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Initial Analysis of The Characteristics of Sweet Orange (Citrus Sinensis) Peel Essential Oils as an Alternative Surfactant in The Tertiary Oil Recovery Method

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ABSTRACT - This study includes synthesis and evaluation of an additive to improve the two main properties of lubricating grease which are; "increasing the dropping point and improving the extreme pressure (EP) properties" of Lithium grease without any negative effect on the other characteristics of lubricating grease. Increasing the dropping point and extreme pressure (EP) properties are the most important factors to widen the application of lubricating grease. The additive is synthesized via two-steps condensation reactions of polyethylene glycol 400 and Boric acid followed by reacting the product with Dodecyl-benzene sulfonic acid in the presence of Xylene as azeotropic solvent. The structure of the synthesized Sulphonyl-Borate ester SPB is confirmed by using FT-IR. Evaluation of the synthesized additive is conducted by blending it with laboratory prepared Lithium grease sample in different ratios. Analysis were carried out to study the effect of additive on the lubricating grease properties, especialy grease consistency ASTM D217, dropping point ASTM D2265, oil separation ASTM D6184, and Four–Ball test ASTM D2783. The results showed that synthesized additive increased the dropping point by 65 % and extreme pressure properties by 66 % of the prepared grease grease sample.

Keywords: biosurfactant, MES, enhanced oil recovery, citrus sinensis

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INTRODUCTION

EOR (Enhanced Oil Recovery) is a tertiary recovery stage that must be carried out to maximize the production of remaining oil in the reservoir when the primary and secondary recovery methods fail. Due to the large number of mature fields that are ineffective when secondary recovery is applied, EOR is implemented in Indonesia (Anam and Purwono 2015). Surfactant injection or surface active agent, which is one of the chemical injections in advanced oil recovery, has the concept of reducing interfacial tension (IFT) on oil/water and stabilizing the emulsion in the fluid by injecting the active substance into the reservoir, thereby altering the wettability of the rock and increasing oil recovery (Li et al. 2018). Additionally, the head and tail of surfactant contribute to the reduction of surface tension between two immiscible fluids(Elmofty 2012); (Gbadamosi et al. 2019).

It is believed that the use of commercially available synthetic-based petroleum surfactants has a negative impact on the environment because they cannot be naturally degraded (they are nonbiodegradable). This creates an opportunity for the development of nature-based surfactants(Hope & Abu 2015). Methyl ester sulfonate (MES) derived from vegetable oil can be developed as an alternative surfactant due to its biodegradability and abundance of basic materials in nature.

Prior research has been conducted on the production of MES using natural raw materials, specifically *Anabasis setifera*. In this study, it was determined that the MES was more eco-friendly and less expensive than commercial surfactants, and that it altered the wettability of the reservoir from oil to water, thereby decreasing the interface tension (Nowrouzi et al. 2020).

Orange peel essential oil has been studied thus far, but primarily for detergent production[7]. Anionic surfactants are the most commonly used surfactants in EOR. The albedo portion of orange peel contains 20-35% pectin, which is composed of pectin acid, which is a component of galacturonic acid and contains a methyl ester group with the formula $RCOOCH_3$ up to 50%, which can be used as an anionic surfactant through the sulfonation stage to become Methyl Ester Sulfate (MES) (Hanum et al. 2012), (Nugroho & Buchori 2019). The synthesis of metyl ester can be accomplished by esterification or transesterification using methanol as a reagent that provides the CH_3 group and operates as a MES purification agent.

METHODOLOGY

The experimental technique was utilized for this study. In the mention of Methyl Ester Sulfonate using transesterification and sulfonation methods.

Characteristics of the MES is tested by a pycnometer for density testing, an Ostwald viscometer for viscosity testing, a pH stick for pH testing, a burette for acid number testing, and a test tube for compatibility testing. This investigation utilized orange peel essential oil, methanol, NaOH, H_2SO_4, NaCl, fenolftalein, and aquadest as its materials.

The Production of Methyl Ester Sulfonate

Transesterification was performed by adding 200 ml of orange peel essential oil to a three-neck flask furnished with a stir bar and heating it at 60. In separate receptacles, heat methanol 44 ml and NaOH 0.5% (w/w methanol) at 60. Put methanol and 0.5% NaOH (w/w methanol) into a three-neck flask containing 60-heated essential oil. Start the mixer motor with 800 revolutions per minute for 90 minutes. Remove the product, then cleanse with 150 ml of hot, 80-temperature distillate water. Centrifuge for 20 minutes to separate glycerol, methanol, water (bottom layer), methyl esters, and triglycerides (top layer). Wash back the top layer of the separation in step 5 using 200 ml of hot distilled water at 80 and separating water from methyl esters and triglycerides using a centrifuge within 20 minutes. After transesterification, the sulfonation process is continued by combining 100 grams of orange peel essential oil methyl ester with 22 ml of H_2SO_4 in a three-neck flask drop by drop. Using a hotplate agitator and constant stirring for 1.5 hours, heat the mixture to 65 and purify MES by adding 30% (wt% of total wt ME and H_2SO_4) methanol. MES can be neutralized by introducing 30% NaOH (Nata, Ma'rifah & Herlina 2014; Supriningsih 2010).

The Production of Brine

Brine is water mingled with a specific concentration of NaCl, which determines the brine's salinity level. The salinity of this investigation is 15,000 ppm (parts per million). Calculating salinity and producing brine can be accomplished as follows:

$$15{,}000 \text{ ppm (NaCl)} = \frac{15{,}000\ mg}{1\ kg} = 15{,}000 \text{ mg/kg}$$

Density Test

The procedure requires the preparation of a 10-ml pycnometer. The unfilled pycnometer is being weighed on a digital scale. Close the pycnometer after completely filling it with MES. Using a digital scale, determine the mass of the pycnometer containing MES and record the results. The MES density can be calculated using the equation provided below.

$$\rho = \frac{m' - m}{v} \qquad (1)$$

Where m is the mass of the empty pycnometer in grams, m' is the mass of the pycnometer filled with MES in grams, and v is the volume of the pycnometer in milliliters.

Viscosity Test

The surfactant solution is subjected to a viscosity test to ascertain the fluid's viscosity value. The Ostwald Viscometer is used for the viscosity test. Prepare the Oswald viscometer and the solution of surfactant. Place 10 milliliters of surfactant solution in the Oswald viscometer. Suck the liquid on the Oswald viscometer using a filler (rubber ball) until it reaches 2 cm above the viscometer's upper limit. Remove the filler and allow the liquid to exceed the maximum level. Time the passage of the surfactant solution from the upper ostwald limit to the lower ostwald limit using a stopwatch. Calculate the viscosity value after noting the flow time. The viscosity of MES can be calculated using the equation provided below.

$$\mu 2 = \mu 1 \times \frac{\rho 2\ t2}{\rho 1\ t1} \quad (2)$$

Where $\mu 2$ is the viscosity of MES in cP, $\mu 1$ is the viscosity of fluid in cP, and is the density of fluid, is the density of MES, t2 is flow time of MES and t1 is the flow time of fluid in second.

pH Test

Using a pH probe, PH testing is performed to determine the acidity or pH levels of the surfactant (Chasani et al. 2014). For instance, the MES surfactant prior to the neutralization process was acidic because H_2SO_4 was added during the sulfonation process; therefore, it had to be neutralized because the EOR step of surfactant injection required a pH value between 6 and 8.

Acid Number Test

The acid number test was conducted to determine the amount of NaOH used to neutralize oil containing 96% methanol and neutralized with NaOH. One gram of MES was weighed to determine the acid number. Mix the MES with up to 5 ml of methanol. The solution is heated and stirred for 10 minutes. Irritating with NaOH and the phenolphthalein indicator until the color turns pink (Eni, Sutriah & Muljani 2017). The acid number of the MES can be calculated using the following equation bellow:

$$\text{Acid Number} = \frac{\text{ml NaOH x N NaOH x 56,1}}{\text{sample weight}} \quad (3)$$

Compatibility Test

A compatibility test is performed to ascertain the surfactant's solubility or brightness level in brine. Surfactants with concentrations of 0.1%, 0.3%, 0.5%, 0.7%, and 1% in saline with a salinity of 15,000 ppm were used in this test. The compatibility test consists of two parts, aqueous Stability and thermal Stability, and is conducted to prevent the deposition of surfactants. In addition, the thermal Stability test is conducted to ascertain the surfactant's resistance at reservoir temperature (60) for a given time period 14.

RESULT AND DISCUSSION

The purpose of this study is to determine the properties of alternative MES surfactants derived from orange peel essential oil. At a brine salinity of 15,000 ppm, the tested properties included density, viscosity, pH, acid number, and compatibility with numerous MES scenarios. These attributes will be compared to those of commercial MES and anionic surfactant SLS.

The Density of the Fluids

Measurement of mass per unit volume of an object. Because density affects solubility in brine and petroleum, the MES density test must be conducted. The MES density value of the essential oil of orange peel as an alternative surfactant has decreased from 0.922 gr/cm^3 to 0.9 gr/cm^3 compared to the density value of the essential oil of orange peel as raw material. In the transesterification and sulfonation processes, the addition of methanol and NaOH solution has an effect on decreasing the density value. In this study, MES has a lower density than commercial MES and SLS surfactants with the same density value, 1.16 gr/cm^3. This suggests that commercial MES and SLS surfactants have a higher molecular weight than MES extracted from orange peel essential oil. Figure 1 compares the density values of essential oils, MES derived from orange peel essential oils, commercial MES, and SLS surfactants. In this study, the 0.922 g/cm^3 density value produced by MES from orange peel essential oil has a reasonable MES solubility rate because it is near to the 1 g/cm^3 density value of the solvent, which is water (Bantacut & Darmanto 2014).

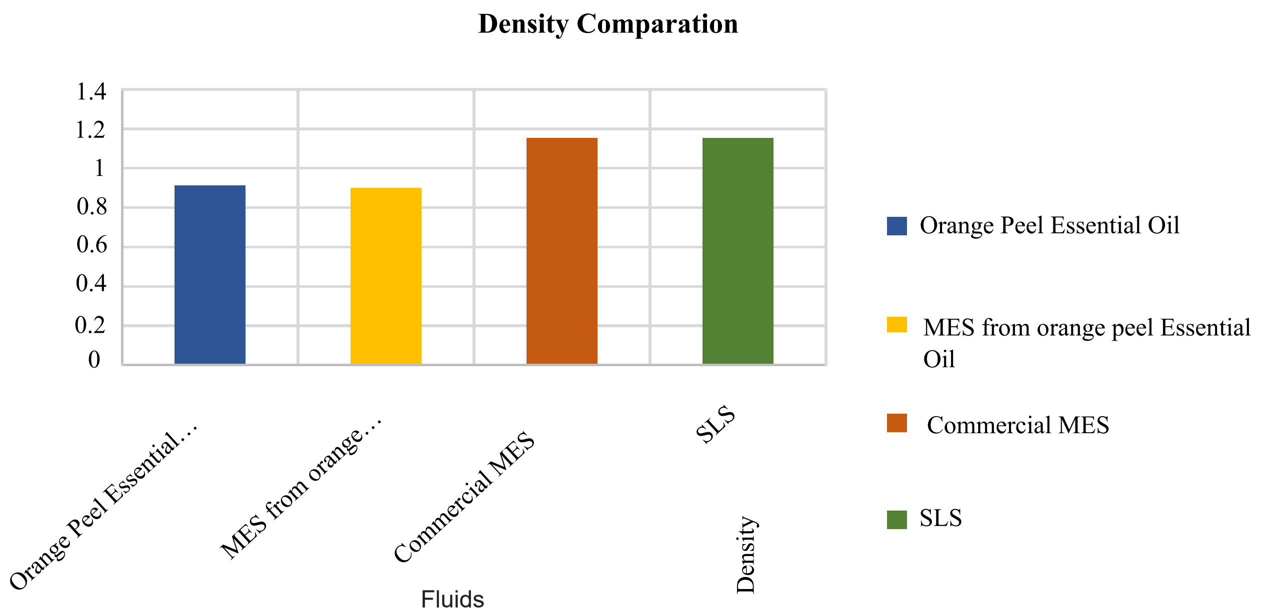

Figure 1
The density of the fluids

The Viscosity of the Fluids

To ascertain the viscosity of the MES surfactant in orange peel essential oil, its viscosity must be measured. The viscosity of the primary material, namely the essential oil of orange peel obtained in this study, was 3.688 cP, while its MES viscosity was 1.36 cP. The viscosity of MES is lower due to the effective completion of the methanol purification procedure. Ultimately, methanol attaches to the salt or di-salt present in the MES as well as the water present in the MES, purifying the impurities and decreasing the viscosity of the MES (Iman et el. 2016). In contrast, the viscosity of commercial MES cannot be measured due to its solid state. Due to the gel form of SLS, its viscosity is significantly greater than the alternative MES surfactant derived from orange peel essential oil. The alternative MES surfactant derived from orange peel essential oil is a watery liquid.

The pH of the Fluids

pH measures the acidity of a liquid. The orange peel essential oil has an acidity level of 4, which, based on this value, indicates that the oil is acidic. Due to the binding between the acidic H_2SO_4 reactant and the methyl ester of orange peel essential oil, the degree of acidity of the MES surfactant after the sulfonation process in this investigation was very low. After the sulfonation process, the pH neutralization process must be continued until the final pH value of MES 7 is attained, which is equivalent to the pH value of commercial MES surfactant and SLS surfactant. In the infusion of surfactants during the EOR production phase, the surfactants' pH must remain neutral or between 6 and 8. If the pH value is greater than 8, the surfactant is alkaline and can cause MES hydrolysis to become salty. Figure 2 depicts the results of an analysis of the pH value of orange peel essential oil, and Figure 3 depicts a comparison of the pH value of orange peel essential oil, MES of orange peel essential oil, commercial MES, and SLS surfactant.

Acid Number of the Fluids

To ascertain how much NaOH is necessary to neutralize MES, the acid number must be determined. The acid number is increased as NaOH neutralizes MES more. The acidity of the orange peel essential oil in this investigation was 0.46 percent. The MES acid number of the orange peel essential oil used in this investigation was 3.048%. In comparison to commercial surfactants, its acid number is 8.42%. In comparison to SLS surfactants, which have an acid number of 3.93 percent, the acid number of commercial surfactants and SLS is greater than the acid number of essential oils for MES surfactants, which is 3.04 percent. Figure 4 depicts the comparison between the acid number values. The greater the acid number, the greater the deterioration of oil triglycerides into free fatty acids, which causes greater harm to the oil (Syed et al. 2019).

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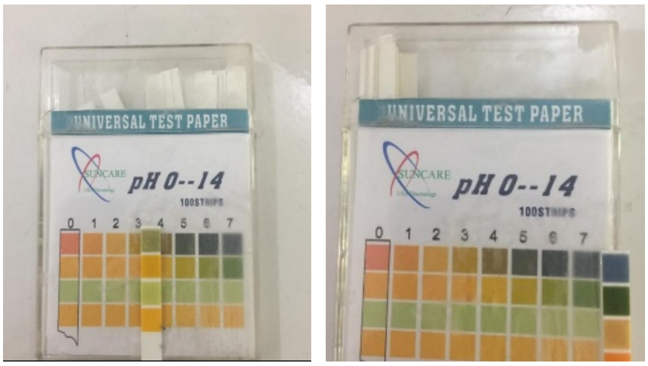

Figure 2
The pH of orange peels essential oil (left) and pH MES of orange peel essential oil (right).

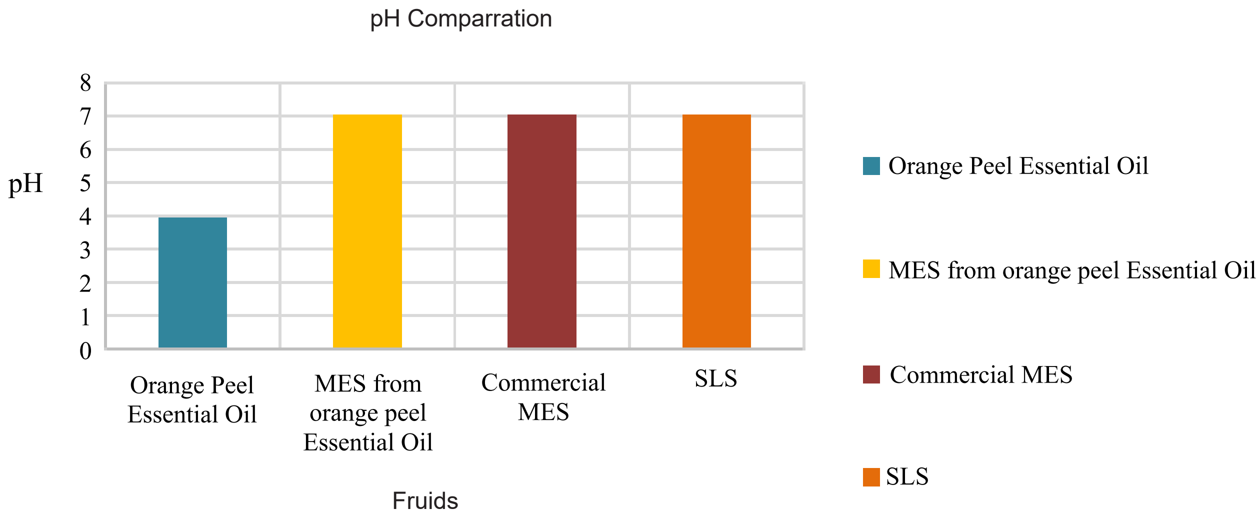

Figure 3
The pH of the fluids.

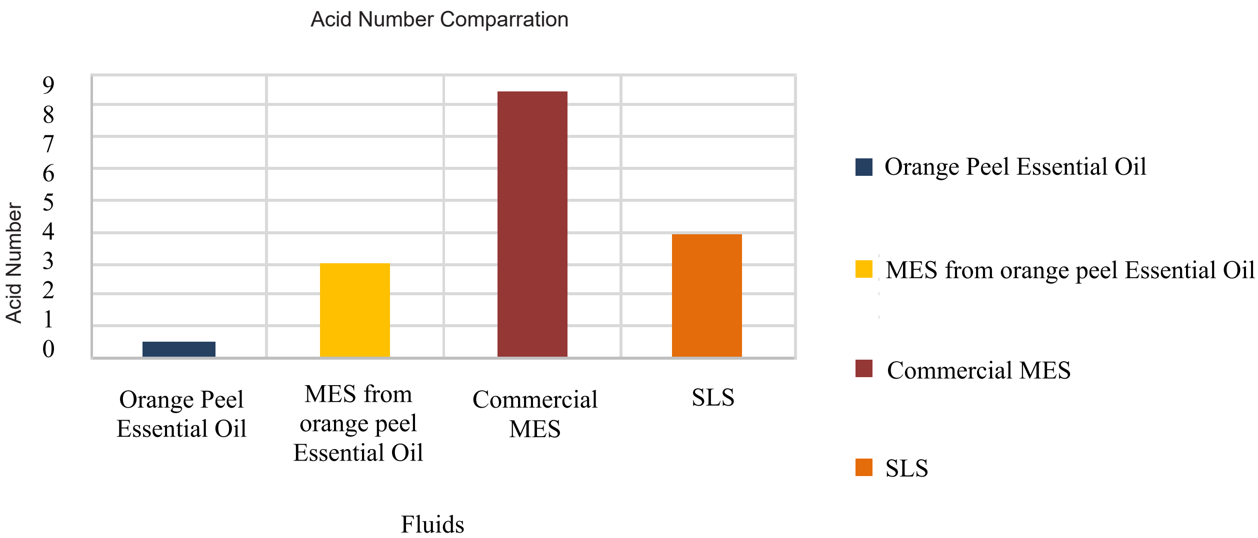

Figure 4
Acid number of the fluids

Compatibility Test

Compatibility tests are utilized to guarantee the stability of a mixture, preventing any potential separation or precipitation that may compromise its efficacy. Surfactants often used in the petroleum world are anionic surfactants resistant to the salinity of the formation water. The injected surfactant must be soluble and stable in reservoir conditions so that the Stability of the solution and thermal stability must be tested because if the answer is unstable such as deposition, it will block the pores of the rock and damage the formation (Muhpidah et al. 2017). Test for compatibility at ambient temperature and 60. The findings of this investigation are presented in Table 1.

Table 1
Compatibility test results of mes from orange peel essential oil.

No	Concentration	*Aqueous Stability*	*Thermal Stability (60˚C)*
1	0.1 %	Clear	Clear
2	0.3 %	Cloudy	Cloudy
3	0.5 %	Cloudy	Cloudy
4	0.7 %	Cloudy	Cloudy
5	1 %	Cloudy	Cloudy

In this study, the MES solution of the essential oil of orange peel with various concentration scenarios, 0.1%, 0.3%, 0.5%, 0.7%, and 1% in brine with a salinity of 15,000 ppm, resulted in a concentration scenario of 0.1% with 15,000 ppm brine that is excellent due to the solution's transparency. At 15,000 ppm salinity, these concentrations are 0.3%, 0.5%, 0.7%, and 1%, none of which form a suspension or clot. Consequently, it can be concluded that all of the scenarios included in this compatibility test are compatible (Hambali, Suryani & Rivai 2013). The formation of two phases or suspensions during the compatibility test is due to the high polarity of this surfactant. Certain surfactant solutions are not clear or cloudy, but that does not mean they cannot be injected (Sugihardjo & Eni 2022).

CONCLUSION

The MES of orange peel essential oil analyzed in this study was included in the initial screening as an alternative surfactant because the values from testing the four initial characteristics were close to the values of the commercial MES and SLS characteristic tests that had been tested by other researchers before. However, to be able to become an alternative surfactant that is applied at the EOR production stage in the petroleum world, MES from orange peel essential oil needs to be continued in further research so that MES from orange peel essential oil becomes a surfactant that can be implemented in tertiary or often tertiary oil production, called Enhanced Oil Recovery (EOR) in the Oil and Gas Field. This is because this research is in its early stages and is carried out on a laboratory scale.

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GLOSSARY OF TERMS

Symbol	Definition	Unit
EOR	Enhanced Oil Recovery	
MES	Methyl Ester Sulfonate	
ppm	Part per million	
IFT	Interfacial Tension	
pH	Potential Hydrogen	
SLS	Sodium Lauryl Sulfate	
ρ	Density	gr/ml
m'	Mass of the pycnometer filled with MES	gr
m	Mass of the empty pycnometer	gr
v	Volume	ml
$\mu 2$	Viscosity of MES	cP
μ1	Viscosity of fluid	cP
t2	Flow time of MES	Second
t1	Flow time of fluid	Second
NaOH	Natrium Hidroksida	
H_2SO_4	Sulfuric acid	

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