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A New Demulsifier Formulation for Crude Oil Emulsions Treatment

By

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ABSTRACT

This work involved formulation of an emulsion breaking chemical or demulsifier from materials locally obtained. Experimental investigation was carried to ascertain its effectiveness in breaking crude oil emulsion. Materials used included locally made liquid soap, starch, camphor, alum, castor oil, and distilled water. Two different demulsifier formulations were made and tested on a crude oil emulsion sample from a Niger Delta field (Oredo Field) and subjected to a temperature of 60°F. A foreign demulsifier, Separol, of the same quantity and under the same experimental condition, served as a basis for comparison (control).

The result of the treatment was a successful separation of oil and water using formulated demulsifier. The separated water volume by the local demulsifier (LDP1) was 31ml, while that separated by Separol was 6ml. This showed the locally formulated demulsifier had better water separation capability than the commercially available imported demulsifier (Separol).

Keywords: Coalescence, Demulsifier, Emulsion, Flocculation, Niger Delta, Saparol.

INTRODUCTION

A Crude Oil Emulsion is a heterogeneous mixture that consists of two immiscible liquids, oil and water. It is formed when excess water is produced from an oil reservoir. In an emulsion, one of the liquid is dispersed in the other liquid in the form of droplets of varying sizes[1]. Depending upon the nature of the dispersed phase, the emulsions are classified as, oil-in-water emulsion, water-in-oil emulsion and complex (multiple) emulsions, that is a combination of water-in-oil and oil-in-water[2]. Crude oil emulsions are kept stable by emulsifying agents such as asphaltenes, resinous substances, silica, silt, iron sulphide, etc, present in the crude oil[3]. It is important to treat emulsions in order to avoid pipeline overloading, corrosion, and increased operation cost. In order to separate both liquids, emulsions are treated by applying heat, electric current, and chemicals or demulsifiers[4].

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[1] Bradley, H.B. (1987): 'Petroleum Engineering Handbook', SPE, Richardson, Texas, Third Edition, pp. 19-1.

[2] Mohammed, A.U., Erakpoweri, T.E., and Onuoha, I. (2013): 'Asphaltene Solvency and Stability of Water in Oil Emulsion-A Case Study of Two Nigerian Crudes', JEPT, ISSN 2225-0573, Volume 3, No.9, pp. 16.

[3] Treating Oil Field Emulsions, fourth edition Petroleum Extension Service, University of Texas, Austin (1990), pp. 8 – 9.

[4] Udonne, J.D. (2012): 'Chemical Treatment of Emulsion Problem in Crude Oil Production', JPGE, Volume 3(7), pp. 135 – 136.

In the past, commercial emulsion-treating chemicals were soap solutions[5]. Presently, several demulsifiers have been manufactured for treating many water-in-oil emulsions. To achieve demulsification of an emulsion, a chemical demulsifier must thoroughly mix with the emulsion and disrupt the emulsifying agent that surrounds the dispersed water droplets[6]. These actions occur in the following processes;

- Flocculation: In this process, the demulsifier attracts the water droplets and brings them together.
- Coalescence: After flocculation, the water droplets fuse together to form single larger drops where the interface film is ruptured.
- Phase separation: At this stage, separation of the oil and water occurs with the water settling below the oil.

MATERIALS AND METHOD

The crude oil emulsion sample used in this research was obtained from an oil field located in Nigeria's Niger Delta region (Oredo Field) Three demulsifier, two laboratory made (LDP1 and LDP2) and a commercially available imported Separol were used in treating this emulsion. The Bottle Test method was used to determine the demulsifier most effective in breaking the emulsion. The result from the test also indicates the smallest amount of demulsifier needed to satisfactorily break the given volume of emulsion. The materials used in formulating LDP1 and LDP2 are shown in Table 1.

Content	**Function**	**Weight/Vol**	
		LDP1	**LDP2**
Alum	To facilitate settling of sediments	5g	5g
Castor Oil	It acts as the lipophilic agent in the demulsifier	30ml	45ml
Starch	Coalescing of the tiny water droplets	5g	5g
Liquid Soap	Destabilization of emulsion film	50ml	25ml

[5] Rafael, M.P., Jorge. A. (2015): 'Iconic Liquids as Surfactants-Applications as Demulsifiers of Petroleum Emulsions', INTECH, 11, pp. 314. Available at http://dx.doi.org/10.5772/59094

[6] Tharwat, F.T. (2013): 'Emulsion Formation and Stability', Wiley-VCH Verlag GmbH & Co. KGaA, London, First Edition, pp. 3. Available at http://www.wiley-vch.de/books/sample/3527319913_c01.pdf

Camphor	It improves the demulsifier performance	10ml	10ml
Xylene	It lightens the oil in the emulsion	-	10ml

Table 1: LDP1 and LDP2 Materials

Apparatus

I. Digital Weigh balance
II. Measuring Cylinder(50ml graduated)
III. Beaker
IV. Magnetic Heat-Stirring machine
V. Filter paper
VI. Prescription bottles (200ml graduated)
VII. Thermostatic Water Bath
VIII. Stop watch
IX. Syringe
X. Micro-pipette

LDP1 Formulation Procedure

I. A solution of 10g of camphor dissolved in 30ml of castor oil was stirred and heated (150°F) in a Magnetic heating and stirring machine until homogeneity of solution is obtained.
II. A mixture of 5g of starch (from cassava flour), 50ml of detergent, and 5ml of Alum solution was prepared in another beaker and added to the camphor-castor oil solution.
III. The new mixture above was further stirred and heated for 2 hours, after which all precipitates or sediments were filtered off.

LDP2 Formulation Procedure

I. A solution of 10g of camphor, 10ml of Xylene and 45ml of castor oil was prepared in a beaker.
II. A second solution of 5g of starch, 5ml of alum solution, and 25ml of liquid soap was prepared also and stirred.
III. Both solutions were combined and heat-stirred in the Hotplate Stirrer machine for 2 hours, afterwards all remaining precipitates were filtered off.

Analytical Procedure

1. Samples were heated in water bath to achieve fluid mobility before placing in the bottles.
2. A 100ml of emulsion were poured into each of the 18 prescription bottles.
3. All prescription bottles were labeled according to the concentration of demulsifier to be used for the analysis. Six bottles for each demulsifier were used with concentrations of 0.2ml, 0.4ml, 0.6ml, 0.8ml, 1.0ml, and 1.2ml of demulsifier.
4. All bottles containing samples with varying dose of demulsifier were agitated to achieve proper mixture.

5. The bottles were placed in the water bath, with water level at the 100ml mark and heated to 60°C for 2 hours.

RESULTS AND DISCUSSION

The Bottle Test results using the three demulsifiers (LDP1, LDP2 and Separol) at a constant treatment temperature of 60°C and at time intervals of 1-120 minutes after heating for 2 hours, are summarized in Tables 2, 3, and 4 respectively. Before carrying out any analysis, all samples were drained of free water after aging for a week. This allowed the water to settle out by gravity. The Basic Sediment and Water (BS&W) and the API of a sample before and after treatment, are summarized in Tables 5.

Volume of Demulsifier(ml)	Separated Water Volume (ml)				
	1min	30mins	60mins	90mins	120mins
0.2	-	-	1.0	1.0	1.0
0.4	2.5	5.0	5.0	5.0	5.0
0.6	2.5	5.0	7.5	7.5	7.5
0.8	7.5	7.5	7.5	7.5	7.5
1.0	2.5	2.5	2.5	2.5	2.5
1.2	7.5	7.5	7.5	7.5	7.5

Table 2: Results of Heat and Chemical Treatment using LDP1

Volume of Demulsifier(ml)	Separated Water Volume (ml)				
	1min	30mins	60mins	90mins	120mins
0.2	-	-	-	-	-
0.4	2.5	2.5	2.5	2.5	2.5
0.6	-	-	-	-	-
0.8	5.0	5.0	5.0	5.0	5.0
1.0	-	-	-	-	-
1.2	-	-	-	-	-

Table 3: Results of Heat and Chemical Treatment using LDP2

Volume of Demulsifier(ml)	Separated Water Volume (ml)				
	1min	30mins	60mins	90mins	120mins
0.2	-	1.0	1.0	1.0	1.0

0.4	-	-	-	0.5	0.5
0.6	-	-	-	0.5	0.5
0.8	2.0	2.0	2.0	2.0	2.0
1.0	-	-	-	1.0	1.0
1.2	-	-	-	1.0	1.0

Table 4: Results of Heat and Chemical Treatment using Separol

Analysis	API @ 60°F	API @ 140°F	BS&W %
Before Treatment	10.28	34.58	0.1
After Treatment	10.38	33.61	0

Table 5: Sample API and BS&W

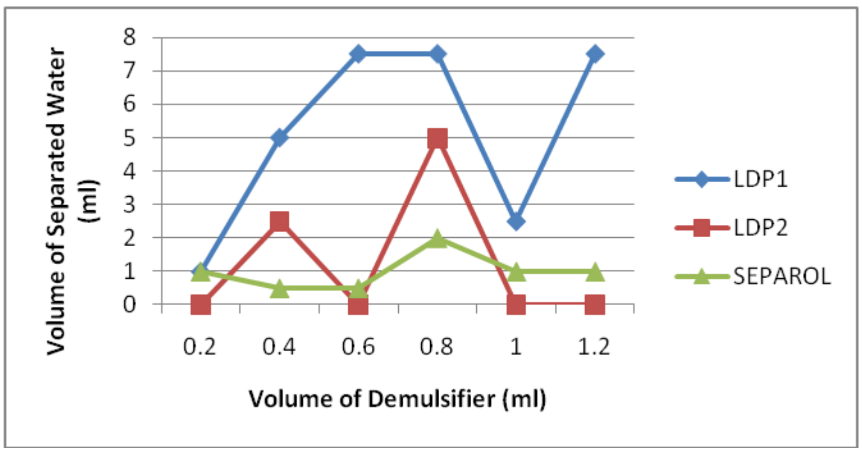

Fig.1: Volume of Separated Water after Treatment

As shown in Table 2 and Figure 1, LDP1 was the most effective demulsifier for treating this particular crude oil emulsion sample, despite the heavy nature of the crude and its pour point of 95°F. All samples were heated in the water bath for two hours before readings were taken. At 1 minute, after heating for two hours, separated water in bottles containing the emulsion with concentrations 0.4ml, 0.6ml, 0.8ml, 1.0ml, and 1.2ml of Formula 1 (LDP1), were 2.5ml, 2.5ml, 7.5ml, 2.5ml, and 7.5ml respectively. At 60 minutes, 1.0ml of separated water was observed for emulsion sample injected with 0.2ml concentration of LDP1 but no further change was observed for the next 60 minutes. A little deviation from normal was observed in the sample dosed with 1.0ml of LDP1 at 1 minute of treatment. As volume of injected demulsifier increased, ideally the volume of separated water ought to increase or be maintained not decrease from 7.5ml to 2.5ml then back to 7.5ml. This may be due to sludge/sediment content in the emulsion sample. Samples treated with 0.4ml and 0.8ml of LDP2 (Table 3) separated 2.5ml and 5.0ml water respectively after 120 minutes. Sediment containing traces of water were observed in other bottles containing LDP2. Perhaps an adjustment of the proportion of materials used may have produced a better result. On the other hand, the total separated water volume by Separol after 120 minutes was 6ml. This proves that there is no demulsifier which can break all emulsions effectively. Ideally for medium to light crude oil emulsions, the API gravity ought to increase due to the separation and extraction of water. However, for heavy crudes (in this case below 20°API) which normally are treated above 180°F, heat may have had a negative effect on difference in density. In special cases, increased heat may cause the density of water to be less than that of oil[7]. Heating well fluids is expensive and can cause a significant loss of the lower-boiling-point hydrocarbons. This results in loss of oil volume because the light ends are boiled off, and the remaining liquid has a lower API gravity and thus may have a lower value. A manual centrifuge was used before and after treatment to determine the BS&W content of crude oil emulsion samples. Also, due to the API gravity of the crude and pour point there was very little separated water from the emulsion hence requiring the addition of Xylene after treatment to the samples in order to reduce its pour point temperature to room temperature. Nevertheless, no free water was observed after treatment.

CONCLUSION

In this work, two demulsifiers were formulated from locally sourced material. They were tested on a crude oil emulsion sample from a Niger Delta field (Oben Field) and subjected to a temperature of 60°F. The results of the treatment was the successful separation of the oil emulsion sample into oil and water. The separated water volume by the local demulsifier (LDP1) was 31ml, while that separated by a foreign demulsifier (Separol) was 6ml. This showed the locally formulated demulsifier had better water separation capability than the commercially available imported demulsifier (Separol).

The results clearly demonstrated that cheap local chemicals with demulsification properties can be used to successfully to break emulsions and enhance the quality of the produced crude. The Demulsifiers (LDP1 and LDP2) contained no organic chloride, bromides, iodides, or lead, hence will not cause any refining problems.

[7] Bradley, H.B. (1987): 'Petroleum Engineering Handbook', SPE, Richardson, Texas, Third Edition, pp. 19-1.