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Formulation of Demulsifying Agent for Water in Oil Emulsion Treatment

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Abstract

The production of crude oil along with water has been a primary problem in the petroleum industry. In this work, an emulsion breaking chemical (LFD) was formulated from locally sourced materials and experimentally compared with an imported commercially available demulsifier (sulphuric acid) to determine its effectiveness in crude emulsion resolution. Materials used are Castor oil, locally made liquid soap, Camphor, Alum, Cassava Starch and distilled water. It was tested on a crude oil emulsion sample from the Niger Delta field at a temperature of 85°F, under the same experimental condition with the imported commercially available demulsifier (sulphuric acid) as the control. The percentage volume of water separated by the locally formulated demulsifier (LFD) was 93.33% while the separated percentage volume of water by commercially available demulsifier (sulphuric acid) was 69.33%. This clearly showed that the locally formulated demulsifier had a better performance in terms of emulsion resolution than the commercially available imported demulsifier (sulphuric acid).

Keywords: Demulsifiers, castor oil, sulphuric acid, liquid soap, camphor, emulsion, alum, cassava starch, sediment

1. Introduction

When two liquids that are immiscible for example oil and water come together in contact, they do not mix homogeneously or dissolve to form a solution, instead one liquid gets dispersed in the other liquid. The dispersion usually occurs in aqueous medium to result in an emulsion. The water present in crude oil can bring about undesirable consequences like: Leaching of additives, corrosion, raise conductivity, etc. (Udonne, 2012). For financial and operational reasons, it is important to isolate the water totally from the crude oils before moving them (from one place to another) or refining them. To diminish the water contained in the crude oil produced, the water/crude oil emulsions must be broken (demulsified). Accordingly, crude oil is a mind-boggling liquid including colloidal particles, for example asphaltene and resins dispersed, it is important to comprehend the mechanisms in charge of the stabilization of these emulsions. (Mohammed *et al.*, 1993).

This crude oil contains basic sediment and water (BS &W) ranging from 2 to 11% which is greater than the specified BS &W (lower than 0.5%). Therefore, it has somewhat been sold as emulsions at low cost because of the high expense for treating emulsions. Water-in-oil emulsions are created during the production of crude oil which is regularly accompanied with water. The emulsion stability ranges from a couple of minutes to years contingent on the inherent characteristics of the crude oil and to some extent, the inherent characteristics of water. (Bhardwaj and Hartland, 1988). So as to reduce the minimum the production problems associated with crude oil emulsions and environmental concerns, petroleum operators need to deter their formation or to break them. At times, when the development of emulsions is an after-effect of poor operation practices, it is possible to deter the formation of emulsion. Nonetheless, in many cases, emulsion formation can be predicted. The exclusion of water during recovery from the oil wells and prevention of agitation is hard to accomplish, and emulsions must be treated. The treatment of water-in-crude oil emulsion include the use of thermal, electrical, chemical process or their blends (Ojinnaka, 2016).

2. Materials and Methods

2.1. Materials

The sample of crude oil emulsion utilized in this research was gotten from an oil field in Niger Delta region of Nigeria. Two Demulsifiers, locally formulated demulsifier (LFD) and a commercially available imported (H_2SO_4) were used in treating this emulsion. The centrifugal agitation method was used to determine the Demulsifier most effective in breaking the emulsion. The materials used in formulating the demulsifier are shown in Table 1 below.

Content	Function	Weight/Vol
Alum	To facilitate settling of sediments.	5g
Castor Oil	It acts as the lipophilic agent in the demulsifier.	30ml
Starch	Coalescing of the tiny water droplets.	5g
Liquid Soap	Destabilization of emulsion film	50ml
Camphor	It improves the demulsifier performance	10ml

Table 1: Materials Used for Locally Formulated Demulsifier (LFD)

Apparatus for the experiment include weighing balance, measuring cylinder (50ml graduated), beaker, magnetic heat-stirring machine, filter paper, measuring cylinder (200ml graduated), Hamilton beach mixer, stop watch, syringe, micro-pipette, thermometer, centrifuge.

2.2. Methods

Water-in-oil emulsion was formed in the laboratory as follows:

- 180ml of crude oil was blended together with (20ml) of liquid surfactant in a beaker for emulsification. The crude oil/surfactant blend was placed in a Hamilton beach mixer for agitation.
- Water of 20ml representing 10% of the emulsion was then gradually added to the oil phase at a consistent rate of agitation. Agitation continued until the emulsion reached ambient temperature without forced cooling.

Figure 1: Hamilton Beach Mixer

Locally formulated demulsifier (LFD) procedure are as follows:

- A solution of 10g of camphor dissolved in 30ml of castor oil was stirred and heated ($150^{\circ}F$) in a Magnetic heating and stirring machine until homogeneity of solution is achieved.
- A mixture of 5g of starch (from cassava flour), 50ml of detergent, and 5ml of Alum solution was prepared in another beaker and put into the camphor castor oil solution.
- All precipitates or sediments were filtered off after the new mix or blend above has been further stirred and heated for 2 hours.

Figure 2: Magnetic Heat-Stirring Machine

2.2.1. Analytical Procedure

The first experiment was done taking sulphuric acid (H_2SO_4) to be its demulsifying agent while the second was carried out using locally formulated demulsifier (LFD).

- A 75ml of emulsified crude oil were poured into each of the 12 measuring tubes. All measuring tubes were labeled according to the concentration of Demulsifier to be used for the analysis. Six bottles of demulsifier were utilized with concentrations of 0.2 milli litre, 0.4 milli litre, 0.6 milli litre, 0.8 milli litre, 1.0 milli litre, and 1.2 milli litre of demulsifier.
- All the cylinders were manually agitated properly to ensure fluid mobility
- All tubes containing samples with varying dose of demulsifier were placed into a centrifuge for agitation to achieve proper mixture.
- The revolutions in one minute (rpm) were noted down.
- After the time of rotation had passed, the test tubes placed in the centrifuge were measured and also the separation of the oil from the water recorded
- The procedure was done again for the entire samples and the results were also recorded.

Figure 3: Centrifuge

3. Results and Discussion

The results of the emulsion resolution using the two demulsifiers (a locally formulated Demulsifier (LFD) and commercially available Demulsifier (H_2SO_4)) at a constant treatment temperature of 85°F and time interval of 2 to 12 minutes and at a varying RPM of 1000 and 1500 summarized in Table 2, 3, 1, 3, 2, 3, 3, 4 and 3.5 accordingly.

Crude Properties	
Density	0.864g/Cm ³
Api	32.46°
Viscosity	2.9 Cp

Table 2: Characteristics of Crude Oil Utilized

Vol. of Demulsifiers(ml)	Separated Water Volume(ml)					
	2min.	4min.	6min.	8min.	10min.	12min.
0	0	0	0	0	0	0

Table 3: Emulsion without Demulsifier at a Speed of 1000 Rpm

Vol. of Demulsifier(Ml)	Separated Water Volume (Ml)					
	2min.	4min.	6min.	8min.	10min.	12min.
0.2	0.5	0.7	0.8	1.0	1.1	1.2
0.4	0.9	1.1	1.3	1.5	2.0	2.2
0.6	2.2	2.5	2.5	2.7	2.8	2.8
0.8	2.9	3.0	3.2	3.2	3.2	3.3
1.0	3.0	3.1	3.3	3.5	3.5	3.6
1.2	3.6	3.7	3.9	4.0	4.0	4.1

Table 4: Emulsion Treatment with Sulfuric Acid at 1000 Rpm and 85 °F

Percentage volume of water separated using H_2SO_4 at 1000 rpm

$$= \frac{\text{Vol. water separated}}{\text{Total vol. of water in the emulsion}} \times 100$$

$$= \frac{4.1}{7.5} \times \frac{100}{1} = 54.67\%$$

Vol. of Demulsifier(ml)	Separated Water Volume (ml)					
	2min.	4min.	6min.	8min.	10min.	12min.
0.2	0.6	0.9	1.3	1.5	1.6	1.8
0.4	1.0	1.4	1.5	1.8	2.2	2.4
0.6	2.3	2.6	2.9	2.9	3.1	3.2
0.8	3.0	3.3	3.6	3.8	3.9	3.9
1.0	3.9	4.3	4.9	5.1	5.1	5.3
1.2	4.2	4.8	4.9	5.2	5.3	5.5

Table 5: Emulsion Treatment with LFD at 1000 Rpm and 85^of

Percentage volume of water separated using LFD at 1000 rpm.

$$= \frac{\text{Vol. water separated}}{\text{Total vol. of water in the emulsion}} \times 100$$

5.5 / 7.5 * 100 = 73.33%

Figure 4: Volume of Separated Water Vs Volume of Demulsifier (ml) at 85^of and 1000 Rpm.

Figure 5: Volume of Separated Water (ml) Vs Time (min.)@1000 Rpm and 85^of

Figure 6: A Bar Charts Representing the Performance of H₂SO₄ and LFD at 1000 Rpm

Vol. of Demulsifier(ml)	Separated Water Volume(ml)					
	2min.	4min.	6min.	8min.	10min.	12min.
0.2	0.5	0.8	0.9	1.0	1.2	1.3
0.4	1.0	1.1	1.4	1.6	1.7	2.3
0.6	2.3	2.5	2.6	2.8	2.9	2.9
0.8	2.9	3.0	3.3	3.3	3.4	3.4
1.0	3.1	3.2	3.4	3.5	3.6	3.7
1.2	4.2	4.5	4.9	5.1	5.2	5.2

Table 6: Emulsion Treatment with H₂SO₄ at 1500 Rpm and 85°f

Percentage volume of water separated using H₂SO₄ at 1500 rpm

$$= \frac{\text{Vol. water separated}}{\text{Total vol. of water in the emulsion}} \times \frac{100}{1}$$

$$= \frac{5.2 \times 100}{7.5 \times 1} = 69.33\%$$

Vol. of Demulsifier(Ml)	Separated Water Volume(Ml)					
	2min.	4min.	6min.	8min.	10min.	12min.
0.2	0.8	1.2	1.5	1.8	2.0	2.3
0.4	1.5	1.9	2.5	3.0	3.3	3.8
0.6	3.0	3.8	4.0	4.2	4.3	4.3
0.8	3.9	4.2	4.5	4.6	4.6	4.7
1.0	4.5	4.9	5.0	5.2	5.5	6.9
1.2	5.1	5.3	5.8	5.9	6.4	7.0

Table 7: Emulsion Treatment with LFD at 1500 Rpm and 85°f

Percentage volume of water separated using LFD at 1500 RPM.

$$= \frac{\text{Vol. water separated}}{\text{Total vol. of water in the emulsion}} \times \frac{100}{1}$$

$$= \frac{7.0 \times 100}{7.5 \times 1} = 93.33\%$$

Figure 7: Vol. of Separated Water Vs Vol. Demulsifier (ml) @ 1500 Rpm and 85°F

Figure 8: Volume of Water Separated (ml) Vs Time (Min) @ 1500 Rpm and 85°F

Figure 9: A Bar Chart Representing the Performance of H2so4 and Lfd @ 1500 Rpm and 85°F

Figure 10: The Schematic Representation of Resolved Emulsion

From Table 3 the experiment was done without a Demulsifier and there was no separated water from the emulsion which shows that no amount of agitation will break an emulsion without a Demulsifier. At a speed of 1000 rpm at 85oF better results were obtained using LFD as shown in Tables 3.3 and Fig 3.3. Percentage of water separated was 73.33%. At a speed of 1500 rpm at 85oF as displayed in Table 7 and Fig 3.5. The amount of water in percentage separated was 93.33%. All the samples were agitated with centrifuge for 12minutes in each case. This shows that locally formulated demulsifiers (LFD) were more effective in emulsion breaking than imported sulphuric acid (H_2SO_4)

4. Conclusion

In oil field and water treatment operations, producer of crude oil is interested in three parts of demulsification. Rate or speed at which the detachment occurs, quantity of water remaining in the crude oil after separation, and quality of the detached water for disposal. In this work, a demulsifier was formulated from locally sourced material (LFD). It was tested on a crude oil emulsion sample from the Niger Delta's field in Nigeria at a temperature of 85oF in comparison with a commercially available imported demulsifier (sulfuric acid). The separated water percentage by volume using the locally formulated demulsifier (LFD) was 93.33%, while the separated water using foreign demulsifier (Sulfuric acid) was 69.33%. The LFD also had a faster rate of separation and a better quality of water separated than the commercially available imported demulsifier (sulfuric acid). The results clearly demonstrated that cheap local chemicals with demulsification properties can be used to successfully break emulsions and enhance the quality of produced crude oil. The locally formulated demulsifier (LFD) is not corrosive and does not contain organic chloride, bromides, or lead, hence will not cause any refining problems

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Appendix

Nomenclature	
BS & W	Basic Sediments and Water
RPM	Revolution per minute
LFD	Locally formulated Demulsifier.

Table 8