Studies on pH Variations in Crude Oil Demulsification

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Abstract— **Braking of emulsion is necessary in many practical applications such as the petroleum industry, agrochemical industry, food industry, pharmaceutical industry, painting and waste-water treatment in environmental technology. Chemical demulsification is the most widely applied method of treating water-in-crude oil emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The effect of chemical demulsification operations on the stability and properties of water-in-crude oil emulsions was assessed experimentally at various crude oil pH. Three different demulsifiers, BE-027, QIT-007 and WAMCO-2 demulsifiers were used for the studies. Result showed that WAMCO-2 gave the best performance with clean produced water and clean oil phase combined with sharp water-oil interphase at pH of 7.68.**

Index Terms— **crude oil, emulsion, demulsifiers.**

I. INTRODUCTION

The destabilization of crude oil emulsions forms an integral part of crude oil production. Petroleum emulsions (typically water-in-oil) readily form with water in the highly turbulent nozzles and piping used for oil production. These emulsions can increase pumping and transportation expenses, corrosion of pipes, pumps, production equipment and distillation columns. The emulsion also caries along other impurities that poisons downstream refinery catalysts (Ekott and Akpabio, 2010). Stable emulsions are typically broken using gravity or centrifugal settling, application of high electric fields and addition of destabilizing chemicals (demulsifiers). Other methods such as pH adjustment, filtration, membrane separation and heat treatment techniques, may also be used. The use of condensed CO_2 has also been suggested and studied by Zaki et al (2003). Methods currently available for demulsification of water-in-crude oil emulsions can be broadly classified as chemical, electrical and mechanical.

In chemical demulsification, chemical known as demulsifier is added to the water-in-crude oil emulsion. These demulsifiers are surface active agents (surfactants) and develop high surface pressure at crude oil-water interface (Abdurahman and Yunus, 2009). It results in replacement of rigid film of natural crude oil surfactants by a film which is conducive to coalescence of water droplets. Chemical demulsification is the most widely applied method for treating water-in-oil and oil-in-water emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The formulation of an emulsion demulsifier for a specific petroleum emulsion is a complicated undertaking. In petroleum system, asphaltenes and resinous substances comprise a major portion of the interfacially active components of the oil (Abdurahman et al, 2007 a,b). Ekott and Akpabio (2010) presented the current state of researches on water-in-oil emulsion stability, destabilization and interfacial rheology and reported a research gap in fully understanding the chemistry of demulsifiers. Ekott and Akpabio (2011) also studied the Influence of Asphaltene Content on Demulsifiers Performance in Crude Oil Emulsions and reported that the solvency of alphaltene content play important role in the Demulsification process of crude oil emulsions and not just the whole asphaltene content.

Specker (2004) discussed asphaltenes and resin as large polyaromatic and polycyclic condensed ring compounds containing heteroatoms. Anderson and Birdi (1991) stated that chemically, asphaltenes and resins represent the pentane or hexane insoluble portion of the oil. Anklem (1997) reported that in the oil industry water comes into contact with crude oil on many occasions, creating emulsions stabilized by various components in the oil, including asphaltenes and resins. Understanding and controlling demulsification is of primary importance for breaking waste emulsions and for using emulsions in industrial processes that require emulsion destabilization as a main step. At drilling site, the recovered oil will contain some water and hydrophilic impurities which need to be removed before shipping and processing. The water concentration may vary, but a target specification for water and sediments removal may be 1% or less (Rowan, 1992). There are many procedures for the neutralization and reduction of the emulsifying agent has been used. For example, Hennessey et al (1995) used the gravity separation, while electrostatic coalescence was used by Bailes et al (1997). Also, centrifugal and filtration methods of emulsion breaking have been used by Lissant (1983). Abdurahman et al (2007b) reported that the percentage of water separated is the best indicator of emulsion stability, because it is a measure of the degree of aggregation or flocculation of individual emulsion water droplets and coalescence of aggregated water droplets. They reported that water phase pH has a strong influence on emulsion stability. Akpabio and Ekott (2010) studied the performance of different demulsifiers on Niger Delta crude oil. In this study three demulsifier chemicals are evaluated for their demulsification performance on crude oil sample at various crude oil pH. The crude oil emulsion was obtained from Qua Iboe oil field operated by Exxon Mobil Nigeria Unlimited.

II. MATERIALS AND METHODS

Fresh crude oil sample was collected from Qua Iboe oil field, Ibeno, Nigeria, at the pressure bleeding point of the well head

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manifold with the aid of clean sample container. Three demulsifier chemicals namely BE-027, QIT-007, and WAMCO-2 which have common use in Mobil QIT oil field were used for the study. Properties of the crude oil were first determined. 10ml of the emulsion was measured using a measuring cylinder and filled in three calibrated centrifuge tube. With the aid of micro syringe, 1ml of each demulsifier chemical was measured and filled in each tube containing the crude oil samples. The tubes were hand shaken, placed and spun in a centrifuge (MODEL: 800-3) at 200rpm for 10 minutes.

To increase the pH of the samples, 0.6M and 0.2M concentration of sodium hydroxide solution (NaOH) were prepared and 1ml of each prepared base solution was added to 10ml of each oil sample and shaken to mix. The pH of the mixtures was determined with the aid of a pH meter (Model: PHS-25) calibrated with a buffer 10.00 solution. 1ml of each demulsifier chemical was then added to the mixtures, hand shaken and centrifuged at 200rpm for 10 minutes. The volumes of separated water were read off after every 1hour. To lower the pH of the samples, 0.6M and 0.2M concentration of hydrochloric acid solution (HCL) were prepared and 1ml of each prepared base solution was added to 10ml of each oil sample and shaken to mix. The pH of the mixtures was determined with the aid of a pH meter (Model: PHS-25) calibrated with a buffer 10.00 solution. 1ml of each demulsifier chemical was then added to the mixtures, hand shaken and centrifuged at 200rpm for 10 minutes. The volumes of separated water were read off after every 1hour. To determine specific gravity, a clean dry 50ml pycnometer (density bottle) was weighed using an electronic weighing balance and then completely filled with distilled water and then weighed again. The pycnometer was emptied, cleaned and dried, then filled with the crude oil sample and weighed.The specific gravity was calculated using equation 1 and converted to 60/60^{o}F using specific gravity reduction table for API determination using equation 2.

$$Specific\ Gravity = \frac{weight\ of\ Sample}{weight\ of\ distilled\ water} \quad (1)$$

The API gravity is obtained from equation 2.

$$API = \frac{141.5}{Specific\ Gravity\ at\ 60/60^{0}F} - 131.5$$

III. RESULTS AND DISCUSSIONS

The studied crude oil emulsion from Qua Iboe oil field had of pH 7.68, specific gravity of 0.8838 and API of 28.604. At crude oil pH of 7.68 the demulsifiers performed differently. At maximum time of observation for (5 hours), QIT-007 demulsifier gave the highest water separation of 4.0ml while WAMCO-2 and BE-027 gave 3.5ml and 0.3ml respectively as shown in table 1. However, the water and oil qualities for WAMCO-2 were clean while the water-oil interface was sharp making WAMCO-2 a better demulsifier to others that gave milky water quality as shown in table 2. The study also shows that WAMCO-2 has a faster separation time of 1 hour to achieve maximum separation of 3.5ml. This presents it as a better demulsifier for quick separation and its attendant benefits.

Similar results were obtained when the pH of the crude oil became more alkaline. WAMCO-2 proved to be the demulsifier of choice considering its water separation capability and quality of produced water.

From table 2, it shows that WAMCO-2 demulsifier alone could give clean water and oil phases separations combined with a sharp water-oil interphase. Considering the resident time to achieve separation, WAMCO-2 was also the best. It was however observed that the demulsifiers performances were influenced by pH variation of the crude oil medium. More water separation was achieved when the crude oil medium was more acidic but the produced water quality was oil, indicating poor demulsifier performance. It was further observed that the best separation was achieved at the crude oil exploited pH of 7.68. WAMCO-2 demulsifier was therefore recommended for use in this oil field.

Table 1: Result for water quantity demulsified from crude oil at various pH values

Time (hrs)	Quantity of water separated in ml														
	BE-027 Demulsifier					**QIT-007 Demulsifier**					**WAMCO-2 Demulsifier**				
	pH 4.25	pH 6.30	pH 7.68	pH 9.63	pH 12.09	pH 4.25	pH 6.30	pH 7.68	pH 9.63	pH 12.09	pH 4.25	pH 6.30	pH 7.68	pH 9.63	pH 12.09
0.1	0.2	0.2	0.2	0.2	0.3	6.0	5.5	3.0	3.5	0.0	6.0	5.3	3.0	5.3	4.5
1.0	0.2	0.2	0.2	0.2	0.3	6.0	5.5	3.0	3.5	0.0	6.0	5.3	3.5	5.3	4.5
2.0	0.2	0.2	0.2	0.2	0.3	6.0	5.5	3.5	3.5	0.0	6.0	5.3	3.5	5.3	4.5
3.0	0.2	0.2	0.3	0.2	0.3	6.0	5.5	3.5	3.5	0.0	6.0	5.3	3.5	5.3	4.5
4.0	0.2	0.2	0.3	0.2	0.3	6.0	5.5	4.0	3.5	0.0	6.0	5.3	3.5	5.3	4.5
5.0	0.2	0.2	0.3	0.2	0.3	6.0	5.5	4.0	3.5	0.0	6.0	5.3	3.5	5.3	4.5

Table 2: Subjective assessment of separated phases of emulsion at various pH values

Phases	Subjective assessment of separated phases after 5 hours														
	BE-027 Demulsifier					QIT-007 Demulsifier					WAMCO-2 Demulsifier				
	pH 4.25	pH 6.30	pH 7.68	pH 9.63	pH 12.09	pH 4.25	pH 6.30	pH 7.68	pH 9.63	pH 12.09	pH 4.25	pH 6.30	pH 7.68	pH 9.63	pH 12.09
Water Quality	Oily	Oily	Oily	Oily	Oily	Milky	Milky	Milky	Milky	Solid milky ppt	Clean	Clean	Clean	Clean	Clean
Oil Quality	Clean	Clean	Clean	Clean	Clean	Clean	Clean	Clean	Clean	Clean	Clean	Clean	Clean	Clean	Clean
Interface Qaulity	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Sharp	Fair	Fair	Fair	Fair	Sharp	Fair	Fair

IV. CONCLUSION

In this study, the performances of three commercial demulsifiers were investigated for crude oil emulsion from Qua Iboe oil field at the crude's natural pH and at varied pH levels. The three demulsifiers used in this study performed differently at the various pH media and showed that demulsifiers performances are affected by the pH of the crude oil medium. WAMCO-2 demulsifier proved better with high water separation, clean water and oil phases and sharp water-oil interphase. Time for maximum water separation for this demulsifier was also good, as small as 6 minutes making it the demulsifier of choice for Qua Iboe Oil fields crude oil emulsions. It is therefore recommended that these commercial demulsifiers should also be studied on crude oil emulsions from other Nigerian oil fields.

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