research is to get the best conditions of the esterification process. The esterification reaction does with the reactants is glycerol with purity of 97.6%, palm oil oleic acid with the molar ratio is 1:1, Methyl Ester Sulfonate Acid (MESA) catalyst 0.5%, and stirring speed 400 rpm. The temperature range of 180°C to 240°C and the processing time between 120 to 180 minutes. The results showed that the best conditions of the esterification reaction at the temperature 240°C and time process are 180 minute. The increasing temperature resulted that the acid number decreases and causing the conversion increased. The maximum conversion is 99.24%, density 0.93 g/cm³, flash point 241°C, pour point -3°C, the boiling point of 244 °C, the acid value of 1.90 mg KOH/g sample, kinematic viscosity 31.51 cSt (40°C), surface tension 37.0526 dyne/cm and GCMS identification, glycerol ester at 22,256 retention time (minutes) and wide area 73.75 (%). From the research results obtained glycerol ester with characteristics suitable for drilling fluid formulations.

1. Introduction

Esterification process of oleic acid with glycerol will produce glycerol ester. In the process, there is the substitution of one (or more) hydrogen atoms on the hydroxyl group with an organic group. Esterification reaction is a reversible endothermic reaction, thus perfect conversion cannot be achieved [1]. If one of the reactants is made excessive, then the equilibrium will shift to the right (ester formation) and molecules collisions will greater and in turn conversion into products greater. Factors that affect the esterification reaction include reaction time, molar ratio, temperature and catalyst. Glycerol ester can be produced from glycerol derived as by-products of biodiesel manufacturing process as much as 12.5% of its production capacity with low purity level because contain components of water and other impurities.

Research of production glycerol ester from glycerol using an acid catalyst has done to obtain a high yield [2], [3], [4], [7]. The molar ratio between glycerol and oleic acid, catalyst concentration, purity of glycerol raw material. Temperature and time process affects the characteristics of glycerol



ester [4], [5], [6], [8], [9]. In soybean producing countries, glycerol from biodiesel industry byproduct is being developed as drilling fluid formulation material for oil well drilling needs. The nature of lubricating and the emulsion of derivate glycerol is used to improve the quality of oil drilling mud by making it as the formulation of oil-based mud (OBM) and water based mud [10], [11], [12]. This research was conducted to obtain the best process of esterification reaction between glycerol with a purity of 97.6% and palm oleic fatty acid on different temperature and processing time.

2. Methods

Esterification reaction is initiated by reaction between glycerol with palm oleic acid using methyl ester oil sulfonic acid as catalysts on three neck flask equipped with a condensor and a magnetic stirrer at temperature 180°C, 210°C and 240°C and reaction time of 120, 150 and 180 minutes [3], [5], [6], [7]. The ratio of glycerol with palm oleic acid is fixed variable, 1:1 [5], with MESA catalyst concentration 0.5% w/w [5]. MESA is the catalyst that is highly acidic with pH 2.2 which derived from palm oil derivatives. The flow rate of nitrogen gas is 100 cc/minute and stirring speed at 400 rpm [5]. Characteristics of glycerol ester as reaction products are known by analyzing the acid number, density with a density meter DMA 4500M Anton Paar, viscosity kinematic (ASTM D 445), the boiling point (ASTM D 86), flash point (ASTM D 92), pour point (ASTM D 97), and chemical composition of glycerol ester with Gas Chromatography Mass Spectrometry. The characteristics are compared with standard base oil that used as drilling fluid formulation.

3. Results and Discussion

3.1 Effect of acid numbers on reaction

Acid number analysis was conducted to determine the residual acid contained in the reaction mixture in produced glycerol ester. Such fatty acids residue was correlated with the content of glycerol esters formed during the reaction. Effect of temperature increases and reaction time process on the acid number can be seen in Figure 1. In general, there is a decline in acid number in certain range of time and temperature. The longer the esterification process is the lower acid number. This is because of the longer reaction time of esterification process, the higher fatty acids converted into glycerol ester. In other hands, longer reaction causing more frequent collisions among reactant molecules and in turn the conversion into products increases. Likewise with different temperature treatment. The higher the temperature is the decline in acid number. The lowest acid numbers found at reaction time 180 minutes and temperature at 240°C, namely 1.90 mg KOH/g sample. A decrease in acid number indicates the conversion of fatty acids into the ester. For comparison, oleic acid had acid number 194-204 mg KOH/g sample. After esterification, the acid number of product mix is 1.90 to 1.96 mg KOH/g sample at temperature treatment 240°C. This is in accordance with the yield of the reaction.

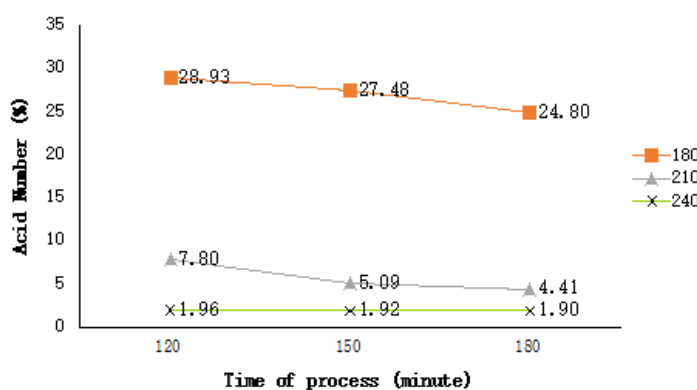


Figure 1. Acid Numbers glycerol ester by temperature and time of esterification process

The yield of the reaction product is the amount of yield in a chemical reaction or a percentage of yield compared to the raw materials processed. In the esterification process, the yield does not reach 100% because the reaction is reversible and in turn perfect conversion cannot be achieved. Water vapor is one factor that reduces the yield of glycerol ester product if not separated from the reactor because it can hydrolyze glycerol esters into glycerol and carboxylic acids. Based on calculations, the highest yield obtained at reaction time 180 minutes and temperature 240°C with nearly maximum yield 99.24%. The high reaction yield showed that the conversion of fatty acids into ester is high. The higher the purity of glycerol, the more ester bonds are formed so that less fatty acids are formed which shows the declining acid numbers and increased reaction yield.

3.2 Kinematic viscosity of glycerol ester

Kinematic viscosity is a number that indicates the amount of resistance in a liquid material to flow or size of shearing resistance of a liquid material. Viscosity test was conducted to determine the resistance of glycerol ester to flow. Figure 2 shows the effect of temperature and reaction time on the kinematic viscosity. The finding show treatment of temperature increase and reaction time produce viscosity values ranging from 31.5 to 75.6 cSt. The higher the temperature and the longer processing time produce the lower viscosity value. The viscosity values found in this research was lower than the viscosity values generated from previous studies ranged between 81-105 cSt [17].

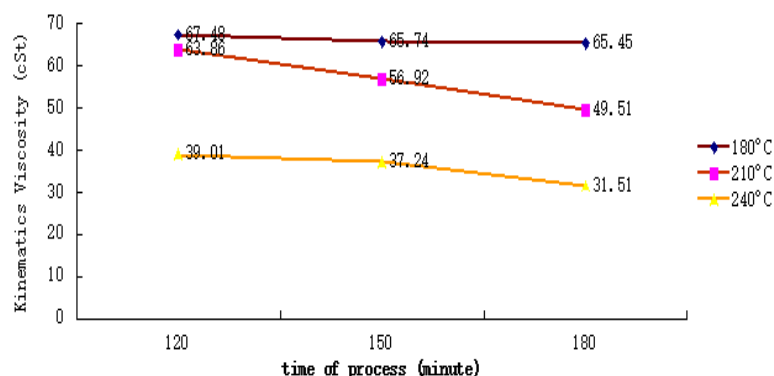


Figure 2. Kinematic Viscosity glycerol ester by temperature and esterification process

The high value of the kinematic viscosity is influenced by carbon chain of oleic fatty acid used in the esterification reaction. Kinematic viscosity values are influenced by the length of the carbon chain, the position and number of double bonds of the fatty acids or alcohols is used in synthesizing ester [13]. The longer the carbon chain is the higher kinematic viscosity value, while the presence of double bonds will reduce the kinematic viscosity value. Kinematic viscosity is also influenced by intermediate compounds such as monoglycerides and diglycerides which having sufficiently high of polarity and molecular weight [14], [17]. The kinematic viscosity of glycerol esters is higher than base oil drilling fluid in marketplace that is 4.5 cSt. High kinematic viscosity indicates the resistance of materials to the changes in temperature. It shows that the resulting glycerol ester has a fairly high resistance on temperature changes, so that when applied to processes that require high temperatures such as drilling fluid OBM, the physical properties of glycerol ester would unchanged.

3.3 Flash point of glycerol ester

Flash point is the temperature at which a number of vapors raised and when mixed with air will form a combustible mixture when given activation energy. Flashpoint indicates the volatility and shows the lowest temperature at which there will be enough flammable vapors to ignite when an *ignition* source is applied. The lower the flashpoint of a material, it will be easier to burn therefore need a specific

handling in storage. Results of testing flash point at different temperature and time can be seen in Figure 4.

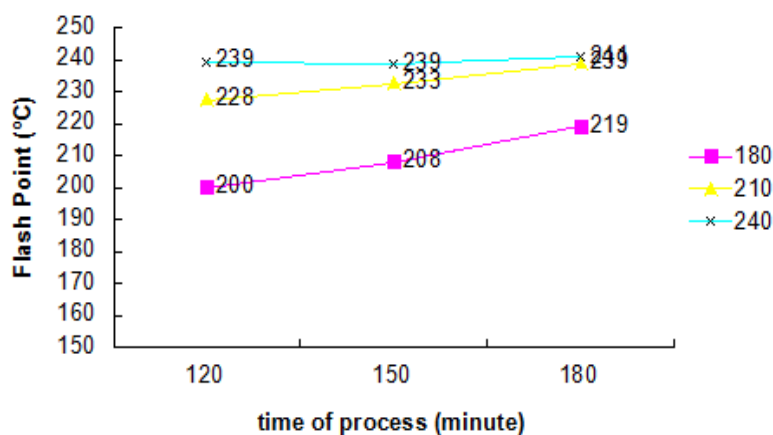


Figure 3. Flash point glycerol ester by temperature and time of esterification process

Generally, glycerol ester produced in this research has high flash point value namely 202°C - 240°C. Figure 4 show that the higher the temperature and the longer the process, the resulting flash point is higher. The higher flashpoint after esterification indicates that there has been a decrease in light fractions content of glycerol ester. In the esterification process, more flammable glycerol components will release a proton from the hydroxyl group to produce activated complex compounds. The release of water and protonated then generate higher flash point of the ester. Flashpoint is influenced by the content of light fractions (residual alcohol) [19], [20], [21]. The lower content of light fraction is the higher the temperature required for ester can be lit. The higher the flash point of a material is the better and the easier for fire handling. The lowest flash point was found from glycerol ester by treatment at 150°C and 120 minutes while the highest was at temperature treatment of 240°C and processing time for 180 minutes. However, the overall flash point finding in this research is still meeting the specification as standardized for oil based mud, namely minimum 85°C for saraline.

3.4 Boiling point of glycerol ester

The boiling point is physicochemical properties that show temperature of glycerol ester starts to boil. Boiling point shows the force of molecules attractions in a fluid, where in the higher attraction force will increase the value of the boiling point. The boiling point is influenced by molecular weight and hydrogen bonding [31], [32]. Figure 4 shows the boiling point of glycerol esters in different time and temperature.

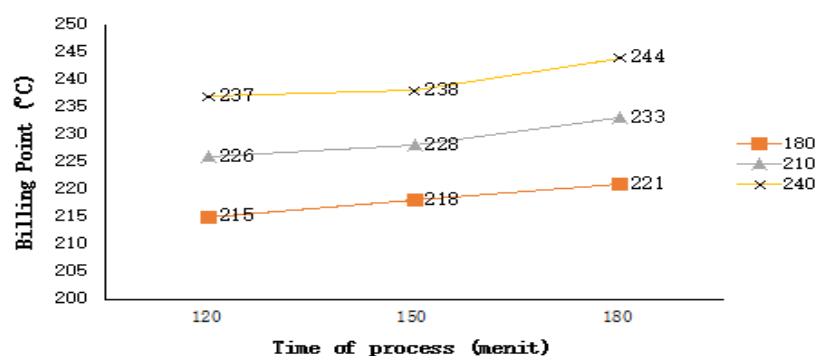


Figure 4. Bolling point of glycerol ester by temperature and time of esterification process

From Figure 4 shows that time and temperature of esterification process affect the boiling point of glycerol ester. The higher of the temperature is the higher value of the boiling point. The higher temperature and the longer reaction time, the boiling point is higher. The highest boiling point found at the temperature 240°C and process time 180 minutes, namely 244°C. In the manufacture of base fluid for drilling fluid, boiling point parameter was important to be observed to prevent the use of base fluid at temperature conditions above the boiling point of the base fluid itself. Particularly, for oil-based base fluid, the high boiling point of glycerol ether is important for use in deep drilling for with oil well temperature and pressure more than 300°C [27]. Commercial base fluid like Saraline begins to boil at 200°C. Other commercial base fluid requires the minimum boiling point at 200°C. Thus, for boiling point parameters, glycerol ester produced is in compliance with the specifications of base fluid used as drilling fluid in oil drilling.

3.5 Pour point of glycerol ester

Pour point indicates the lowest temperature in which a material is still able to flow. The lower pour point of a material, such materials are capable of low increasingly low temperatures. Pour point indicates that at the lowest temperature, oil can still flow and when the oil is at its lowest temperature, the oil will be frozen and cannot flow. The analysis results of glycerol ester pour point with different temperature and time is shown in Figure 5.

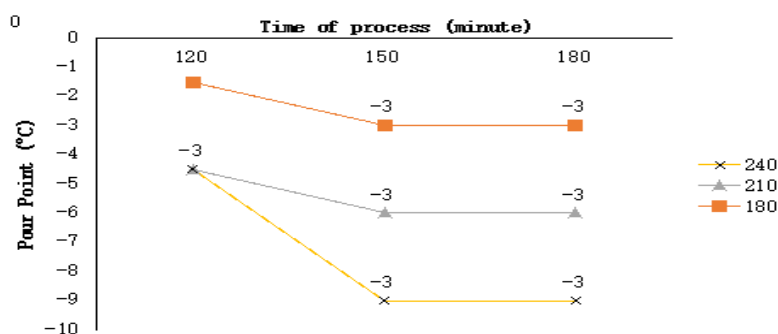


Figure 5. Pour point of glycerol ester by temperature and time of esterification process

Figure 5 shows that pour point of glycerol ester with different temperature and process time is fluctuated, ranging from 0°C, -1.5°C to -3°C. The best average of pour point is process time of 150°C and 180°C namely -3°C. The commercial base fluid has pour point of -20°C and the maximum of 18°C. Thus, for the pour point parameters, glycerol ester produced in compliance with the specifications of drilling fluid in oil drilling. Especially for oil-based mud (OBM), the lower pour point of glycerol esters is important for use in drilling, particularly offshore drilling. By knowing the pour point of a base oil that is used for oil drilling, it can be calculated at which temperature the oil can still be pumped or not or to calculate how much water vapor (steam) required as heater to keep the oil still can be pumped out from the well-bore

3.6 Interfacial tension

Interfacial tension is the force that holds the surface of a particular phase together. Interfacial tension is always smaller than the surface tension because the adhesion force between two liquids that do not mix each other is greater than the adhesion between the liquid and the air. The surface tension of a liquid is the energy required to increase the surface area of liquid by unit area [19]. Surface tension between water and glycerol esters was tested under ambient pressure at 30°C. The surface tension of a liquid is depends on several factors such as the type of fluid, temperature, pressure, and density. If the

liquid molecules are large, such as water, the surface tension is usually high. Likewise, the density, the higher the density of the liquid, the higher the energy required to break the wall surface of the liquid due to the increased attractiveness among molecules. Interfacial tension between water and glycerol esters was tested using tensiometer. Droplet radius of Glycerol ester is 1.475 mm, and the value of interfacial tension is 37.0526 dyne/cm. The test of interfacial tension shows that glycerol esters are not water soluble.

3.7 Chemical composition analysis of glycerol ester by GCMS method

GC-MS testing methods were performed to determine the composition of fatty acid constituent of glycerol ester derived from esterification reaction. Detection of fatty acids types and triglycerides is using gas chromatography (GC), followed by mass spectrometry (MS) analysis. GC method was performed for separation, quantification, and analysis of fatty acids by first made its fatty acid derivatives, as well as MS analysis to determine the fragmentation of saturated and unsaturated fatty acids, and the location of double bonds of fatty acids. Analysis by GCMS method was performed on glycerol ester derived from the greatest conversion of esterification reaction. According to the analysis results, it appears that the number and types of esters from the perfect separation of esterification produce peaks with different retention times (Figure 6). Short chain esters are polar than the long chain. Laws of like dissolve like ester stated that the type of esters with longer chain will be retained in the column, while the short-chain ester will pass along eluted out of the column. Short chain polar will appear earlier than a nonpolar long chain. Fatty acid having a single carboxylic groups and nonpolar hydrocarbon chains, causing the fat does not dissolve in water [1], [31], [33].

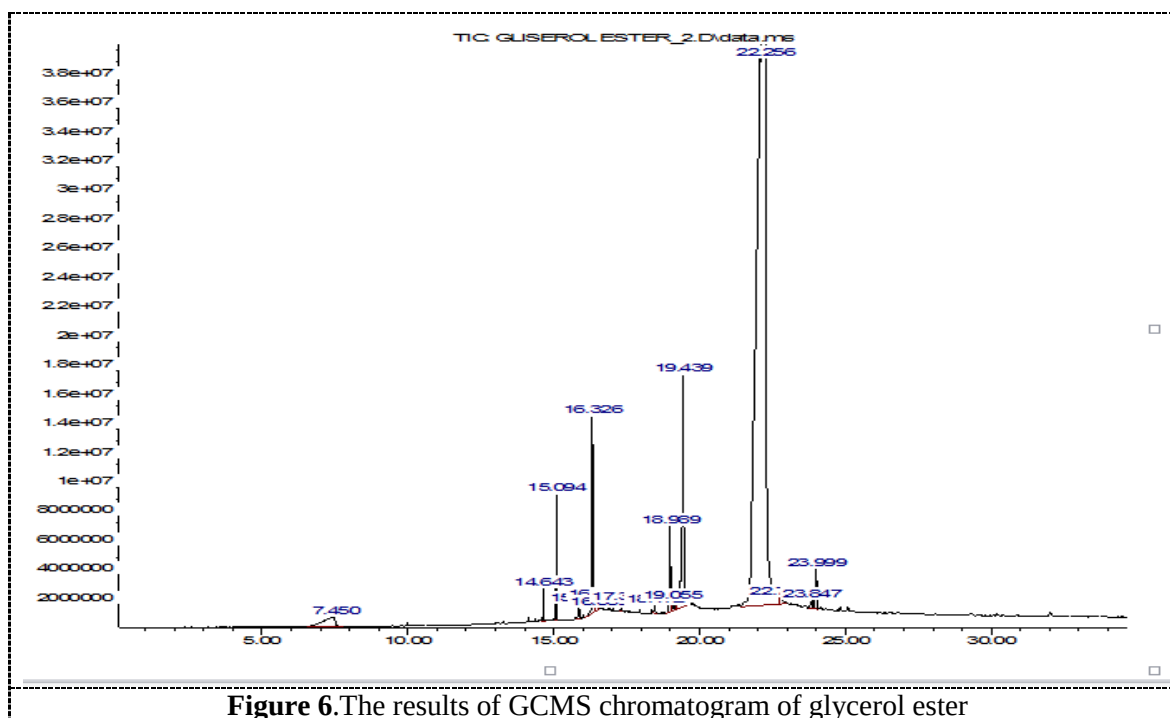


Figure 6. The results of GCMS chromatogram of glycerol ester

Chromatogram analysis shows that glycerol ester consists of ester compounds with 3 highest peaks. First, linoleic acid as the first highest peak that is an unsaturated fatty acid with two double bonds had a retention time of 16.32 minutes and the area 14.32%. Second, palmitic acid, that is long-chain saturated fatty acid with a retention time of 19.42 minutes and area 6.08%. The last highest peak is glycerol monooleate with a retention time of 22.256 (minutes) and area 73.75 (%).

4. Conclusion

Esterification reaction between glycerol as the byproduct of biodiesel industry with palm oleic acid produce higher value-added glycerol ester. One potential use of glycerol esters is as one component in the formulation of drilling fluids for oil drilling needs. To be used in petroleum drilling industry, the glycerol must have characteristics in accordance with the base fluid derived from petroleum derivatives. Raw materials used in the esterification reaction are glycerol with a purity of 97.68%, which is reacted with palm oleic acid and methyl ester sulfonic acid (MESA) as the catalyst from palm oil derivatives. The results showed that the success of the esterification reaction is influenced by the increasing temperature and processing time. The best characteristic of glycerol ester is obtained from the reaction at a temperature of 240°C and processing time of 180 minutes, with the largest rate of decline in acid number and generates maximum conversion of 99.24%, density of 0.93 g/cm³, flash point 241°C, pour point -3°C, boiling point 244°C, acid value 1.90 mg KOH/g sample, kinematic viscosity 31.51 cSt (40°C), and surface tension 37.0526. Glycerol esters are used as the base oil in the drilling fluid is a product that is more environmentally friendly and renewable because it comes from palm oil derivatives.

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