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EVALUATING THE EFFECTIVENESS OF DEMULSIFER IN WATER AND OIL EMULSION

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ABSTRACT

This study evaluated the effectiveness of demulsifiers in water and oil emulsion. Emulsified water is for the most part present in unrefined petroleum as an after effect of blending happenings amid production operations. The development of emulsion prompts issues transportation and production. For the purpose of this study three objectives were drawn to guide the study. The main materials used in this project research is the emulsion sample which was obtained from three different oil fields and companies. The study was carried out using four synthetic demulsifiers; Amine bunches (groups), Polyhydric Alcohol, Acid and Polymeric demulsifiers which were utilized for water-in crude oil emulsions demulsification. Finding from the study revealed that the effectiveness of any demulsifier is dependent on the dielectric constant of demulsifier, emulsion sample, PH value of the demulsifier, the HLB of demulsifier and emulsion. The emulsion success comes about because of the nearness of interfacial obstruction inhibiting combination of the scattered water droplets. The study also revealed that the best technique to conquer the issue is to demulsify the crude by utilizing demulsifiers. The demulsifiers will destabilize the interfacial film between the droplets. Demulsifiers with amine and polymeric groups were utilized for breaking of water-in crude oil emulsion, in this study. The relative rate of water partition were resolved through breaker tests. The polymeric group demulsifier performed very well on breaking emulsion than amine group demulsifiers. The study recommends that the methods of evaluating a demulsifier's effectiveness discussed in this project work should be adopted and this involves the derivation of correlation for the efficiency of demulsifier to a particular parameter which is observed to change as emulsion resolution efficiency changes.

KEY WORDS: *Emulsion, Crude oil, Water, demulsifier and solvent.*

1.0 INTRODUCTION

One of the most important tasks of the petroleum industry today is the control of oil field emulsion treatment and prevention. Emulsion can be defined as a combination of two naturally immiscible liquid which are mainly water and oil. A typical emulsion has either water droplet dispersed in oil or oil droplet dispersed in water. (ELF PTM, 1992). Emulsion do not occur naturally, rather, they form in the well bore during the production process crude oil, water and minute particles of fossils, salts, clay, silt and other impurities, gets violently mixed up together as they flow to the surface. During this process of mixing, an emulsion is formed from the violent agitation of the fluids (Frank, 1973). Figure 1 shows what happens as fluid flows through a construction in a tubing string, the same phenomenon is obtainable during petroleum production.

The stability of the emulsion is determined by the type of emulsifying agent present, which are chemical substances that keep the mixture of oil and water in an emulsified form. These substances are at times dissolved or suspended in formation waters (Evans, 1996). It is important to note that not all water mixed up with the oil is required for the formation of emulsion. Thus, after the emulsion has been formed, water is left at the base called FREE WATER. Emulsion causes damages mainly corrosion of surface production equipment, refinery equipment, well head components and scaling of water. Crude oil emulsion has poor market value because of its high water content. Emulsion treatment is very important for production engineers, and has necessitated the setting up of different treatment plants designed to take care of emulsion problems.

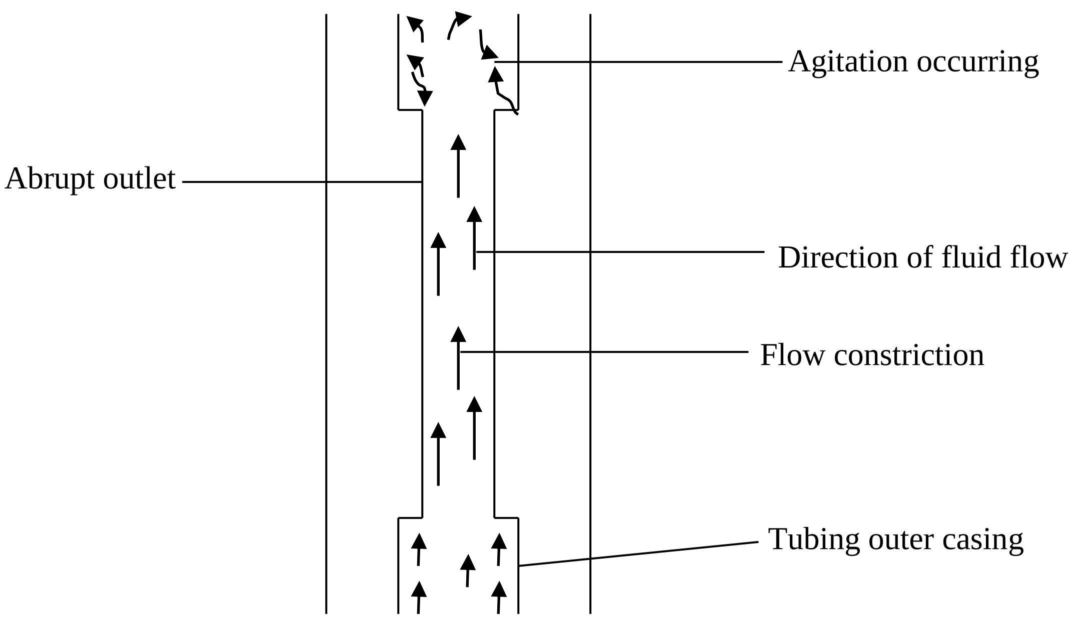

Fig. 1: Fluid flow through a tubing string

Over the years, different ways of resolving emulsions have been developed. (APES, 1974). Heat treatment, gravity settling methods or a combination of two or more methods. As for back as the 19th century, crude emulsion was called "Cut Oil" and the only way to treat them was the use of heat, but this method did not prove satisfactory enough. As years went by, different treatment method where adopted to complement the heating process. Emulsion treatment using chemicals (demulsifiers) has proven to be the most effective way of solving the emulsion problems. In Nigeria, different demulsifiers have been introduce to march different crude oil emulsions and they are known by their trade names such as: SERVOCC6002, SERVOCC PRODEC-EMBX-7, TEROLITE, HOECHEST, SEPAROL, BODAC, BORITE ISOBUTY ALCOHOL, and D9090. E.T.C., some are locally made while others are imported (Graham, 1980, Mkpadi & Okonkwo 1986).

Demulsifiers are so far the best solutions to emulsion problems but sometimes, they fail to perform leading to:

1) Corrosion of surface production equipment
2) Damaging refining equipment or well head components and
3) Scaling of water

Demulsifiers, by nature of their chemical make-up distort the equilibrium in a typical emulsion. As a results of this, water and oil assume different phases, although this does not always occur since some demuslifiers are very inactive in crude oil emulsion. The reason for this is that the emulsifying agent may not be compatible with the demulsifier used. It is a fact that emulsifying agent statbilzes the emulsion and so any manufactured demsulsifier should attack it directly. Where the emulsifier is successful, it alters the chemical nature of the emulsifying agent to function as a demulsifying agent. This only occurs when the emulsifier being applied, correctly matches or is in some way compactable with the emulsifying agent. Emulsifying agents have been discovered to change with time, thus the emulsifying agent in a particular filed could be calcium salt at another time it could be Kalonite or other metallic salts (Frank 1973). A clear evidence of a change in the emulsifying agent is seen when an emulsifier selected to effectively treat an emulsion from a field suddenly becomes efficient, when this happens, a fresh screaming and ranking exercise is carried out in other to select a better demulsifiers. This is done empirically, where every single demuslsifiers is subjected to a series of test until the optimum is identified.

This wastes time and money and a number of times, wrong selections have been made. It is thus necessary to come up with a faster and more reliable means of determining the most efficient demuslsifier for a particular oil field emulsion and a means of knowing the composition of the emulsifying agent at the same time. This research is aimed at introducing a more reliable method of determining the most effective demulsifier to use in a particular oil field emulsion by evaluating the effectives of demulsifier on water and oil emulsion.

2.0 LITERATURE REVIEW

Emulsion Theory

Emulsion are stable mixtures of oil and water in which one is dispersed in the other. Oil and water are immiscible liquids having different size grade phases, with the finer size grade of the dispersed phase more stable in the emulsion (APES, 1974).

There are basically two types of emulsions:

i) The water dispersed in oil (water in oil emulsion).
ii) The oil dispersed in water (oil in water emulsion).

In the water in oil emulsion, water is the dispersed medium while oil is the continuous medium, as seen in fresh untreated crude oil which comes to the surface emulsified with the formation water. Other examples are vegetable oils for cooking and oil based drilling fluids (Krik, 1979).

Crude oil emulsions contain strong natural surfactants in minute amounts which gives stability to the emulsion. These surfactants migrate from the oil to the oil water inter-phase. When the emulsion is stored over a period of time without being treated, it begins to age. This ageing is as a result of the formation of fines and crystals emulseded in the rigid interfacial skin which makes the emulsion grow strong. When an emulsion ages, it means it becomes more stable and more difficult to resolve (Kwant, 1975).

A stable emulsion is one that cannot easily be resolved or broken but remains unresolved by gravity settling after a 24 hours period (Mkpàdi and Iniodi, 1985). Breaking an emulsion, means separating the water from the oil by physical or chemical methods.

Factors Affecting Emulsion Stability

The stability of crude oil emulsion depends on the following (Mkpadi and Iniodi, 1985):

1) The properties of the oil
2) The amount of water in the crude
3) The salinity of the produced water
4) The type of emulsifying agent.
5) Shear history.

Property of the Oil

The density of crude oil are measured in API units. With respect to API gravities, the crude oils are classified into three groups. The heavy, the medium and the light crude. The heavy crude has an API of below 20, medium above 27 and light crude between 35 and 44.

Heavy crude produce less stable emulsion and are required to be heated to obtain good dehydration. Medium crude produce emulsion which are not stable as those produced by heavy crude. Light crude are even easier because of their low viscosity.

Water in Crude

Emulsions are stable at low water cuts (5%). Above 30%, the water present is known as “free-water” because, it settled out of the emulsion on its own without external influences. This means that the higher the water cut, the less stable the emulsion (Frank, 1973).

Salinity of Produced Water

Highly saline formation water helps stable emulsions to form during production. As earlier mentioned, these water contains surfactants and other salts which when mixed with the oil, causes the water molecules to be strongly attracted to the oil molecule.

Type of Emulsifying Agent

The type of emulsifying agent present in an emulsion, plays a major role in its degree of stability. Emulsifying agents associated with crude oil emulsions are, lines of clays, inorganic salt compounds and fossil fines (Evans, 1996).

Emulsification

Emulsification is the process, by which oil, water and some impurities are vigorously mixed together to form a stable mixture (APES, 1974). The stability of the mixture is enhanced by an emulsifier. An emulsifier is a surfactant (Surface Acting Agent). It is a substance possessing dual solubility, thus part of it is water soluble-and the other is oil soluble.

Examples of emulsifiers are drilling muds, napthenic acids, and aromatic compounds. In the process of emulsification, the emulsifiers make it possible for the fluid in the non-continuous phase (in water) to diffuse into the continuous phase fluid (oil).

Demulsification

Demulsification is a term used to explain resolution of crude oil emulsion using demulsifiers. It is simply emulsion resolution with chemicals. A demulsifier is a 30-50% solution of active material in an organic solvent (Kwant, 1975). Demulsifiers are also defined as (Surfactants) surface-active-agents which reduce the surface of an emulsion to the original surface tension of oil and water and thus separating the two.

The organic solvent has two functions:

1) It reduces the viscosity of the pure demulsifiers so that it can be easily injected in the flow stream.
2) To form a solution with the demulsifier so that it does not separate into its original components by gravity effects (Kwant, 1975).

There are three basic types of demulsiflers namely:

1) The nonionic demulsifiers e.g. phenol, polyethers
2) The cationic demulsifiers e.g. sulphates
3) The anionic demulsifiers e.g. oxylates

The process of demulsification is simply the action of a demulsifier in a crude oil emulsion. After the application of the chemical, enough mixing energy is applied to the mixture which helps it to migrate from the continuous phase to the oil-water inter-phase of separate parts of the molecule (Oil and water molecule).

The chemical absorbs in their inter-phase, thereby resulting in the displacement of the naturally present emulsifier. A concentration then develops which causes a local higher surface tension and this causes the inter-phase to swell and burst.

Two steps are identified in this process.

i) Floccualtion: Disperse water droplets forms clusters in the oil medium.
ii) Coalescense: Clustered water droplets merge together to form bigger droplets. This is a process that affords settling out of larger water droplets by gravity effect. Coalesance will only occur if two or more unstable water droplets merge together to form a single larger droplet.

The prerequisites for coalescence are:

1) The emulsion should be in motion and
2) Demulsifier must be present

Demulsifier Application

There is no simple designation of specific demulsifier for the treatment of specific emulsions but there are some demulsifiers that give consistent results when applied, such as:

i) Polyglycol Esters: They are characterized by quick brightening of the emulsion but frequently tends towards slower water droplets coalescence.
ii) Low Molecular Weight: They generally show good demulsificant properties and rapid water settling.
iii) Sulphonates: They show fair water droplet performance.

The limiting factors in these results are that the same conditions under which these chemicals were applied must be maintained and demulsifier chemicals are not know by chemical compositions. Thus, it will be extremely difficult to identify a demulsifier.

Demulsifiers are applied in specific quantities to emulsion samples. Some emulsion requires more than others for effective results. Applying the correct dose of chemical to the emulsion will lead to selecting the optimum chemical to be used for a particular emulsion as long as application conditions are maintained. For the selection of the optimum chemical, the improved bottle test will be used. A representative sample of fluid is taken and transferred into several test bottles. Several demulsifying chemicals are added to the emulsion to determine which chemical will best treat a given emulsion. The optimum chemical will provide the clearest, separation of oil and water (the sharpest inter-phase) at lowest temperature and lowest cost per barrel treated.

3.0 METHODOLOGY

Laboratory analysis was carried out using emulsion samples and demulsifiers.

MATERIALS

The materials used in this research are emulsion sample obtained from different oil fields and companies in Niger Delta, Nigeria labelled as Sample A,B and C, and three demuldifiers.

The demulsifiers used are:

Demulsifier 1 – Isobutyl alcohol
Demulsifier 2 – D9096
Demulsifier 3 – Tetrolite
Xylene solvent was used as dilutant for the concentrated demulsifiers samples.

Experiment 1: Measurement of pH

Apparatus

pH – Meter (electrometric)
Prob (Electrode)

Procedure

The crude oil sample was put in a 50ml beaker and it was placed in the pH meter. After which the prob was standardized with buffer 4 solution to boost the strength of the electrode and to ensure accurate sensitivity. The prob was then inserted into the emulsion sample and the reading was taken from the pH meter. After checking each sample, the prob was cleaned and dipped in a solution to ensure purification.

Experiment 2: Measurement of Density

Apparatus

Density bottle (pignometer)
Weighing balance

Procedure

The empty density bottle was washed and weighed to get the weight of the bottle, which was 25.33 grams with a volume of 50ml; this was done to ensure accurate results. The density bottle was filled with emulsion sample and the reading was taken when the dial stabilized. The density bottled was washed and filled with another emulsion sample and the reading was taken until the reading of the last sample was taken.

Experiment 3: Viscosity Measurement

Apparatus

Red Wood viscometer no. 1
Stop watch,
Kohlrausch flask,
Thermometer,
Filter paper

Procedure:

Clean the viscometer cup properly with CCl4 and dried it to remove traces of solvent. The viscometer is leveled using the leveling screws and the outer bath is filled with water. The ball valve is placed on the jet to close it while the test oil is poured into the cup up to the tip of indicator. A clean dry Kohlrausch flask is placed below the discharging jet. A clean thermometer and a stirrer is inserted into the cup and covered with a lid. The water in the bath is heated slowly with constant stirring. When the oil in the cup attains 80°C the heating is stopped. The ball valve is lifted up and the stop watch starts. Oil from the jet flows into the flask. When the lower meniscus of the oil reaches the 50 ml mark on the neck of receiving flask, the stop watch is stopped. The time taken for 50 ml of the oil to collect in the flask is recorded. The experiment was repeated to get more readings.

Experiment 4: Determination of the basic sediment and water (BS & W)

Apparatus

Electrical centrifuge, centrifuge tubes, tube racks.

Materials

Emulsion samples
Demulsifier samples
Solvents

Procedure

Two centrifuge tubes of 100ml were filled to the 50ml mark with Xylene solvent and 10ml of the first demulsifier samples was added to the solvent and mixed properly after which the emulsifier mixture was poured into the crude oil sample until the level of the fluid in the tube reached the 100ml mark.

The mixture was shaken vigorously and heated to 70^oC for 10mins. The tubes were then removed and placed in a centrifuge in such a way that one tube was directly opposite the other. The centrifuge was allowed to spin at 1500 RPM for 10 mins at the same temperature of 70^oC.

The height of the sediment and water in the tube was read of directly.

Experiment 5: Bottle test (screening and ranking)

Apparatus

25ml test tube with corks
Graduated pipette and dropper
Demulsifiers sample
Emulsion sample

Procedure

Each test tube is filled with 25ml of the emulsion sample, and shaken vigorously and allowed to heat for 60^oC. 1 drop of demulsifier sample is added to the emulsion sample, followed by 2 drops, 3 drops, 4 drops and 5 drops. Each test tube is shaken vigorously for 10mins to ensure effective mixing and allowed to stand for another 10mins after which the water level and emulsion level are recorded. The same procedure was carried out with different demulsifier and emulsion samples.

4.0 RESULTS AND DISCUSSION

TABLE 1: pH Values For W/O Emulsion & Demulsifier

EMULSION SAMPLE	pH VALUE OF EMULSION	DEMULSIFIER SAMPLE	pH VALUE OF DEMULSIFIER
Well 1	6.01	Isobutyl alcohol	7.10
Well 2	5.59	D9096	6.10
Well 3	6.15	Tetrolite	7.10

TABLE 2: Viscosity Measurement of W/O Emulsion.

EMULSION SAMPLE	VOLUME OF W/O EMULSION SAMPLE (ml)	Viscosity of Sample (min/sec)
Well 1	25	41
Well 2	25	1.41
Well 3	25	2.19

TABLE 3: Density Measurement of W/O Emulsion Sample.

EMULSION SAMPLE	CRUDE DENSITY ($glcm^3$)
Well 1	0.906
Well 2	0.905
Well 3	0.902

(BS & W) EXPERIMENT 1, USING DEMULSIFIER 1

Demulsifier -Isobutyl alcohol
Solvent - Xylene
Treating temp - 60^oC
Quantity of emulsion - 40ml
Quantity of demulsifier - 10ml
Retention time - 20 minutes

TABLE 4: (BS & W) Result Using Demulsifier 1 (Isobutyl Alcohol)

Emulsion sample	Volume of emulsion	Volume of oil	BS & W	Volume of resolved water
Well 1	40	30.6	9.2	8.5
Well 2	40	29.4	10.2	9.5
Well 3	40	32.5	7.5	7.0

(BS & W) EXPERIMENT 2, USING DEMULSIFIER 2

Demulsifier -Tetrolite
Solvent -xylene
Treating tem -60^o C
Quantity of emulsion sample -40ml
Quantity of demulsifier -10ml
Retention time -20 minutes

TABLE 5: (BS & W) Result Using Demulsifier 2 (D9096).

Emulsion Sample	Volume of emulsion (ML)	Volume of oil	BS & W	Volume of resolved water
Well 1	40	28.0	12.0	11.9
Well 2	40	33.0	6.6	6.0
Well 3	40	35.2	5.0	4.8

(BS & W) EXPERIMENT 3 USING DEMULSIFIER 3

Demulsifier - Tetrolite
Solvent - Xylene
Treating temp - 60^oC
Quantity of emulsion sample - 40ml
Quantity of Demulsifier - 10ml
Retention time - 20 minutes

TABLE 6: (BS & W) Result Using Demulsifier 3 (Tetrolite)

Emulsion Sample	Volume of emulsion (ML)	Volume of oil	BS & W	Volume of Resolved water
Well 1	40	30.6	9.4	8.5
Well 2	40	30.4	9.6	9.0
Well 3	40	28.0	12.0	11.8

IMPROVED BOTTLE TEST USING WELL 1 AND DEMULSIFIER 1

W/O emulsion sample - Well 1
Demulsifier - Isobutyl Alcohol
Treating temp - 40^oC
Quantity of emulsion - 25ml
Quantity of Demulsifier - 1—5 drops
Retention time - 20 minutes

TABLE 7: (Improved Bottle Test Using Well 1 and Demulsifier 1)

Chemical concentration in drops	Volume of Emulsion	Volume of Resolved water	Volume of oil
1	25	1.2	23.5
2	25	2.5	22.0
3	25	5.0	20.0
4	25	5.2	12.8
5	25	5.2	19.8

IMPROVED BOTTLE TEST USING WELL 2 AND DEMULSIFIER 2

W/O emulsion sample - Well 2
Demulsifier - d9096
Treating temp - 40^oC
Quantity of emulsion - 25ml
Quantity of Demulsifier - 1—5 drops
Retention time - 20 minutes

TABLE 8: (Improved Bottle Test Using Well 2 and Demulsifier 2).

Chemical concentration in drops	Volume of Emulsion	Volume Resolved water	Volume of oil
1	25	2.0	23.5
2	25	3.5	21.5
3	25	3.5	21.5
4	25	2.0	23.0
5	25	1.9	23.1

IMPROVED BOTTLE TEST USING WELL 3 AND DEMULSIFIER 3

W/O emulsion sample - Well 3
Demulsifier - Tetrolite
Treating temp - 40^oC
Quantity of emulsion - 25ml
Quantity of Demulsifier -1drops
Retention time -20 minutes

TABLE 9: (Improved Bottle Test Using Well 3 and Demulsifier 3).

Chemical concentration in drops	Volume of emulsion	Volume resolved water	Volume of oil
1	25`	0.8	24.2
2	25	1.5	23.5
3	25	3.0	22.0
4	25	4.2	20.8
5	25	5.0	20.0

5.0 DISCUSSION

The pH measurement revealed that for accurate emulsion resolution, Isobutyl alcohol demulsifier works best in well 1, D9096 in well 2 and tetrolite in well 3 respectively, with demulsifier pH higher than emulsion pH. This is in accordance with Strassner (1968). Results of Viscosity measurement showed that well 2 had the lowest flocculation rate of the three emulsion samples, thus the demulsifer will be effective in well 2. While the density measurement showed a decreasing trend from well 1 to 3, indicating more emulsion of water in oil. The basic sediment and water (BS&W) analysis, showed that the demulsifier Isobutyl Alcohol and D9096 was more effective in well 3, while Tetrolite was effective in well 1 with a higher volume of oil and lower volume of water resolved respectively. Analysis of the improved bottle test using Isobutyl Alcohol showed that, there was effective emulsion resolution as the drops of the demulsifier increased, with maximum efficiency at a drops. While D9096 improved bottle test showed a maximum efficiency using 3 drops of the demulsifier in the emulsion. While Tetrolite improved bottle test showed that maximum efficiency was attained using 5 drops.

6.0 CONCLUSION

The results of this work reveals that for maximum efficiency to be obtained for water in oil emulsion, the pH of the demulsifier should be higher than that of the emulsion, while the viscosity and density of the emulsion is low for higher flow rate and water in oil emulsion respectively. The BS&W analysis showed that Isobutyl alcohol was the most efficient demulsifier of the three by reducing more water in oil. The improved bottle test results, showed that D9096 was most efficient in water in oil emulsion with the least number of drops.

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