Demulsification Studies on Western Onshore Crude Oils

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Abstract: Western onshore fields are known as mature fields and the problems associated with mature fields are encountered in day to day operations. Water content of different fields are showing uptrend and field operator requires new products (Demulsifiers) to deal with the problems. Some of the field produces heavy while some produces paraffinic oil. To break this kind of emulsion (Heavy oil emulsion) it requires high temperature and higher doses of demulsifier. Demulsification of heavy oils is a well known issue and requires thorough investigation in terms of evaluation of the product at high temperature along with dose optimization to get better water quality after Demulsification. The paper deals with Demulsification studies of individual oil and studies on their mixes. Oils were treated with different demulsifiers at different temperatures. Product optimization studies were also taken up to select the best product which can be field implemented.

Keywords: Demulsifier, Emulsion, Crude oil

1. Introduction:

Crude oil is rarely produced alone. It is generally mixed with water, which creates a number of problems during oil production. Produced water in the field is obtained in two ways: some of the water may be produced as free water and some of the water may be produced in the form of emulsions. Treatment of emulsion is a tedious issue because of number of operational problems like tripping of separation equipment in gas, in oil separating plants, production of off-specification crude oil, and creating high pressure drops in flow lines. To meet crude specification for transportation, storage, exportation and to reduce corrosion and catalyst poisoning in downstream-processing facilities, emulsions have to be treated to remove the dispersed water and associated inorganic salts.

Emulsion:

An emulsion, in physical chemistry is mixture of two or more liquids in which one is present as droplet, of microscopic distributed throughout the other.

A crude-oil emulsion can be classified into three broad groups:

- water in oil emulsion
- oil in water emulsion
- multi or complex emulsion

The stability of inter- facial films, and the stability of the emulsions depends on a number of factors, including the heavy material in the crude oil (e.g., asphalatene, resins, and waxes), solids (e.g., clays, scales, and corrosion products), temperature, droplet size.

The water in Oil emulsions consist of water droplets in a continuous oil phase, and the oil in water emulsions consist of oil droplets in a continuous water phase. In the oil industry, W/O emulsions are more common and therefore, the O/W emulsions are sometimes referred to as “reverse” emulsions. Multiple emulsions consist of tiny droplets suspended in large droplets and are more complex.

Mechanism involved in Demulsification:

Demulsification:

It is the separation of an emulsion into its component phase, is a three step process. The first step is flocculation (aggregation, agglomeration, or coagulation). The second step is coalescence. Both of these steps can be the rate-determining step in emulsion breaking.

Flocculation or aggregation:

The first step in Demulsification is the flocculation of water droplets. During flocculation, the droplets clump together and aggregates are formed. The droplets are close to each other, even touching at certain points, but do not lose their identity. Coalescence at this stage only takes place if the emulsifier film surrounding the water droplets is very weak. The rate of flocculation depends on the following factors.

- Water content in the emulsion.
- Temperature of the emulsion is high.
- Viscosity of the oil is low.
- Density difference between oil and water is high.

Coalescence:

Coalescence is the second step in Demulsification. It is a process in which tiny droplets of water combined or merge to form a large droplet.

- High rate of flocculation increases the collision frequency between droplets.
- The absence of mechanically strong films that stabilize emulsion.
- High water cut increases the frequency of collisions between droplets.
- High temperature reduces the oil and interfacial viscosities thereby increasing the droplet collision frequency.

Sedimentation or creaming:

In this process water droplets settle down in an emulsion because of their higher density. Its opposite process, creaming, is the rising of oil droplets in the water phase. Sedimentation and creaming are driven by the density difference between oil and water and may not result in the breaking of emulsion. Unresolved emulsion droplets accumulate at the oil in water interface in surface equipment and form an emulsion pad.

A pad in surface equipment causes several problems including the following:

- Occupies space in the separation tank and effectively reduces the retention or separation time.
- Increase the BS&W of the treated oil.
- Increase the residual oil in the treated water

Emulsion pads are caused by:

- Ineffective demulsifiers (unable to resolve the emulsion)
- Insufficient demulsifiers (insufficient quantities to break the emulsion effectively)
- Low temperatures.
- The presence of accumulating solids.

Because emulsion pads cause several operational problems, their cause should be determined and appropriate actions taken to eliminates them.

Methods:

Crude oil emulsions must be separated completely before the oil to be transported and processed further. The separation of emulsion into oil and water requires the destabilization of emulsifying films around water droplets. This process is accomplished by any, or a combination, of the following method:

- Chemical methods - adding chemical demulsifiers.
- Thermal methods - Increasing the temperature of the emulsion.
- Electrical methods - Applying electrostatic fields that promote coalescence.

- Mechanical methods – Reducing the flow velocity that allows gravitational separation of oil, water, and gas.

Demulsification methods are application specific because of the wide variety of crude oils, brines, separation equipment, chemical demulsifier, and specification. Furthermore, emulation and condition change over time, which adds to the complexity of the treatment. Heat application method is used to treat emulsion better chemical demulsifier to promote destabilization followed by settling time with electrostatic grids to promote gravitational separation.

Chemical Method

In this method of emulsion treatment is adding demulsifier. These chemicals are designed to neutralize the stabilising effect of emulsifying agent. Demulsifier are surface acting agent that when added to emulsion, move to the oil in water interface, elate or weaken the rigid film, enhance water droplet coalescence. Ideal emulsion breaking with demulsifier requires a actual selectivity of chemical, appropriate quantity of chemical, appropriate mixing of chemical and sufficient retention time in separator for the water droplets to settle down. It is may also required the addition of heat, electric grids, and coalesces to facilitate or completely resolve the emulsion.

Chemical selection

Selection of the appropriate demulsifier is critical for emulsion breaking. However, with the increasing understanding of emulsion mechanisms, the availability of new and improved chemicals, and new technology, research, and development efforts, selection of the right chemical is becoming more scientific. Many of the failure of past have been eliminated.

Demulsifier chemicals contain the following component:

- Solvents
- Surface active ingredients
- flocculants

Testing procedures are available to select appropriate chemicals. These tests include:

- Bottle tests
- Dynamic simulators
- Actual plant tests

All test procedure have limitations. Hundreds of commercial demulsifier products are available that may be tested. Changing condition at separation facilities result in a very slow selection process, especially at large facilities; therefore, it is important at such facilities to maintain a record of operational data and testing procedures as an ongoing activity.

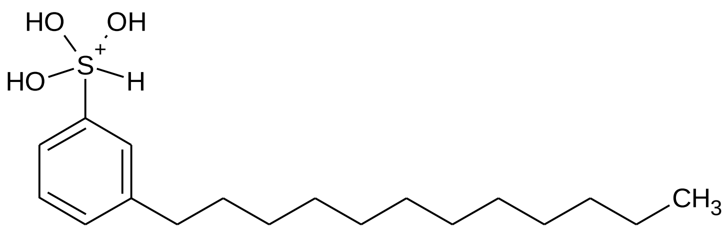
Several factors effect demulsifier performance including:

- Temperature
- PH
- Type of crude oil
- Brine composition
- Droplet size and distribution

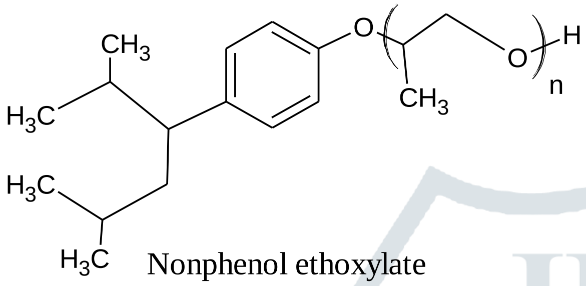
Demulsifiers are typically formulated with polymeric chains of:

- Ethoxylated phenols
- Ethoxylated alcohols and amines
- Ethoxylated resins
- Ethoxylated oxides

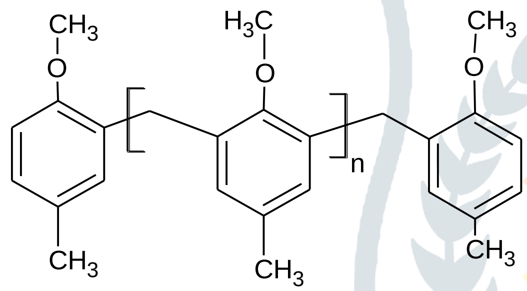
Fig 1. Structures of Demulsifiers



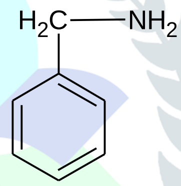
Dodecylbenzene sulphonic acid



Nonphenol ethoxylate



Nonphenol with EO+PO complex



Benzylamine

Fig 2: Oil sample

Fig 3: Samples of various demulsifier

Fig 4: Separation of water after Demulsification

The above figure shows that the demulsifier displaces the indigenous surfactants in the interfacial film**.**

To ensure better performance, a demulsifier should meet the following criteria.

- Dissolve in the continuous oil phase.
- Partition into the water phase.
- Possess a high rate of adsorption at the interface.
- Have an interfacial activity high enough to suppress the IFT gradient, thus accelerating the rate of film drainage and promoting coalescence.

2. Experimental work:

- The oil sample was preconditioned by heating at 40-50^{o} C for 1 hour.
- The oil sample was dose with pre-decided dose of 300-800ppm of 2-20% demulsifier solution (Xylene or Toluene).
- It was then shaken 50 times vigorously for homogenization, removing the cap periodically for the gases to seep out.
- The oil sample was then heated to 65^{o} C.
- The oil sample was then shaken 150 times more for complete homogenization and left for curing for 1 hour at 65^{o} C.
- Then oil sample was taken from around middle level of the beaker and water content was measured using IP-358 method (Dean stark method).

3. Results: (Bottle test)

Table-1.

Source : Western onshore field (Oil Sample I)
Volume : 10 lit.
Free water: 2 lit. After heating 1 hr @ 70˚C
Blank W/C: 40 %

No.	Name		Dose		Results			
	Name of the product	Name of the Product	Dose in ppm	Dose in ppm	Initial water separation (ml)	After 1hr water separation (ml)	Water clarity	Water content %
1	Product-A	-	300	-	Nil	10 ml	Clear	N.A
2	〃	-	500	-	Nil	50ml	Sticky	N.A
3	Product-B	-	300	-	Nil	Nil	Clear	N.A
4	〃	-	500	-	Nil	25 ml	-	N.A
5	Product-C	-	300	-	Nil	Nil	-	N.A
6	〃	-	500	-	Nil	10 ml	-	N.A
7	Product-D	-	300	-	Nil	10ml	-	N.A
8	〃	-	500	-	Nil	50 ml	Crystal clear	N.A
9	Product-E	-	500	-	Nil	Nil	-	N.A
10	〃	-	800	-	Nil	45 ml	Brownish	N.A
11	Product-F	-	500	-	Nil	15 ml	Clean	N.A
12	〃	-	800	-	Nil	65 ml	Clean	N.A
13	Blank	-	-	-	Nil	-	-	-

Table-1.1

Source : Western onshore field (Oil Sample I)
Blank W/C: 40 %

No.	Name		Dose		Results			
	Name of the Product	Name of the Product	Dose in ppm	Dose in ppm	Initial water Sep.(ml)	After 1hr sep. (ml)	Water clarity	Water content %
1	Product-A	Product -G	500	500	25 ml	50ml	Clean	2.0%
2	Product-B	Product -G	500	500	Nil	40 ml	Clean	4.0%
3	Product-D	Product -G	500	500	Nil	60ml	Crystal clear	4.0%
4	Product-E	-	1000	-	30ml	60ml	Clean	2.8%
5	Product-F	-	1000	-	15ml	50ml	Crystal clear	3.2%
6	Product-H	-	1000	-	Nil	50ml	clear	2.4%
7	Blank	-	-	-	Nil	Nil	-	-

Table-1.2

Source –Western onshore field (Oil Sample II) Dozing@40˚C
Blank w/c – 65% Curing@60˚C

No.	Name		Dose		Results			
	Name of Product	Name of Product	Dose in ppm	Dose in ppm	Initial water Sep.(ml)	After 1hr sep. (ml)	Water clarity	Water content %
1	Product-A	-	300	-	85 ml	110ml	Clean	1.6%
2	Product-A	-	500	-	80 ml	110ml	〃	1.4%
3	Product-B	-	300	-	100ml	115ml	〃	1.2%
4	Product-B	-	500	-	120ml	120ml	〃	1.2%
5	Product-D	-	300	-	Nil	110ml	〃	1.6%
6	Product-D	-	500	-	100ml	125ml	〃	3.2 %
7	Blank	-	-	-	-	-	-	-

Table 1.3

Source- Western onshore field (Oil Sample III+IV, ratio 6:1) Dozing@ 40˚C
Blank W/C- 65% Curing@ 60˚C

No.	Name		Dose		Results			
	Name of the product	Name of the product	Dose in ppm	Dose in ppm	Initial water Sep.(ml)	After 1hr sep. (ml)	Water clarity	Water content %
1	Product-A1	-	500	-	15 ml	110ml	Clean	1.6%
2	Product-B1	Product -G	400	400	15 ml	100ml	〃	1.2%
3	Product-E	-	500	-	110ml	130ml	〃	1.0%
4	Product-E	-	800	-	125ml	125ml	Brownish	2.8%
5	Product-F	-	500	-	90	130ml	Muddy& Sticky	1.6%
6	Product-A	Product -G	400	400	125ml	125ml	Clean	0.8 %
7	Blank	-	-		-	-	-	-

4. Discussion:

Demulsification studies were taken up on three different heavy oils to know the effect of different Demulsifiers. Crude oil sample I was heated up to 70˚C to remove the free water available in the crude and demulsification studies were taken up after removing the free water. Crude oil was treated with different demulsifiers (Product A-F) at different doses of 300-800 ppm. The results have been depicted in table 1.
The products which were providing better results viz. (A, B & D) were mixed with another Product G and further evaluated. Similarly product (E, F & H) were also evaluated at a higher dose of 1000 ppm. The results are shown in table no.1.1.
Three products A, B, & D were also evaluated on crude oil sample II. The results have been tabulated in table no.1.2
The efficiency of five different products (A1, B1, E, F & A) were investigated on mixed crude oil sample of III & IV. The efficiency of demulsifiers were also studied by mixing them together (Product B1 & G) and (A & G) and is depicted in table 1.3.

5. Conclusions:

Out of many products evaluated Product F at a dose of 800 ppm was found to be effective on crude oil sample I.
Similarly two products viz.Product B & Product D at a dose of 500 ppm was found to be effective on crude oil sample II and can be further evaluated in the field.
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Product E & Product F at a dose of 500 ppm gave good results on mixed crude oil (Sample III+IV in the mixed in the ratio,6:1) and the water cut was also obtained in the range of 1-1.6 %.
All the samples studied are heavy oils in nature so the final conclusion can be drawn after field trial of the products.

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