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Demulsification of a Nigerian crude emulsion using ethoxylated-resoles and their xylene modified blends

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Abstract. Demulsification is a method used to reduce or disrupt the water - crude oil emulsion system without uttering the initial composition of the crude oil. This process is done by the introduction of chemicals called demulsifiers, which break the emulsion into aqueous and organic phases. In this study, the demulsifier formulated was the base-catalyzed phenol-formaldehyde resin known as the resoles, with the ratios of phenol to formaldehyde, varied between 1.0:1.2 and 1.0:2.0. The different samples of resoles where then ethoxylated to make them more hydrophilic using different weights (10, 15 & 20 g) of polyethylene glycol (PEG). Screening of the ethoxylated demulsifiers was done using the established bottle test procedure, at 70 °C, the concentration of 50 ppm, and 20 minutes of residence or separation time, in order to select the most effective demulsifier, based on the amount of water removed from the emulsion. The best chemical-demulsifier produced was the ethoxylated resole, which was then blended with xylene at varying percentages (0, 20, 40, 50, and 80 % weight/weight) and was further screened, using the bottle test method. From the analysis, it was obtained that the most effective ethoxylate-xylene demulsifier blend was sample DR3, and made of formaldehyde to phenol ratio of 1.8:1, 20 g of PEG 400 blended with 20 % xylene. The demulsifier gave a water separation efficiency of 85.7 %, compared with the commercial demulsifier, which yielded 72.7 %. The result indicates the practical significance of solvent modified demulsifiers for separating crude oil emulsions in the petroleum industries.

Keywords: Bottle test, crude oil emulsions, ethoxylated resoles, Resoles, Xylene

1. Introduction

The crude oil reserve in Nigeria has been estimated to be about 2.09 x 1011 ft3. And she is ranked as the sixth-largest oil producer amongst the crude oil-producing nations in the world, with a production capacity of 2.5 x 106 barrel per day (BPD) [1-3]. Crude oil exploration, production, and its sales in Nigeria play a very crucial role in the nation's economy, and it has accounted for more than 90 % of her overall national earnings since oil was discovered in Nigeria in 1956, [4]. The problem with most production wells in Nigeria is the presence of water, coproduced with the crude-oil, giving rise to greater than 2 % basic sediments and water (BS&W) content of the crude oil. The high BS and W is

responsible for the low market value of crude oil [5] produced from this part of the world since it is difficult to meet the international market specifications of lesser than 0.5 %.

Water-in-oil emulsion develops during oil production, and it is often associated with coproduced and or injected water sufficiently agitated at the wellbore and pipelines as the crude oil-water mixture flows from the reservoirs to the manifold, separators, and at the surface facilities [4, 6]. Furthermore, the shear-blending of the crude oil and water phases during production and the presence of the natural surfactants in the crude-oil contribute to the formation of such stable emulsions [7-9]. The water poses several processing problems due to the extreme changes in the Physico-chemical properties of the oil. And these include increased density, viscosity, high-pressure drop in the pipelines, and other challenges related to corrosion [5, 10], which together increase the cost per unit price of crude oil produced. And in most cases, the formed emulsions usually have much higher viscosities than just the water or crude oil alone [5, 10, 11]. Hence the water in the formed emulsion must be disentangled [12] from the mixture by careful treatment, separated and appropriately removed. The ease of separation of petroleum emulsions is a function of the type and the degree of stability of the formed emulsion systems. An emulsion is said to be stable when the emulsion persists in any environment or overcome changes in its physicochemical properties with time [6]. The degree of emulsion stability varies with age, and it is dependent on the characteristic properties of crude petroleum. [13]. Petroleum or crude oil is made up of a series of hydrocarbons [14, 15], such as asphaltenes, naphthenes, alkanes, and aromatic components (the carboxylic acids, phenols), other organic matter, inorganic salts, and metals [16]. A notable amount of nitrogen and sulfur-containing compounds may also be present as well. Crude oil is a compound mixture of organic matters. Its content tends to vary due to its sources or location, age, and depth [17]. Grouping of crude-oil or petroleum noted for aiding the water-in-oil emulsion formations includes resins, asphaltenes, and waxes. They can exist either in their dissolved and/or particulate form within the crude oil emulsion. They are usually bonding materials [18]. Asphaltenes is a very high polar component of crude oil that contains compressed naphthenic and aromatic rings. Most of these chemical compounds sometimes, form films at the surface of the oil, while others are surface active agents. Hence, the probability that unstable or stable emulsion mixtures will be formed varies largely on the constituents of the different crude oils. Emulsions are formed from the fusion of two or more immiscible liquids and can also be referred to as colloidal systems in which tiny droplets of an immiscible liquid are completely dispersed in another mobile or liquid medium, which is usually aided by some emulsifying agents present in the petroleum or crude-oil [19]. Emulsions are part of the two/three phase systems of compound mixtures known as colloids. Emulsions can be grouped into either water-crude oil or oil-water emulsions, with the former, being more frequently occurring in crude oil production wells [20]. And emulsions can be found in various areas such as in agriculture, pulp and paper, food, biological fluids, petroleum, mining, pharmaceuticals industries etc [21].

There are four main treatment methods employed in breaking or demulsifying crude oil emulsions. And they include chemical, thermal, mechanical, and electrical processes [22]. From the operational cost point of view, the chemical-demulsification method is the most efficient method used in the petroleum production industries for the demulsification of crude oil emulsions [22, 23].

Polymeric demulsifiers are some of the readily used chemical compounds that are capable of breaking water-in-oil emulsions. These demulsifiers can easily diffuse into the water-crude oil interfacial boundary and hence reduce the surface tension or break the connecting interfacial film between them. The surface-active agents present in the crude oil possess some functionalized active groups capable of penetrating into the water-crude oil interface to form a thin interfacial layer that can easily be broken, using chemical demulsifiers [24]. Demulsifiers are surface-active compounds that help in the separation of emulsions into crude oil and water phases, usually at minimal dosages or in parts per million (PPM). Some demulsifiers are polymeric in nature, while others are surfactant based on ionic, anionic, or non-ionic structures that are crucial in separating crude oil-water emulsions [15]. The demulsification of water-in-oil emulsions is usually a challenging task. And this is because of the two immiscible liquid phases involved [25].

In this work, resoles (or phenol-formaldehyde resins) were first produced, [1, 4], and ethoxylated with polyethylene glycol (PEG 400), before it was modified using various percentages of xylene as the solvent [4]. The resultant three-components demulsifier was then used to effect the separation of a Nigerian crude-oil emulsion using the bottle test method. The test method of analysis is an experimental procedure where different quantities of the demulsifying agents are introduced into a series of graduated centrifuge tubes containing the emulsion samples to be separated. At the lapse of the set separating time, then the appearance and the extent of phase distribution or separation at the interface between the two phases are recorded [26].

2. Materials and Methods

2.1 Materials
The water-crude oil emulsion was collected from an onshore facility in Nigeria's Niger-Delta region, 37 % formalin or formaldehyde solution, phenol solution (industrial grade), 30 % sodium hydroxide solution, 99.9 % xylene (Technical grade), 20 % hydrochloric, acid, polyethylene glycol (PEG) 400 (Technical Grade).

2.2 Equipment/Apparatus
Uniscope Laboratory water-bath, (model No: SM801A) and centrifuge (Model No: SM800B), pH-meter (Jenway, Model No: 3520), A 2-in-1 Hot plate/magnetic stirrer (Thermo-Scientific, Model No: SP13015), reflux condenser, ESCO Ductless fume cupboard, Scout Pro weighing balance (Model No: SPU2001), quick-fit mercury-in-glass thermometer ($0\text{-}100^0$C), 250 ml 3-neck flat bottom flask (Pyrex), 250 and 500 ml beakers (Pyrex), measuring cylinder (Pyrex), sample bottles, graduated centrifuge bottles, and Dean's stark trap.

2.3 Production of Demulsifiers
The Resoles were first produced using the method described by [1]. The procedure used is known as the condensation polymerization where two reactants – formaldehyde and phenol are reacted to form the resoles, using 30 % sodium hydroxide (NaOH) as the catalyst. The molar ratios of the formulated resins varied from 1.2-2.0 of formaldehyde to 1.0 mole of phenol, carried out at a temperature of 70 ^{o}C, 3 hrs reaction time, and a pH of 9 to give the different phenol-formaldehyde resins (A, B, C, D, and E respectively.

The samples of resoles obtained were then ethoxylated using polyethylene glycol (PEG 400). The ethoxylation reaction was carried out in a 250 ml 3-necked flask, fitted with a reflux condenser, a magnetic stirrer, a quick-fit thermometer, and a dean-stark trap. 10.5 g of each of the resole samples (A, B, C, D, and E) was respectively weighed and mixed with the polyethylene glycol (20 g, 15 g & 10 g, respectively) in benzene as the reaction medium. 20 % hydrochloric acid (1 drop) was then added as a catalyst. The reaction mixture was then refluxed at a temperature of 65 ^{o}C for 2 hrs. Finally, the solvent benzene was removed by increasing the reaction temperature above 82 ^{o}C to separate the benzene from the product, and to obtain the ethoxylated-phenol formaldehyde resin. The different weights of PEG (20g, 15g, & 10g) used during the ethoxylation process were labeled as R1, R2, and R3, respectively. The ethoxylated phenol-formaldehyde resins were thus labeled as AR1, AR2, AR3, BR1, BR2, BR3, CR1, CR2, CR3, DR1, DR2, DR3, ER1, ER2, and ER3 respectively.

2.4 Basic Sediment and Water Test (BS&W)

The BS&W was performed on the oil emulsion so as to determine its water content [1]. The oil samples were first poured into a container and stirred to blend well. The blended crude oil emulsion sample was added to each of the centrifuge bottles, up to half of its full level. Solvent xylene was then added to the centrifuge bottles to make up to the 10 ml mark. The bottle was shaken thoroughly to homogenize its content and then placed in a hot water bath set at 60 °C for 15 mins. The bottles were then arranged in their compartment within the centrifuge machine and allowed to spin at 1500 rpm for 10 mins. The centrifuge bottles were then removed, and the BS&W in each of them noted and recorded. Hence from equation 1, the basic sediment and water were calculated.

$$\% \text{ BS\&W} = 2x. \tag{1}$$

2.5 Screening of Demulsifiers

The bottle test procedure or method (BTM) described by [1, 12] was employed to screen all the formulated demulsifiers.

In this method, the crude oil emulsions were poured into the centrifuge bottles and immersed in the hot water bath set at the required temperature for 15 mins. Each of the prepared demulsifiers was then dosed or injected, at the concentration of 50 ppm, into the centrifuge bottles. They were then uniformly agitated by overturning the tubes several times before contacting them in a hot water bath for about 20 mins until it reached the set temperature of 70°C. The bottles were then taken out of the hot water bath and placed in the centrifuge chamber and spun at 1500 rpm for 15 mins. The volume of water separated was noted and recorded for each of the demulsifier used.

3. Results and Discussion of Results

3.1 Performance of Phenol-Formaldehyde Demulsifiers

The phenol-formaldehyde demulsifiers were prepared at varying phenol to formaldehyde (PF) ratios of 1.2:1, 1.4:1, 1.6:1, 1.8:1 & 2.0:1, and labeled as samples A, B, C, D, and E respectively. Analysis of the formulated PF demulsifiers (or resoles) was done using the bottle test procedure described in section 2.3.3. Results of the analysis from Figure 3 show that the percentage water separation increases steadily as the formaldehyde-phenol (F/P) mole ratio is increased until it got to a maximum at 1.8:1 F/P before it began to decrease. This agrees with the work of other researchers [4] that the solubility of the phenol-formaldehyde resin in the aqueous phase of the crude oil emulsion increases as its formaldehyde content in the demulsifier is increased. The effect of this is the ability of the demulsifier to destabilize the water – crude oil emulsion system, which results in its separation. But beyond this point (1.8:1), an inversion takes place, causing a decrease in its water separation efficiency. The overall best demulsifier was sample D, which gave water separation of 43 %.   Details are in Figure 1-10.
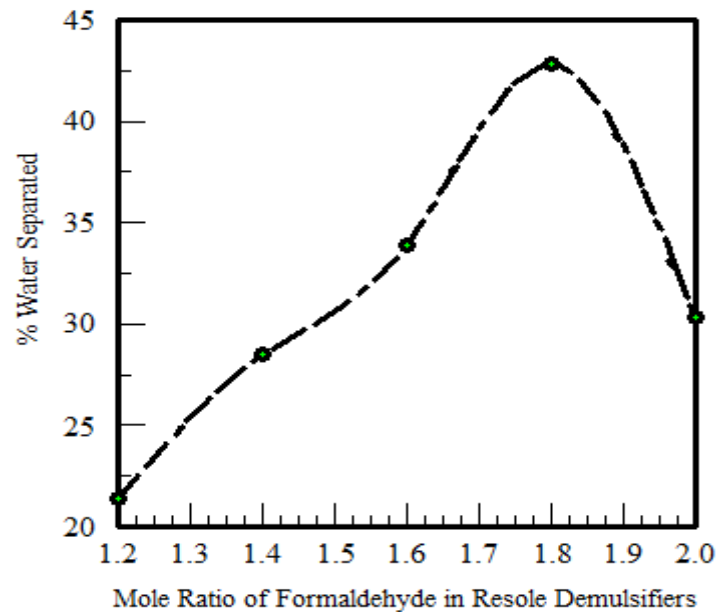
Figure 1: The Effect of Mole Ratio on the Performance of the Resoles

3.2 The Effect of Ethoxylation on Demulsifier Performance
The formulated resole-demulsifiers labeled samples A, B, C, D, and E were each ethoxylated using 10, 15, and 20 g of the polyethylene glycol or PEG 400, respectively, to give the ethoxylated resole-demulsifiers. The results are as displayed in Figures 2 – 4.
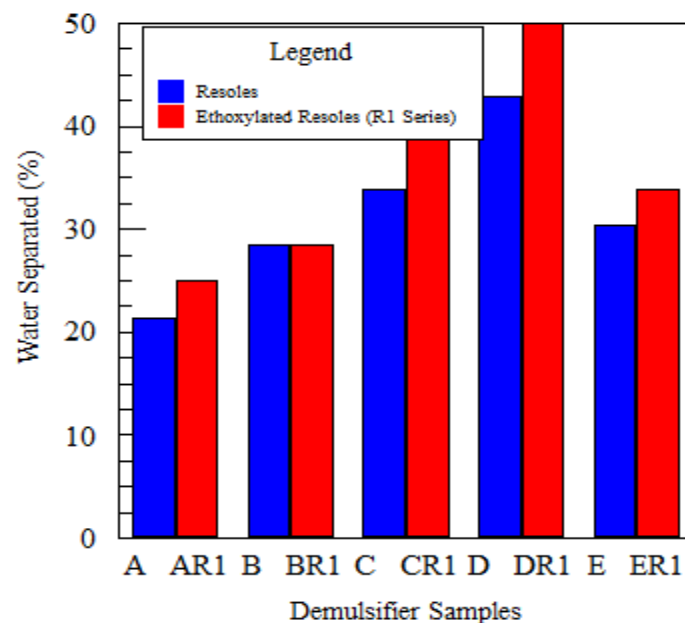

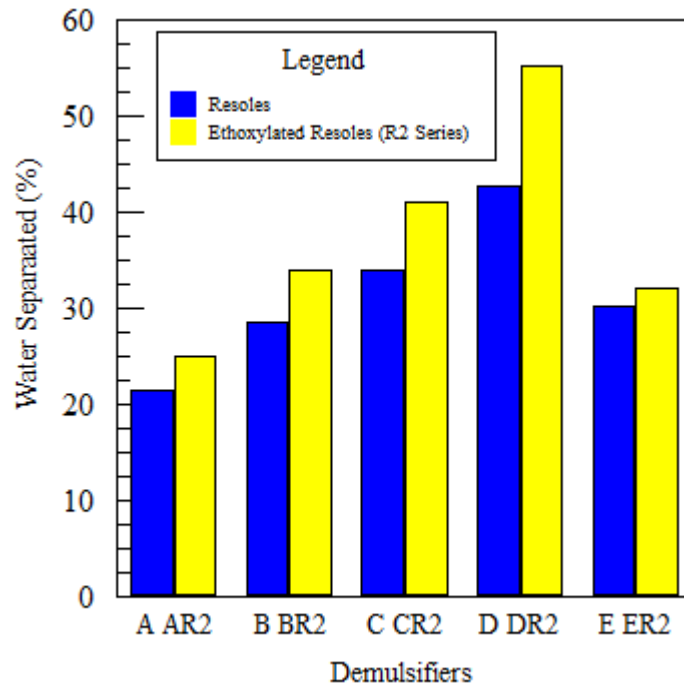**Figure 2**: Comparison of resole and ethoxylated resole demulsifiers using 10 g of PEG 400 (R1)

Figure 3: Comparison of resole and ethoxylated resole demulsifiers using 15 g of PEG 400 (R2)
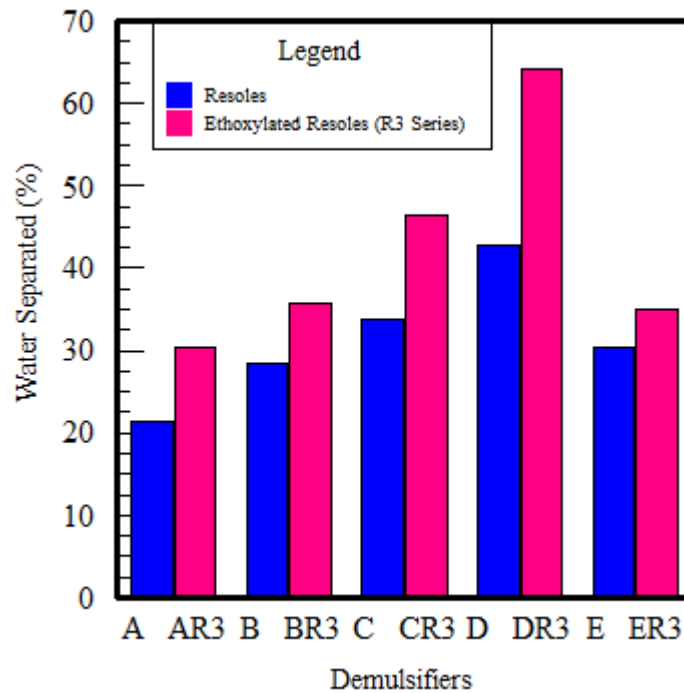

Figure 4: Comparison of resole and ethoxylated resole demulsifiers using 20 g of PEG 400 (R3)

Figures 2–4 show the performance of the ethoxylated resole-demulsifiers using the different quantities (10, 15, and 20 g) of PEG 400, in comparison with the non-ethoxylated resole-demulsifiers, (A, B, C, D, and E). Figure 2 shows the performance of the ethoxylated demulsifiers (AR1, BR1, CR1, DR1, and ER1) using 10g of PEG 400, for the ethoxylation. And from Figure 2, it was observed that all the ethoxylated-demulsifiers gave higher percentages of water separation during the demulsification

process than the resole-demulsifiers (A, B, B, C, D, and E). The ethoxylation of the resole-demulsifiers was observed to have significantly enhanced their performance, in comparison with the resole-demulsifiers. This may be attributed to the increased solubility of the ethoxylated in the aqueous phase of the crude-oil emulsion. Except for BR1, which separated the same volume of water as the resole B, others (AR1, CR1, DR1, and ER1) were, between 11.9 to 16.8 %, better than A, C, D, and E resole demulsifiers. It was also observed that there was a steady rise in the amount or percentage of water separated, as the formaldehyde–phenol (F/P) mole ratios in ethoxylated resole-demulsifiers were increased, from AR1 to ER1, until it got to a maximum with DR1 at 1.8:1 F/P mole ratio. The same trends were observed in Figures 3 and 4. However, the ethoxylated resoles (AR2, BR2, CR2, DR2, and ER2) using 15 PEG 400 (Figure 3) and (AR3, BR3, CR3, DR3, and ER3) using 20 g of PEG 400 (Figure 4), exhibited much better water separation efficiencies. R2 series in Figure 3 were, between 5.6 and 29.2 % more efficient than their resole counterparts, while the R3 series (Figure 4) were, between 15.5 and 50 % more efficient than their resole counterparts. The best-ethoxylated demulsifiers, from Figures 3 and 4, were DR2 and DR3. And they produced 55.3 and 64.2 % water separation efficiency respectively, in comparison with the 42.8 % produced by the resole demulsifier. From Figures 2-4, it was observed that the percentage of water separated using the ethoxylated-demulsifiers increased as the weight of the PEG 400 used in the ethoxylation process was increased from between 10 and 20 g, and at a constant F/P mole ratio. Using 10, 15, and 20 g of the PEG 400, in the ethoxylation of the resole-demulsifiers, yielded R1 (AR1, BR1, CR1, DR1, & ER1), R2 (AR2, BR2, CR2, DR2, & ER2), and R3 (AR3, BR3, CR3, DR3, & ER3) series of ethoxylated-demulsifiers, respectively. They produced maxima water separation capacities of 50, 55.3, and 64.2 % for DR1, DR2, and DR3, respectively. It was observed that the R3 series generally produced the highest percentages of water separation followed by the R2 and then R1 series and have been displayed in Figure 5.

Figure 5 shows the general performance of the ethoxylated demulsifiers. Their excellent performance, especially the R3 series, which contains the highest quantity (20 g) of PEG 400, may be attributed to the increase in the hydrophilic chain length, and hence the excellent demulsifying power exhibited by them [24].
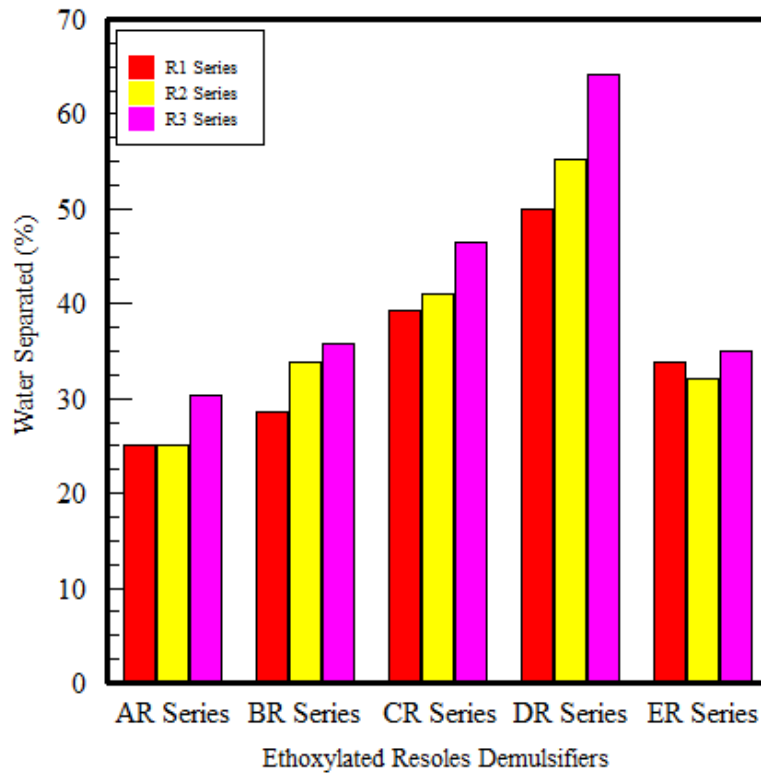
Figure 5: Comparison of ethoxylated resole demulsifiers using 10, 15 and 20 g each of PEG 400

In Figure 6, the rates of water separation from the oil emulsion sample were measured. The rates were recorded in terms of the percentage volume of water that was separated in a given time. And over the entire time period, as shown in Figure 6, all the ethoxylated resoles recorded higher rates of water separation. However, the quantity of water separated for both demulsifiers increased with time.
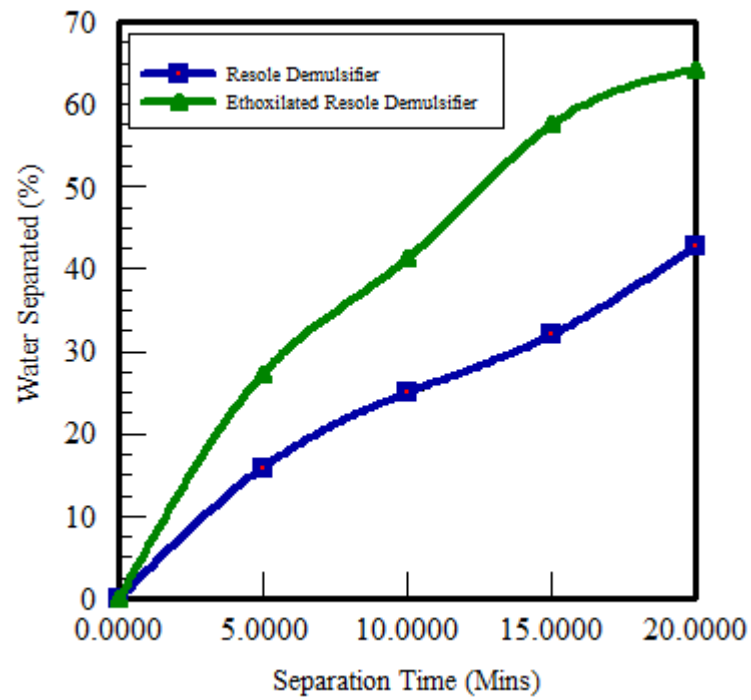
Figure 6: Comparison of the performance of ethoxylated resole-demulsifiers and resoles.
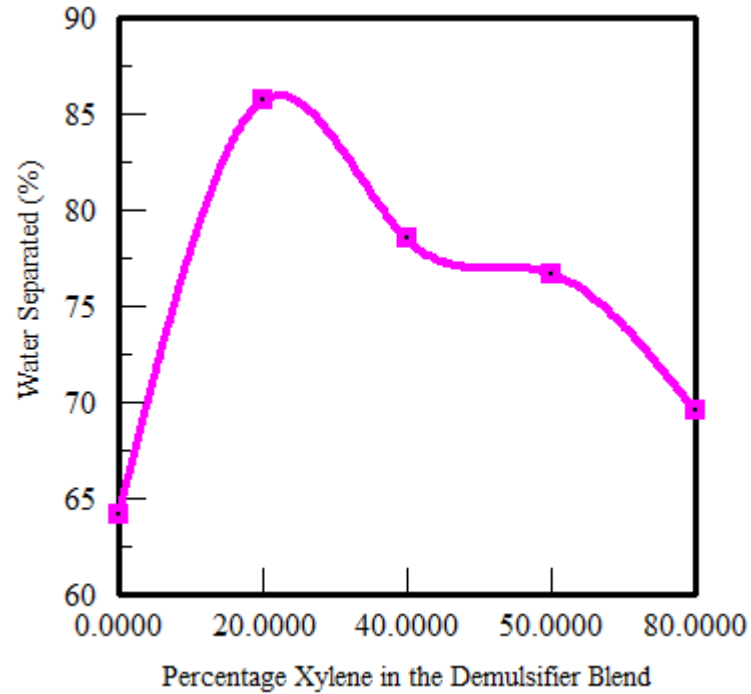

Figure 7: Effect of Solvent (Xylene) on Ethoxylated Demulsifier Performance

3.3 Effect of Solvent on Demulsifier Performance

Here, the effect of modifier or solvent on the demulsifier's performance was carried out. The ethoxylated demulsifier or DR3, which gave the highest percentage water separation, was selected and blended with the modifying agent or xylene at varying weight percentages. The results are displayed in Figure 7. It was observed that the percentage of water separated (or its efficiency) increased as the percentage content of xylene was increased from 0 to 80 %, in the demulsifier – xylene blend. The percentage of water removed increased from 64 % at 0 % xylene blend to a maximum of 85.7 % at 20 % xylene blend before it steadily decreased to 69.6 % at 80 % xylene blend. The percentage of water separation obtained from the emulsion sample was observed to have significantly increased when the xylene-ethoxylated-demulsifier blends were used. And the percentage values were all higher than the maximum % value obtained when only the ethoxylated-demulsifier was used to separate the same crude-oil emulsion. Thus the use of solvents as a diluent or modifier enhances the performance of demulsifiers in breaking crude oil emulsions. The obtained results agree with the findings of other researchers who also observed that solvents or co-solvents promote the separation or de-emulsification of crude oil emulsions [27]. Figure 8 gives the plot of the rates or percentage water separation with time for all the xylene – demulsifier blends. From Figure 8, it was observed that the water separation capacities of the different xylene - demulsifier blends (DR3X0, DR3X20, DR3X40, DR3X50, DR3X80) increased at different rates, with the 80/20 % demulsifier-xylene blend (DR3X20), producing the highest rates (from the 6th up until the 20th min) of performance or water separation from the emulsion sample. The ethoxylated-demulsifier without the xylene blend (DR3X0) showed the least water separation rates, all through the demulsification time considered. This may be attributed to the solvent's ability to carry the demulsifying agent to the interface of the oil and water at a much faster rate than it would have occurred when it is absent. When no solvent is added, the rate of dispersion of the demulsifier agent in the emulsion sample is then strictly dependent on the degree of mixing. This step is slower and usually results in low water separation or demulsification of crude oil emulsions [11]. This is illustrated in Figure 9, where a comparison of the water separated using the ethoxylated-demulsifier with and without the addition of solvent xylene, further validated the demulsification power of solvent (xylene)-demulsifier blend.
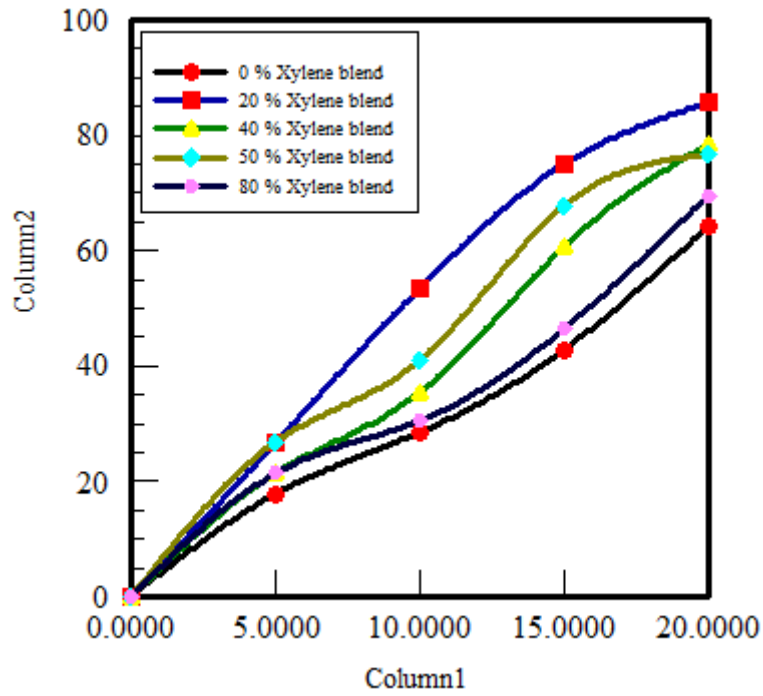
Figure 8*: Effect of time on the separation rates of demulsifier-solvent blends*
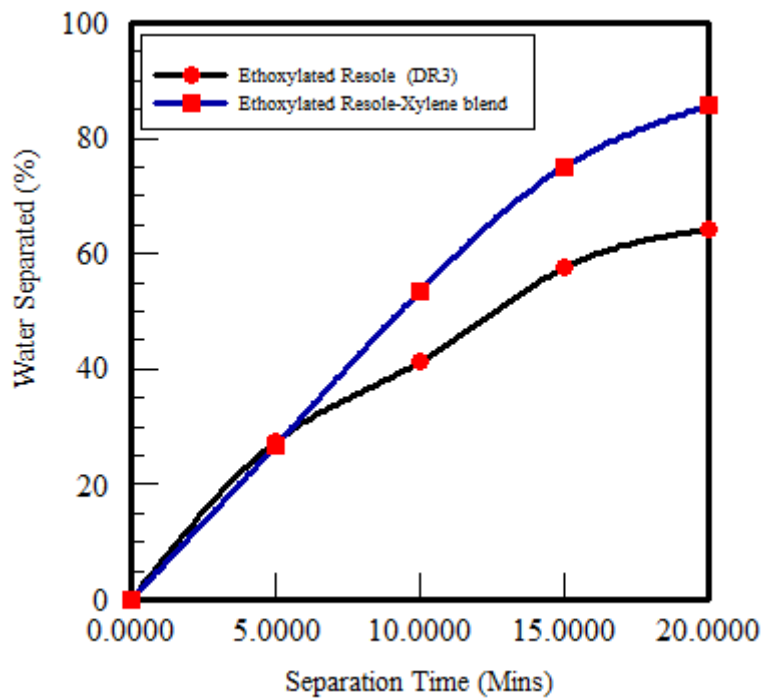

Figure 9: Comparison of the extent of water separation of the ethoxylated-demulsifier and Xylene blend, (DR3X20) and ethoxylated-demulsifier alone (DR3).

3.4 Comparison DR3X20 with A Commercial Demulsifier (CDE)

Figure 10 shows the result of the analysis of the commercial demulsifier (CDE) carried out at the temperature and concentration of 70 ^{0}C and 50 ppm, respectively, compared with the optimum of the ethoxylated-emulsifier, DR3X20. The bottle test analysis showed that the formulated demulsifier-solvent blend had a high water separation efficiency of about 85.7 %, while that of the commercial demulsifier was 73 % for a residence time of 20 minutes. In addition, it was observed that from the 5th to 20th minute, the rates of water separation or demulsification of crude oil emulsion were much higher for DR3X20 than the commercial demulsifier (CDE).
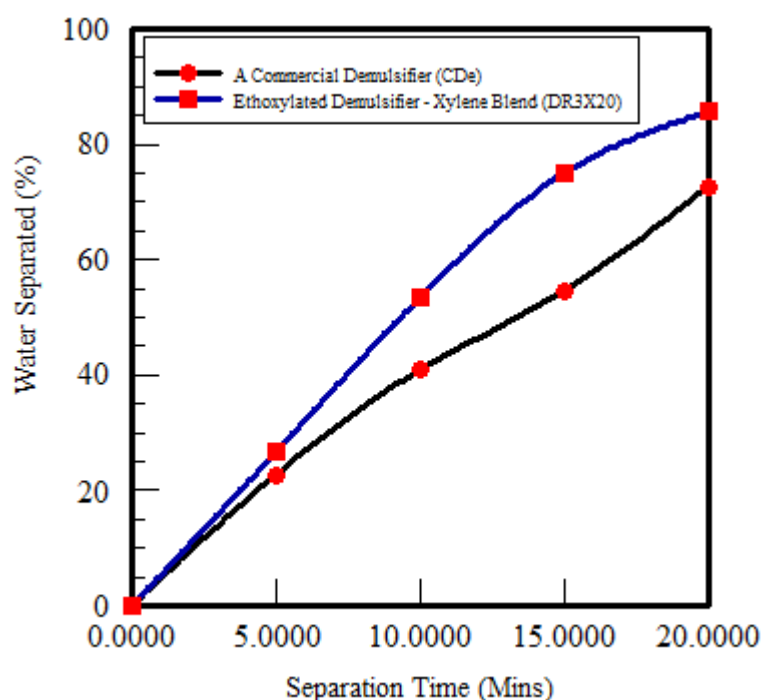

Figure 10: Comparison of the optimum demulsifier – xylene blend with A commercial demulsifier

4. Conclusion

The demulsification of the crude-oil emulsion systems is pivotal at ensuring the production of high market-valued crude-oil and also to prevent the processing equipment from being unduly exposed to the corrosive nature of the basic and acidic salt components present in the aqueous portion of the emulsion. And the type of the demulsifiers selected, significantly dictates the success of the demulsification process. Demulsifiers are crude oil emulsion specific. What works well in location A, may fail in another location, hence the need to continually formulate and test demulsifiers on crude oil emulsions from both onshore and off-shore production fields.

In this study, three different types of demulsifiers were produced and tested. And it was observed that

- The demulsification capacities, in terms of the % water removed, of resoles increased as the formaldehyde – phenol mole ratios (F/P) were increased. It, however, got to a maximum at a 1.8:1 F/P mole ratio before it began to decline.

- The ethoxylated resoles performed better than the resole demulsifiers. A maximum of 64.2 % water separation efficiency was obtained from resole-ethoxylates in comparison to the 42.8 % obtained with the resole demulsifiers alone.
- The separation rates, i.e., more water separation, were obtained per time for the ethoxylated resoles than the resoles alone, across the test period considered.
- The ethoxylated resole-xylene blend (DR3X20), was the most efficient demulsifier, and it gave 85.7 % water separation efficiency. The DR3X20 demulsifier was also more efficient than the commercial-grade demulsifier that gave 72.7 %.
- All the ethoxylated resole–xylene modified demulsifiers were more efficient than the best unmodified ethoxylated resole demulsifier, which produced water separation.

Acknowledgments

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