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FORMULATION, COMPOUNDING AND ASSESSMENT OF DE-EMULSIFIERS FOR THE DE-EMULSIFICATION OF NIGERIAN CRUDE OIL EMULSION

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Abstract

Chemical de-emulsification is an emulsion treatment method, which involves the addition of chemicals known as de-emulsifiers to break crude oil emulsions. Resoles (base catalyzed phenol formaldehyde resins) and polyester-based de-emulsifiers were formulated and blended at various ratios to produce a single de-emulsifier. The formaldehyde to phenol ratios for the resoles varied from 1.2:1 – 1.8:1 and the polyesters were produced at 120^0C, 162^0C and 183^0C. Performance analyses of the de-emulsifiers were carried out using the bottle test method at a temperature of 70°C, concentration of 50ppm and residence time of 20 minutes. The most effective de-emulsifier selected was based on the volume of water expelled from the crude oil emulsion. The results were also analysed using Minitab 17 utilizing a Pareto, Normal effect, Interaction and contour plots to study which of mole ratios, blend ratios, temperature and their combined effects have the most significant effect on de-emulsification. Results showed that the most effective de-emulsifier was sample F3X made of 80% resole (1.8:1) and 20% polyester sample 3 produced at 183^0C, combined with xylene at a concentration of 50%. This de-emulsifier obtained a water separation efficiency of 81.8% compared to a commercial de-emulsifier, which gave an efficiency of 73%.

Keywords: *De-emulsification; Resoles; Polyesters; Xylene; Blend.*

1. Introduction

Crude oil can be described as a naturally occurring liquid, which can be found under the surface of the earth and is formed by the heating and compression of these organic matters over a long period of time. It consists of complex mixture of hydrocarbons [1-3], inorganic salts, organic matter as well as minute amounts of metal [4]. In Nigeria, crude oil was discovered in Oloibiri, Bayelsa State in 1956 and is currently ranked the 6th largest oil producer in the world. The exploration, production and sales of crude oil in Nigeria plays an important role in the country's economy as it accounts for a whopping 90% of her gross earnings [5].

An emulsion is a colloidal system in which small drops of one liquid are dispersed in another liquid and water–in–oil emulsions, where water is dispersed in the external oil phase [6] are common especially during hydrocarbon production when it is co-produced with water at the reservoir, or with injected water at the well bore [7-8]. The two liquids (oil and water) are immiscible but with the natural surfactants or emulsifying agent such as asphaltenes and resins contained in the crude oil, an emulsion is produced [9-10]. The presence of emulsions is undesirable because of its associated problems such as increased viscosity, density, pressure drop, rigid films that are difficult to break, reduced handling capacity of pipes and corrosion of processing facilities which all lead to higher operational cost [11-12]. To minimize the problems related to the production of crude oil emulsions such as increased production costs and corrosion, as well as environmental concerns, petroleum operators need to prevent the

formation of these emulsions by breaking or separating them [13-14]. Consequently, after the de-emulsification process crude oil for sales is expected to comply with product specifications such as maximum allowable amount of basic sediment and water content as well as salt content.

Several methods currently available for de-emulsification of crude oil include chemical, electrical, thermal, mechanical methods or their combination [15]. Chemical de-emulsification involves the use of chemicals known as de-emulsifiers) to reduce the stability of the emulsions and assist in its coalescence and eventual separation [16]. De-emulsifier formulations involve a combination of two to four different chemistries (chemicals), in carrier solvent(s) such as isopropanol, methanol, xylene or diesel. This treatment method is the most widely applied method because of the ease of application of the chemicals, low cost as well as minimal heat and settling time requirements [17-18].

The characteristics and physical properties of crude oil undergo a significant amount of change upon emulsification. Changes such as increase in density, viscosity and water cut of crude oil could lead to corrosion of pipelines as well as increase processing and production costs. These adverse effects could make the production of certain oilfields less economical. It is therefore, imperative that effective methods of treatment be employed in order to curb this challenge.

This research aims at identifying and formulating an effective de-emulsifier using a combination of chemistries (chemicals) that would help break crude oil emulsions into two clear water and crude oil phases and hence facilitate reduced operational cost involved in oil processing. In addition, locally formulated and effective de-emulsifiers will also reduce the importation of de-emulsifiers, thereby conserving our hard earned foreign exchange.

2. Experimental and procedure

2.1. Materials

Crude oil used was obtained from Agbami, a deepwater field, located off the Niger Delta, Nigeria. Phenol crystals (99% purity, Technical grade), formaldehyde (37% purity, Baker analysed), sodium hydroxide pellets (99% purity, Riedel-de Haen analysed), xylene (99.9% purity, Baker analysed), maleic anhydride, polypropylene glycol (PPG) and 86% phosphoric acid were all of analar grade.

2.2. Apparatus/Equipment

The equipment used include the following; Hot Plate with Magnetic Stirrer (Thermo Scientific Model SP13015), Fume Cupboard (ESCO Ductless), Water Bath (Uniscope Laboratory Model SM801A), pH meter (Jenway Model 3520), Centrifuge (Uniscope Laboratory Model SM800B), Weighing Balance (Scout Pro Model SPU2001), Quick Fit Thermometer (0-100^{0}C), 250mL 3-neck flat bottom flask, Beakers (250mL and 500mL), 250mL Measuring Cylinder, Reflux Condenser, Centrifuge Bottles, Spatula, Stirring Rod and Sample Bottles. All the glassware were Pyrex product.

2.3. Methods

Figure 1 below shows the flow chart of the methods employed in this research work and the brief description of each method is highlighted below.

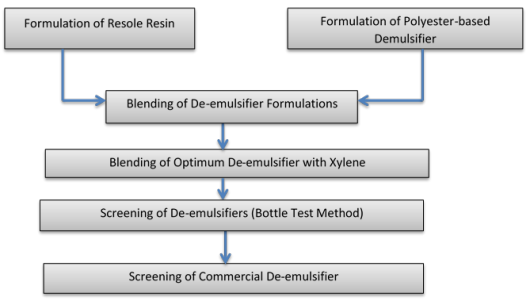

Figure 1. Flowchart of the experimental work

2.3.1. Formulation of resoles

Resoles are produced by a condensation polymerization reaction between phenol and formaldehyde in the presence of a basic (alkaline) catalyst, NaOH. 67mL of formaldehyde was measured and 142.4g of phenol crystals was added and stirred to dissolve. The pH of the solution was adjusted to 9 by introducing the prepared 30% (w/v) sodium hydroxide solution in drops until desired result was achieved. The solution was then charged into a 3-neck flat bottom flask fitted with a reflux condenser and quick fit thermometer. The experiment was set up in a fume cupboard and allowed to run for the required 3 hours with uniform agitation at a temperature of 70^0C. The pH of the solution was adjusted to 9 every 30 minutes using the sodium hydroxide solution. The resoles produced were then allowed to cool, after which they were transferred into appropriately labeled sample bottles. The procedure was then repeated using varied quantities of phenol crystals and formaldehyde solution shown in Table 1. Each formulation was scaled up/down based on a 200mL batch size.

Table 1. Contribution of raw materials in resole formulation

Sample Name	F:P ratio	Molar mass of phenol (g)	Volume of formaldehyde (mL)	Scale up/down value	New mass of phenol (g)	New volume of formaldehyde (mL)
A	1.2:1	94.0	44.2	1.5	142.4	66.9
B	1.4:1	94.0	51.5	1.4	134.9	73.9
C	1.5:1	94.0	55.2	1.4	131.4	77.2
D	1.6:1	94.0	58.9	1.36	128.1	80.3
E	1.7:1	94.0	62.6	1.33	124.9	83.2
F	1.8:1	94.0	66.2	1.3	122.6	86.1
G	2.0:1	94.0	73.6	1.24	116.5	91.2

2.3.2. Formulation of polyester-based de-emulsifier

97.54 parts, 1.96 parts and 0.5 parts of polypropylene glycol (PPG), maleic anhydride and phosphoric acid respectively were accurately weighed, charged into the reactor and heated at low stirring speed to the reaction temperatures for a residence time of five hours, as shown in Table 2.

Table 2. Reaction conditions for polyester based de-emulsifier formulations

S/N	Sample	Reaction temperature, (^{0}C)	Reaction time, (hr)
1	1	120	5
2	2	162	5
3	3	183	5

2.3.3. Blending of de-emulsifiers

2.3.3.1. Blending of resole and polyester based de-emulsifiers

These de-emulsifiers were blended based on weight ratios between resole Sample A and polyester sample 1. Blends for de-emulsifiers B-G follow the same pattern as with de-emulsifier sample A shown in Table 3.

Table 3. Blending Resole Sample A and Polyester-based Sample 1

Sample	Mass of polyester based de-emulsifier (g)	Mass of Pf de-emulsifier A (g)
A1a	10	0
A1b	8	2
A1c	5	5
A1d	2	8
A1e	0	10

2.3.3.2. Blending de-emulsifiers with solvent (xylene)

After screening the De-emulsifiers produced in Table 3, the most effective of the de-emulsifier sample was then blended with xylene. This is shown in Table 4.

Table 4: Blending of de-emulsifier with solvent xylene

Mass ratio (de-emulsifier : xylene)	Mass of de-emulsifier (g)	Mass of xylene (g)
20:80	2	8
30:70	3	7
50:50	5	5
70:30	7	3
80:20	8	2

2.3.4. Screening procedure

2.3.4.1. Basic Sediment and Water Test (BS&W)

This test was done first to know the percentage of water contained in the crude oil emulsion**.** Untreated crude oil samples obtained were first thoroughly agitated to homogenize. The homogenized crude oil sample was then poured into centrifuge bottle to about 50% of the bottle volume. Pure xylene was added to the bottle to make it up to 100% and shaken vigorously for thorough mixing. The centrifuge bottle was then placed in a water bath and for 15 mins at a temperature of 60°C. The sample was placed in a centrifuge and spun at 1500rpm for 10mins. The percentage water and basic sediment BS and W in the tube was recorded as 'x'. Then from eqn (1) the % BS&W was calculated. The '2' accounts for the pure xylene solvent used.

$$BS\&W\ (\%) = 2x \qquad (1)$$

2.2.4.2. Bottle test method

Screening of de-emulsifiers was done to determine how effective the formulated and compoundded de-emulsifiers (Tables 3 and 4) respectively are in breaking the water-in-oil emulsion.

The method described by Efeovbokhan *et al.* [7] was adapted and used. The centrifuge bottles containing the crude petroleum emulsion were immersed in a water bath at the temperature of 70^0C for 5 minutes for temperature stabilization. 50 ppm of the de-emulsifier was then injected into each bottle using a micropipette and uniformly agitated by overturning 100 times. The bottles were put back in the water bath for 20 minutes after which they were placed in a centrifuge set at 1500rpm for 20 minutes.

2.2.5. Screening of commercial de-emulsifier

The commercial de-emulsifier was also screened at 70°C as discussed in section *2.2.4.2* while varying residence time, with an interval of 5 minutes from 5-20 minutes. The volume of water and oil separated from the emulsion system was observed and the % water separation calculated using equation 2.

$$\%\,\boldsymbol{Volume\ of\ water\ separated} = \frac{\boldsymbol{volume\ of\ water\ separted}}{\boldsymbol{Total\ volume\ of\ water\ in\ the\ emulsion}} \qquad (2)$$

3. Results and discussions

3.1. Effect of mole ratio on the performance of phenol-formaldehyde de-emulsifier

Screening (analysis) of formulated de-emulsifiers was done using the bottle test method. The results obtained are shown in Figure 2.

From Figure 2, the percentage volume of water separated increased steadily to a maximum value of 40% at phenol to formaldehyde molar ratio of 1:1.8. It was observed that a further increase in the molar ratio beyond 1:1.8 results in a decline in the efficiency of water separation of the resole de-emulsifier. This is in conformity with the work of other researchers [7] that the

performance of resole de-emulsifiers increases with its molar ratio of formaldehyde relative to phenol. This is because methyl-ol content of resole do not only increase with increasing molar ratio of formaldehyde; it is also soluble in the aqueous phase of the crude oil emulsion making more of the de-emulsifier available at the inter phase to alter the surface tension. This action promotes the rapid coalescence of water droplets and hence water separation. It was also seen that a further increase in the mole ratio beyond 1.8:1 results in a decline in the efficiency of water separation of the de-emulsifier. This agrees with Hanapi *et al.* [17], who suggested that the F:P ratio of resole resins be limited to 1.2:1 - 1.8:1 to avoid inversion in solubility.

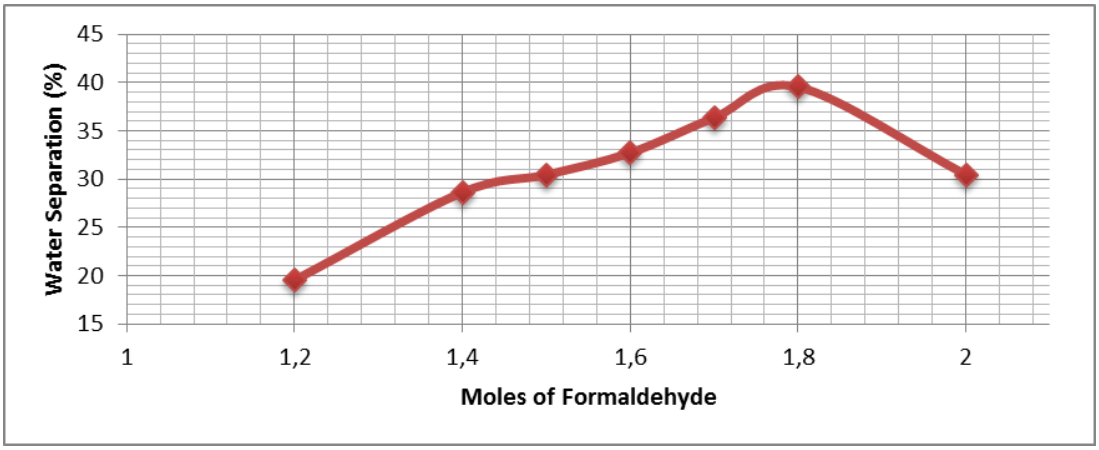

Figure 2. Effect of mole ratio on performance of resole

3.2. Effect of de-emulsifiers blend on de-emulsification process

Phenol-formaldehyde de-emulsifiers produced were blended with a polyester-based de-emulsifier to produce a new set of de-emulsifiers that were screened so as to determine their effectiveness in separating crude oil emulsions. The results are shown in Figures 3-5.

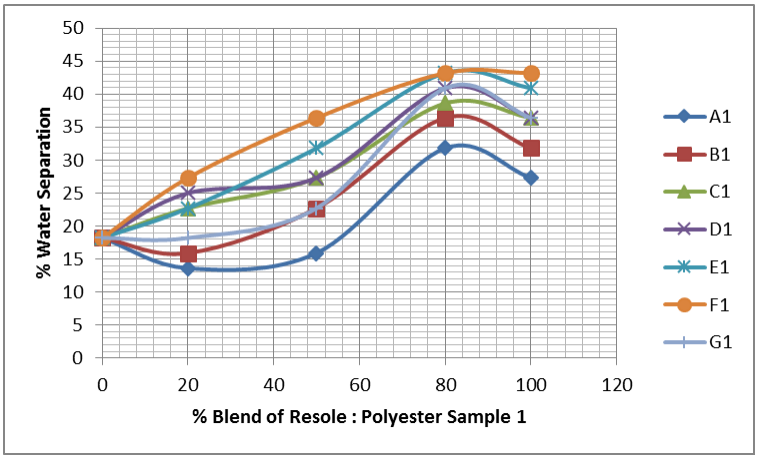

Figure 3. The effect of blend of resole and polyester sample 1 on de-emulsification

From Figure 3, it was observed that the de-emulsifier blend F1 made of F:P (1.8:1) and polyester sample 1 gave the overall best performance in the de-emulsification process run 1. The maximum performance (water separation) of 36.4% occurred at a blend of 80% sample F and 20% sample 1. The blend A1 made of F:P (1.2:1) and polyester sample 1 produced the least performance. This suggests that the higher the molar ratio of F:P de-emulsifier in the blends, the higher the efficiency of the de-emulsifier. Blend E1 made of F:P (1.7:1) and poly-

ester sample 1 was seen to completely overlap with blend F1 at the higher blend ratios. This shows that the optimum blend for maximum water separation lies between the blends E1 and F1.

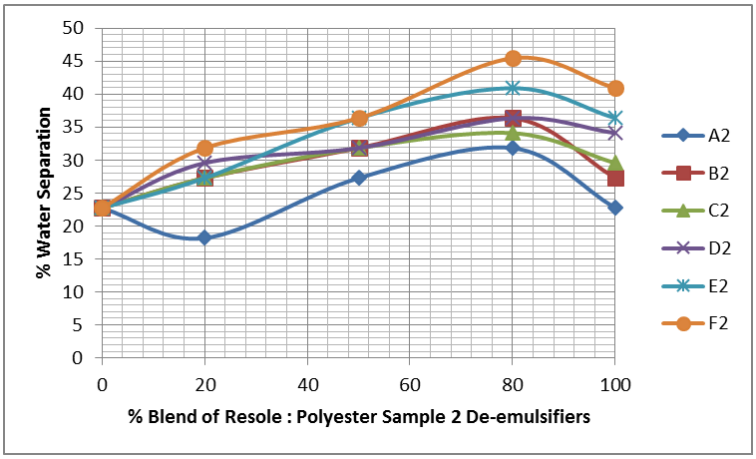

Figure 4. The effect of blend of resole and polyester sample 2 on de-emulsification

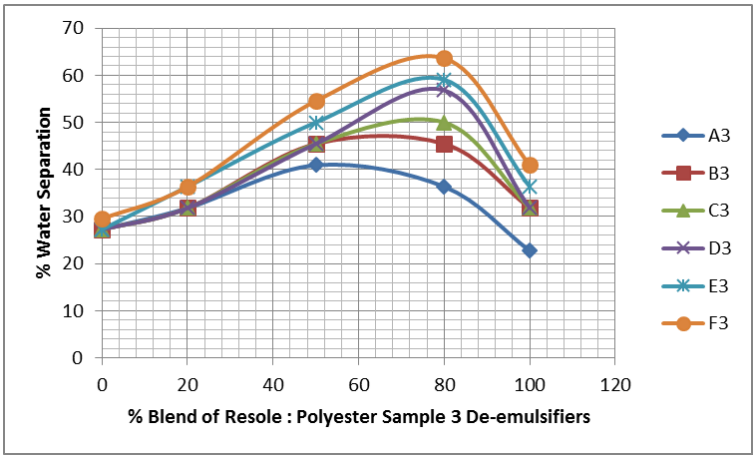

Figure 5. The effect of blend of resole and polyester sample 3 on de-emulsification

Figures 4 and 5 follow exactly the same pattern as Figure 3. Except that Figure 4 are blends produced from resole samples and polyester sample 2 while Figure 5 are blends produced from resole de-emulsifier samples and polyester sample 3. The polyester samples were obtained at different reaction temperatures – sample 1 was produced at a temperature of 120°C, sample 2 at 162°C and sample 3 at 183°C. From Figures 3 – 5, de-emulsifier samples obtained by blends of resole and polyester produced at higher temperatures generally performed best compared to the others. The increasing order of performance is A1 < A2 < A3, C1 < C2 < C3, F1 < F2 < F3, etc. There was an overall improvement in performance comparing the individual resole de-emulsifiers with the blended de-emulsifiers. From Figure 2 the highest percentage water separation obtained for the individual resole de-emulsifiers was 40% while for some of the blended de-emulsifiers E2 and F2 respectively gave 41 and 45.5% water separation efficiency as seen in Figure 4. But in Figure 5, all the blended samples performed better than the individual resole de-emulsifiers. The highest was 63.6% water separation efficiency for F3, 59% for D3, 57% for E3, 50% for C3, 46% for B3 and 41% for A3.

From Figures 3 to 5, the maximum value of percentage water separation for all the blends, except for A3, occurred at a blend of 80% resole and 20% polyester samples. And in all the

three runs represented by Figures 3 to 5 respectively the F1, F2 and F3 blends gave the best water separation of 36.4, 45.5 and 63.6%.

3.3. The effect of solvent (xylene) blend with de-emulsifier F3 on de-emulsification

The effect of introducing a solvent to the best blended de-emulsifier on water separation efficiency was carried out using xylene. Here xylene was mixed with F3 (F3X) in increasing percentage order of 0%, 20%, 30%, 50%, 70% and 80% as a modifying agent to further enhance its performance. Figure 6 shows the performance of the xylene/F3 blends on the de-emulsification of the Nigerian crude oil emulsion.

Figure 6 shows that the water separation efficiency increases with increasing xylene concentration, up to 50%, after which subsequent increase resulted in a steady decline in de-emulsifier efficiency. Maximum water separation of 81.8% was obtained at a blend of 50% xylene and 50% F3 de-emulsifier. It was observed from Figure 6 that all the blends produced better water separation than just F3 alone (shown as intercept on the Y-axis). These results are in agreement with the results obtained by other researchers [19] that co-solvent or solvent addition enhances de-emulsification process.

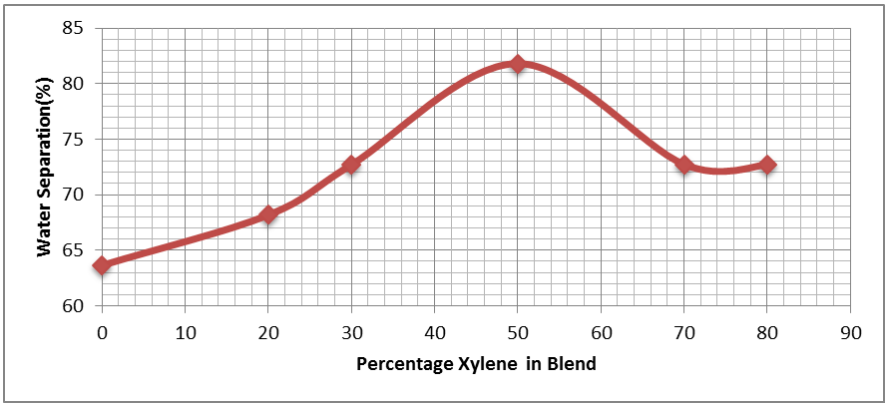

Figure 6. The effect of solvent (xylene) on de-emulsifier performance

3.4. Comparison with commercial de-emulsifier

The commercial de-emulsifier was screened and tested against F3X subject to the same bottle test conditions. Here rate of water separation and percentage water separation were measured. Figure 7 shows the comparative tests carried out on both de-emulsifiers. It was observed from Figure 7 that rate of water separation measured for 20 minutes at intervals of 5 minutes, was higher for F3X than the commercial de-emulsifier. Also the percentage water separation efficiency was 72.7% compared to 81.8% for F3X de-emulsifier.

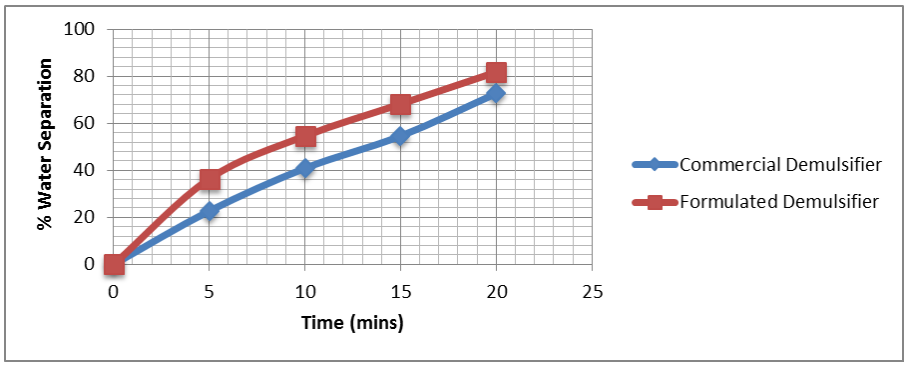

Figure 7. Comparison of F3X de-emulsifier blend with a commercial de-emulsifier

3.5. Determining the factors which have the most significant effect

The results obtained from screening analysis of the formulated and compounded de-emulsifiers were further analysed using Minitab 17. This was to determine which one or combined factors (mole ratio, blend ratio and polyester sample) have the most pronounced effect on de-emulsification. A Pareto Chart, Normal Effects and Contour Plots were used for the analysis.

3.5.1. Pareto Plot

The Pareto chart was used to determine which factors have statistically significant effects on the response or percentage water separation. The reference red line indicated on the chart helped to identify which effects (whether singly or combined) are significant to the response. The farther a factor is from the red line the more significant its impact of the response. From the Pareto Chart in Figure 8, it was seen that mole ratio (A) has the most significant impact on the volume of water expelled from the emulsion, followed by blend ratios (B) and the combined effect of blend ratio/ temperature of in which the polyester sample was prepared (BC).

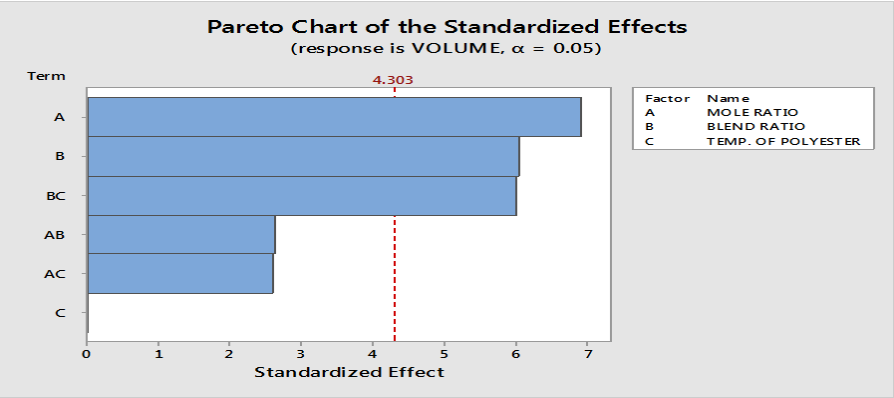

Figure 8. Pareto plot of the effects of various factors on efficiency of de-emulsifier

3.5.2. Normal Plot

The Normal effects plot (Figure 9) was used to compare the relative magnitude and the statistical significance of both the main and interaction effects. The factors that have significant effects are shown in red and those without significant effects are shown in blue. The further a factor is from the red line, the more significant the effect it has on the corresponding response.

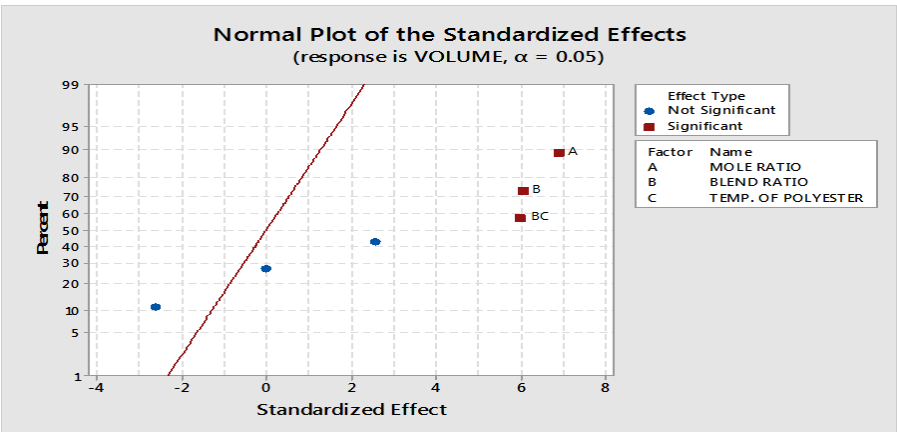

Figure 9. Normal effects plot for optimization of efficiency

From Figure 9, it was observed that the mole ratio (A) at which the resoles were produced has the most significant effect of 7 and relative magnitude of 89%. The blend ratio (B) and the combined effect of the blend ratio and temperature of polyester type (BC) produced the same effect of 6 but relative magnitudes of 73 and 59% respectively on the de-emulsification process.

3.5.3. Contour plot

A contour plot (Figure 10) is a graph used to determine the potential relationship between three variables. Contour plots exhibit the 3-dimensional relationship in two dimensions, with x- and y-factors (predictors) plotted on the x- and y-scales and response values represented by contours.

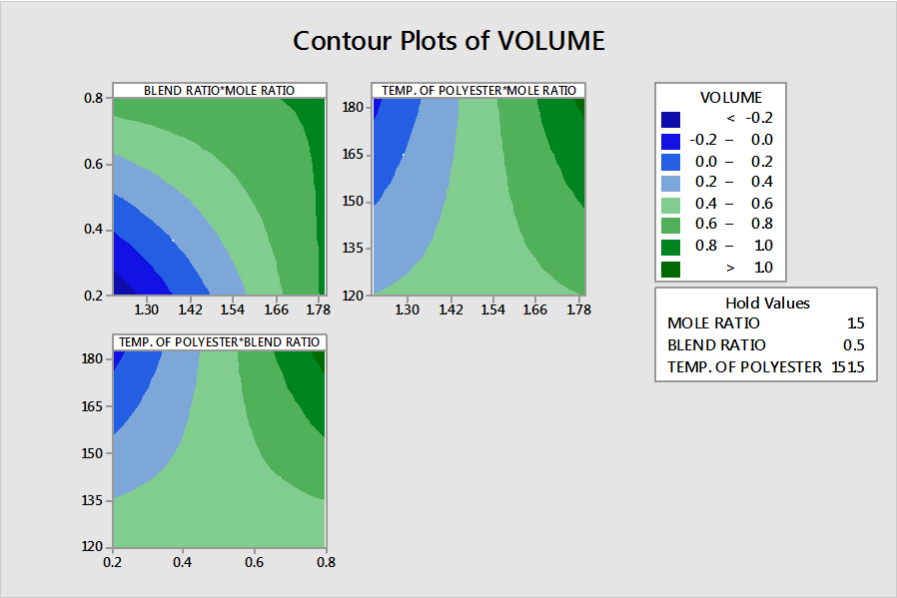

Figure 10. Contour Plots of Volume

From Figure 10, the plots show the effects of mole ratio, blend ratio and temperature of polyester on the volume of water expelled from the crude oil emulsion. The first plot showed the combined effect of blend ratio and mole ratio if temperature of polyester were kept constant at 151.5^{0}C. The darkest green region revealed the blend ratio and mole ratio interaction that will cause the highest amount of water to be expelled from the crude oil emulsion while the dark blue region showed the combination with the least effect. Plot 2 which showed the combined effect of temperature of polyester and mole ratio when the blend ratio was held constant at 0.5 and plot 3 which showed the effect of temperature of polyester and blend ratio when mole ratio was kept constant at 1.5, produced similar effects indicated by the contours. The darkest green showed the range of temperatures and mole ratios in which their combined effect will be significant. The darker blue showed the ranges where the combined effect of temperature and mole ratio will be insignificant. Exactly the same trend was observed for plot 3. The contours are well interpreted and read from the legend.

4. Conclusions

This study showed that de-emulsifier performance increases with increase in F: P ratio for the resoles reaching an optimum beyond which there is an inversion or a reduction in its water separation efficiency. Water separation efficiency is enhanced when blends of phenolic resin (or resole) and polyester - based de-emulsifiers are used. Also, blending compounded de-emulsifiers with a diluent (xylene) produces very effective agents for the de-emulsification of crude oil emulsions. The high water separation rates and efficiency of the compounded F3X

de-emulsifier attained over the commercial sample being used in the Nigerian oil Industry, will lead to an improved operation in the de-emulsification unit of the industry.

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