Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 11, Issue 1, March 2016 , p.p(234-244)
ISSN 1992 – 0849

EXPERIMENTAL STUDY TO FIND ALTERNATIVE DEMULSIFIER TO TREAT EMULSION CRUDE OIL

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Received date : 27 / 4 / 2015 **Accepted date : 30 / 11 / 2015**

ABSTRACT

When crude oil is produced from an oil field well, it is generally accompanied with variable proportions of water, which makes the separation of water from crude oil commercially difficult. In this research it was found the best alternative demulsifier (belongs to the researchers) from the demulsifiers (unknown chemical formula) that is used in the wet oil treatment. Which is highly effective and less costly in economic terms of their counterparts. The crude oil that we made our research is taken from Jamboor field in Iraq. (Specific gravity = 0.6417) and the water quantity 0.18 ml, if we used organic component Benzene with demulsifier (special formula belongs to researchers), we will see that the quantity of water in crude 0il is (0.17 ml).

Keywords: *Alternative Demulsifiers, Treatment crude oil, Water Drops, Melted Paraffin , Wet crude oil, water-in-oil emulsion.*

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دراسة تجريبية للإيجاد بديل كاسر الاستحلاب لمعالجة النفط الرطب

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تاريخ استلام البحث: ٢٧ / ٤ / ٢٠١٥ تاريخ قبول البحث: ٣٠ / ١١ / ٢٠١٥

الملخص

عندما يتم استخراج النفط الخام من الحقول النفطية فانه يحتوي على نسب معينة من الماء الذي لا يمتزج معه بسبب الشد السطحي الفاصل بينهما الناتج من المركبات البارافينية التي تحيط بقطرات الماء، مما يجعل عملية فصل قطرات الماء من النفط الخام صعبة اقتصاديا وتسمى هذه الحالة مستحلب الماء في النفط الخام. وفي هذا البحث تم ايجاد بديل كاسر الاستحلاب الافضل (العائد للباحثين) من الكواسر الاستحلاب (الغير معلومة صيغته الكيميائية) التي يتم استعماله في معالجة النفط الرطب. والذي يكون ذات فعالية عالية وأقل كلفة من الناحية الاقتصادية من نظيراتها. نفط الخام المستخدم في هذا البحث تم أخذه من حقل الجمبور(كركوك–العراق)، الوزن النوعي له يساوي ٠.٦٤١٧ والماء المتواجد بيه (٠.١٨)ml، فعند إجراء البحث باستخدام البنزين كمادة عضوية مع كاسر الاستحلاب (العائد للباحثين)، نلاحظ بأن كمية الماء والتي تم معالجته تكون (٠.١٧)ml.

الكلمات الدالة : بديل كاسر الاستحلاب ، معالجة النفط الخام ، قطرات الماء ، ذوبان البارافين : النفط الرطب ، الماء في النفط المستحلب.

1. INTRODUCTION

Demulsification is the breaking of a crude oil emulsion into oil and water phases. From a process point of view, the oil producer is interested in three aspects of demulsification: rate or the speed at which this separation takes place & amount of water left in the crude oil after separation and quality of separated water for disposal. A fast rate of separation, a low value of residual water in the crude oil, and a low value of oil in the disposal water are obviously desirable. Produced oil generally has to meet company and pipeline specifications. For example, the oil shipped from wet-crude handling facilities must not contain more than 0.2% basic sediment and water (BS&W) and 10 pounds of salt per thousand barrels of crude oil. This standard depends on company and pipeline specifications. The salt is insoluble in oil and associated with residual water in the treated crude. Low BS&W and salt content is required to reduce corrosion and deposition of salts. The primary concern in refineries is to remove inorganic salts from the crude oil before they cause corrosion or other detrimental effects in refinery equipment. The salts are removed by washing or desalting the crude oil with relatively fresh water. When crude oil is produced from an oil field well, it is generally accompanied with variable proportions of water. This water is emulsified by surface-active substances naturally present in the crude, which makes the separation of water prior to crude commercialization difficult. A number of research groups have investigated the various mechanisms of water-in-oil emulsion stabilization, a good review of which has been issued recently[1]. Various techniques are used to break these emulsions, among which the most widely used consists of adding small amounts of so-called “demulsifiers”. These surface-active molecules adsorb at the oil-water interface and accelerate the phase separation. Nowadays, the mechanism for this destabilization is however not yet fully understood. A number of demulsifiers are proposed by suppliers and the choice of the most efficient one is a long and difficult task. Moreover, during the well life, the production conditions (temperature, salinity) can change and it is very often necessary to proceed to the selection of another additive. The different demulsifiers are generally tested through a “bottle-test” method, which consists of adding a given demulsifier in small bottles containing freshly sampled emulsion from the field production and following the percentage of decanted water as a function of time. Screening of additives is then performed rather empirically. In this paper, we present first, on the basis of bottle testing, a physicochemical approach of demulsification that gives some insight into the operative mechanisms. This approach is based on earlier observations

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carried out while the phase behavior of surfactant-water hydrocarbon mixtures for micro emulsion formulation was being investigated. [2,3] It was then found that the rate of phase separation is maximum when a particular three-phase behavior, namely, a micro emulsion phase in equilibrium with both excess water and oil phases, is observed when the system has reached its final equilibrium. Produced oilfield emulsions can be classified into three broad groups: water-in-oil, oil-in-water, and multiple or complex emulsions. Water-in-oil emulsions consist of water droplets in a continuous oil phase, and oil-in-water emulsions consist of oil droplets in a water-continuous phase. Figures. (1) and (2) show the two basic (water-in-oil and oil-in-water) types of emulsions. Multiple emulsions are more complex and consist of tiny droplets suspended in bigger droplets that are suspended in a continuous phase[5]. Figures. (3) and (4) shows Photomicrograph of oil in water emulsion and Fig.(5) shows an example of a multiple emulsion[4,6].

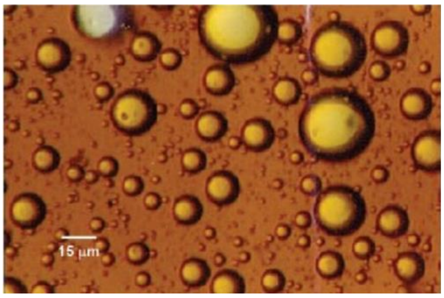

Fig.(1): Photomicrograph of a water in oil emulsion

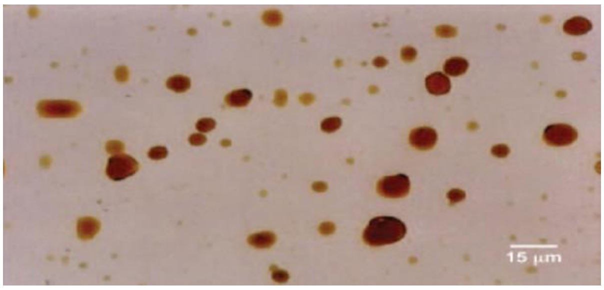

Fig.(2): Photomicrograph of oil in water emulsion

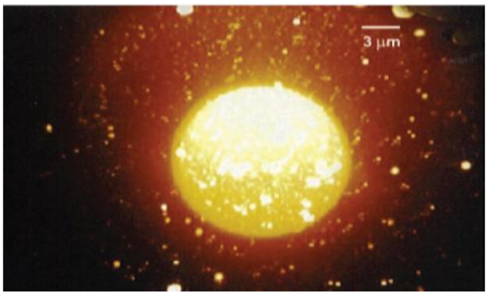

Fig.(3): Photomicrograph of an emulsion showing interfacial films (magnified)

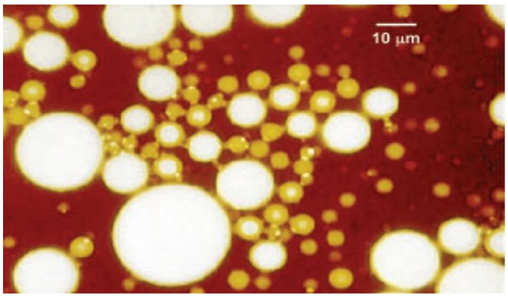

Fig.(4): Photomicrograph of an emulsion showing interfacial film

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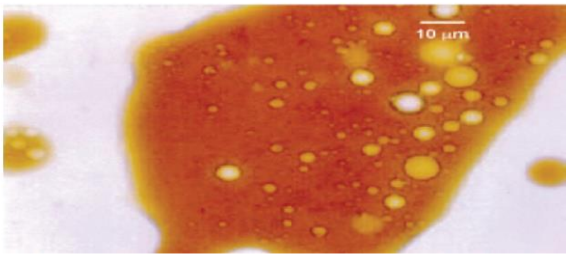

Fig. (5): Photomicrograph of oil in water emulsion

When the dispersed droplets are larger than 0.1 µm, the emulsion is a macro emulsion[6, 4]. Emulsions of this kind are normally thermodynamically unstable (i.e., the two phases will separate over time because of a tendency for the emulsion to reduce its interfacial energy by coalescence and separation). However, droplet coalescence can be reduced or even eliminated through a stabilization mechanism. Most oilfield emulsions belong in this category. In contrast to macro emulsions, there is a second class of emulsions known as micro emulsions. These emulsions form spontaneously when two immiscible phases are brought together because of their extremely low interfacial energy. Micro emulsions have very small droplet sizes, less than 10 µm, and are considered thermodynamically stable. Micro emulsions are fundamentally different from macro emulsions in their formation and stability. The parameters that effect on emulsion crude oil stability water concentration & mixing speed effect and temperature[4]. Crude oil emulsions must be separated almost completely before the oil can be transported and processed further. Emulsion separation 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 methods: Thermal methods & Mechanical methods and Chemical methods. The most common method of emulsion treatment is adding demulsifiers. These chemicals are designed to neutralize the stabilizing effect of emulsifying agents. Demulsifiers are surface-active compounds that, when added to the emulsion, migrate to the oil/water interface, rupture or weaken the rigid film, and enhance water droplet coalescence. Optimum emulsion breaking with a demulsifier requires a properly selected chemical for the given emulsion; adequate quantity of this chemical; adequate mixing of the chemical in the emulsion; and sufficient retention time in separators to settle water droplets. It may also require the addition of heat, electric grids, and coalesces to facilitate or completely resolve the emulsion. Demulsifier chemicals contain the following components: Solvents & Surface-active ingredients and Flocculants [7, 8, 9, 10, 11].Solvents, such as benzene, toluene, xylene, short-chain alcohols, and heavy aromatic naphtha, are generally

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carriers for the active ingredients of the demulsifier. Some solvents change the solubility conditions of the natural emulsifiers (e.g., asphaltenes) that are accumulated at the oil/brine interface. These solvents dissolve the indigenous surface-active agents back into the bulk phase, affecting the properties of the interfacial film that can facilitate coalescence and water separation. Surface-active ingredients are chemicals that have surface-active properties characterized by hydrophilic-lipophilic balance (HLB) values. For a definition and description of HLB, see the literature [5]. The HLB scale varies from 0 to 20. A low HLB value refers to a hydrophilic or water-soluble surfactant. In general, natural emulsifiers that stabilize a water-in-oil emulsion exhibit an HLB value in the range of 3 to 8[5]. Thus, demulsifiers with a high HLB value will destabilize these emulsions. The demulsifiers act by total or partial displacement of the indigenous stabilizing interfacial film components (polar materials) around the water droplets. This displacement also brings about a change in properties such as interfacial viscosity or elasticity of the protecting film, thus enhancing destabilization. In some cases, demulsifiers act as a wetting agent and change the wettability of the stabilizing particles, leading to a breakup of the emulsion film. Flocculants are chemicals that flocculate the water droplets and facilitate coalescence.

2. EXPERIMENTAL WORK

2.1.APPARATUS

2.1.1.WATER CONTENT TESTING: the ASTM D 95 Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation .The apparatus is used for testing water in the range from 0 to 25 % volume in petroleum products, tars, and other bituminous materials by the distillation method.

2.1.2. CONICAL PLATE CENTRIFUGEC: is a type of centrifuge that has a series of conical discs which provides a parallel configuration of centrifugation spaces. The conical plate centrifuge is used to remove solids (usually impurities) from liquids or to separate two liquid phases from each other by means of an enormously high centrifugal force. The denser solids or liquids which are subjected to these forces move outwards towards the rotating bowl wall while the less dense fluids moves towards the center. The special plates (known as disc stacks) increase the surface settling area which speeds up the separation process. Different stack designs, arrangements and shapes are used for different processes depending on the type of feed present. The concentrated denser solid or liquid is then removed continuously, manually or intermittently, depending on the design of the conical plate centrifuge. This

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centrifuge is very suitable for clarifying liquids that have small proportion of suspended solids.

2.2. MATERIALS

Organic materials used in this research is Toluene 60% (country of origin U.S.A) and Benzene 40% (country of origin Turkey) either demulsifier components it (CHINZC-29614) (country of origin China) and demulsifier with special formula belongs to researchers.

2.3.Procedure

After pumping the crude oil from the reservoir it will restored in big tanks and waited for about 24 hours, so the large water drops which covered by paraffin components are collected in the bottom of treatment tank because of its high density (these will threw out and are not needed); but the tiny water drops which covered by the same paraffin components will not collected in the bottom of treatment tank because of its low density. In this research it is required to choose the best demulsifier one to melt paraffin components and release the shear stress of water drops (their diameters are more than 0.1 μm) that exist in crude oil. So these water drops broken easily when we supply electric voltage. After the treatment crude oil the rate of water percentage must not increase 12 ppm in one barrel because if it increases from this rate, it will cause corrosion in the refinery operation. The crude oil that was used in the present research is taken from Jamboor oil field in Iraq. (Specific gravity = 0.6417) and the water quantity 0.18 ml that we take this reading by the apparatus water content as seen in figure 6 (a & b). Then we took 25 ml from crude oil with 25 ml organic component (Benzene or Toluene) leading to make hydrocarbon components with the same physical properties and reduce the viscosity of crude oil, then added amount of alternative demulsifier (found by the researchers) or original demulsifier (CHINZC-29614) that used in industry treatment (0.2 – 0.5) ml. First of all we took toluene component with crude oil with original demulsifier (CHINZC-29614) that used in industry treatment and we take the water quantity reading from the apparatus named centrifuge as seen in Fig. (7). The working conditions of this apparatus is 1800 rpm with 50 ^{o}C. This procedure repeated again with benzene. Then this experiment repeated again with toluene and benzene but we added the alternative demulsifier (special formula belongs to researchers) instead of original demulsifier. These water quantities are compared with each other to know which water quantity is higher as shown in Figures (8, 9, 10, 11).

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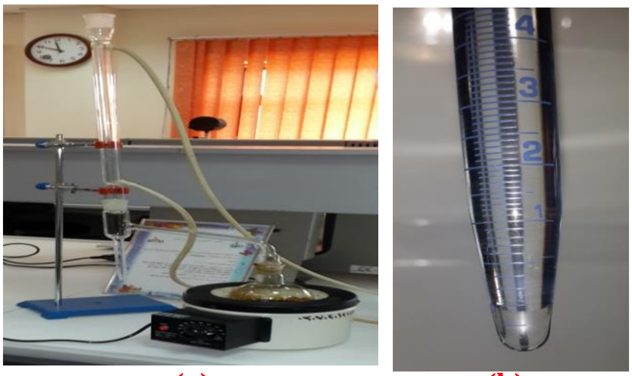

(a) (b)

Fig.(6): apparatus water content

Fig.(7): apparatus centrifuge

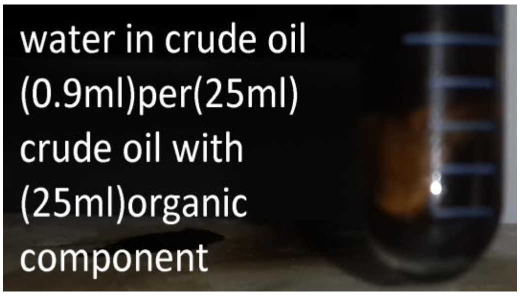

Fig.(8): Toluene with(0.2ml) demulsifier

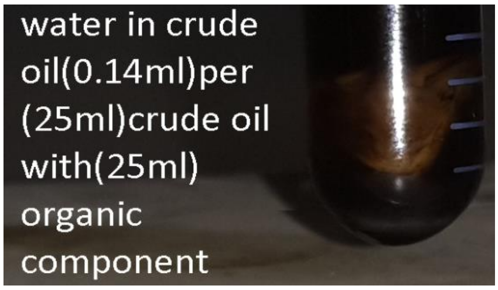

Fig.(9): Benzene with(0.2&0.4ml)demulsifier

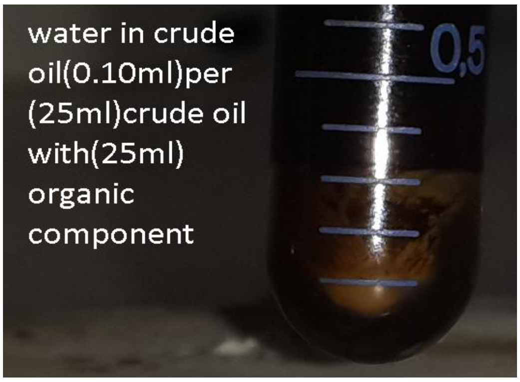

Fig.(10): Benzene without demulsifier

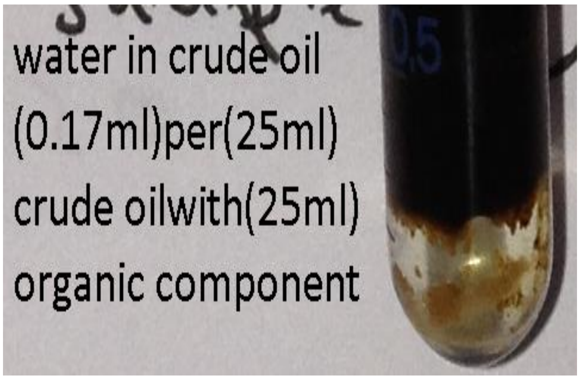

Fig.(11): Benzene with alternative demulsifier

3. RESULT AND DISCUSSION

Table (1)	
Toluene (25 ml) Crude oil (25 ml) Demulsifier (CHINZC-29614)	
vol. of Demulsifier (ml)	water content (ml)
0.2	0.9

Table (2)	
Toluene (25 ml) Crude oil (25 ml) without Demulsifier (CHINZC-29614)	
vol. of Demulsifier (ml)	water content (ml)
0	0.6

Table (3)	
Benzene (25 ml) Crude oil (25 ml) Demulsifier (CHINZC-29614)	
vol. of Demulsifier (ml)	water content (ml)
0.2	0.14
0.4	0.14

Table (4)	
Benzene (25 ml) Crude oil (25 ml) without Demulsifier (CHINZC-29614)	
vol. of Demulsifier (ml)	water content (ml)
0	0.10

Table (5)	
Benzene (25 ml) Crude oil (25 ml) (special formula belongs to researchers)	
vol. of Demulsifier (ml)	water content (ml)
0.18	0.17
0.36	0.17

If we seize to the Tables (1) and (2) , when we use organic component (Toluene) with demulsifier (CHINZC-29614), we will see that the quantity of water in crude oil is 0.9 ml, and repeating the experiment without adding original demulsifier (CHINZC-29614), we will see the water quantity is 0.6 ml. This shows that the original demulsifier (CHINZC-29614) effects to the melt of paraffin components and the water quantity different between them is (0.3 ml). While

If we look at the Tables (3) and (4) we when we use organic component (Benzene instead of Toluene) will see that the water quantity different between them is (0.4 ml)., this shows changing organic component has an effect to melt the paraffin components and the water quantity increases. Now let us see the table 3 if we increase the amount of demulsifier to double size, the water quantity will not change, this means that increasing demulsifier has no effect to melt more paraffin components. Then, let us seize to Table (5) , we used organic component Benzene (which is better than Toluene as we saw), with demulsifier (special formula belongs to researchers) the water quantity is increased to (0.17 ml), the water quantity different between the table 3 is (0.3 ml).this shows that this special demulsifier is better than the original demulsifier (CHINZC-29614) to melt the paraffin components which covers around water drops and this make the electric penetration be easy which is used in treatment industry of crude oil, because this paraffin components has no electrical conductivity and prevents breaking membranes of water drops. As a result these special demulsifier will be more economical from the original demulsifier (CHINZC-29614). Wide range of water concentration is covered in this study over the range of 10–50% by volume.

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