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A Comparative Evaluation of Solid-State Catalysts for Synthesis of Non-Ionic Surfactant Based Oleic Acid for Enhanced Oil Recovery (EOR)

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Abstract. The Enhanced Oil Recovery (EOR) process with chemical techniques carried out by injecting chemicals such as surfactants, can be an alternative to increase oil production, especially in old oil wells. This study investigated the best formulation of non-ionic surfactants based on the mole ratio of oleic acid and PEG-400 as well as catalyst types such as KOH and p-TSA 1%, which are used in surfactant synthesis to be able to increase oil production. The tests carried out are the value of acid, saponification, ester, and iodine, FTIR, NMR as well as a test of compatibility, phase behavior, and IFT. The results showed that the best formulation of ester polyethylene glycol oleate with reaction temperature conditions of 130°C was at a mole ratio of 1: 4 using a 1% p-TSA catalyst with a value of acid is 3,61 mg KOH/g, saponification is 144,12 mg KOH/g, ester is 140,51 mg KOH/g and iodine is 76,70 g I2/100 g. The compatibility tests and phase behavior show that this surfactant can be developed in chemical EOR with an IFT value of 2,6 x 10^{-1} mN/m.

Keywords: Enhanced oil recovery, oleic acid, solid-state catalysts, synthesis

INTRODUCTION

In recent years, global energy consumption has increased exponentially due to population growth, economic growth, and technological development (Gallego et al., 2021). As a result, oil reserves, particularly in Indonesia, have tended to decline, and currently, the rate of new oil discoveries has begun to decline. While petroleum will continue to be needed in the future, both as a source of energy and as a raw material for various important products, long-term efforts should therefore focus on increasing the recovery from exploited fields (Saxena, 2019 ; Al Wahaibi, 2019). To overcome these problems, especially to increase the production from old oil wells, oil recovery can be implemented

Enhanced Oil Recovery (EOR) includes a variety of techniques that aim to increase the productivity and life of oil fields (Nwidee et al., 2016). Chemical EOR is a technique in which oil is recovered by chemical injection and is one of the cheapest and most developed EOR techniques and can be used for medium-viscosity crude oil, regardless of the type of rock formation (Druetta & Picchioni, 2020). The chemical EOR technique is a non-thermal EOR that requires relatively low costs (Gbadamosi et al., 2019). The most common chemicals used in chemical EOR techniques are polymers, surfactants, alkalis, surfactant-polymer (SP), and alkali-surfactant-polymer (ASP) (Nwidee et al., 2016).

The surfactant can reduce the interfacial tension (IFT) until 10^{-3} N/m and can increase the oil recovery by dissolving the oil (in the form of an emulsion) at a low IFT so that the oil can be washed away with the formation water flowing toward the production well (Sagir et al., 2020). Surfactants in EOR can reduce the interfacial tension between the oil and water phases from the remaining water flooded in a reservoir. In addition, because surfactants have hydrophilic and hydrophobic properties, where the hydrophilic group will bind the residual water and the hydrophobic group will bind the oil phase in the reservoir, the wettability between the oil and the rocks in the reservoir will increase, So that the oil recovery (SOR) can also increase(Atta et al., 2021; Olajire et al., 2014). Different types of surfactants have been used in chemical EOR, both non-ionic and anionic surfactants. non-ionic surfactants generally show better performance than anionic surfactants because non-ionic surfactants are much more tolerant of high salinity compared to anionic surfactants(Chen et al., 2021). Non-ionic surfactants do not ionize in water, however, they have high resistance to high salinity.

Some examples of non-ionic surfactants are polyoxyethylene stearyl ether, nonylphenol, propylene glycol monostearate, alcohol ethoxy stearate, etc. (Shachi et al., 2018).

There were several studies on the development of non-ionic surfactant and their applications, such as non-ionic biosurfactants from tannic acid for EOR application was obtained ultra-low IFT with a value of 0.052 N/m and resulted in about 90% OOIP (original oil in place) (Seo et al., 2018) (Khayati et al., 2020); a non-ionic surfactant from pure saponin was gained for EOR in sandstone and carbonate reservoirs and the experiments resulted decreased the oil-water IFT by 77.31% and the oil recovery was improved by 6.23 - 8.4% OOIP ; the study of polyethoxylated non-ionic surfactant with different ethylene oxide units were combined with low-salinity brine show that IFT decreased with increasing salinity in oil-wett carbonate reservoirs (Souayeh et al., 2018).

Surfactant synthesis using vegetable oils such as palm oil is recommended due to its abundant availability and eco-friendliness. Surfactants from vegetable oils have been extensively studied in Indonesia using palm oil as raw material such as oleic acid (Putra et al, 2020). The use of palm oil as a surfactant will not interfere with or compete with food. Palm oil which is traditionally processed is used for food about 85-90%. And only 10-15% of palm oil is used for non-food applications. Palm oil which is a natural oil and fat is a triglyceride compound. In the conversion processing, these triglycerides are processed into three stages, namely the form of crude glycerine into glycerol, splitting into crude fatty acids through further processing for food. In contrast, triglyceride molecules are hydrolyzed into crude fatty acid methyl esters through a transesterification reaction which can be processed for non-food applications (Mba et al., 2015) (Yeona et al., 2012). The synthesis of palm oil-based surfactants, such as oleic acid, has previously been carried out by (Putra et al., 2020), an esterification process between oleic acid and PEG-400 using a sulfuric acid catalyst. (Irawan et al., 2018) also investigated the synthesis of polyethylene glycol monooleate (PMO) using a potassium hydroxide (KOH) catalyst. Furthermore, (Abdullah et al., 2017) synthesized polyethylene glycol monooleate using cesium heteropoly-acid (Cs HPA) catalyst.

Further research was conducted on the synthesis of palm oil-based non-ionic surfactants, such as oleic acid and polyethylene glycol, through an esterification process using an acid catalyst, i.e. para toluene sulfonic acid (*p*-TSA) and a base catalyst, i.e. potassium hydroxide (KOH). The synthesized non-ionic surfactant, ester polyethylene glycol oleate, has properties that have the potential to be applied to chemical EOR techniques, especially based on the results of its phase behavior test which can produce Winsor Type III emulsions and low IFT values.

EXPERIMENTAL SECTION

Materials

The materials used in this study were technical oleic acid (PT. Brataco), technical PEG-400 (PT. Brataco), potassium hydroxide (Merck No. 1.05033.1000), para toluene sulfonic acid (p-TSA) (Sigma Aldrich No. 402885-100G), hydrochloric acid (Smart-Lab No. 030822004), potassium iodide (Merck No. 1.05051.0500), carbon tetrachloride (Merck No. 1.02222.2500), sodium thiosulfate (Merck No. 1.06516.1000), technical ethyl acetate (PT. Smart-Lab Indonesia), technical 96% ethanol (PT. Smart-Lab Indonesia), iodine (Merck No. 1.04761.0100), acetic acid glacial (Smart-Lab No. 250722003), silicon oil, phenolphthalein (PP) indicator, formation water, crude oil of field X.

Synthesis of Surfactants Based Oleic Acid and Polyethylene Glycol

The process used to synthesize ester polyethylene glycol oleate is an esterification process carried out by reacting oleic acid and PEG-400 with the used molar ratio i.e. 1:1, 1:2, 1:3 and 1:4 in a three-necked flask as a reactor with a Dean-Stark that has been connected to a condenser, heated with a temperature of 130°C and stirring with a magnetic stirrer at 300 rpm. After approaching 130°C, the catalyst was added to the reactor about 1% of the total weight of the reactants, the catalysts were *p*-TSA and KOH. The reaction was carried out for 6 h and samples were taken every hour. The product of this reaction was extracted in a separatory funnel using technical ethyl acetate and aquadest in a 1:1 ratio until the pH was neutral (6-7) and evaporated until no solvent dripped. The final product is then characterized, while the sampling product is only identified by an acid value test(Irawan et al., 2018). The acid value test results of the sampling products were converted into % conversion of free fatty acids using the following formula (A Hawash et al., 2020):

$$X_{FFA} = \frac{A-B}{A} \times 100\%$$

Keterangan :

X_{FFA} = Free fatty acid conversion (%)

A = Acid value of raw materials (mg KOH/g)

B = Acid number of treatment after esterification (mg KOH/g)

Characterization of Polyethylene Glycol Oleate

Fourrier transform infra-red (FTIR)

This test was conducted to determine the substitution group in surfactant of ester Polyethylene glycol oleate. The FTIR spectrum was obtained from a Shimadzu FTIR instrument IR Prestige-21 series. The sample was scanned in the wave number range of 4000-400 cm^{-1}.

Nuclear magnetic resonance (NMR)

Samples were analyzed using ^{1}H-NMR 500 MHz JNM-ECZ500R, ^{13}C-NMR 125 MHz JEOL, JNM ECA 500 to determine and ensure the compound structure of the synthesized surfactant sample was dissolved in

$CDCl_3$. The surfactant solution was put into an injection tube and then placed in the NMR device for analysis.

Interfacial tension (IFT)

Samples were measured using a Spinning Drop Tensiometer-SDT SN 30015499. First, fill the capillary by setting down the sample drop (light phase) with a syringe and cannula into the closing plug to create a meniscus (surface curvature) on the closing plug. Submerge the open end of the capillary in the liquid of the heavy phase, stir briefly, and draw up sufficient liquid with the piston rod such that the complete reference cone can still just be seen in the capillary. Slide the reference cone with the piston rod forward slightly to create a meniscus of the heavy phase at the opening of the capillary. Bring this meniscus into contact with the sample drop. Place the capillary in the sample chamber. Then determine the image scale and touch-sensitive button menu info for acceleration and release speed. Touch-sensitive button sets capillary speed/launch drop. Adjust the touch-sensitive button to set the temperature and the touch-sensitive button to set the light, further control the camera position. Carrying out the interfacial tension measurement is carried out in the Advance software.

RESULTS AND DISCUSSION

Synthesis of Surfactants Based Oleic Acid and Polyethylene Glycol

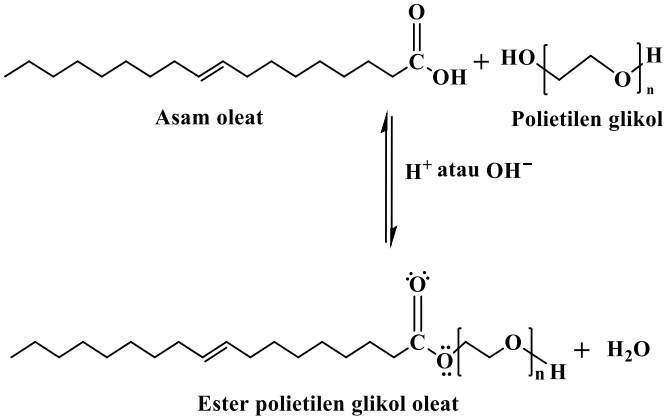
The synthesis process of ester polyethylene glycol oleate is made by the ratioof oleic acid and polyethylene glycol, respectively, such as 1:1, 1:2, 1:3 and 1:4. In this study, polyethylene glycol acts as alcohol to react with oleic acid to obtain ester polyethylene glycol oleate. The comparison was made by exaggerating the amount of moles of its polyethylene glycol to obtain a product with a high conversion of free fatty acids. Le Chatelier's principle of the law of equilibrium states that the equilibrium of a chemical reaction depends either on the concentration of a reactant or, in this case, the use of a smaller amount of alcohol during ester production may decrease the result due to insufficient alcohol concentration to shift the equilibrium reaction toward completion (A Hawash et al., 2020).

In this esterification, catalysts are used to accelerate the reaction rate by lowering the activation energy by changing the reaction mechanism so that the reaction proceeds faster. Esters can be formed chemically through an esterification process using acid and base catalysts (Amani et al, 2014). Ester polyethylene glycol oleate is produced as the main product and water is a by-product.

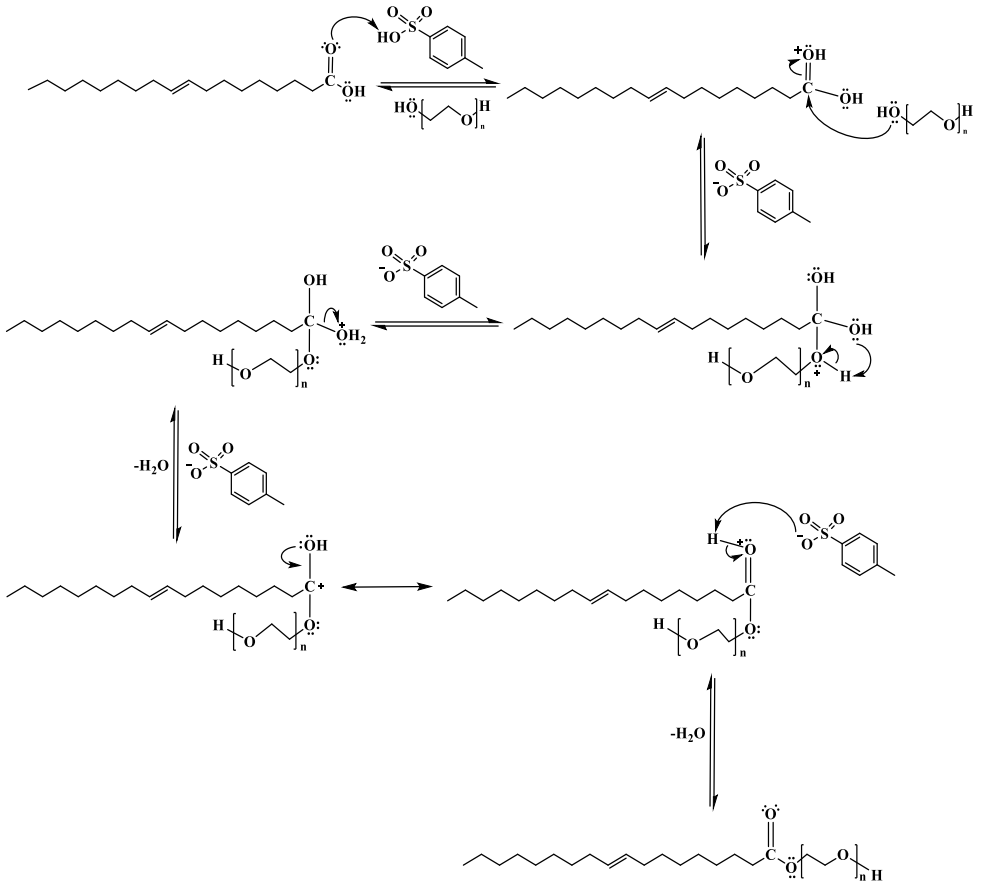
The reaction equation (**Scheme 1**) shows that the esterification of oleic acid with polyethylene glycol is reversible; therefore, the reaction cannot be complete. As the reaction approaches completion, the equilibrium can be shifted by removing one of the products, such as water because water molecules can hydrolyze the products back to form fatty acid and alcohol (Pongpoman et al., 2020).

The esterification reaction mechanism that occurs in the synthesis of polyethylene glycol oleate esters (**Scheme 2**) begins with carbonyl oxygen attacking the H^+ of the acid catalyst and deprotonating its OH group. This causes the positively charged carbonyl oxygen and *p*-TSA compounds to become conjugated bases. A pair of electrons from the carbonyl double bond (π bond) is pushed onto the carbonyl oxygen to better stabilize the positive charge while creating an electron-poor carbon center (Abdullah et al., 2017; Pathak, 2015).

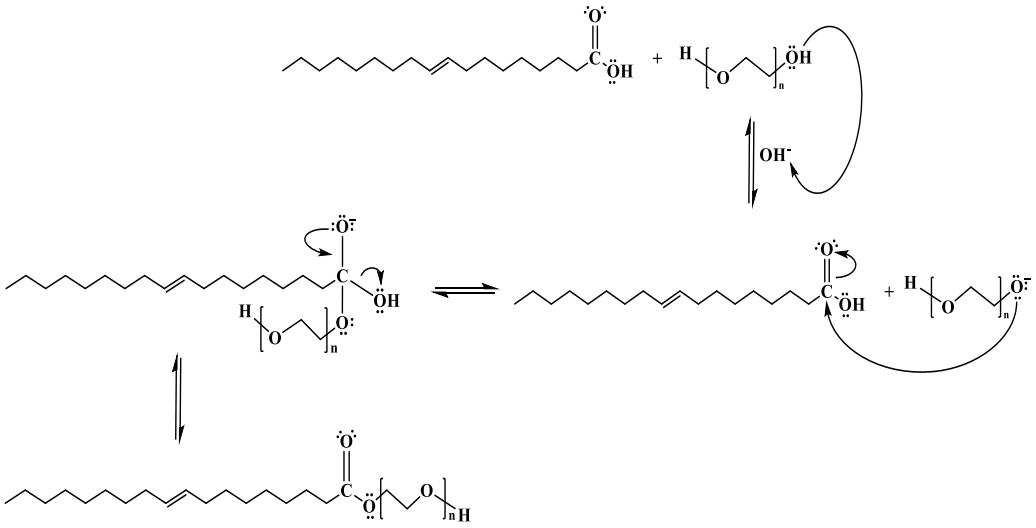
In addition, the hydroxyl groups of polyethylene glycol as nucleophilic, attack the electron-poor carbons (electrophiles) to form intermediates. Then, the positively charged hydroxyl group of polyethylene glycol is deprotonated by the hydroxyl group of carboxylic acid, stabilizing the oxygen atom of polyethylene glycol. The release of hydroxyl group protons of polyethylene glycol creates an activated complex and protonation of the hydroxyl carboxylate group occurs followed by the release of water molecules (Patel et al., 2015). Finally, the positively charged carbonyl oxygen is deprotonated by the conjugated base to form an ester polyethylene glycol oleate with water as a by-product.



Scheme 1. Esterification of oleic acid and polyethylene glycol with acid or base catalysts



Scheme 2. Mechanism of oleic acid and polyethylene glycol esterification reaction with *p*-TSA



Scheme 3. Mechanism of esterification reaction of oleic acid and polyethylene glycol with KOH

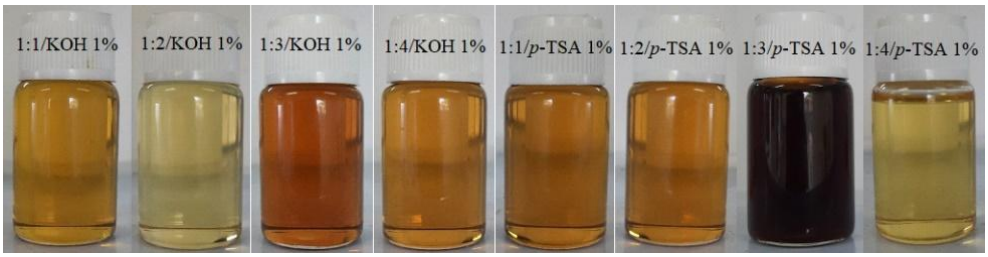


Figure 1. Product of Polyethylene glycol oleate

The mechanism of esterification reaction with a base catalyst in **Scheme 3**, in the process of exchanging the hydroxy group (-OH) of a carboxylate with the alkoxy group (-OR) of an alcohol and producing water, is the process that determines the rate because it is very slow. This is due to the process of exchanging the hydroxy group (-OH) of a carboxylate with the alkoxy group (-OR) of an alcohol, starting with the formation of the activated complex. This activated complex compound is unstable and to reach the activated complex state, it is necessary to have an energy called the activation energy. For a chemical reaction to occur, the activation energy, which is the potential energy, must be exceeded, which can be overcome by the presence of a catalyst.

The products of synthesis, all have the form of a liquid and the color of the product has an average orange color and there are also yellow and brown (**Figure 1**). The formation of brown products is due to the addition of *p*-TSA catalysts which are carried out simultaneously or quickly, causing accelerated side reactions. According to observation data from various other parameters, it can be seen in terms of physical observation or color that the optimum is in the condition of 1:4 (oleic acid : PEG 400) using 1% p-TSA with a lighter yellow color.

Characterization of Polyethylene Glycol Oleate

Acid value of the final product

Acid value analysis is performed to determine the remaining free fatty acids contained in the product. The remaining free fatty acids usually have a negative correlation with the content of ester polyethylene glycol oleate formed during the reaction (Berghuis et al., 2019).

Based on **Figures 2**(**a**) and **2**(**b**), the ester polyethylene glycol oleate synthesized using a 1% KOH catalyst, produces the lowest acid value at a 1:4 molar ratio of 6.01 mg KOH/g, and that synthesized using a 1% *p*-TSA produces the lowest acid value at a 1:4 molar ratio of 3.61 mg KOH/g. The ester polyethylene glycol oleate synthesized with *p*-TSA 1% has a lower acid value. This is because acid catalysts remain effective during the reaction in fats that still contain free fatty acids . The results also showed that acid catalysts have better catalytic activity than alkaline catalysts.

Free fatty acid conversion of sample products

In this study, sampling was carried out every hour to determine the optimization time of free fatty acid conversion in the esterification process of polyethylene glycol oleate. The optimum free fatty acid conversion was at a molar ratio of 1:4 using KOH catalyst and *p*-TSA 1% was 98.63% and 98.62%, respectively, after 4 h of reaction (**Figure 3**). The Free fatty acid conversion tends to decrease after the reaction time of 4 h, indicating that the reaction has reached an equilibrium state within four hours (Patel et al., 2015). The optimal time, the amount of esterification products does not increase anymore because the state has reached equilibrium at that time.

Saponification value of ester polyethylene glycol oleate

The saponification value can be interpreted as a measure of the ester bond content (Wypych, 2017). Therefore, in this study, the saponification value was used to determine the amount of ester value in the sample. **Figure 4** (**a**) shows that the higher the number of moles of PEG-400 used in the synthesis of ester polyethylene glycol oleate using a 1% KOH catalyst, the lower the value of saponification. While synthesized using a 1% *p*-TSA catalyst shows that the higher the number of moles of PEG-400 used in the synthesis of ester polyethylene glycol oleate, the higher the value of saponification (**Figure 4**(**b**)), which shows that there are more ester bonds. The higher the value of saponification, the smaller the free fatty acids, and conversely, the lower the value of saponification, the higher the free fatty acids. The highest saponification value obtained with *p*-TSA catalyst is at a molar ratio of 1:4, which is 144.12 mg KOH/g.

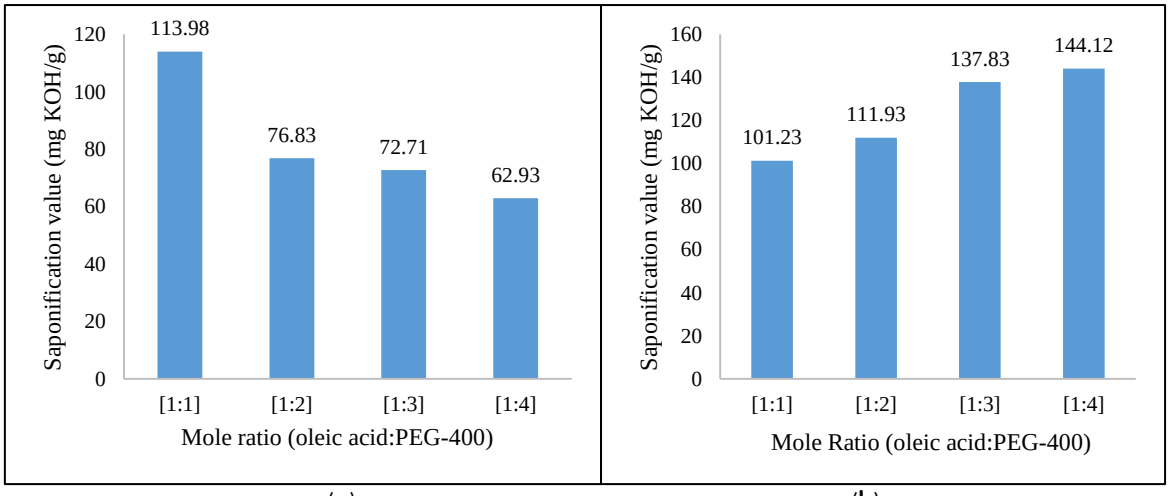
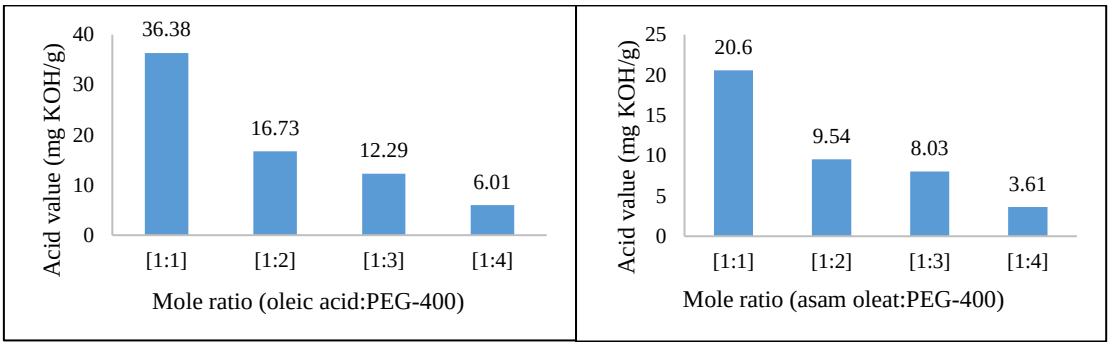


Figure 4. Graph of saponification value of polyethylene glycol oleate (**a**) KOH and (**b**) *p*-TSA

Ester value of ester polyethylene glycol oleate

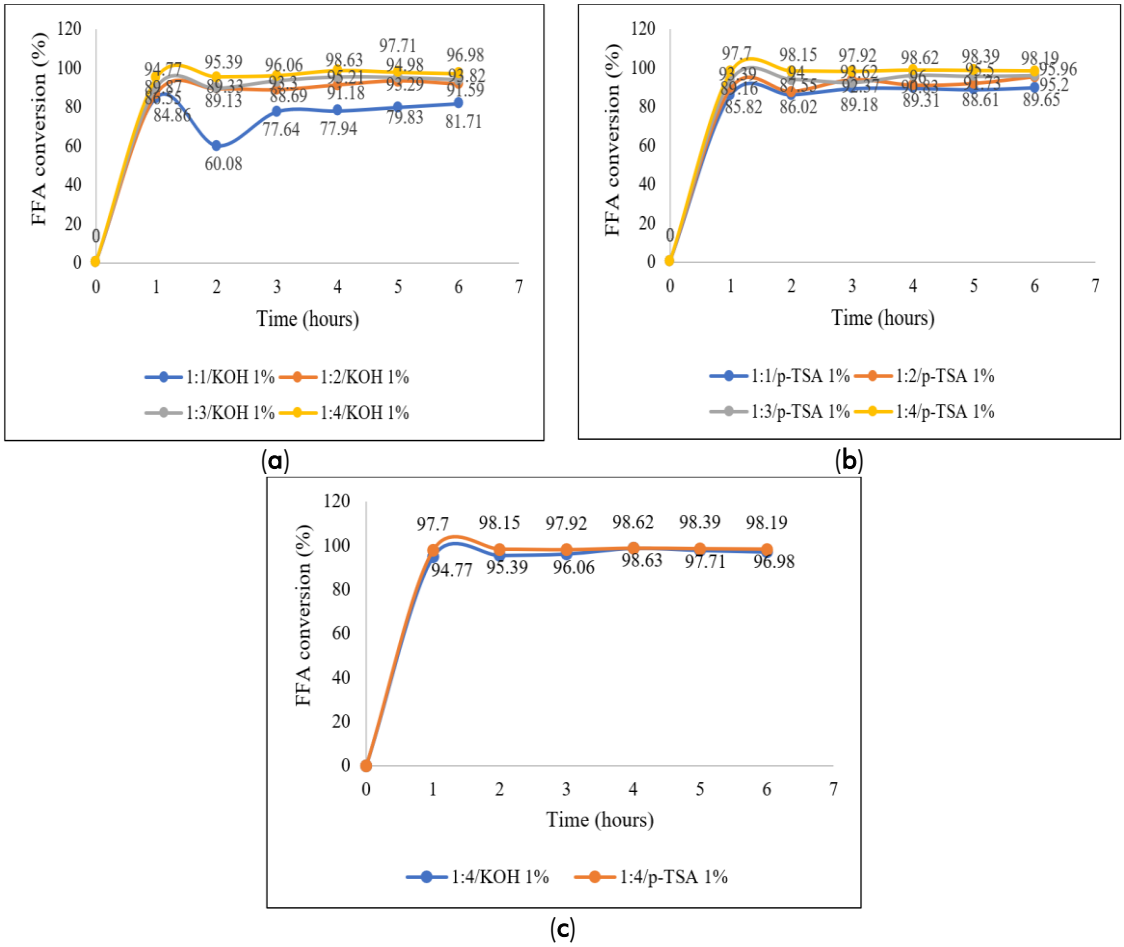
The ester value is the number of milligrams of potassium hydroxide required to hydrolyze the ester in one gram of the sample. A high value of esters indicates the presence of high levels of esters and low content of fatty acids (Belsare et al., 2017).

The best results of ester polyethylene glycol oleate synthesis with 1% KOH catalyst based on the ester value are obtained at a molar ratio of oleic acid to PEG-400 of 1: 1 with an ester value of 77.6 mg KOH/g, while the best results with a 1% *p*-TSA catalyst are obtained at a molar ratio of oleic acid to PEG-400 of 1:4 with an ester value of 140.51 mg KOH/g (**Figure 5**(**a**) and **5**(**b**)). Comparing the two, it is known that the optimum result of the esterification reaction of oleic acid and PEG-400 is obtained with a molar ratio of 1: 4 using a 1% *p*-TSA catalyst. This is because the use of acidic catalysts can optimize ester formation due to the presence of protons (H^+) derived from acidic catalysts and more easily release protons. After all, they are completely ionized. While the base catalyst will absorb water when dissolved in alcohol so the higher the moles of alcohol used for the esterification process, the higher the possibility of water being absorbed in the base catalyst. If too much water is absorbed, the catalyst will not be working optimally (30) and can block the reaction of converting free fatty acids into esters.



(**a**) (**b**)

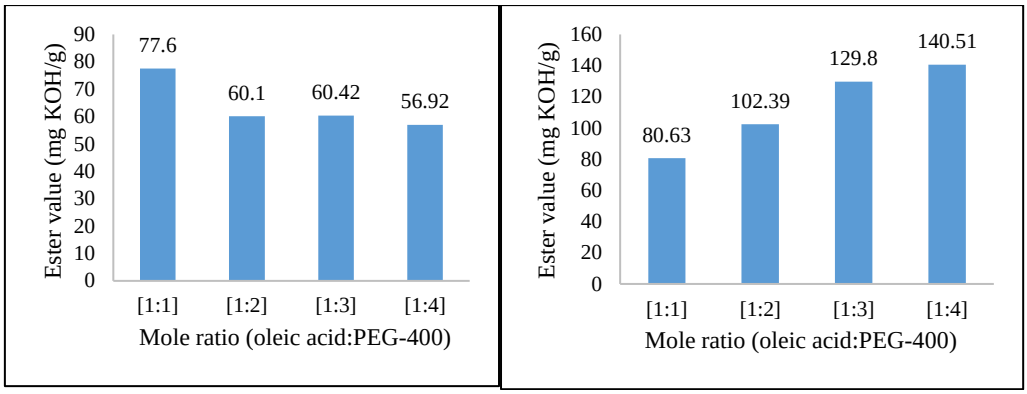
Figure 2. Graph of acid value of polyethylene glycol oleat (**a**) KOH and (**b**) *p*-TSA



(**a**) (**b**)

(**c**)

Figure 3. Graph of free fatty acid conversion (**a**) 1% KOH; (**b**) *p*-TSA and (**c**) KOH and *p*-TSA.



(**a**) (**b**)

Figure 5. Ester value graph of polyethylene glycol oleate (**a**) KOH and (**b**) *p*-TSA.

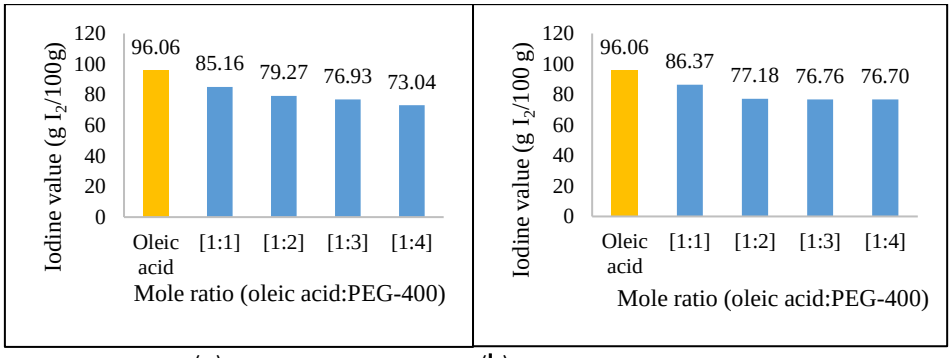
Iodine Value of Ester Polyethylene Glycol oleate

Iodine number is a measure of unsaturation (double bond) in fats, oils, and fatty acids (Spitz, 2016). The iodine value of polyethylene glycol oleate with molar ratio from 1:1 to 1:4 using a 1% KOH catalyst decreased from 96.06 g I_2/100 g to 85.16 – 73.04 g I_2/100 g when compared to the iodine value of oleic acid also tested in this study (**Figure 6**(**a**)). The iodine value of ester polyethylene glycol oleate synthesized using a 1% *p*-TSA catalyst with a mole ratio of 1:1 to 1:4 also decreased when compared to the iodine value of oleic acid, from 96.06 g I_2/100 g to 86.37 – 76.70 g I_2/100 g (**Figure 6**(**b**)). The decrease in iodine value indicates that the esterification reaction is going well, so it can slightly reduce the oil unsaturation functional groups of ester polyethylene glycol oleate.

Synthesized ester polyethylene glycol oleate, either synthesized with KOH or *p*-TSA catalysts were analyzed by FT-IR to determine the functional groups contained in the non-ionic surfactant and to ensure that the ester compounds were actually been formed. FTIR spectra of polyethylene glycol oleate synthesized using KOH catalysts (**Figure 7**(**a**)) showed peaks in wavenumber 1095.36 – 1098.60 cm^{-1} of C—O—C bonds (**Table 1**) and all mole variations show these peaks. C—O—C bonds are in range 1050 – 1250 cm^{-1} (Turkun, 2019). The FTIR spectrum of oleic acid shows the absorption of carbonyl groups (C=O) for carboxylic acids in the area of 1708.15 cm^{-1}, where the area shifts to 1730.64 – 1732.44 cm^{-1} in the FTIR spectrum of polyethylene glycol oleate which shows carbonyl groups for ester compounds. The peak at 3434.17 – 3440.92 cm^{-1} which shows the strain of hydroxyl groups derived from the PEG-400 structure (Khan et al., 2018)

FTIR spectra of polyethylene glycol oleate synthesized using *p*-TSA (**Figure 7**(**b**)) show the presence of C-O-C bond absorption in wavenumber of 1090.52 – 1097.68 cm^{-1} (Oulette & Rawan, 2018) and similarly to synthesized using KOH, all mole variations show these peaks. The FTIR spectrum of oleic acid shows the absorption of the carbonyl group (C=O) for carboxylic acids in the area 1708.15 cm^{-1}, where the area shifts to 1732.58 – 1733.84 cm^{-1} in the FTIR spectrum of polyethylene glycol oleate showed carbonyl groups for ester compounds. The peak at 3399.91 – 3454.87 cm^{-1} shows the strain of the hydroxyl group derived from the structure of PEG-400 (Khan et al., 2018)

When comparing the spectra of both (**Figure 7** (**c**)) of the mole variation that produces the highest ester value, both showed the absorption area of the O—H group at a wavelength of 3440.92 cm^{-1} (KOH catalyst) and a wavelength of 3399.91 cm^{-1} (*p*-TSA catalyst). The peaks of the O—H group in the polyethylene glycol oleate ester spectrum synthesized using *p*-TSA catalysts seem sharper. The sharper the FTIR spectrum provides information the more elements that have the homogeneity of the bond.



(**a**) (**b**)

Figure 6. Iodine value graph of polyethylene glycol oleate (**a**) KOH and (**b**) *p*-TSA.

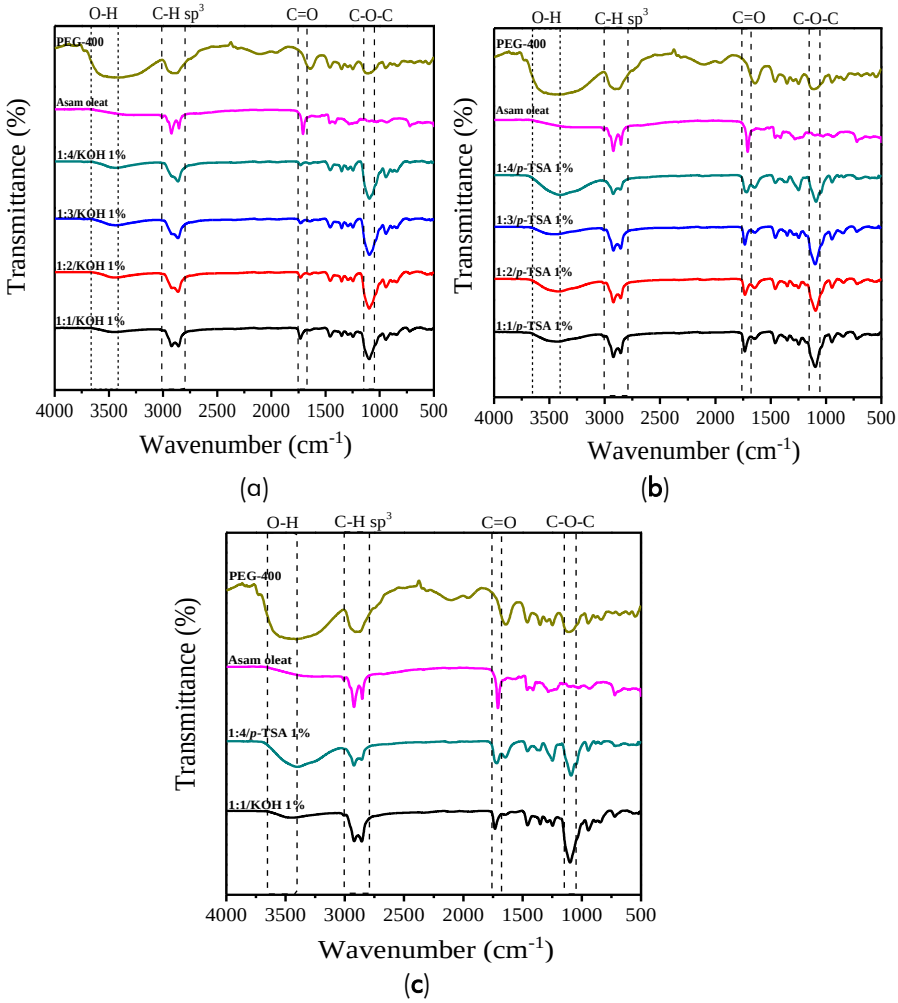


Figure 7. FTIR spectrum Overlay of polyethylene glycol oleate (**a**) KOH; (**b**) *p*-TSA and (**c**) KOH and *p*-TSA.

Table 1. Wavenumber absorption area on ester polyethylene glycol oleate

No.	Functional groups	Wavenumber (cm^{-1})	
		KOH catalyst	*p*-TSA catalyst
1.	C–O–C	1095.36 – 1098.60	1090.52 – 1097.68
2.	C=O (ester)	1730.64 – 1732.44	1732.58 – 1733.84
3.	O–H	3434.17 – 3440.92	3399.91 – 3454.87
4.	C–H sp^3	2857.07 – 2921	2855.74 – 2923.07

Chemical structure of ester polyethylene glycol oleate

In this study, ^{1}H-NMR and ^{13}C-NMR analyses were performed to ensure that the desired polyethylene glycol oleate compounds were formed. The chemical shift (δ) is measured concerning the proton absorption of the reference compound. The most commonly used reference compound is tetramethylsilane (TMS). TMS can be used as a reference compound because it has protons that are protected enough to appear in the upfield region. The sample peak is measured based on how far it is shifted from the TMS (Turkun, 2019).

In ^{1}H-NMR, the ester products (**Figures 8** (**b**) and **8** (**c**)) have peaks in the range of chemical shift (δH) of 4.20 ppm, while in ^{1}H-NMR of oleic acid (**Figure 8** (**a**)), these peaks do not appear, indicating that the spectrum is characteristic of completely formed ester products (Oulette & Rawn, 2018). The chemical shift (δH) of 4.20 ppm (2H; *t*) indicates a peak with triplet multiplicity due to the presence of 2H bound to the C atom adjacent to CH_2 (**Figure 8**) of PEG-400 which has become an ester. The chemical shift of 4.20 ppm is the CH_2 group at C which leads to the downfield area because it is influenced by the carbonyl group of oleic acid because the carbonyl group is an electron-pulling group (electronegative) so the protons in the CH_2 group become deshielding. This is because the carbonyl group pulls the electron density away from the carbon, which also affects the electron density around the proton (Putra et al., 2020). In ^{1}H-NMR of oleic acid, there is a peak with a chemical shift of 11.1 ppm, indicating the presence of H derived from the carboxylic group (Yadav et al., 2014), while the peak does not appear in ^{1}H-NMR of ester products, both synthesized using KOH and *p*-TSA catalysts.

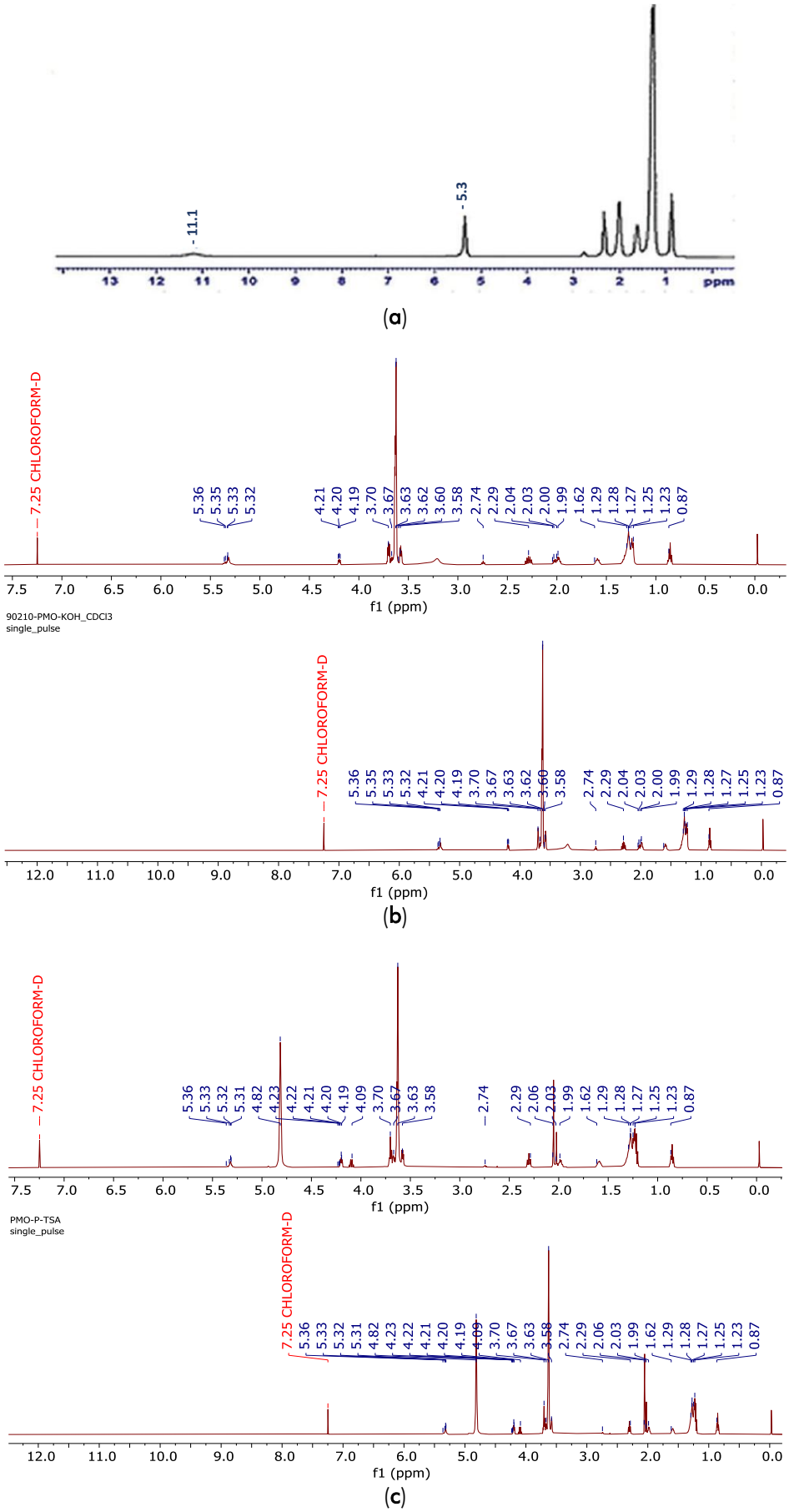


Figure 8. ^{1}H-NMR spectrum of (**a**) oleic acid (**b**) polyethylene glycol oleate (KOH) and (**c**) polyethylene glycol oleate (*p*-TSA).

Furthermore, the peak in the chemical shift of 5.36 ppm (2H; *q*) appears in ^{1}H-NMR in ester and oleic acid products, which with quartet multiplicity indicates the presence of H from CH which is double bonded to CH also (-CH=CH-) which is a structure derived from oleic acid and the two CH bonds are also adjacent to CH_2, so it can be known that there is no breaking of the double bond during the esterification process (Gunawan & Nandiyanto, 2021).

In ^{13}C-NMR spectrum of oleic acid, there is a peak with chemical shift (δC) at 180.58 ppm indicating the presence of carbonyl carboxylic acid (38), where it is also detected in the ^{13}C-NMR spectrum of the synthesized ester product (**Figures 9** (**b**) and **9** (**c**)), at the chemical shift (δC) 177.96 ppm (KOH) and 175.36 ppm (*p*-TSA). This is possible because there are still free fatty acids that have not been completely converted into ester products. In contrast to the ^{1}H-NMR spectrum, the synthesized ester product does not show the presence of a carboxylic acid peak. According to Foris (Jenie et al., 2014), this is possible due to the exchange of protons between OH-carboxylate with deuterium from the NMR solvent $CDCl_3$, which causes the peak to shrink or disappear completely, or to appear in the downfield but it is not visible because it is below the baseline, so it does not appear in the NMR spectrum.

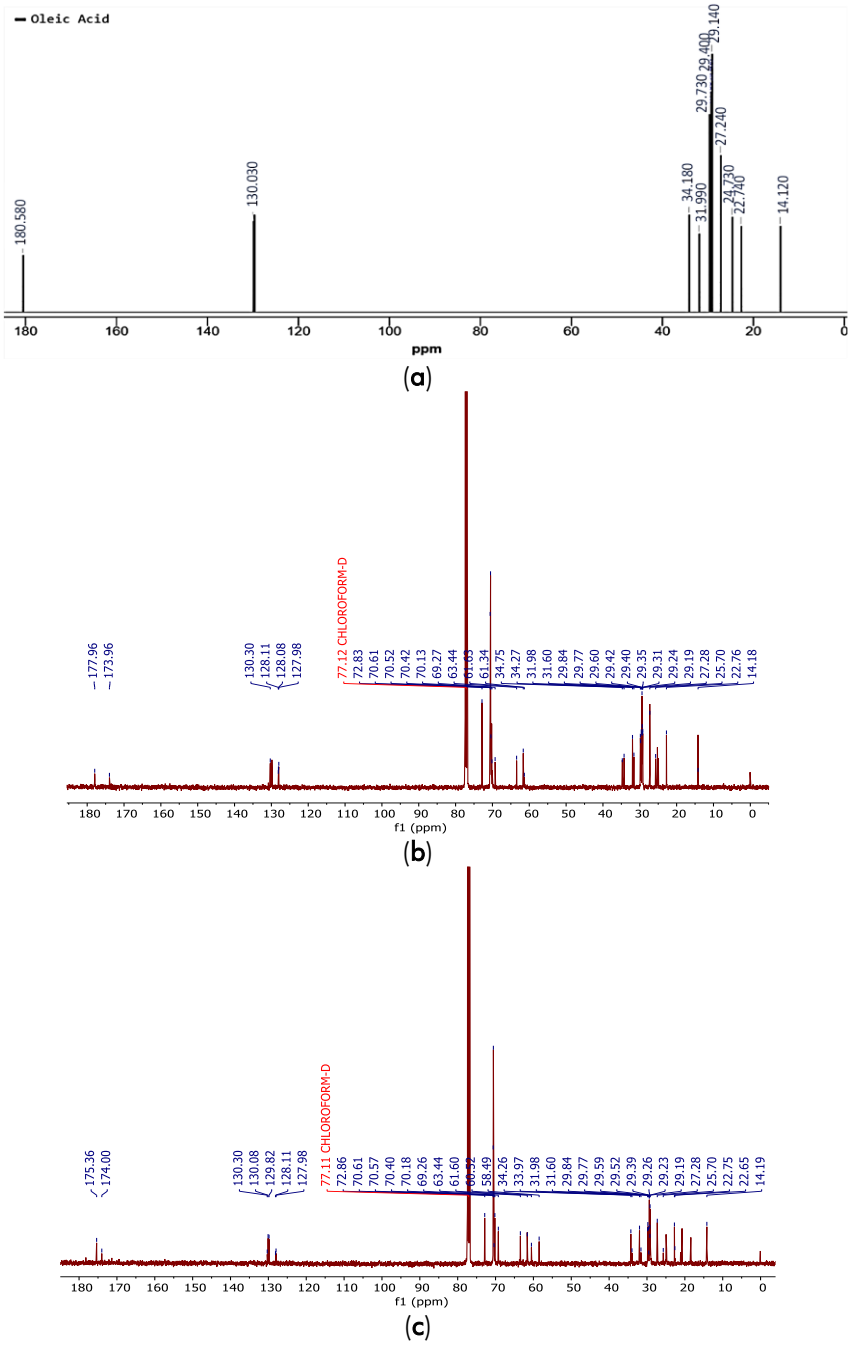


Figure 9. ^{13}C-NMR spectrum of (**a**) oleic acid (**b**) polyethylene glycol oleate (KOH) and (**c**) polyethylene glycol oleate (*p*-TSA).

The presence of ^{13}C-NMR spectrum of the ester polyethylene glycol oleate at chemical shifts of 173.96 ppm (KOH) and 174.00 ppm (*p*-TSA) indicates the presence of the carbonyl carbon (—C═O) of the ester or is a typical peak for the ester because it does not appear in the ^{13}C-NMR spectrum of oleic acid (Jenie et al., 2014). The appearance of a peak at a chemical shift of 130.03 – 130.30 ppm indicates the presence of C double-bonded to C (—CH═CH—) (Foris, 2015), showing that there is no breaking of the double bond during the esterification process.

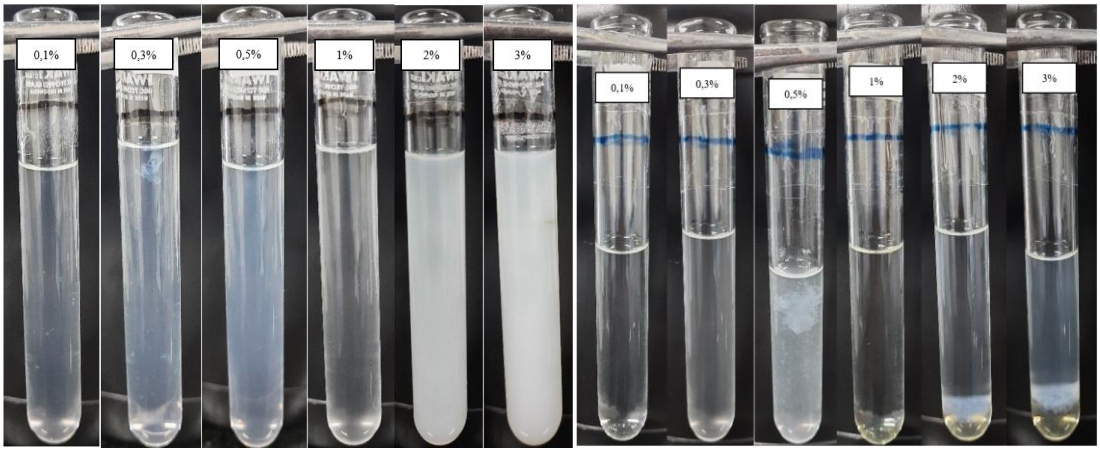
Compatibility test of ester polyethylene glycol oleate

The compatibility test is one of the important tests that aims to determine the solubility or suitability of surfactants in the formation of water. Compatibility test is done with temperature conditions of the reservoir which is usually around 60°C. Compatible solutions are those where the condition is clear and no precipitate is formed (Mazur et al., 2020). Clear compatibility results can be an indication that the possibility of clogging in the reservoir at the time of the EOR process will be low (Priyanto et al, 2021).

Ester polyethylene glycol oleate synthesized with KOH catalyst has nothing to completely clear or completely soluble solutions (**Figure 10** (**a**)), therefore, for the results of the compatibility test of ester polyethylene glycol oleate synthesized with KOH catalyst in this study, it was confirmed that none of them are compatible, the surfactant is not considered exactly for the Reservoir in question. Ester polyethylene glycol oleate can give a completely soluble result in the formation of water exactly with a surfactant concentration of 0,1% in **Figure 10** (**b**) due to the presence of C—O—C Group in PEG-400. The group can bind to water molecules to make the surfactant can be easily soluble(Mazur et al., 2020).

The results of the compatibility test with a surfactant concentration of 1% to 3% on polyethylene glycol oleate ester synthesized with *p*-TSA catalyst showed the occurrence of surfactant precipitation it is because although non-ionic surfactants are more tolerant to high salinity, most are not resistant to high heat, which makes the IFT increase at high temperature so that it will separate (Sagir et al., 2020)

The precipitation of surfactants at a concentration of 1% to 3% in the formation water (**Figure 10** (**b**)) also shows that with increasing temperature, hydrogen bonds in the surfactant can become loose and make the type of solubility of surfactant molecules in the formation water decreased drastically decreased (Ivanova et al., 2020). Ester polyethylene glycol oleate is soluble in water formation when without heating in an oven with a temperature of 60 °C. This shows that non-ionic surfactants are not resistant to high enough temperatures so it can be said that their stability properties are poor.



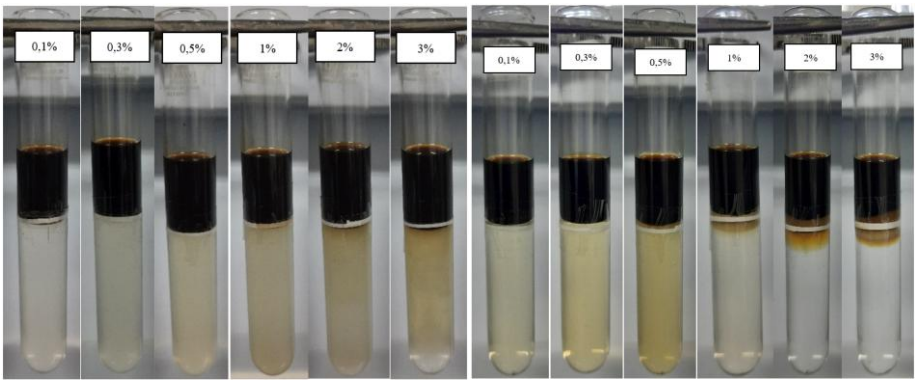
(**a**) (**b**)

Figure 10. Results compatibility test of polyethylene glycol oleate were synthesized using (**a**) KOH (**b**) *p*-TSA.

Table 2. Result compatibility test of polyethylene glycol oleate in formation water

Mole ratio oleic acid:PEG-400	Catalyst	Solubility					
		0.1%	0.3%	0.5%	1%	2%	3%
1:1	KOH 1%	++	++	++	++	+	+
1:4	*p*-TSA 1%	+++	++	+	-	-	-

notes: +++ = soluble (compatible)
++ = slightly soluble (less compatible)
+ = less dispersed, like milky (no compatible)
– = precipitation (no compatible)



(**a**) (**b**)

Figure 11. Results phase behavior test of polyethylene glycol oleate synthesized using (**a**) KOH and (**b**) *p*-TSA.

Table 3. Result of IFT test

Mole ratio	Catalyst	Concentration	IFT Value
1:1	KOH	3%	11 x 10^{-1} mN/m
1:4	*p*-TSA	1%	2.6 x 10^{-1} mN/m

Phase behavior test of ester polyethylene glycol oleate

The phase behavior test is performed to analyze the type of microemulsion formed in the mixed solution of oil, surfactant, and water formations (Kurnia et al., 2021). The most expected test result in this phase behavior test is the middle phase emulsion (Winsor Type III), because according to (Zulkifli et al., 2020) the best type of microemulsion for EOR process purposes is Winsor Type III, followed by Winsor Type I and Winsor Type II.

Ester polyethylene glycol oleate synthesized using KOH catalyst showed no emulsion (**Figure 11** (**a**)), while it is synthesized using *p*-TSA catalyst can produce Winsor type III emulsion, which is the use of surfactant concentration of 1% to 3% and also no surfactant precipitate at the bottom of the tube, contrary to the compatibility test results (**Figure 11** (**b**)). With the use of a surfactant concentration of 0.1%, the results are compatible or clear in the compatibility test, but the results of the phase behavior test do not form a middle phase emulsion.

Winsor Type III (mid-phase emulsion) forms an oil-in-water (o/w) emulsion. o/w type emulsion is an emulsion consisting of oil droplets dispersed in water, with oil as the inner phase and water as the outer phase. In Winsor Type III emulsions, both oil and water are dissolved by surfactants and are often considered to be bicontinuous because they are in equilibrium with excess oil and water. This type of microemulsion is very important in EOR because of its very low IFT, thermodynamic stability, and ability to dissolve excess oil and water (Ahmed & Elraies, 2018).

Interfacial tension test of ester polyethylene glycol oleate

The value of the interfacial tension (IFT) is the energy value that maintains the stability of the separation of the two-phase interface. The two-phase interface becomes easier to solve when the IFT is reduced (Deng et al., 2021). The Interfacial Tension (IFT) test is usually performed as a preliminary test before proceeding to preliminary tests such as core flooding and other advanced tests. The surfactant must produce a low IFT before proceeding to core flooding

The use of 1% surfactant concentration resulted in an IFT value of 2.6 x 10^{-1} mN/m (**Table 3**), where the IFT value can already produce Winsor type III emulsions in phase behavior tests. In contrast, ester polyethylene glycol oleate synthesized using KOH catalysts cannot produce these emulsions even at the highest concentration of 3% because the IFT value is still quite high at 11 x 10^{-1} mN/m. High IFT values can lead to miscibility between water and oil, therefore water cannot properly mobilize the remaining oil in the reservoir (Ahmed & Elraies, 2018).

CONCLUSIONS

In this study, it can be concluded that the best formulation in the esterification process of ester polyethylene glycol oleate with a temperature condition of 130°C was at a molar ratio of 1 : 4 (oleic acid: PEG-400) using 1% *p*-TSA with an value of acid is 3.61 mg KOH/g, saponification is 144.12 mg KOH/g, ester is 140.51 mg KOH/g and iodine is 76.70 g I_2/100 g which was also confirmed by FTIR and NMR analysis. The compatibility test results of ester polyethylene glycol oleate synthesized using *p*-TSA catalyst showed the most compatible results with the use of 0.1% surfactant. The surfactant was able to produce Winsor type III emulsion in the phase behavior test using a surfactant concentration of 1% without surfactant precipitation at the bottom of the tube and with an IFT value of 2.6 x 10^{-1} mN/m, so this type of surfactant is still potential enough to be developed in chemical EOR.

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