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Optimization of Phenolic Based De-Emulsifiers

¹V.E. Efevbokhan, ¹K.M. Olayemi, ²P.A.L. Anawe and ¹O.G. Abatan

¹Department of Chemical Engineering,

²Department of Petroleum Engineering, Covenant University, Km 10 Idiroko Road, P.M.B. 1023, Ota, Ogun State, Nigeria

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Corresponding Author:

V.E. Efevbokhan,
Department of Chemical Engineering,
Covenant University,
Km 10 Idiroko Road,
P.M.B. 1023, Ota, Ogun State, Nigeria

ABSTRACT

The de-emulsification of a Nigerian crude oil emulsion has been investigated using locally formulated base and acid catalyzed phenol formaldehyde resins with varied formaldehyde to phenol molar ratios. The bottle test method was used for the screening process and the best de-emulsifier was chosen based on the largest volume of water removed from the crude oil emulsion. The screening process was done at temperatures of 50 and 70°C and de-emulsifier concentrations of 20 and 50 part per million (ppm), respectively. A factorial design was done to determine the best combination of de-emulsification conditions for optimal performance. The results were optimized and analyzed using software called Minitab 16 utilizing pareto chart, normal effects, main effects and interactions plots. From the analysis, it was found that the optimum set of conditions for best performance of the resole de-emulsifier were 50 ppm, 70°C and 1.8:1 concentration, screening temperature and formaldehyde to phenol molar ratio, respectively. While for novolak de-emulsifiers, they were 50 ppm, 70°C and 0.1:1. Increasing temperature and concentrations were found to enhance de-emulsification performance with all the resole and novolak de-emulsifiers.

Key words: Resole, novolak, de-emulsifiers, de-emulsification, emulsions

INTRODUCTION

Nigeria oil reserve is abundant and it is estimated to be about 209 billion cubic feet with its net oil export of over 2.5 million barrels per day (Energy Information Administration, 2007). But one of her oil fields-Obagi oil field in Rivers, Port Harcourt is having emulsion problem. The Basic Sediment and Water (BS and W) of the crude oil is 2-12% which makes it higher than the specified 0.5%. This problem makes crude oil produced from this region to have low market value because it is difficult to meet international market specifications.

Water-in-oil emulsions are common occurrences during crude oil production. They are formed when oil and water are co-produced with sufficient agitation or injected water in reservoir, at well bore, in pipelines during flow of the mixture from the reservoir to the manifold and separators and at surface facilities (Al-Sahhaf *et al.*, 2009). Emulsion stability ranges from a few minutes to years depending on the nature of

the crude oil mixtures (Bhardwaj and Hartland, 1998). Crude oil is a complex mixture of hydrocarbons (Aske, 2002; Rhee *et al.*, 1989) ranging from the paraffins to naphthenes and aromatics. It varies in color from clear to tar-black and in viscosity, from that of water to almost solid. It exists in the reservoirs in most cases as gas at the top followed by the oil and then water at the bottom (Hyne, 2001). Hence, during the production of crude oil, water accompanies the oil being produced. It has been reported that an equivalent volume of water accompanies the daily production of some 60 million barrels of crude oil (Ivanov and Kralchevsky, 1997). Owing to the various factors that affect production, a relative amount of this water can become completely dispersed in the crude oil as tiny droplets to form water in oil emulsion where oil is the continuous phase and water the dispersed phase. In most cases, crude oil emulsions result from the natural surfactants such as asphaltenes and resins contained in the crude oil which, when mixed with water, emulsifies the water into the oil (Sjblom *et al.*, 1992). This produces stable water-in-crude oil

emulsion which often has a much higher viscosity than either the crude oil or water alone (Kokal and Wingrove, 2000; Kokal *et al.*, 2001). The film formed by the adsorption of asphaltenes and resins around the water droplets, is generally strong and difficult to break. The amount and nature of the emulsifying agents determines the stability of the emulsion (Bhardwaj and Hartland, 1998). The stable crude oil emulsion is characterized by high viscosity and rigid film results with significant formation damage to the reservoirs which increases the Basic Sediment and Water (BS and W) of oil. It also increases the operational and capital cost. Crude oil emulsion occupies larger volume of pipes thereby reduce the pipes handling capacity and causes corrosion of processing equipment (Becher, 1985). This necessitates the need to prevent crude oil emulsions formation or break them so as to minimize the production and processing problems associated with such emulsions (Gafonova, 2000). Several methods have been used in the de-emulsification of crude oil such as thermal, electrical and chemical methods. Chemical method which involves the use of chemical agents called de-emulsifiers break the stabilized oil/water interface with small doses at lesser time. For de-emulsification to occur, this interfacial film has to be broken (Aveyard *et al.*, 1992). These specialty chemicals basically work by weakening the stabilizing film hence promoting coalescing and settling. A great number of de-emulsifiers have been formulated and used. Many more are still being formulated because the performance of de-emulsifiers is known to be crude oil specific and as field conditions change, the de-emulsifier requirements also changes. What works excellently well for crude A may perform very poorly for crude B and vice versa. Sometimes, two or more de-emulsifiers may have to be combined in certain ratios for meaningful de-emulsification to take place. The formulation of commercial de-emulsifiers is largely based on empirical approaches in an attempt to get the most effective which can work in shorter separation time and at smaller dosages (Selvarajan *et al.*, 2001). Other factors that promote the effectiveness of a chemical de-emulsifier include sufficient mixing at the oil-water interface, right dosage and temperature (Kokal and Al-Juraid, 1999). A good de-emulsifier must possess ability to partition into the water and oil phases. There must be sufficient concentration of the de-emulsifier in droplets to ensure high diffusion flux to the interface (Krawczyk, 1990). De-emulsifiers that have been proposed for use include organic substances and/or surfactants such as sulphonates (Porter, 1994), polyglycol ethers (Saywer *et al.*, 1994), epoxy resins, polyamines (Myers, 1992), polyols, oxylated phenols, e.g., alkanolamine and nonylphenol ethoxylate derivatives (Easton and Thomas, 1989). The increasing economic need to eliminate emulsion and reduce the Basic Sediment and Water (BS and W) in order to meet strict crude specification for the Nigerian oil industry has led to this research work, to develop varied phenol-formaldehyde (phenolic) based de-emulsifiers and tested against a commercial de-emulsifier sample using the popular bottle test method in a laboratory setting. Factorial design to study the

interplay and inter-relationship of mole ratios, concentration and temperature (multi variables) for de-emulsifier's optimum performance was carried out.

MATERIALS AND METHODS

Materials: Crude oil emulsion sample used was obtained from an onshore oil field in Port Harcourt, Rivers State, Nigeria. The various chemicals used include: Phenol crystals (99% purity, Technical grade), Formaldehyde (37% purity, Baker analyzed), Sodium hydroxide (99% purity, Riedel-de Haen), Sulfuric acid (98% purity, Sigma-Aldrich analyzed) and xylene (99.9% purity; Baker analyzed). All chemicals were used without further purification.

Apparatus/equipment: A batch reactor comprising of a 250 mL 3-neck flat bottom flask to which were mounted a reflux condenser and a quick fit thermometer (0-250°C range) was set up inside a fume cupboard. The third neck (opening) on the reactor served as the charging port for the reactants and catalyst. Other equipment used includes pH meter, centrifuge machine, graduated centrifuge bottles and water bath.

Procedure for preparing resol and novolak resins: The 30% solution of caustic soda was first prepared. Based on a molar ratio of 1.2:1 of formaldehyde to phenol (F:P), accurately weighed and melted phenol was added into measured formaldehyde solution in a beaker. The mixture was stirred slowly as the pH was adjusted by adding drops of caustic soda solution until the desired pH was reached. The mixture was then charged into the reactor set up and heated for 3 h at the desired temperature. The pH was monitored and adjusted when necessary every 30 min to maintain it at the desired set value. Uniform agitation was ensured to prevent caking. At the end of three hours, the reaction mixture was then cooled and stored in an appropriately labeled sample bottle. Six different molar ratios, 1.2:1, 1.3:1, 1.4:1, 1.5:1, 1.7:1 and 1.8:1 of F:P were used in the formulations to examine their effects on the crude oil emulsion system. Temperature was varied depending on the type of resin desired: For low mole ratio resins (1.2-1.3:1), reaction temperature used was 95°C and at pH of 7.5. The resins in the intermediate mole ratio range (1.4-1.5:1) were prepared at 75°C at pH of 8 while the resins in the high mole ratio range (1.7-1.8:1) were prepared at 55°C and pH of 9. Reaction time was constant at 3 hours for all the formulations examined.

For the novolak resins, the reaction procedures followed the same process as described for the resoles except that two mole ratios of 0.1:1 and 0.8:1 at a desired pH of (1 or 5), reaction time and temperature of 4 h and 100°C were respectively used.

Factorial design of experiment: The Design of Experiment (DOE) helped to study multiple experimental factors or variables at multiple levels. It was necessary in order to know the optimized value for each of the de-emulsifier formulated.

Using two levels and three factors, a software called “Minitab 16” ran a 2³ design of experiment table. The three factors considered were mole ratio of formaldehyde to phenol, temperature of de-emulsification and concentration (in ppm) used. From the various F:P ratios, the de-emulsifiers obtained were coded for ease of reference (Table 1).

Table 1: Formulated de-emulsifier samples and their codes

Mole ratio formaldehyde	Phenol	pH of reactant mixture	De-emulsifier sample type
1.2	1	7.5	Q
1.3	1	7.5	R
1.4	1	8.0	S
1.5	1	8.0	T
1.7	1	9.0	U
1.8	1	9.0	V
0.1	1	1.0	W
0.1	1	5.0	X
0.8	1	1.0	Y
0.8	1	5.0	Z

Table 2: Low and high level factor Variables for de-emulsifier pair Q and T

Factors	Variable levels	
	Q	T
Concentration (ppm)	20	50
Temperature (°C)	50	70
F:P ratio	1.2:1	1.5:1

Table 3: 2³ Full factorial design and its responses for de-emulsifier pair Q and T

Std order (C1)	Run order (C2)	Centre point (C3)	Block (C4)	Concentration (ppm) (C5)	Temperature (°C) (C6)	Mole ratio (C7)	% Volume of water removed (C8)
2	1	1	1	50	50	1.2	23
5	2	1	1	20	50	1.5	38
6	3	1	1	50	50	1.5	39
8	4	1	1	50	70	1.5	44
7	5	1	1	20	70	1.5	42
1	6	1	1	20	50	1.2	20
3	7	1	1	20	70	1.2	25
4	8	1	1	50	70	1.2	28

Table 4: 2³ Full factorial design and its responses for de-emulsifier pair R and U

Std order (C1)	Run order (C2)	Center point (C3)	Block (C4)	Concentration (ppm) (C5)	Temperature (°C) (C6)	Mole ratio (C7)	% Volume of water removed (C8)
7	1	1	1	20	70	1.7	44
8	2	1	1	50	70	1.7	46
1	3	1	1	20	50	1.3	28
5	4	1	1	20	50	1.7	41
4	5	1	1	50	70	1.3	33
3	6	1	1	20	70	1.3	32
2	7	1	1	50	50	1.3	31
6	8	1	1	50	50	1.7	43

Table 5: 2³ Full factorial design and its responses for de-emulsifier pair S and V

Std order (C1)	Run order (C2)	Centre point (C3)	Block (C4)	Concentration (ppm) (C5)	Temperature (°C) (C6)	Mole ratio (C7)	% Volume of water removed (C8)
5	1	1	1	20	50	1.8	44
4	2	1	1	50	70	1.4	43
1	3	1	1	20	50	1.4	35
7	4	1	1	20	70	1.8	47
8	5	1	1	50	70	1.8	50
3	6	1	1	50	50	1.4	37
6	7	1	1	50	50	1.8	46
3	8	1	1	20	70	1.4	41

The de-emulsifiers were then paired to run the 2³ DOE table. The pairing for the resoles were de-emulsifiers A and D, B and E and C and F while the pairing for the novolaks were de-emulsifiers GandI and HandJ. Table 2 shows an example of the two levels of each factor for one of the pairs used. The full factorial designs were made for all the de-emulsifier pairs with “Minitab 16” and the performance of the de-emulsifier calculated as % volume of water separated using Eq. 1:

$$\text{Volume of water separated} = \frac{\text{Volume of water separated}}{\text{Volume of emulsion}} \times 100 \quad (1)$$

The full factorial designs carried out with their corresponding responses for each pair of de-emulsifiers are shown in Table 3-7.

Basic Sediment and Water test (BS and W): The basic Sediment and Water test was first done to know the percentage of water in the crude oil emulsion. Crude samples were collected and agitated to homogenize. The sample was poured into centrifuge bottle to 50% of its level. Pure xylene was used to make it up to 100%. It was shaken vigorously to

Table 6: 2³ Full factorial design and its responses for de-emulsifier pair W and Y

Std order (C1)	Run order (C2)	Centre point (C3)	Block (C4)	Concentration (ppm) (C5)	Temperature (°C) (C6)	Mole ratio (C7)	% Volume of water removed (C8)
1	1	1	1	20	50	0.1	20
3	2	1	1	50	50	0.1	25
4	3	1	1	50	70	0.1	28
2	4	1	1	20	70	0.1	25
8	5	1	1	50	70	0.8	21
7	6	1	1	50	50	0.8	17
5	7	1	1	20	50	0.8	13
6	8	1	1	20	70	0.8	19

Table 7: 2³ Full factorial design and its responses for de-emulsifier pair X and Z

Std order (C1)	Run order (C2)	Centre point (C3)	Block (C4)	Concentration (ppm) (C5)	Temperature (°C) (C6)	Mole ratio (C7)	% Volume of water removed (C8)
6	1	1	1	20	50	0.8	12
4	2	1	1	50	70	0.1	22
2	3	1	1	20	70	0.1	18
3	4	1	1	50	50	0.1	23
6	5	1	1	20	70	0.8	18
7	6	1	1	50	50	0.8	15
8	7	1	1	50	70	0.8	2
1	8	1	1	20	50	0.1	19

homogenize. This was placed in a water bath at temperature of 60°C for 15 min. The sample was put in a centrifuge and spun at 1500 rpm for 10 min. The percentage water and bottom sediment in the tube was recorded as ‘x’. The BS and W (%) = 2x.

Bottle test method: The bottle test method was used for screening the de-emulsifiers formulated. The screening process consists of a series of centrifuge bottles spun in a centrifuge machine to effect the emulsion separation. The bottles containing the emulsion were first immersed in a water bath at the required temperature for 5 min. Twenty percent solution of each of the formulated de-emulsifiers was prepared using xylene as solvent. This was then dosed or injected at the required concentration of 20 or 50 ppm into each of the centrifuge bottle and uniformly agitated by overturning 100 times. The bottles were then returned to the water bath for 20 min to acquire the right temperature of 50 or 70°C. At the end of 20 min, the bottles were placed into the centrifuge bottles chamber and spun at 1500 rpm for 20 min. Then the total volume of water drop, appearance of the water/oil interface (filaments, turbidity and sludge) and clarity of the water were observed and recorded. The most effective single de-emulsifier was obtained based on the water separated from emulsion system.

RESULTS

The screening process of the commercial and formulated de-emulsifiers was done using crude oil emulsion. The results are as given in Table 3-7 where the factorial design of experiment were analyzed using software called “Minitab 16”.

Factorial optimization: Optimization of the best conditions for de-emulsification obtained from the factorial design was

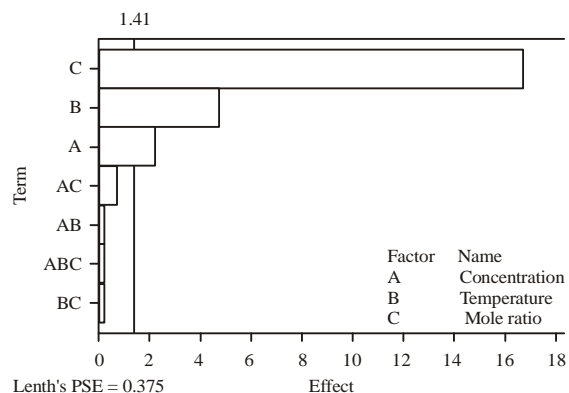


Fig. 1: Pareto chart for de-emulsifier pair Q and T

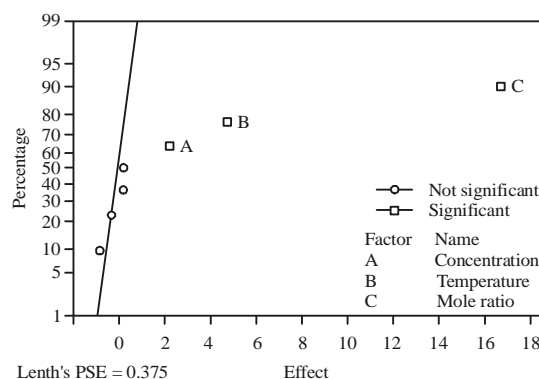


Fig. 2: Normal plot for de-emulsifier pair Q and T

carried out using Minitab 16 to analyze its output or responses in Table 3-7. The analysis tools used were Pareto plot, Normal plot, Main effects plot and Interaction plot. The results are graphically presented in Fig. 1-14.

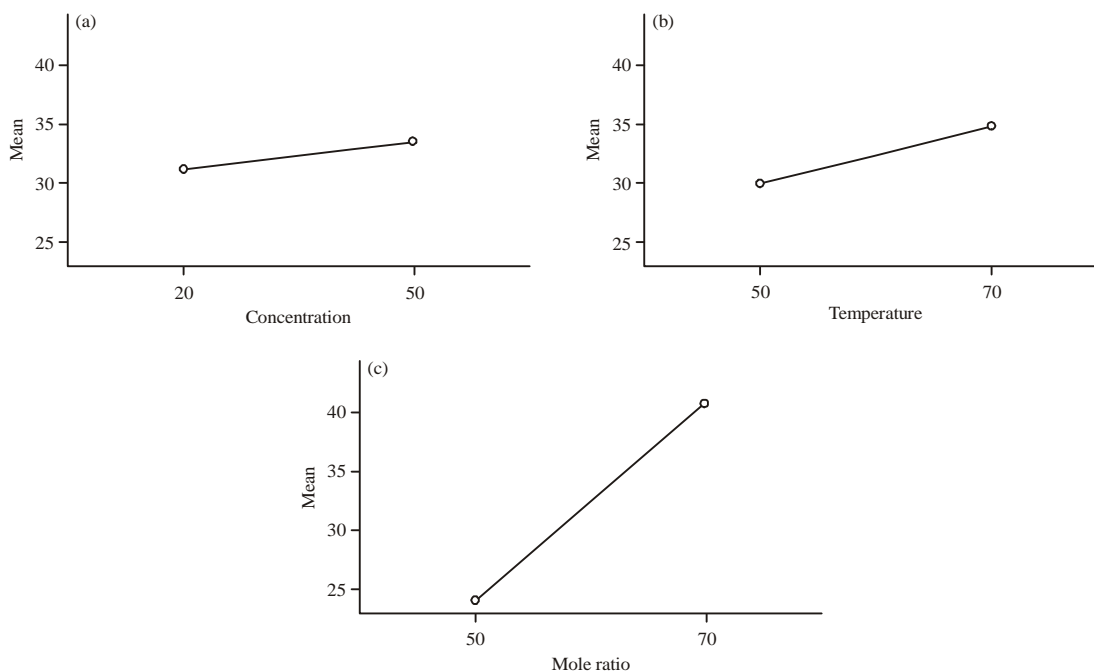


Fig. 3(a-c): Main effects plot of de-emulsifier Q and T

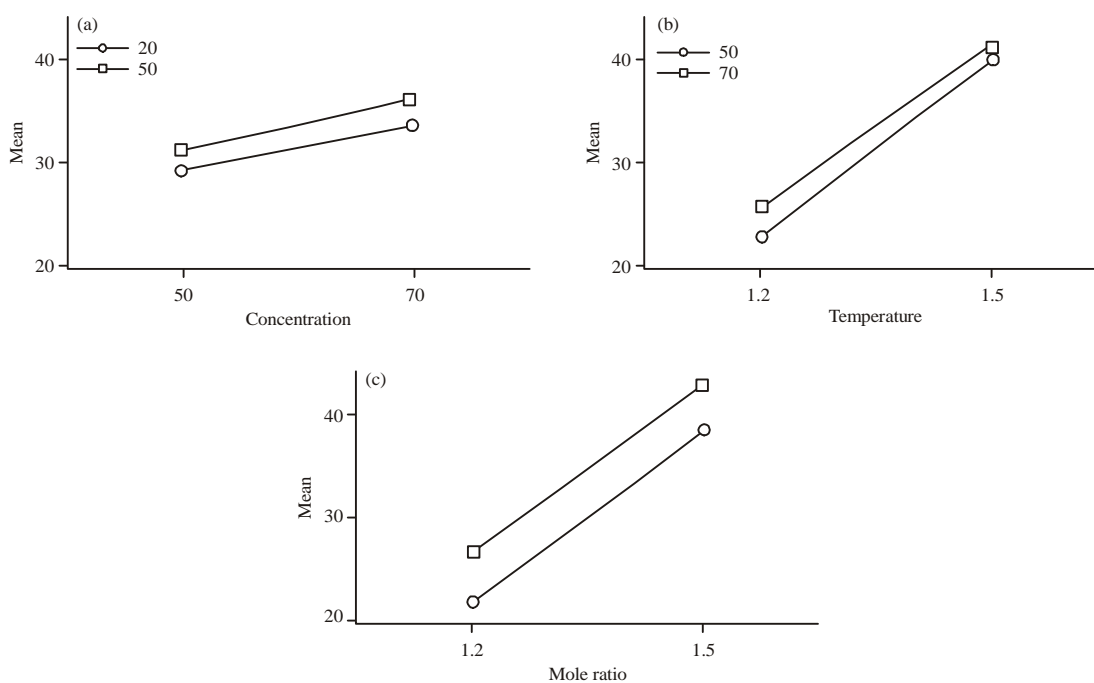


Fig. 4(a-c): Interactions plot of de-emulsifiers Q and T

Pareto chart (Analysis of resole de-emulsifiers pairs Q and T, R and U and S and V): Pareto charts (Fig. 1) were made in order to know the statistical significance of the main and interaction effects of the three variables (concentration, temperature and mole ratio) investigated during the de-emulsification process. The reference (red line) on the chart helps to indicate which effects are significant. The charts considered the effects of each variable and their

combined or interaction effects of the de-emulsifier pair on de-emulsification. The same effects and trend were observed for the other two de-emulsifier pairs R and U and S and V.

Normal effects plot (Analysis of resole de-emulsifiers pairs Q and T, R and U and S and V): Normal effects plot (Fig. 2) was made to compare the relative magnitude and the statistical significance of both main and interaction effects.

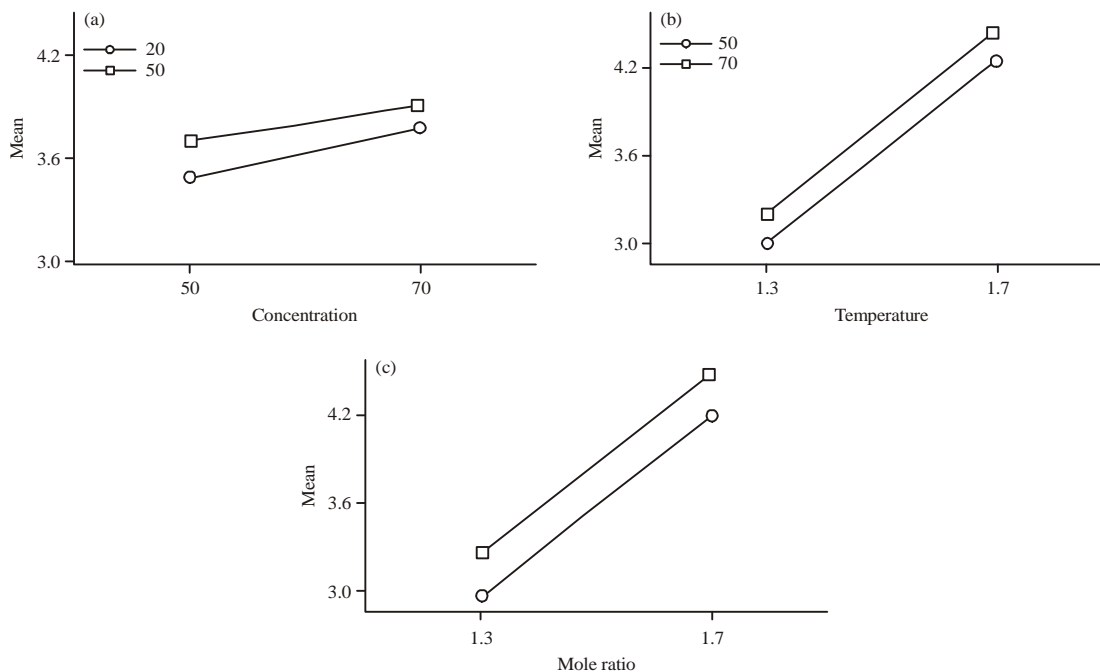


Fig. 5(a-c): Interactions plot of de-emulsifiers R and U

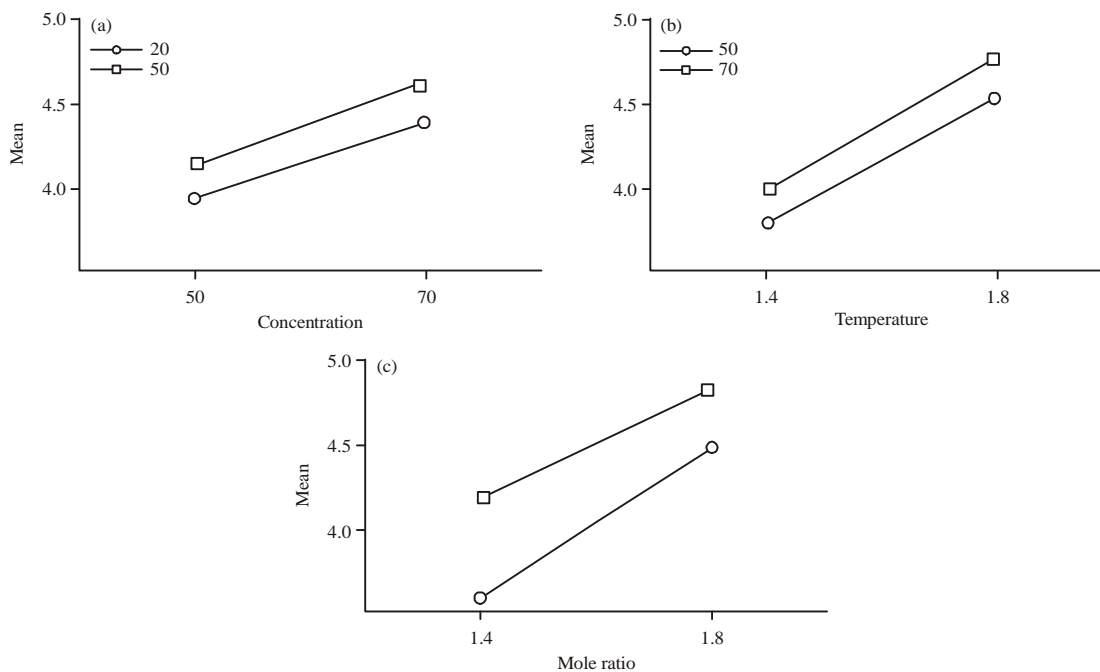


Fig. 6(a-c): Interactions plot of de-emulsifiers S and V

Minitab 16 drew a line to indicate where the points would expectedly fall if all effects were zero. Points that do not fall near the line indicated significant effects. In Fig. 2 for de-emulsifier pair Q and T, using the volume data from Table 4 and for de-emulsifier pairs R and U and S and V, there were three significant effects (at $\alpha = 0.05$) which

included-concentration (A), temperature (B) and mole ratio (C). 3.1.3. Main effects plot (analysis of resolde de-emulsifiers pairs Q and T, R and U and S and V).

Figure 3 gives the main effect plot which was used to show how the volume of water separated from the crude oil emulsion responds to one or more of the factors. A horizontal

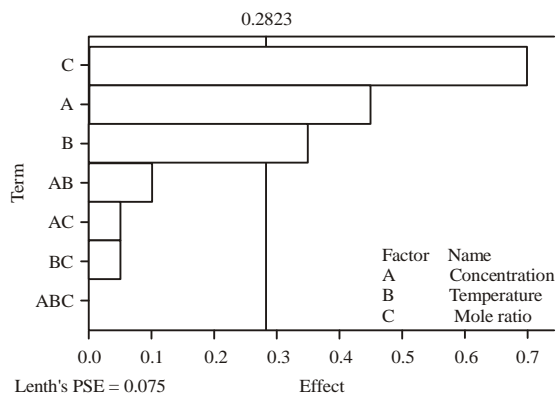


Fig. 7: Pareto chart for novolak de-emulsifier pair W and Y

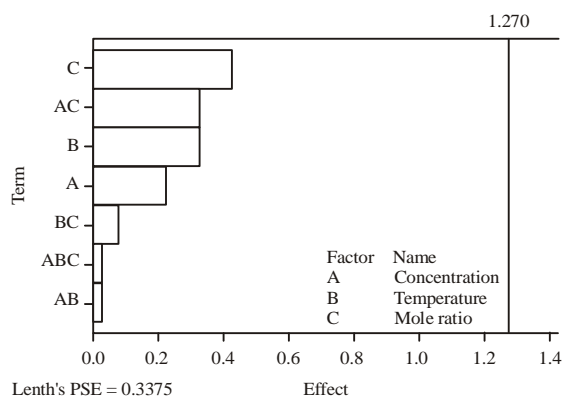


Fig. 8: Pareto chart for novolak de-emulsifier pair X and Z

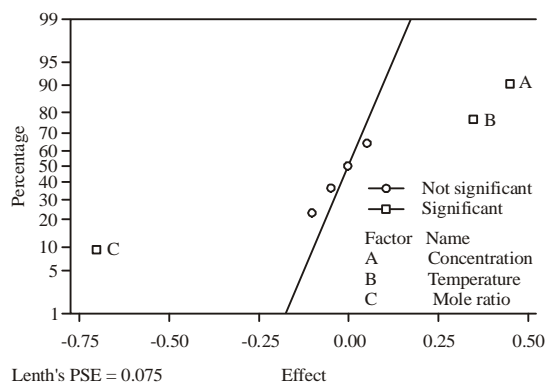


Fig. 9: Normal plot for novolak de-emulsifier pair W and Y

line (parallel to the x-axis) means there is no main effect present and a line that is not horizontal shows there may be a main effect present. The larger the slope is, the stronger the effect of the variable on the de-emulsification process. The relative magnitude of the effects of the factors can be seen by comparing the slopes of the lines on the plots.

Interaction effects plot (Analysis of resole de-emulsifiers pairs Q and T, R and U and S and V): The interactions plot (Fig. 4) is used to visualize the interaction effect of two factors on the performance or response of the de-emulsifiers

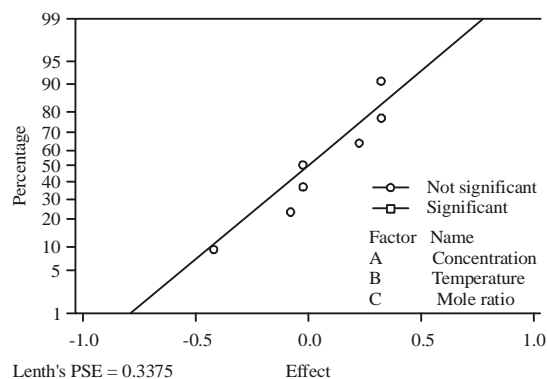


Fig. 10: Normal plot for novolak de-emulsifier pair X and Z

and to compare the relative strength of the effects. Minitab 16 was used to draw interactions plots for the three factors-concentration, temperature and mole ratio. An interaction is present when the change in the response mean from the low to the high level of a factor depends on the level of a second factor. The greater the degree of departure from being parallel, the stronger the effect.

Factorial optimization for novolaks de-emulsifier pairs W and Y and X and Z: Same optimization process was carried out for novolak de-emulsifiers using the same tools that were used for resole and are described as follows.

Pareto chart (Analysis of novolaks de-emulsifiers pairs W and Y and X and Z): Figure 7 and 8 gave completely different analyses of the two de-emulsifier pairs in which Minitab used an α -level of 0.05 to draw the reference line. For the de-emulsifier pair W and Y, reference line cuts across the three main factors-mole ratio, temperature and concentration being investigated (Fig. 7).

Normal plot (Analysis of novolaks de-emulsifiers pairs W and Y and X and Z): In Fig. 9, the three variables considered showed significant effects in the de-emulsification process. Temperature extended the farthest from the reference line indicating that it has the greatest effect on the de-emulsification and was closely followed by concentration (ppm) of the de-emulsifier while mole ratio of formaldehyde to phenol in the novolak de-emulsifier negatively influenced de-emulsification.

Main effects (Analysis of novolaks de-emulsifiers pairs W and Y and X and Z): For the two de-emulsifier pairs W and Y and X and Z shown in Fig. 11 and 12 the three variables mole ratio, temperature and concentration produced similar effects on the crude oil de-emulsification.

Interaction effects plot (Analysis of novolaks de-emulsifiers pairs X and Y and Y and Z): In Fig. 13 and 14, different effects of the variables were observed. From Fig. 13 the lines in the temperature-mole ratio plot and the concentration-mole

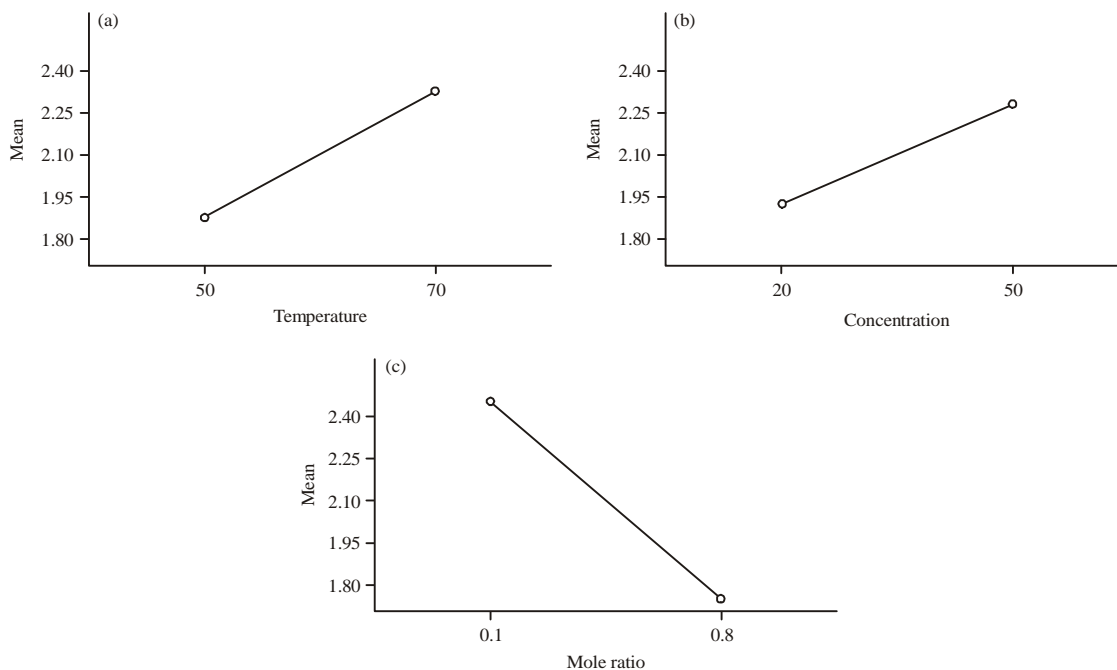


Fig. 11(a-c): Main effects plot for novolak de-emulsifier pair W and Y

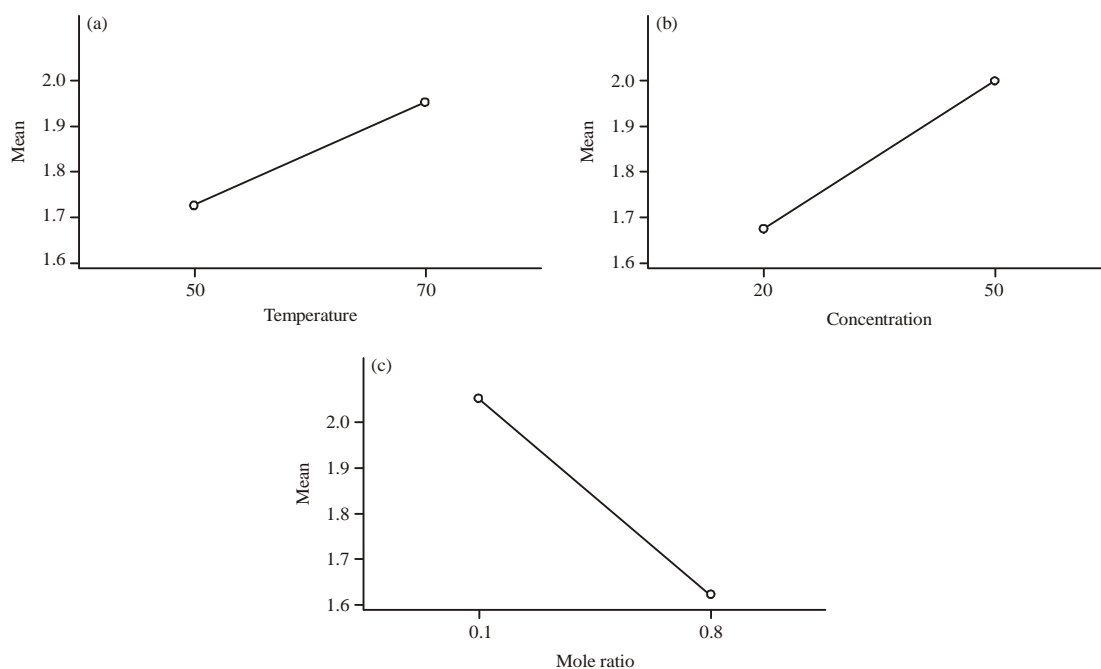


Fig. 12(a-c): Main effects plot for novolak de-emulsifier pair X and Z

ratio plot are parallel to each other. However, the lines in the temperature-concentration plot are not parallel to each other indicating that there exists an interaction effect between temperature and concentration. The negative slopes of the lines in the temperature-mole ratio and concentration-mole ratio plots indicate that the interactions between these variables do not enhance de-emulsification.

DISCUSSION

Pareto chart (Analysis of resol de-emulsifiers pairs Q and T, R and U and S and V): For Pareto charts (Fig. 1), Minitab 16 used an α -level of 0.05 to draw the reference red line. The farther the graph of the variable extends from the red line the more significant the effects of such variable. For de-emulsifier

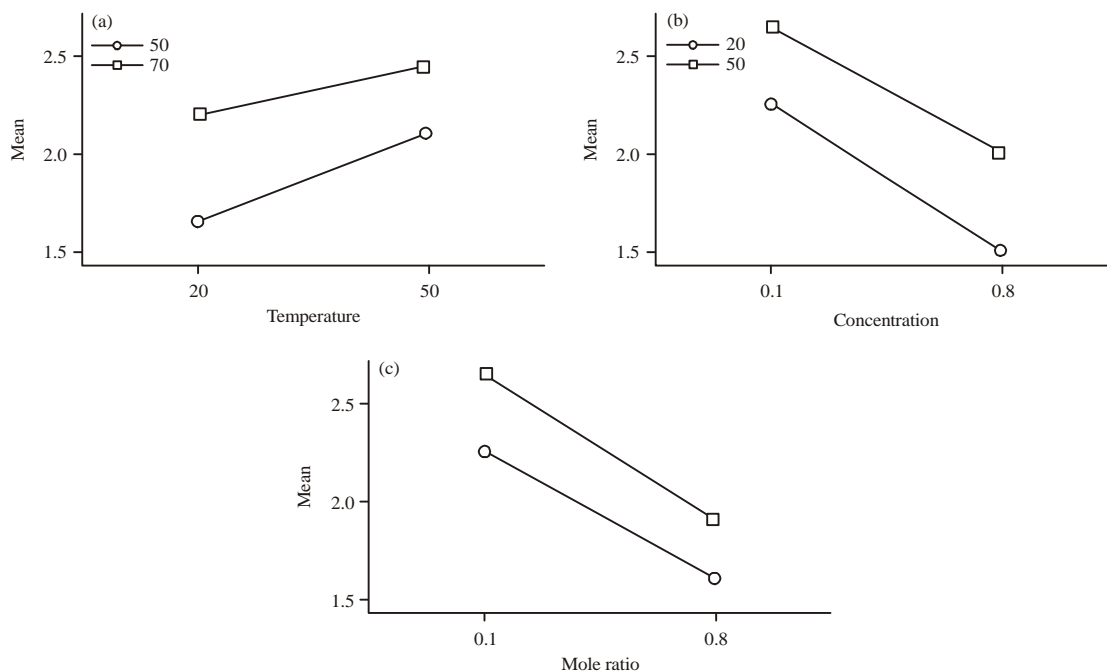


Fig. 13(a-c): Interaction effects plot for novolak de-emulsifier pair W and Y

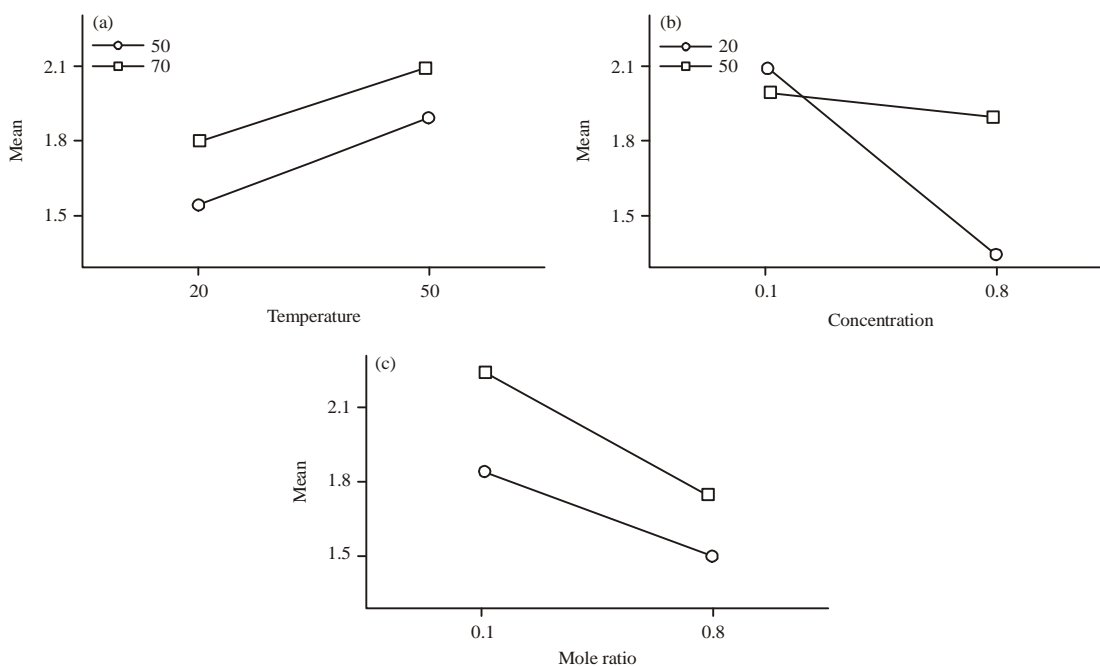


Fig. 14(a-c): Interaction effects plot for novolak de-emulsifier pair X and Z

pair Q and T shown in Fig. 1, it was observed that the effect of each variable had significant effects on de-emulsification. Mole ratio (denoted by C) had the largest effect on de-emulsification because it extended the farthest from the red line. This was minimally followed by temperature (denoted by B) and concentration (denoted by A) gave the least effect. The combined-concentration and temperature

interaction (denoted by AB, temperature and mole ratio interaction (denoted by BC), concentration and mole ratio (denoted by AC) and concentration, temperature and mole ratio (denoted by ABC) had no effect on the de-emulsification process because they did not extend beyond the reference line. The same effects were observed for samples B and E and C and F.

Normal effects plot (Analysis of resole de-emulsifiers pairs Q and T, R and U and S and V): In Fig. 2 for de-emulsifier pair Q and T, using the volume data from Table 5 and for de-emulsifier pairs R and U and S and V, there were three significant effects (at $\alpha = 0.05$) which included-concentration (A), temperature (B) and mole ratio (C). Again mole ratio (denoted C) was seen to have the largest effect for all pairs of de-emulsifiers on the de-emulsification process because it lies farthest from the reference line. This was also minimally followed by temperature (denoted by B) and concentration (denoted by A) having the least effect.

Main effects plot (Analysis of resole de-emulsifiers pairs Q and T, R and U and S and V): From Fig. 3 the plots indicate that for concentration, the volume of water removed increased as concentration was increased from 20-50 ppm. For Temperature effect, volume of water removed increased as temperature was increased from 50-70°C and for mole ratio, the volume of water removed increased as the mole ratio increased from 1.2:1-1.8:1. The relative magnitude of the effects of the factors can be seen by comparing the slopes of the lines on the plots. It was observed from the plot that effect of mole ratio on de-emulsification was more significant with a main effect of 42% followed by temperature of 35% main effect and 32% main effect for concentration. The plots of concentration and temperature showed no much difference in the magnitude of their effects compared to the plot of mole ratio where there was a significant magnitude of its effect on the de-emulsification process.

Interaction effects plot (Analysis of resole de-emulsifiers pairs Q and T, R and U and S and V): As seen in Fig. 4, the lines are slightly parallel to each other in the concentration-temperature and temperature-mole ratio plots. This showed that there were no interaction effects between these factors. However, in the concentration-mole ratio plot, the lines are not parallel to each other; hence, there was an interaction present. This meant that at high concentration the volume of water separated, increased as mole ratio increased. For de-emulsifier pair R and U (Fig. 5) the concentration-temperature plot, the lines are not parallel to each other. This showed the presence of an interaction between these factors on de-emulsification. While for de-emulsifier pair S and V, the temperature-mole ratio plot gave lines that were not parallel to each other which, showed that there was an interaction present (Fig. 6). At higher temperature, the volume of water separated increased as mole ratio was increased.

Hence, from the plots obtained from Minitab 16, the overall optimized de-emulsification conditions for the de-emulsifiers gave 50 ppm concentration and 70°C temperature and mole ratio of F:P as 1.8:1.

FACTORIAL OPTIMIZATION FOR NOVOLAKS DE-EMULSIFIER PAIRS W AND Y AND X AND Z

Pareto chart (Analysis of novolaks de-emulsifiers pairs W and Y and X and Z): Figure 7 showed significant effects of all the three variables. Mole ratio extended farthest

from the reference line which meant that mole ratio had the highest effect on the de-emulsification process. This was closely followed by temperature and minimally by concentration. But for de-emulsifier pair Y and Z (Fig. 8), the reference line did not cut across any of the bars which meant that none of the variables was significant at an alpha level of 0.05.

Normal plot (Analysis of novolaks de-emulsifiers pairs W and Y and X and Z): From Fig. 9, the mole ratio (C), extended to the opposite side of temperature (A) and concentration (B). This means that mole ratio less than 1 of formaldehyde as in the case of novolaks cannot enhance de-emulsification of water-in-crude oil emulsions. The differences between the various novolak de-emulsifiers were in their molar ratios and pH of preparation. Table 1 shows the novolak de-emulsifier samples W, X, Y and Z. While the molar ratio of phenol was kept constant at 1, that of formaldehyde was either 0.1 or 0.8 and at pH of either 1 or 5. If the formaldehyde mole ratio is high, the resin will have high methylol content and enormous water solubility. Thus the de-emulsifiers with lower formaldehyde mole ratio resins (novolaks) have much less methylol content and hence low water solubility. This was what accounted for the poor performance of the novolak de-emulsifier (Fig. 9 and 10) in the de-emulsification the crude oil emulsion used. The de-emulsifier pair X and Z did not produce any noticeable effects on de-emulsification (Fig. 10).

Main effects (Analysis of novolaks de-emulsifiers pairs W and Y and X and Z): It was observed that the volume of water removed increased as the concentration (ppm) of de-emulsifiers and temperature of de-emulsification were increased, respectively. While the mole ratio of formaldehyde to phenol in the novolak de-emulsifier adversely affected rather than to enhance de-emulsification. The volume of water removed decreased as mole ratio of formaldehyde to phenol was increased from 0.1:1 to 0.8:1. This negated the observed trend in resoles where, the percentage water removed increased as the mole ratio of formaldehyde to phenol was increased from 1.2:1 to 1.8:1. The method of preparation of the two de-emulsifiers may have been responsible for the observed difference in performance between them. While the resoles were prepared in basic or alkaline medium, the novolaks were prepared in acidic medium. Also, the molar ratios of the formaldehyde in the novolak de-emulsifiers were all below 1 mole.

Interaction effects plot (Analysis of novolaks de-emulsifiers pairs X and Y and Y and Z): From Fig. 13, both concentration and temperature enhanced de-emulsification. That is, the volume of water removed increased with increasing concentration and temperature. But in Fig. 14, the lines in the temperature-concentration plot are slightly parallel to each other indicating that there was no temperature-concentration interaction effect on the de-emulsification process. However, in the temperature-mole ratio and concentration-mole ratio plots, the lines are not parallel to each other. Both of these interacting variables had

no overall positive effects on de-emulsification. This was the reason for the negative slopes observed in these plots. Their interactions are inversely proportional to each other in the de-emulsification process. Hence, from Fig. 14, decreasing mole ratio and increasing temperature, decreasing mole-ratio and increasing concentration of de-emulsifiers and vice versa favored de-emulsification. Though, the extent of water separation from the crude oil emulsion was far lower than that obtained from resole de-emulsifiers.

Thus from Fig. 7-14, the optimized de-emulsification conditions for novolak de-emulsifiers pairs W and Y and X and Z are concentration 50 ppm, temperature 70°C and mole ratio of 0.1:1 (F:P).

In comparison to works carried out by other researchers Temple-Heald *et al.* (2015), Al-Sabagh *et al.* (2009) and Pena *et al.* (2005), where base catalysed ethoxylated phenolic resins were mostly investigated, the phenolic resins promoted coalescence of droplets (water separation) giving optimum performance as the resins' hydrophilic property (or water solubility), concentration, temperature and molecular weight (mole ratios) were increased.

CONCLUSION

For the resole de-emulsifiers, performance increased as the molar ratio of formaldehyde to phenol was increased from 1.2:1 to 1.8:1.

For the novolak de-emulsifiers, performance decreased as the molar ratio of formaldehyde to phenol ratio was increased from 0.1:1 to 0.8:1.

In the de-emulsification process using resole de-emulsifiers, the most significant singular factor is the mole ratio of formaldehyde to phenol.

Temperature-mole ratio interaction had the greatest combined effect on the de-emulsification process.

The performance of all the formulated de-emulsifiers increased as the temperature of de-emulsification was increased.

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REFERENCES

Al-Sabagh, A.M., M.R. Noor El-Din, S. Abo-El Fotouh and N.M. Nasser, 2009. Investigation of the demulsification efficiency of some ethoxylated polyalkylphenol formaldehydes based on locally obtained materials to resolve water-in-oil emulsions. *J. Dispersion Sci. Technol.*, 30: 267-276.

Al-Sahhaf, T.A., M.A. Fahim and A.M. Elsharkawy, 2009. Effect of inorganic solids, wax to asphaltene ratio and water cut on the stability of water-in-crude oil emulsions. *J. Dis. Sci. Technol.*, 30: 597-604.

Aske, N., 2002. Characterization of crude oil components, asphaltene aggregation and emulsion stability by means of near infrared spectroscopy and multivariate analysis. Ph.D. Thesis, Norwegian University of Science and Technology.

Aveyard, R., B.P. Binks, P.D.I. Fletcher, X. Ye and J.R. Lu, 1992. The Resolution of Emulsions, Including Crude Oil Emulsions, in Relation to HLB Behavior. In: *Emulsions: A Fundamental and Practical Approach*, Sjoblom, J. (Ed.). Springer Science and Business Media, Netherlands, ISBN: 9780792316183, pp: 97-110.

Becher, P., 1985. *Encyclopedia of Emulsion Technology*. Vol. 2, Marcel Dekker, New York.

Bhardwaj, A. and S. Hartland, 1998. Studies on build up of interfacial film at the crude oil/water interface. *J. Dispersion Sci. Technol.*, 19: 465-473.

Easton, T. and B. Thomas, 1989. De-emulsification of oils. United States Patent 4888107. <http://www.freepatentsonline.com/4888107.html>

Energy Information Administration, 2007. Primary energy consumption by source and sector United States of America. Energy Information Administration, USA.

Gafonova, O.V., 2000. Role of asphaltenes and resins in the stabilization of water-in-hydrocarbon emulsions. M.Sc. Thesis, The University of Calgary, Alberta, Canada.

Hyne, N.J., 2001. *Nontechnical Guide to Petroleum Geology, Exploration, Drilling and Production*. 2nd Edn., Pennwell Books, USA., ISBN: 978-0878148233, Pages: 575.

Ivanov, I.B. and P.A. Kralchevsky, 1997. Stability of emulsions under equilibrium and dynamic conditions. *Colloids Surfaces A: Physicochem. Eng. Aspects*, 128: 155-175.

Kokal, S. and J. Al-Juraid, 1999. Quantification of various factors affecting emulsion stability: Watercut, temperature, shear, asphaltene content, de-emulsifier dosage and mixing different crudes. Proceedings of the Society of Petroleum Engineers annual Technical Conference and Exhibition, October 3-6, 1999, Houston, Texas.

Kokal, S. and M. Wingrove, 2000. Emulsion separation index: From laboratory to field case studies. Proceedings of the Society of Petroleum Engineers Annual Technical Conference and Exhibition, October 1-4, 2000, Dallas, Texas.

Kokal, S., A. Al-Yousif and N.S. Meeranpillai, 2001. Very thick crude emulsions: A field case study of a unique crude production problem. Proceedings of the Society of Petroleum Engineers Annual Technical Conference and Exhibition, September 30-October 3, 2001, New Orleans, Louisiana.

Krawczyk, M.A., 1990. Mechanisms of de-emulsification. Ph.D Thesis, Illinois Institute of Technology.

Myers, D., 1992. *Surfactant Science and Technology*. Wiley-VCH, New York, USA., ISBN: 3-527-89586-8, Pages: 360.

- Pena, A.A., G.J. Hirasaki and C.A. Miller, 2005. Chemically induced destabilization of water-in-crude oil emulsions. *Ind. Eng. Chem. Res.*, 44: 1139-1149.
- Porter, M.R., 1994. Use of Surfactant Theory. In: *Handbook of Surfactants*, Porter, M.R. (Ed.). Blackie Academic and Professional, United Kingdom, pp: 26-93.
- Rhee, C.H., P.C. Martyn and J.G. Kremer, 1989. Removal of oil and grease in oil processing wastewater sanitation. District of Los Angeles County, California.
- Saywer, C.N., P.L. Mccarty and G.F. Parkin, 1994. *Chemistry for Environmental Engineering*. 4th Edn., McGraw Hill, Singapore, ISBN: 0-070113908-7.
- Selvarajan, R., S. Ananthasubramaniam and A.M. Robert, 2001. Aqueous dispersion of an oil soluble de-emulsifier for breaking crude oil emulsions. US Patent No. 6,294,093.
- Sjoblom, J., L. Mingyuan, A.A. Christy and T. Gu, 1992. Water-in-crude oil emulsions from the Norwegian continental shelf, 7. Interfacial pressure and emulsion stability. *Colloids Surf.*, 66: 55-62.
- Temple-Heald, C., C. Davies, N. Wilson and N. Readman, 2015. Developing new surfactant chemistry for breaking emulsions in heavy oil. *J. Pet. Technol.*, 66: 30-36.