Application of Physico-Technological Principles in Demulsification of Water-In-Crude Oil System

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Abstract
The presence of water-in-oil emulsion in petroleum industry presents serious pipeline challenges and flow problems such as corrosion, scaling and plugging of in-field flow lines plugging. These problems are attributed to the presence of asphaltene and resinous compounds in the crude oil. Application of a suitable approach for the treatment of crude oil emulsion remains a major concern in the petroleum industry. This paper discusses the use of light gasoline as diluents to reduce the viscosity of a 17^{o} API heavy crude oil emulsion. Several demulsification bottle tests were carried out. Addition of up to 25ml of gasoline led to an increase in API gravity of the crude oil from 17 to 24, indicating improved crude quality. The results also show increased water separation in response to corresponding increase in gasoline blending ratios which was most effective at gasoline blends between 5ml and 10ml. The crude oil and gasoline blend samples dosed with 2ppm of demulsifier chemical, NALCO EC2111A, a reduced injection rate from 5ppm, currently used on the operator's oilfield showed considerably higher rates of water separation with huge savings in demulsifier costs.

Keywords: Demulsifier, emulsion, viscosity, gasoline, diluents.

1. Introduction

Crude oil is found in the reservoir in association with gas and saline formation water. As the reservoir becomes depleted, a time will be reached when water is co-produced with oil. The number of wells now co-producing water with crude oil is steadily increasing; these immiscible fluids are readily emulsified by the simultaneous action of shear and pressure drop at the well head, chokes and valves (Bhattacharyya, 1992). Presence of emulsions is very common in the petroleum industry. They form naturally during the crude oil production and their presence may have a strong impact on the crude oil production as well as facilities employed. Emulsions are also formed during flow through valves, chokes or pumps. Emulsions are stable when the crude oil phase contains natural surfactants. It is known that the viscosity of water-in-oil emulsions can be strongly increased by increasing its water volume fraction and by decreasing the temperature (Nour et al., 2010). Reducing such a high viscosity requires better understanding of emulsion properties. According to Mat et al (2006), emulsion can be categorized into stable, unstable and meso-stable emulsions according to stability and operational definitions:

Stable emulsions will persist for days, weeks and longer. They showed the viscoelastic properties and viscosities are at least three orders of magnitude greater than that of the starting oil. In addition, stable emulsion will increase with viscosity over time. It has been postulated that the stability is derived from the strong viscoelastic characteristics that were caused by the presence of asphaltenes and resins in some cases. Increasing alignment of asphaltenes at the oil-water interface may cause an increase in viscosity. *Unstable emulsions* usually persist for only a few hours after mixing stops. These emulsions are ready to separate into oil and water due to insufficient water particle interactions. However, the oil may retain small amounts of water, especially if the oil is viscous. *Meso-stable emulsions* are probably the most common emulsion that are formed in the fields. These emulsions can be red or black in appearance. This emulsion has the properties between stable and unstable emulsions. It is suspected that these emulsions contains either insufficient asphaltenes to render them completely stable or contains too many destabilizing materials such as smaller aromatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Meso-stable emulsions may also degrade to form layers of oil and stable emulsions.

Knowledge of the factors, which help the stabilization of these emulsions and the manner in which these emulsions are stabilized are necessary for their proper demulsification (Bhardwaj and Hartland, 1998). The predominant mechanism whereby petroleum emulsion is stabilized, is through the formation of a film consisting of a physical, cross-linked network of asphaltenic molecules, which aggregate through lateral intermolecular forces to form primary aggregates or micelles at the oil-water interface (Auflem, 2002). The film is elastic with viscous properties. This interfacial film plays an important role in stabilizing the water droplets against coalescence and these films offer extremely high resistance to drainage. The parameters that control film drainage include film viscosity and elasticity. Film drainage depends on a number of factors including interfacial tension and tension gradient, as well as the rheological properties of bulk and surface phases (Aveyard et al., 1992).

Many researchers suggested that stable water-in-oil emulsions can be produced by a variety of compounds and mixtures. While asphaltenes and resins clearly play an important role in the formation of stable emulsions, there are oils with significant amounts of asphaltenes, which do not produce stable emulsions. Certain type of compounds in the asphaltenes and resins with surfactant properties likely play a major role in producing stable emulsions. Compounds with higher solubility in the oil phase than in the aqueous phase are the most likely emulsifying agents to produce stable water-in-oil emulsions. Waxes and sea water particles such as clays can contribute to the stability of water-in-oil emulsions, but cannot by themselves produce stable emulsions. Similarly, surfactants produced during the photo-oxidation of oil are assumed to still require the presence of asphaltenes and resins to produce stable water-in-oil emulsions. Photo-oxidation of oil means that emulsions formed with fresh crude are unstable, while after exposure to light, the crude forms stable emulsions (Lee, 1999). Thus, essential to the formation of stable water-in-oil emulsion are sufficient amounts of certain polar compounds, such as nickel porphyrins, found in the asphaltenes and resins of crude oil. If insufficient amounts of these polar compounds are present in the oil, then the presence of waxes and other particles will not lead to the formation of stable emulsions.

Demulsification or emulsion breaking is necessary in many practical applications such as the petroleum industry, coating, painting, and waste water treatment in environmental technology (Kim, 1995). Demulsification has gained importance because the use of steam and caustic injection or combustion process, for in-situ recovery of heavy crude oils, is complicated by the production of viscous emulsions of oil, water and clay. The demulsification of crude oil emulsions forms an integral part of crude oil production. Destabilization of water-in-crude oil emulsion is carried out by using either of four methods such as mechanical, chemical, thermal, or electrical. Other methods such as pH adjustment, filtration, membrane separation and heat treatment techniques, may also be used (Gafonova, 2000). Knowledge of the properties and characteristics of the emulsion and the mechanisms that are taking place during coalescence of water droplets are required in a fast separation (Ese et al., 1999).

Separation may not naturally occur with time depending on the properties of the oil and the emulsions formed may not easily break under gravity. Therefore, the use of chemicals that work as demulsifiers is commonly employed. Chemical demulsification is the most widely applied method of treating water-in-oil and oil-in-water emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The stability of emulsions is largely affected by the nature of the interface/film and surfactant adsorption mechanisms (Kim, 1995). The process of chemical demulsification of a water-in-crude oil emulsion involves the acceleration of the coalescence as well as the film rupture process. Dispersed water droplets approach each other and flatten to form a thin film of continuous oil phase between them, the outward drainage flow of the film can create gradients in interfacial tension which then oppose and slow down such drainage. The rate of coalescence will depend upon the factors that bring the droplets together (e.g. concentration), and on the balance of forces that stabilizes and disrupt the interface. The tendency for the drops to coalesce will be the van der Waals forces when the lamellae are thin enough, and the restoring forces will be the Gibbs-Marangoni effect. This effect will operate due to the distortion and increase in surface area of the drops as they get close together. Therefore the stability of emulsions is largely affected by the nature of the interfacial film and surfactant adsorption mechanisms. Injecting the chemical at drilling sites can provide great benefits as it will reduce pressure drop in pipelines and/or enhance the emulsion separation and handling. Hence, it is important for the industry to find an efficient way of testing and evaluating these chemicals in the laboratories before applying them in the field. An efficient testing method will lead to an optimization and potential reduction of the quantity of the chemical needed for this purpose, resulting in monetary and most important, environmental benefits. So far, mainly bottle testing has been employed to conduct such measurements. In the present study, the bottle test method is applied in demulsifying crude oil from a flow station in Nigeria's Niger Delta, blended with varying ratio of gasoline as diluent.

2. Materials And Methods

The method employed in this work entails the following:

a) Blending of the crude oil sample with light petroleum fraction (gasoline) which acts as diluents and subsequent addition of chemical demulsifier -NALCO EC2111 A.

b) Laboratory test on the samples to determine specific gravity and API gravity.

c) Centrifugation of the samples using centrifuge apparatus to determine water content (BS&W)

The crude oil was obtained from Shell Petroleum Development Corporation Obigbo flow station located in Rivers State, Nigeria. The crude oil produced from the respective oil wells are transported through flow lines to the Obigbo flow station where chemical injection pumps are used to dose appropriate amounts of demulsifier to the incoming crude at the bleeding point before the separator. Bottle tests were conducted in the laboratory to determine the best crude oil-gasoline (diluents) blend with demulsifier for the crude emulsion produced from the fields.

2.1 Sample Collection for Bottle Test

At the Obigbo flow station, samples were collected at the wellhead manifold pressure with the aid of a sample container.

The pressure of the bleeding point was opened sufficiently so as to get a homogenized sample of fluid. The sample container was rinsed with the sample before the collection. The following rules were observed while performing the bottle test experiment:

1. The samples were as fresh as possible.
2. The samples used for the bottle test were true representative of the crude oil emulsion at the Obigbo fields.
3. The same condition of agitation and temperature were simulated as the experiment was performed.

2.2 Blending Of Crude Oil Sample with Gasoline

Six test bottles labeled A, B, C, D, E and F were used for this test. The crude oil was blended with different ratios of gasoline (0ml, 5ml, 10ml, 15ml, 20ml and 25ml) and filled into the labeled test bottle accordingly. Thus sample A was not blended with gasoline (blank sample).

According to Stokes' law (HTS Consultants, 2007), the settling velocity of water droplet in an oil continuous phase is proportional to the diameter of the droplet squared, the difference in density between the oil and water phases, and the inverse of the viscosity of the oil, mathematically expressed as:

$$\frac{dx}{dt} \alpha \frac{d^2 \left(\rho_{water} - \rho_{oil}\right)}{\mu}$$

$where:$

$\frac{dx}{dt}$ = rate of creaming of the dispersed water phase.

$d =$ diameter of the water droplet

$\rho_{water} - \rho_{oil} =$ relative difference in density of the emulsion phase and

$\mu =$ viscosity of the emulsion

Thus, addition of low-boiling diluents to the heavy crude oil emulsions will increase the difference in density of its emulsion phases, and also the viscosity of the continuous phase. This then enhances flocculation and coalescence of the crude's dispersed water droplets according to equation [1], and thus improving the rate of demulsification and dehydration.

2.3 Determination of Specific Gravity and API Gravity

Specific gravity test was carried out on the blended samples A to F and pure gasoline using the standard laboratory test method. The materials used were crude oil/gasoline blends, labeled A to F; gasoline sample; distilled water; pycnometers (density bottle); beaker; measuring cylinder; and electronic balance. The balance was set at zero point before an empty, clean dry 50ml pycnometer was weighed. The pycnometer was filled with the sample and excess liquid coming out through the capillary tube was wiped off. The pycnometer together with sample was then weighed. The pycnometer was also filled with distilled water and weighed. The experiment was carried out at room temperature of 28^0C. The procedure was repeated for all the samples and the specific gravity was calculated as follows:

$$Specific\ gravity = \frac{weight\ of\ sample\,(g)}{weight\ of\ distilled\ water\,(g)}$$

$$Specific\ gravity = \frac{m_2 - m_1}{m_3 - m_1}$$

where:

$m_1 =$ weight of empty pycnometer

$m_2 =$ weight of pycnometer + sample

$m_3 =$ weight of pycnometer + distilled water

The API gravity was determined using the equation [2] below:

$$^0API = \frac{141.5}{Sp.Gr.(60^0 F / 60^0 F)} - 131.5$$

The values of specific gravity and API gravity were calculated and recorded.

2.4 Determination of BS&W:

Laboratory test was carried out to determine the Basic Sediment and Water (BS&W) of the unblended and blended samples A to F, first without addition of chemical demulsifier, then followed by addition of 2 to 3 drops (about 2ppm) of chemical demulsifier - NALCO EC 2111A to the samples. Graduated centrifuge tubes, measuring cylinders (I0ml), centrifuge and stop watch were used to carry out the tests. Six different small graduated centrifuge tubes were filled with samples A to F to the 10ml mark. The blend samples were mildly agitated by manually shaking the tubes 15 times to ensure thorough mixing of both the oil and the gasoline. The samples were centrifuged for 10 minutes at about 3000rpm. All samples were treated equally.

The basic sediment content, water content and the sum of the basic sediment and water were read and recorded. The procedure was repeated with the addition of 2 to 3 drops (about 2ppm) of chemical demulsifier- NALCO EC2I11A to the newly filled centrifuge tubes. The readings obtained were also recorded.

3. Results and Discussion

3.1 Results

The results of the specific gravity, API gravity and bottom sediment and water (BS&W) of the unblended and blended crude oil are presented in the table below. Detailed samples calculations are shown in the appendix.

Table 1. *Specific Gravity, API Gravity of Crude Oil/Gasoline Blends and % water separation*

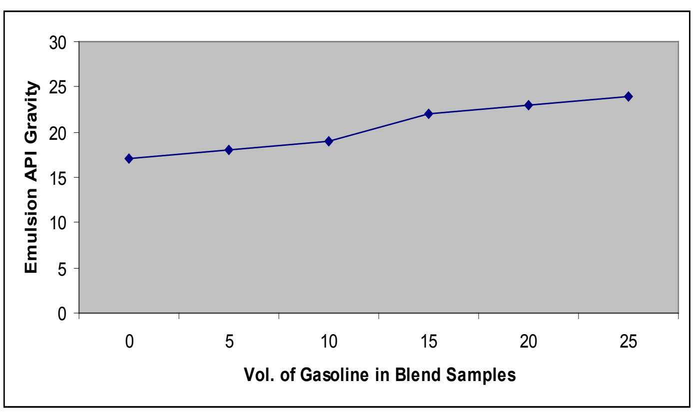
Sample Label	Crude Emulsion (%)	Oil Gasoline (%)	Specific Gravity	API Gravity	% Vol. Water separation Without Demulsifier	% Vol. Water separation With Demulsifier
A	100	0	0.955	17	6.25	8.75
B	95	5	0.947	18	11.25	13.75
C	90	10	0.939	19	15.00	16.25
D	85	15	0.924	22	16.25	17.50
E	80	20	0.918	23	17.50	17.75
F	75	25	0.909	24	18.75	21.25
G	0	100	0.771	52	-	-

4. Discussion of Results

Figure 1 shows the effect of gasoline blending on emulsion API gravity. From the results presented in table 1, an increase in the blending ratio of gasoline gives corresponding increase in the API gravity of the crude oil emulsion. This is a remarkable improvement achieved by gasoline blends since a high API gravity is an indication of the quality of petroleum products.

Also, the degree of water separation which is a function of the lightness of the emulsion is shown in figure 2. The ease of water separation increases with increasing volume of the gasoline blended with the crude oil emulsion. Blend A (blank) gave a poor resolution of the emulsion even with a chemical demulsifier. This was due to lack of diluents. The addition of 5ml of diluents in blend B enhanced the rate of water drop which improved progressively in Blends C through D to F without demulsifier dosage. The rate of water drop was more enhanced with dosage of 2ppm chemical demulsifier.

Fig.1. *Effect of Gasoline blending on emulsion API Gravity*



Importantly, one of the properties of crude oil which often determines its export and sales volume is its BS&W. with the drastic rate of water drop from the crude oil due to addition of diluents, analysis of the top, dry crude will give a BS&W $\leq$ 0.2% which falls within the range of operator's specification for sale or export.

Fig.2. *Effect of Gasoline Blending on Volume of Water Separated*

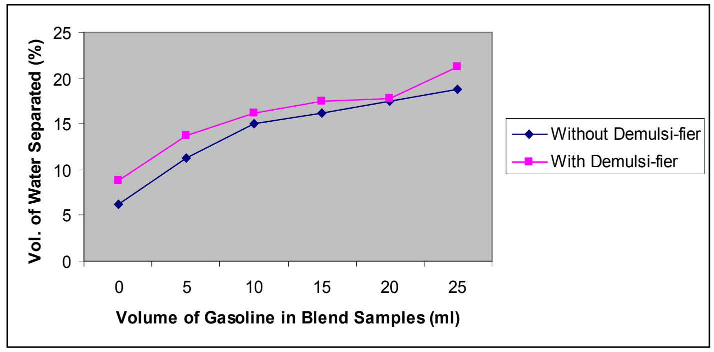
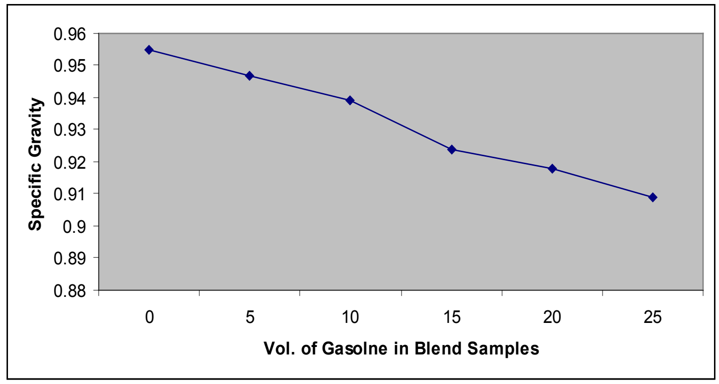


Fig.3. *Effect of Gasoline blending on emulsion Specific Gravity*



The crude oil produced with trace BS&W as blending ratio increased had the following qualities:

1. Low probability of corroding export lines including sub-sea lines and at refinery.
2. Lower cost pumping and hence ease of handling, and
3. Low potential to scale or plug flow lines, manifold, and processing facilities.

Figure 3 shows the decrease in specific gravity of the emulsion as percentage volume of diluents increases. The specific gravity drops from 0.9555 to 0.909 as diluents increases from 0 to 25ml.

5. Conclusion

The laboratory study of blending the heavy crude oil emulsion with different gasoline ratios at the field's wellhead temperature and a 2ppm demulsifier treatment has satisfactorily proven to be an effective method for tackling oilfield emulsion problems due to a number of reasons. First, gasoline is regarded as a compatible and effective diluents for reducing the absolute viscosity of the heavy emulsion crude without the use of additional heat except that attained at the wellhead. This improved the crude flow through facilities with relatively little pumping cost.

Secondly, gasoline enhances the process of demulsification by creating emulsion blends that are less tight and hence easily resolved with a low dosage of demulsifier chemical. Results from this study indicate that the rate of water separation increases with increase in gasoline blending ratio. This reduces the excessive use of demulsifier and hence optimizes the purchase cost of demulsifier.

Thirdly, gasoline also improved the quality of the dry crude oil and separated effluent water. Using gasoline as diluents produced dry crude which fall within the range of the operator's specification of ≤ 0.2% BS&W. This effect reduces the risk of corrosion in flow lines and export pipeline and at refineries. It will also reduce the risk of catalyst poisoning during refining operation. More importantly, it increases the market preference of the crude oil.

Finally, the advantages of this process over the use of heat and some other emulsion control measures include its ease of execution since it does not require the specification and design of any special unit operation equipment. Only a pump and the erection of an injection point may be necessary, hence it requires relatively little capital and time for execution in newly developed oilfields.

Although the bottle test has existed for years and continues to be a source of guidance when addressing oilfield emulsion problems, it is only suitable for laboratory experimentation. It is therefore recommended that pilot plant and field trials should be carried out to enable the effects of the gasoline blends be seen under large scale production conditions.

6. References

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7. Appendix

7.1 Specific Gravity Calculation (move to appendix)

The readings obtained from the tests were computed and the following calculations were made:

$$Specific\ gravity = \frac{m_2 - m_1}{m_3 - m_1}$$

Where

m_1 = wt. of empty pycnometer = 28.52g

m_2 = wt. of pycnometer + sample = 66.85g

m_3 = wt. of pycnometer + distilled water = 78.24g

For Sample A; (100% crude oil), m_2 = 75.99g.

$$Specific\ gravity = \frac{66.85 - 28.52}{78.24 - 28.52}$$
$$= 0.771$$

For Samples B to F similar calculations were made and results shown in Table 2.

7.2 API Gravity Calculation (move to appendix)

From the values of specific gravity obtained, the API gravity can be calculated using the following relationship.

$$^0API = \frac{141.5}{Sp.Gr.(60^0 F / 60^0 F)} - 131.5$$

For 100% gasoline;

$$^0API = \frac{141.5}{0.771} - 131.5$$

$$= 52.03$$

7.3 BS&W Calculations: (move to appendix)

The percentage volume of water separated was calculated as follows for samples with and without demulsifier:

$$\%Vol.of\ water\,separated = \frac{vol.of\ water\,separated\,(ml)\,x100\%}{total\,vol.\ of\ sample\,(ml)}$$