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Biodiesel and Diesel Oil Performance as Carrier for Palm Oil Methyl Ester Sulphonate Surfactant for Application in Oil Well Stimulation in Limestone Reservoir

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Abstract

Formation damage is defined as any type of a process that results in a reduction of the fluid flow from the reservoir into formation which causes a decrease permeability reservoir and the performance of wells. Oil well Stimulation technique can be used as an alternative to solve the formation damage. Oil well stimulation technique requires applying of surfactant that can reduce surface tension and interfacial surface tension, preventing from emulsion blocking, and wettability alteration to water-wet. Methyl Ester Sulphonate (MES) Surfactant of palm oil is an anionic surfactant derived from renewable natural resources that environmental friendly. In its application, the surfactant requires the carrier. This paper provides a brief discussion of the mechanism of the use of diesel and biodiesel as a carrier. The results showed that both the carrier can be used as

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a good carrier in oil well stimulation activities in limestone reservoir in OK field, and the formulation are MES 1% in the biodiesel carrier or MES 5% diesel carrier.

Keywords: Oil Well Stimulation; MES; Palm Oil; diesel; biodiesel.

1. Introduction

The oil drain often faces the problem that caused the decline in the productivity of oil wells. One cause of the decline in oil productivity is due to formation damage [1]. Formation damage or oil wells formation damage is a process that destructive for reservoir permeability that result in reduced fluid flow from reservoir to the production wells formation or injection wells, where the damage is caused by plugging the bore well, perforation holes, or formation around the perforation holes. One alternative to prevent, reduce or overcome the formation damage is the stimulation of oil wells (well stimulation).

Well stimulation or stimulation of oil wells is one way to improve the productivity of oil wells. Stimulation method that can be done is by injecting chemicals substance or known as chemical stimulation. Chemical stimulation is defined as stimulate efforts of oil well by injecting chemicals substance to produce optimum oil from estimated quite potential reserves. The commonly used chemical substance is addition of surfactants, acids, salts and solvents [2].

Surfactant (surface active agent) is a substance with active surfaces that can reduce interfacial tension between oil and water due to amphifilik structure, namely the existence of two groups that have different degrees of polarity in the same molecule. Hydrophilic group is easily soluble in water, while the hydrophobic group are soluble in oil [1]. Surfactants can lower the interfacial tension among fluid, the fluid with rock, and fluid with hydrocarbons. In addition, surfactant can break the surface tension of oil emulsion bound with rocks (emulsion block), reducing the occurrence of water blocking and change rock wettability became water wet. Under such conditions, oil becomes easy flowing and thus water cut can be reduced.

Surfactant which has been widely used in the petroleum industry is petrochemical-based surfactants. This surfactant produced from petroleum derived products that currently more limited in number, therefore it need surfactant-based renewable resources and performed well, such as Methyl Ester Sulphonate (MES) surfactant. Methyl Ester Sulphonate Surfactant that synthesized from palm oil is an alternative that can be used for oil well stimulation. Utilization of palm oil into MES surfactant can be done considering the content of C16 and C18 fatty acids (palmitic acid, stearic acid, and oleic acid) has excellent detergency properties. In addition, the MES surfactant has an advantage over petrochemical-based surfactants, such as: lower production cost (around 57%) than petrochemical-based surfactants (linear alkilbenzen sulphonate, LAS), good dispersion characteristics, good detergency properties especially at hard water, resistant to high temperature, soluble in organic solvents and inorganic [3]. Due to these properties, then the MES surfactant can be applied as oil well stimulation for damaged petroleum wells.

Utilization of surfactants as oil well stimulation requires a media agent (carrier). Carrier media in well stimulation usually is diesel oil. This carrier is used to remove asphaltene sediment. Besides require carrier, Surfactants as oil stimulation agent, also required an additives selection. Additives selection was conducted to determine the best type and concentration of additives that soluble in oil as oilbase stimulation agent. Each of these additives are added in the oilbase surfactant formula and have their respective functions, such as the addition of salt (NaCl) is used to obtain optimal salinity so that the value of interfacial tension is low; addition of aromatic solvents useful for dissolving aspaltene and paraffin sediment on formation. After the addition of additives, performance test will be performed for produced oilbase surfactant formula. Performance test consisted of thermal stability test, wettability test and behavior phase test.

This research was aimed to obtain information of the best carrier for palm oil based MES surfactant for oil well stimulation applications in limestone reservoir in OK Oil Field.

2. Material and Method

2.1. Materials

Materials used in this study are methyl ester sulphonate surfactant made from palm oil, fluid samples from OK Oil Field, biodiesel and diesel. Research's instrument consisted of vortex mixer, hotplate stirrer, purification tanks, thermometers, analytical balance, glassware, pipettes, and oven. Spinning drop interfacial tensiometer and pH meters was used for analysis.

2.2. Methods

The research is divided into several stages namely MES surfactant production process from palm oil, performance analysis and test for the resulting MES surfactant, MES surfactant formulations for application in oil well stimulation and performance test of surfactant formula for applications in oil well stimulation.

Production process of MES surfactant from palm oil

Palm oil is the base ingredient for methyl ester production as raw material for MES anionic surfactant production. Methyl ester olein obtained through transesterification process that produces methyl ester and glycerol. Methyl esters were separated from glycerol and purified from impurities. Then, MES anionic surfactant will be synthesized by sulfonation of palm oil methyl ester with SO_3 reactants gas. MES anionic surfactant made based on technology production processes that have been developed by SBRC-IPB researchers team with process conditions adapted to the application of oil well stimulation

Analysis and Performance test of MES Anionic Surfactant

Produced MES Anionic surfactant then analyzed for physico-chemical properties to determine the suitability of the application for oil well stimulation. Test was conducted on the iodine number, acid number, the active ingredient, viscosity, pH and the value of interfacial tension, and density

Surfactant Formulations for Well Stimulation Applications

At this stage, the MES-based surfactant formulations and additives at certain concen-trations using diesel and biodiesel as carrier. The analysis is interfacial tension test/IFT. The selected best formulation is formula that able to provide the lowest fluid interfacial tension

Performance Test of MES Surfactant Formula for Well Stimulation Applications

Performance test of surfactant formula for application in oil well stimulation are include: heat resistance test, interfacial tension test (IFT), wettability test and behavior phase test.

3. Result and Discussion

3.1. Production Process of MES surfactant from Palm Oil

Palm oil raw material used in this study is the fraction of olein. Palm olein is liquid fraction of palm oil fractionation results that have been purified. Palm olein was selected as raw material because fatty acid constituent composition of palm olein is dominated of long chain carbon ($C_{16:0}$, $C_{18:1}$). The longer lipophilic carbon chain on surfactant molecules structure then the possibility of the surfactant more soluble to oil will be greater and with active group to bind to the fraction of water causes both surfactant solubility in oil or water getting better.

Table 1: Analysis result of palm oil methyl ester

Analysis	Units	Result
Free Fatty Acid	%	0.13
Acid value	mg KOH/g	0.94
Iodine number	mg Iod/g	61.77
Saponification number	mg KOH/g	207.63
Density	g cm^{-3}	0.8718
Viscosity (29 ^{o}C)	cP	-
Water content	%	0.13
Total Glycerine	%-massa	0.06
Esters	%-massa	95.55

Methyl esters are produced by transesterification process, that is triglycerides reaction process with alcohol using alkaline catalyst to produce alkyl esters of fatty acids and glycerol. Based on the analysis of free fatty acids, it is known that the free fatty acid content in palm oil raw materials is less than 2%. Due to the reason, conversion of palm oil into methyl ester is only use one stage of the reaction, namely transesterification process. In transesterification process, methanol is added as much as 15% (v/v) of the total palm oil raw materials to be processed and mixed with KOH as much as 1% (v/v) of the total to form methoxide solution. Then palm oil and methoxide solution mixed in transesterification reactor. Transesterification process lasted for 1 hour, at a temperature of 60 °C with stirring. Then, the process of settling was conducted to separate crude methyl ester and glycerol produced. The next step is washing process of crude methyl ester to eliminate impurities material such as soap residue, catalyst, glycerol residue, and and others. The washing process is done using warm water 30% (v/v) of the total crude methyl ester to be purified, which is performed three times. The last process is drying to reduce moisture content and methanol which still contained in methyl ester to produce pure methyl ester. The analysis results of physicochemical properties of palm oil methyl ester (ME) is presented in Table 1. The produced metil esters then synthesized into MES surfactant by reacting methyl esters of palm olein with SO_3 gas reactants using Falling Film Sulfonation Reactor. In general, the MES surfactant products is dark blackish.

3.2. Analysis and Performance Test of Produced MES Anionic Surfactants

MES anionic surfactant of palm oil is then analyzed for physico-chemical properties to determine the suitability for application in oil well stimulation. MES analysis results are presented in Table 2.

Table 2: Analysis result of MES surfactant

Analysis	Units	Result
Acid value	ml NaOH/g sample	7. 47
Iodine number	mg iod/g sample	35.55
Active content	%	12.54
Density	g cm^{-3}	0.91735
Viscosity	cP	1.92
pH		7±0.2
Foam stability		50%

Iodine number is a measure of the average number of unsaturated components of the oil or fat that expressed in weight of iodine, which is the number of milligrams of iodine absorbed per gram of sample [4]. Iodine number is one indicator to determine the successful addition of sulphonate group in the methyl ester carbon chain. Iodine number obtained from the analysis is 35.55 mg iodine/g sample.

The active ingredient is one of the parameters that indicate the quality of surfactant. If the active ingredient is high, then the performance of surfactant will be good. Active ingredient testing method is a two-phase titration method or EPTON methods. The principle of this test is the active ingredient titration of anionic using cationic surfactants with methylene blue indicator.

Viscosity is a measure of fluid viscosity that states the size of friction in the fluid. Mass density is a measurement of mass per unit volume. pH value is used to express the degree of acidity or alkalinity of a solution. pH is defined as kologaritma activity of dissolved hydrogen ions (H^+). MES pH value was 7 ± 0.2.

3.3. Surfactant Formulations for Well Stimulation Applications

The formulation process begins by dissolving the surfactant on organic and inorganic carrier, namely diesel and biodiesel. Determination of surfactant concentration is done by dissolving surfactant in the carrier (diesel and biodiesel) as a carrier agent in the formulation. MES with a concentration of 0 to 6% is dissolved in the carrier medium (diesel and biodiesel), stirred using stirrer for 1 hour then measuring the interfacial tension between the surfactant formula with water field formation OK. This is done to observe response of interfacial tension between water formation with the carrier that is used after the addition of surfactant. Relationship graph between MES in the diesel and biodiesel carrier with interfacial tension (IFT) presented in Figure 1.

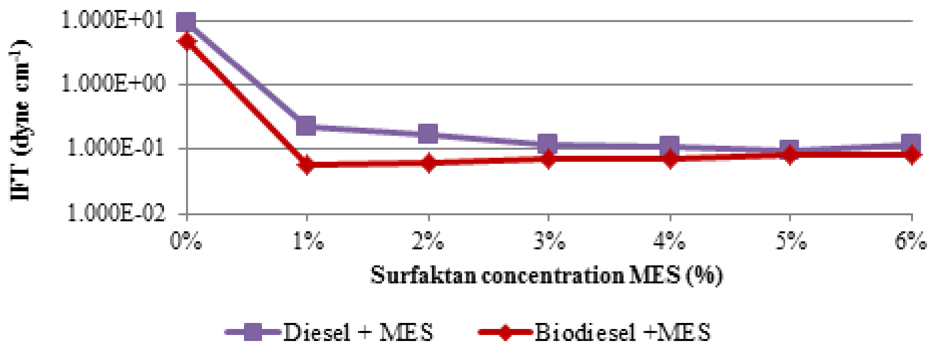


Figure 1: IFT Value at various surfactant concentrations with oilbase carrier in limestone reservoir in OK field

Figure 1 shows that the IFT value generated by the surfactant in diesel carrier experiencing concentration decrease from 0 to 5 percent, where the higher the concentration of surfactant, the lower IFT values obtained and the opposite occurs in surfactant with biodiesel carrier. The lowest IFT value produced from surfactant with diesel carrier is 5% ie $7.164x10^{-2}$ dyne cm^{-1} whereas the optimum concentration of MES on biodiesel carrier is at concentration of 1% with IFT value $6.257x10^{-2}$ dyne cm^{-1}.

Optimal salinity is required to get very low oil-water interfacial tension value. Therefore, NaCl addition test is performed to reduce the interfacial tension value of surfactant formula for oil well stimulation. This test is done by adding NaCl to formation water of each of wells as much as 1.0%.

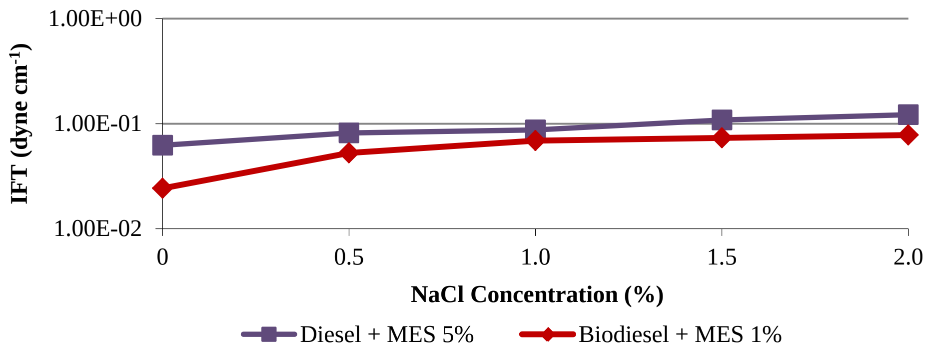


Figure 2: Effect of NaCl addition of in limestone reservoir formations water in OK Fields on IFT value of 5% surfactant formula with biodiesel and diesel carrier

Figure 2 shows that the addition of NaCl as much as 1% to water formation OK field against MES surfactant

5% with diesel or biodiesel carrier cannot lower the value of interfacial tension of surfactant formula. This is maybe caused by high salinity of water formation in OK field that reaches 23 000 ppm, that exceeding the optimum salinity of MES surfactant namely 10 000 ppm. In addition, as showed at Table 3, the highest ion content is sodium ions (Na^+) and chloride ions (Cl^-). Both of these ions can react to form NaCl, so that the levels of salt in injection water and OK field formations high enough and also cause no decrease in interfacial tension of surfactant formula.

Table 3: Analysis results of water formation in OK field

Parameter	OK brine water	OK water injection	Unit
pH	7.2	8.0	-
Turbidity	5.95	3.68	Pt Co
TSS	48	28	mg L^{-1}
TDS	21190	19990	mg L^{-1}
Conductifity	24.95	21.95	mΩ cm^{-1}
Salinitas	23.0	22.6	ppt
Hardness, $CaCO_3$	832.67	860.69	mg L^{-1}
Chloride, Cl	19421.46	19005.03	mg L^{-1}
Ammonia, NH_3	25.80	24.11	mg L^{-1}
Sulphate, SO_4	72.79	108.01	mg L^{-1}
Free Clorin, Cl_2	<0.01	<0.01	mg L^{-1}
Phenol	0.10	0.09	mg L^{-1}
Oil & Grease	59.0	19	mg L^{-1}
BOD_5	20.83	11.53	mg L^{-1}
COD	155.98	77.99	mg L^{-1}
Barium, Ba	150.13	20.88	mg L^{-1}
Iron, Fe	1.31	0.75	mg L^{-1}
Sodium, Na	2828.57	5842.38	mg L^{-1}
Magnesium, Mg	39.08	36.73	mg L^{-1}
Calcium, Ca	171.16	207.32	mg L^{-1}

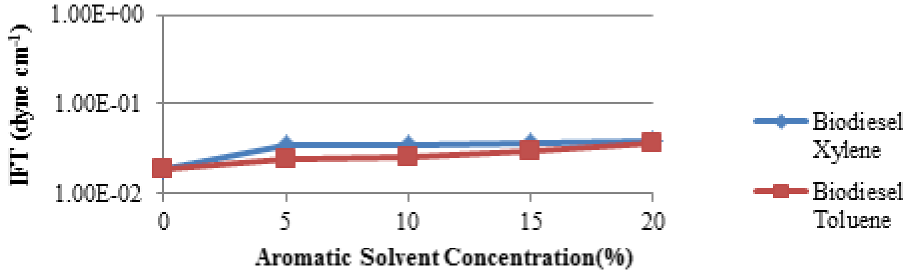


Figure 3: Graph of aromatic solvent effect on IFT value on biodiesel carrier

Asphaltene has insoluble properties in straight-chain hydrocarbons such as diesel and kerosene [1]. Aromatic solvents that have a good ability to dissolve asphaltene are toluene and xylene. According to [5], aromatic solvent that has a good ability to dissolve asphaltene is toluene and xylene. Toluene and xylene also has the ability to dissolve paraffin which may also precipitate together with asphaltene. Aromatic solvents are mixed into the formulation is toluene and xylene. Formula with optimal MES concentrations is mixed with various concentrations of aromatic solvents i.e 5, 10, and 15% and stirred at 40 °C. Parameters determine the best concentration of aromatic solvent is interfacial tension. The measurement results of the effect of aromatic solvent addition with IFT values on diesel and biodiesel carrier can be seen in Figures 3 and 4.

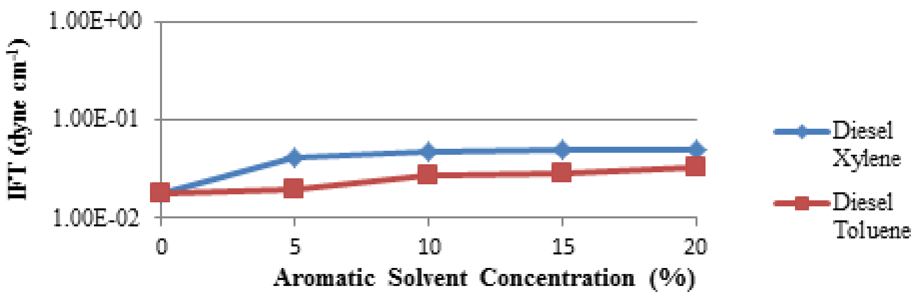


Figure 4: Graph of aromatic solvent effect on IFT value on diesel carrier

Figure 3 shows that at limestone reservoir in OK field, the addition of aromatic solvents on MES surfactant oilbase formula with diesel and biodiesel carrier able to increase the IFT value and it is not good to use surfactant formula as oil well stimulation agent. This increase may be related to low aspalthene contained in. Analysis result of crude oil in OK field showed that visually the oil is liquid and solid black. Asphaltene content in OK oil accounted for 6% or around 0.06 grams per gram of oil samples, indicating the amount of asphaltene contained in the oil is quite low (Table 4).

Table 4: Analysis results of OK oil

Analysis	Units	Result
Form (at temperature room)	-	Liquid
Color	-	Black
Asphaltene	g/g sample	0.0681
Density	g/cm^3	0.8662
API Gravity 15 ^{0}C	^{0}	24.89
API Specific Grafity	^{0}	0.9048
Viscosity	cP	1.40

3.4. Performance Test of MES Surfactant Formula for Well Stimulation Applications

Surfactant formula that produced as oil well stimulation is formula MES 1% with biodiesel carrier (Biodiesel +

MES 1%) and formula MES 5% with solar carrier (Diesel + MES 5%). The two formulas then tested for the performance. Surfactant formula with the best MES concentrations, optimal salinity and the best aromatic solvent concentration can be indicated by performance in changing the wetting properties of rock, the formation of emulsions, and endurance formula in hot temperatures. The tests are including heat resistance, wettability, and phase behavior.

Thermal Stability Test

Thermal stability test carried out by heating the oil base surfactant formula at reservoir temperature, 121 °C, for seven days in the oven. Surfactants formula are expected able to maintain interfacial tension (IFT) value for seventh day or at least still at 10^{-2} dyne cm-1. Observation was carried out daily on surfactant solution and measurement of interfacial tension value. These observations were made to see the trend of changes in the value of interfacial tension that occurs during heating at reservoir temperature. The analysis results of surfactants interfacial tension with biodiesel and diesel carrier after thermal stability testing can be seen in Figure 5.

Figure 5 shows that oil base surfactant formula with biodiesel or diesel carrier, until the third day still able to maintain the value of IFT, and after the third day of an increase in the IFT value. The increase in temperature to near the temperature of the reservoir is effective in lowering the value of IFT [6].

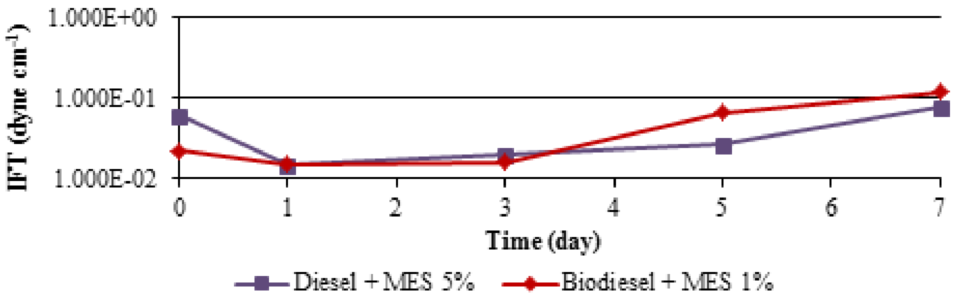


Figure 5: Graph of thermal stability test on oilbase surfactant formula in limestone reservoir of OK Field

Phase Behavior Test

Phase behavior test was intended to see the performance of the oil base surfactant solution with water fluid formations of limestone reservoir of OK field. In the process of oil well stimulation, surfactant solution is injected into the well, then soaking for some time and after that the surfactant solution and the fluid from the reservoir is pumped back through the same well. Visually observations were made by looking at changes in the surfactant mixture of oil base with formation water fluid in OK field.

Stages of phase behavior testing is the formation water sample and surfactant solution which has been prepared inserted into 50 ml threaded tube with ratio between oil base surfactant samples: formation water is 80:20. Then the sample was kept in the oven according to the reservoir temperature (121°C) for 60 minutes. After that the rotary mixing turned on with a speed of 6 rpm for 1 h at reservoir temperature (121°C). After mixing process for 1 hour, the sample is removed and stored at a temperature of 60°C and taken the photos (calculated as the observations for 0 hour. Photo was taken back after 10, 60, 120, 240, 720, 1440, and 2880 minutes. The results of analysis of phase behavior of surfactant formula was presented in Figure 6 dan Table 5.

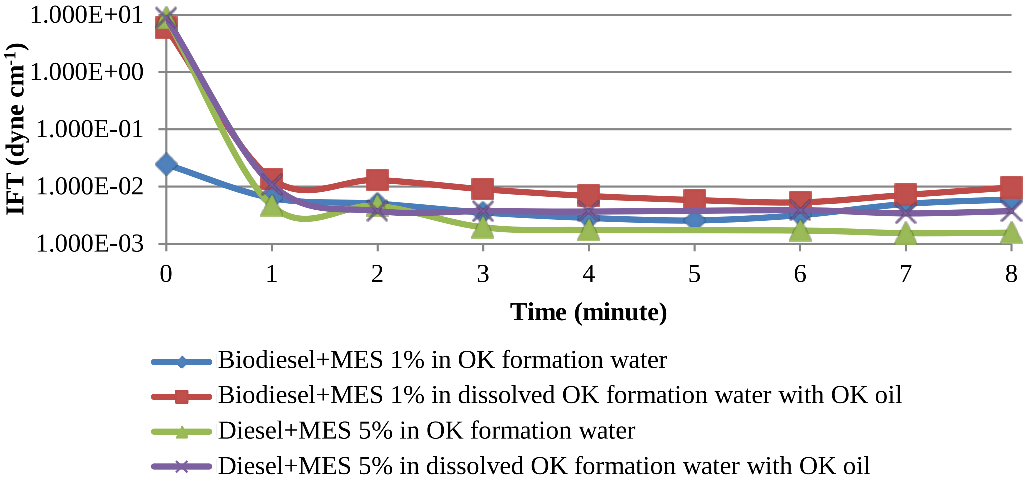
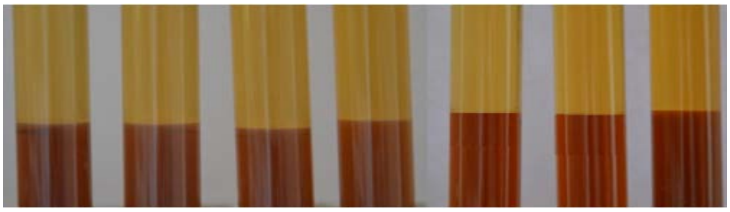
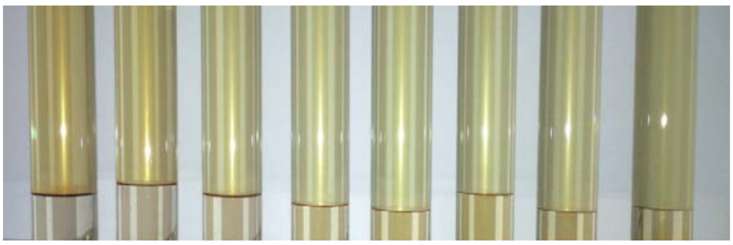


Figure 6: Graph of phase behavior test on oilbase surfactant formula in limestone reservoir in OK Field

Table 4: Results of phase behavior test on oil base formula formula in limestone reservoir in OK Field

Formula	Picture
Diesel + MES 5%	 **10 min 1 hr 2 hr 4 hr 12 hr 24 hr 48 hr**
Biodiesel + MES 1%	 **10 min 1 hr 2 hr 4 hr 6 hr 12 hr 24 hr 48 hr**

4. Conclusions and Recommendation

From the research, it can be concluded that biodiesel carrier can be used as an alternative to diesel carrier in oil well stimulation in limestone reservoir tin OK field. MES surfactant concentration used as well stimulation agent is 1% formulated with biodiesel carrier or 5% MES surfactant formulated with diesel carrier, as shown from the results of formula performance test, where up to a third day of thermal stability test, both oil base formulas with biodiesel and diesel carrier are able to maintain the IFT value, and in phase behavior test, up to 48 hours of observation time, does not form an emulsion and IFT values can still be maintained up to 10^{-3} dyne/cm.

The research was conducted by comparing the carrier biodiesel with diesel as a carrier commonly used in oil well cleaning activity. The availability of biodiesel in the oil field is still difficult to obtain, so the oil industry needs other alternative carrier with environmentally friendly as the solution.

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