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Evaluating the Stability of Emulsion Fluid Synthesized with Palm Oil Mill Waste for Enhancement of Hydrocarbon Withdrawal from Niger Delta Oil Fields

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ABSTRACT

The economic withdrawal of oil and gas from the Niger Delta oil wells has given rise to a lot of wells being abandoned as production declined to below the economic limit. Tertiary recovery of the remnant oil will demand a strategy to squeeze the remnant oil locked in the pores of the reservoir formation. One such technique is emulsion flooding. This paper evaluates the stability of a locally formulated emulsion fluid synthesized from the waste (palm oil mill effluent, and empty palm fruit bunch) of the palm oil mill industry. The palm oil mill effluent and empty palm fruit bunch were characterized using Gas Chromatography - Mass Spectroscope, the oil component as indicated from the characterization was extracted using a centrifuge and separating funnel. The empty fruit bunch was burnt in an open space, and the ash was further homogenized using an electric blender. 350g of the ash was dissolved in 500 ml of distilled water, and the solution after thorough stirring, was filtered to remove undissolved particles. The oil extracted from the palm oil mill effluent, and the ash solution were mixed in a ratio of 30/70 and stirred vigorously to form emulsion fluid. The emulsion was evaluated for stability through visual observation, centrifugal test by varying the temperature from 30oc to 100oc with the RPM varied from 1000 to 1200, the interfacial tension between oil /ash solution of the emulsion fluid, shear stress determination, and droplet size distribution analysis. The result showed emulsion stability (%) of 100%, 99.5%, 99.2%, 98.8%, 98.3%, 97%, 96%, and 96% for temperature (oc) of 30, 40, 50, 60,70,80,90 respectively. The analysis indicated that the emulsion sample has low interfacial tension, and moderate viscosity, and it is stable, and suitable for moderate-temperature reservoirs.

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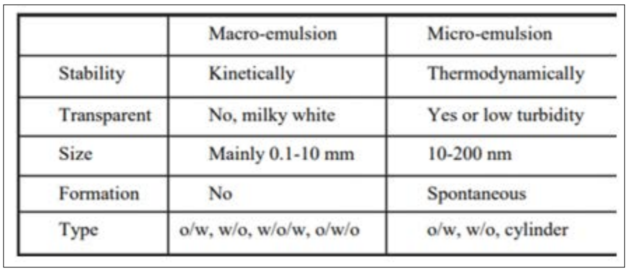
Introduction

Emulsions can be categorized into two varieties namely: micro-emulsion and macro-emulsion. The stability of micro- emulsions are temperature dependent. They have a droplet size of 100nm and are characterized by their low interfacial tension and high power of solubility. Macro-emulsions have larger droplet size, normally greater than 100nm, and have low reaction rate, and resist change due to heat. For a three components of the emulsion system, the micro-emulsion is the counterpart of the macro-emulsion since they both belong to the system but with different characteristics. The study of micro-emulsion began in the late 1960s, encouraged by the long emulsion stability and ultra-low interfacial tension of the micro-emulsion. The petroleum industry started research into the tertiary micro-emulsion recovery method EOR research in the [1].



	Macro-emulsion	Micro-emulsion
Stability	Kinetically	Thermodynamically
Transparent	No, milky white	Yes or low turbidity
Size	Mainly 0.1-10 mm	10-200 nm
Formation	No	Spontaneous
Type	o/w, w/o, w/o/w, o/w/o	o/w, w/o, cylinder

Figure 1: Comparison between Micro-emulsion and Macro-emulsion source Healy et al., (1975)

The viscosity of emulsions increases with increasing water fraction [2]. The rheology properties of emulsions are important factors affecting the swept volume and displacement efficiency. The emulsion behaviors include different characteristics such as newtonian fluid, expansion fluid, pseudoplastic fluid, and viscoelastic fluid [3].

The interfacial rheology method is the most common method for measuring the rheological properties of emulsions. It includes a shear test and an expansion test, and they are used to measure the shear rheological property and expansion rheological property, respectively. The shear test method utilizes a stress rheometer with a double-wall ring geometry [4]. The preparation of a stable emulsion involves the alteration of interfacial behavior by surfactant or/and heavy oil solid grains to prevent its driving force which is responsible for coalescence [5].

Another criterion for stable emulsion formation is that the droplet size must be small enough to allow that the thermal collisions forces acting on the continuous phase molecules to produce Brownian motion which prevents settling [6]. The characteristics of an emulsion constantly vary from the moment of formation to the time of total phase inversion.

Accordingly, fresh emulsions can demonstrate a different characteristic, compared to aged samples. This is attributed to the variation in the oil type due to the presence of absorbable components, differences in emulsifier adsorption rate, and its ability in producing a film at the interface. When the mixture is subjected to a considerable change in the temperature or pressure, the emulsion characteristics such as viscosity or droplet size can alter significantly [7].

[8]. Summarized the current development in emulsion behavior, droplet size distribution, viscosity, rheology and interfacial tension properties of emulsions for enhanced oil recovery. stability of oil-water emulsion depends on the oil content, stability decreases with increase in oil content of the emulsion [9]. The existence of creaming of drops of emulsion phase is as a result of the variation in density between the dispersed and the continuous phases, the rate at which the droplet coalescence depends on factors such as; type of surfactant and it`s concentration, droplet diameter, volume fraction of the dispersed phase [10].

A model relating the droplet stability period and inter-facial properties of emulsion droplet size was developed to evaluate the stability of emulsion as well as the theoretical analysis of alkali-surfactant-polymer concentration effect on the stability of emulsion. The stability of oil-in-water emulsions during ASP flooding were studied using the emulsion stability model (Civan model) based on two-phase separation. The effect of ASP on characteristics of the emulsion was explored by quantitative analysis of film strength and measurement of inter-facial tension, and zeta potential. The results showed that the Civan model is suitable in evaluating the stability of the O/W emulsion.[11].

The surfactant introduced to the oil–water system causes a reduction in surface tension and also adsorption at the interface while forming an interface film with a certain strength, which protects the dispersed phase and makes it difficult to merge after colliding with each other [12]. Solid particles suspended in oil–water systems are also good emulsifiers. A particle emulsifier is the same as the usual surfactants. Adsorption reduces the interfacial area and hence lowers the free energy of the system. Furthermore, unlike surfactant, such particles need not be amphiphilic—the only requirement is that they should be partially wetted by both fluids.[13]. The size and distribution of emulsion droplets have a great influence on the stability of the emulsion. Broadly, emulsion stability is directly proportional to the droplet size.[14].

An experimentally investigation on the effects of process factors on emulsion stability was carried out on an emulsion sample prepared by using 100 ml colloid mill with sorbitan monooleate (SM) as emulsifier. The factors investigated were, ratio of oil/water, stirring intensity, emulsifier dosage, emulsifying temperature and mixing time. The results showed that the most influencing variables are: emulsifier dosage, 0.5%; oil/water ratio, 1:1; stirring intensity, 2500 rpm; and mixing temperature, 30°C [15].

Different water ratios of water-in-heavy-oil (W/O) emulsion samples were prepared with heavy oil from Bohai Bay, China. Mixtures of water-in-oil emulsions and light crude oil samples with various mixing ratio (1:9, 2:8, 3:7) were studied, respectively using the electron microscope, and the rheometer. The viscosity of water-in-oil emulsion droplets' distribution obtained were used to evaluate the emulsion stability, and the effect of reduction in viscosity. The outcome of the study indicated that water-in-oil emulsion droplets size distribution range is directly proportional to water ratio in the emulsion [16].

Materials and Methods

The palm oil mill effluent was characterized using the conventional technique of quantitative chemical analysis of heating the sample in a water bath to a temperature 60oC was done by making the sample suitable for AAS analysis. Ten milliliter of the sieved palm oil mill effluent was injected into the graphite furnace cuvette, controlled electrical heating process of the cuvette dried the sample and removed the matrix before atomization, the hollow cathode lamps provided exact elemental output of light focused through the center of the graphite furnace cuvette to activate measurement as atomization was ongoing. The sample was found to contain (oil, sodium, potassium, magnesium, phosphate, calcium, and ammonium). The oil, and water elements of the sample were separated using a separating funnel. Furthermore, ash was obtained from the empty palm fruit bunch by burning the bunch, then blending the ash and finnaly b filtering the ash with a sieve. 350g of the filtered ash was dissolved in 500ml of distilled water to form an ash solution. The oil extracted from the palm oil mill effluent and the ash solution from the empty palm fruit bunch were mixed in a ratio of 30:70, the mixture was stirred vigorously to form an emulsion. The rheology of the formulated emulsion was tested, followed by stability tests using the visual observation, centrifugal test, inter-facial tension test, and droplet size test.

Specific Gravity Determination

A hydrometer was used to determine the specific gravity of the emulsion sample extracted from the palm oil mill effluent,the oil was poured into a 100cc of graduated cylinder, the hydrometer was inserted into the graduated cylinder until the principal floatation was observed. Once the hydrometer became stable, the specific gravity was read from the graduations of the measuring cylinder and the API gravity was computed using the formula below:

$$\mathbf{API} = \frac{141.5}{S.G} - 131.5$$

Density Determination

A digital densimeter (Rudolph`s DDM 2910-Densitometer) was set to gram per milliliter (g/ml) unit of measurement, and immersed in 5ml of the emulsion sample till the entire sensing element become submerged. The densimeter was allowed stabilized and display the density reading.

Viscosity Determination

A viscometer was used to carry out the evaluation. The emulsion sample was sucked into the viscometer at a certain marked level, and was allowed to flow down from the marked level at the recording of a stop watch as T1 in seconds. The process was repeated to get the second reading of Time required in flowing down as T2 in seconds. The mean of the two times recorded was gotten and multiplied with viscometer constant C which is 0.1 to get the actual mean viscosity.

Temperature and pH Determination

The oil was poured in a cylindrical beaker 100cc. A thermometer was inserted into the beaker containing the emulsion sample, and observations were made to where the mercury level stopped. The temperature was recorded as T. cooler change was observed by dipping a litmus paper in the emulsion sample.

Evaluation of Emulsion Stability

Visual Observation

The formulated Emulsions` stability was evaluated by allowing the emulsions to stay seven days (7 days) to observe any signs of separation, creaming or sedimentation.

Centrifugal Test on Formulated Emulsion

Centrifuge applies the force of gravity to accelerate separation of liquid phase in an emulsion. 40ml of the formulated emulsions were respectively poured into the centrifuge tubes and capped with lids while placing the tubes opposite each other in the centrifuge, the tube was balanced correctly, and the lids closed, then placed in a rotor, varied centrifugal temperature of 30oC to 100oC were used to test the thermodynamic effect on emulsion stability, A centrifuge machine was brought and cleaned for use, the machine was connected to a power source and the emulsion samples were poured into the glass wares in the spinning centrifuge and cocked. The centrifuge operation was carried out first at 1200rpm varied in different temperatures of 300C, 40, 50, 60, 70, 80, 90, 100 . Calculation of the emulsion stability, involves the determination of the initial volume of the emulsion and the volume of the separated water at each temperature. the initial volume of the emulsion is 100 mL. From the centrifugal test, the volume of the separated water at each temperature is known. The emulsion stability In percent at ech temperature is calculated:

$$\text{Emulsion Stability (\%)} = \frac{1 - vol\ of\ separated\ water}{initial\ vol.of\ emulsion} * 100$$

Determination of Interfacial Tension Between the Emulsion`s oil and Ash Solution

Spinning drop tensiometry (SDT) is a technique for measuring the interfacial tension between two fluids. In this work, spinning drop tensiometer (Kruss Data Physics) was used to determine the interfacial tension between oil and ash solution used in formulating the emulsion samples. The rotating cylinder and drop information system of the tensiometer were appropriately cleaned and dried, the rotating cylinder was filled with the heavier fluid (Ash Solution) and then a drop of oil was created using the drop information system. The cylinder was rotated at constant speed of 1000RPM, the images of the drop was captured by a high speed camera. Finally the drop length (L), drop width (W), and the ratio aspect (L/W) were measured, then the inter-facial tension (IFT) were calculated using Vonnegut equation:

$$\text{IFT} = \left(\frac{\rho\Delta\omega^{2L^3}}{4\pi^2}\right)$$

Shear Stress Determination

The capillary viscometer method measures shear stress by analyzing the flow of fluids through a narrow capillary tube. In this work the (Ubbelohde viscometer) was used to determine the shear stress of the emulsion sample. This viscometer consists of a narrow cylindrical glass tube (capillary tube), with a uniform diameter (R) and the length (L) a reservoir container to hold fluids and the stop watch to measure flow rate (Q) and a manometer to measure pressure difference (Δp). The reservoir was filled with the emulsion sample, and connected to the capillary tube, the pressured drop, flow rate and temperature were measured. Finally shear rates were calculated using the equation:

Results

The emulsion sample was allowed to stand for seven day, it showed no creaming during this period of visual observation.

Table 1: Rheology of Formulated Emulsion Sample

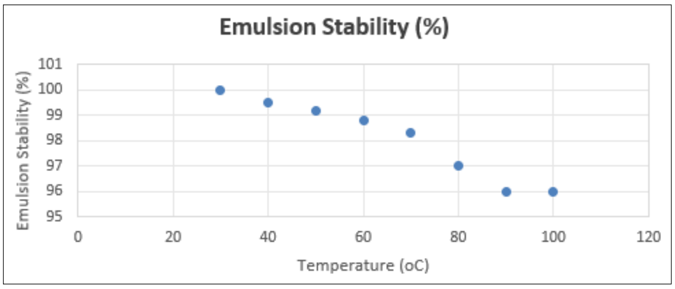
IFT	Density	Viscosity	S.G	API	pH
12.39	0.92	1.70	0.85	34.38	6.9

Table 2: Centrifugal Test of Emulsion Sample

Temp. (oC)	30	40	50	60	70	80	90	100
Water Separation(ml)	0	0.5	0.8	1.2	1.7	3.0	4.0	4.0

Table 3: Emulsion Stability (%) Versus Temperature (Oc)

Temp. (oC)	30	40	50	60	70	80	90	100
Emulsion Stability (%)	100	99.5	99.2	98.8	98.3	97	96	96



Graph 1: Emulsion Stability(%) versus temperature (oc)

Table 4: Shear Stress of Emulsion Samples at Different Shear Rates

Viscosity pa.s	Shear stress@10s-1 shear rate	Shear stress@50s-1 shear rate	Shear stress@100s-1 shear rate
1.70	0.017	0.085	0.17

Table 5: Droplet Size Distribution with Mean, Median and Standard Deviation of the Emulsion Sample

Droplet size	mean	median	Standard deviation
20-40um	20	18	8

Discussion

Centrifugal Test Analysis

The centrifugal test results provide valuable insights into the thermal stability of the emulsion, which is crucial for oil reservoir flooding operations. The emulsion shows excellent stability at 30°C, with no water separation.Water separation increases with temperature, indicating that the emulsion's stability decreases as temperature rises. The rate of water separation increases gradually with temperature, suggesting a gradual degradation of the emulsion's stability. The emulsion's stability appears to degrade significantly above 70°C, with a substantial increase in water separation. The emulsion's stability is acceptable up to 60°C, making it suitable for oil flooding operations in moderate-temperature reservoirs.To maintain emulsion stability, injection temperatures should be kept below 60°C

Inter-Facial Tension (IFT) between Oil and Palm Bunch Ash Solution of Emulsion Samples Analysis

Interfacial Tension (IFT), is a measure of the energy at the interface between two immiscible liquids, such as oil and water. in the context of emulsions, IFT is a critical parameter that influences the stability and behavior of the emulsion. An IFT value of 12.39 mN/m (milliNewtons per meter) is relatively low, which suggests that the emulsion has a moderate to high degree of stability.

Droplet Size Distribution of Emulsion Sample Analysis

The droplet size distribution of an emulsion is a critical factor that influences its stability, texture, and overall performance. The mean and median droplet sizes are relatively close, indicating a fairly symmetrical distribution. This suggests that the emulsion has a consistent droplet size, which is beneficial for stability. A standard deviation of 8 μm indicates a moderate degree of polydispersity (variation in droplet size). This means that while most droplets are around 18-20 μm, there are some larger and smaller droplets present. A moderate symmetrical distribution can be beneficial for stability, as it allows for some flexibility in the droplet size distribution. The range of 20-40 μm indicates that there are some larger droplets present, which can be detrimental to stability.

Larger droplets can cream or sediment more easily, leading to phase separation. However, the droplet size distribution suggests that the emulsion has a moderate degree of stability, the consistent mean and median droplet sizes combined with a moderate symmetrical distribution indicate a relatively stable emulsion.

Shear Stress in Emulsion Sample Analysis

Most emulsions exhibit shear thinning behavior, where shear stress increases with shear rate but at a decreasing rate, (Derkach, S.R 2009., Dickinson, E.2015). This is beneficial for enhanced oil recovery, as it allows the emulsion to maintain its viscosity and flow easily through porous rock formations. Emulsions with higher viscosity tend to have higher shear stresses, indicating stronger resistance to flow. A Viscosity of 1.70 Pa·s,exhibited by the emulsion sample indicates a non-Newtonian fluid with relatively high viscosity. This is beneficial for oil reservoir flooding as it can improve sweep efficiency and oil displacement. Shear stress Increases with shear rate (0.017 @ $10s^{-1}$, 0.085 @ $50s^{-1}$, and 0.17 @ $100s^{-1}$), revealing moderate shear thickening behavior. This suggests the emulsion can maintain its structure under various flow conditions. Based on this, the emulsion sample appears to be stable for flooding oil reservoirs. The high viscosity and moderate shear thickening behavior indicate that the emulsion can reduce fingering and channeling, leading to more efficient oil displacement; the high viscosity and shear thickening behavior can help to displace oil more effectively. the emulsion can maintain its structure under various flow conditions, reducing the likelihood of coalescence or breakdown.

Rheological properties of emulsion sample Analysis

Interfacial Tension (IFT) of 12.39 mN/m is low and indicates better emulsion stability, the emulsion sample density of 0.92 g/cm^3 is close to water density, suggesting high water content emulsion. Viscosity of 1.70 Pa·s (1700 cP) is a moderate viscosity, indicating relatively stable emulsion.The Specific Gravity (SG) of 0.85 is lower than the specific gravity of water, confirming high water content emulsion. The API Gravity of 34.38 shows that the emulsion is light thereby confirming its ability to flow. The pH of 6.9 is a neutral pH indicating minimal impact on emulsion stability. Overall, based on these properties, the emulsion sample appears relatively stable. The low IFT and moderate viscosity contribute to its stability.

Conclusion

- The emulsion sample has shown relative stability based on the results of the analysis.
- The sample has a low inter-facial tension and moderate viscosity.
- The stability evaluation of the emulsion sample indicated that the emulsion ris stable across a range of temperatures with an acceptable decrease in stability at higher temperature
- The emulsion is suitable for flooding a moderate temperature reservoir

Recommendation

Further testing and evaluation under reservoir specific conditions are recommended to confirm the field performance of this emulsion sample

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