



Empirical Modeling of the Precipitation Formation of Naphthenic Acid in An Idealized System

^{1*}Attahiru, A., ²Muhammad, A.B., ²Muhammad, C. and ¹Baba, H.

¹Department of Chemistry, Niger State College of Education, Minna, Nigeria,

²Department of Pure & Applied Chemistry, Usmanu Danfodiyo University, Sokoto, Nigeria,

ABSTRACT

The tendency of naphthenic acids to precipitate out of solution when in contact with the metal ions present in the formation water, present a formidable challenge for the petroleum industry. In this study, empirical modeling of naphthenic acid precipitation in idealized system was investigated. Response surface design based on Box-Behnken statistical design was used for the analysis. The result of the analysis revealed that the relative amount of naphthenate precipitate formed increases with increase in naphthenic acid concentration, calcium ion concentration, pH of formation water and percent water cut, as indices have significant effect on the formation of the precipitate. The predicted yield values for the options by the optimizer were 1.62%, 2.86% and 7.94% and validated values obtained empirically are 2.05 ± 0.16 , 3.36 ± 0.24 and 8.80 ± 0.14 respectively. These values were quite close of less than 1% differences for all the solutions predicted by the optimizer, this indicates that the model developed were well fitted and highly reliable. Validated yield of 2.05 ± 0.16 under the optimal condition given in solution was the best option for the minimizing the naphthenate precipitate. In general, the observed effects of the factors suggest that precipitation of the naphthenic acid can be minimized with acidic formation water that contains relatively low concentration of calcium ions concentration particularly when the concentration of the naphthenic acid in the crude oil is as low as possible.

Keywords: Naphthenic Acid, Naphthenate, Formation water, Water cut, idealized system.

INTRODUCTION

The definition of naphthenic acids is vague. Gunstone *et al.*, (2007) defined naphthenic acids as “carboxylic acids containing one or more alicyclic rings”, and example that they gave were monocyclic acids. Similarly, Bataineh *et al.*, (2006) defines naphthenic acids as “petroleum acids containing naphthene or cycloparaffin structure”.

The term ‘naphthenic acid’ is often used to account for all carboxylic acids present in crude oil, including acyclic and aromatic acids. Nearly all crude oils contain some naphthenic acids. Heavy crudes from geologically young formations have the highest acid content while paraffinic crudes usually have low acid content (Lengger, *et al.*, 2015; Priyanka *et al.*, 2015). Naphthenic acids are known to be produced during the in-reservoir biodegradation of petroleum hydrocarbons and they are considered to be a class of biological marker, closely linked to the maturity and the biodegradation level of the fields (Lochte and Littmann, 2013; Headly *et al.*, 2018). Recently, more and more oilfields

face severe flow assurance problems due to formation of deposits and soaps, generally termed naphthenates (Simon *et al.*, 2008). The presence of naphthenic acids in crude oil is of significant concern to the petroleum industry. These acids are associated with the corrosion of refinery equipment, blockage of the surface equipment, leading to the incurrance of additional cost to the consumer. (Arla *et al.*, 2007; Frank *et al.*, 2008; Fahim *et al.*, 2010; Tamilarasan *et al.*, 2012; Jorge *et al.*, 2016).

Calcium naphthenate are formed through interaction of naphthenic acids in crude oil with calcium ions (Ca^{2+}) from the formation water under right condition of pH and temperature to form solid deposit of calcium naphthenat (Sarac and Civan, 2007; Clark and Veil, 2009; Ashafizadeh *et al.*, 2012). Mapolelo *et al.*,

Received 07 October, 2021

Accepted 04 December, 2021

Address Correspondence to:

abdullahiattahiru74@gmail.com

(2011) described naphthenic acids by general formular $C_nH_{2n}+ZO_2$, where n represents the number of carbon atoms in the molecules and Z specifies hydrogen deficiency in the case of cyclic naphthenic acids. This formular implies the presence of one carboxylic group and the general formular has been used widely in mass spectrometry studies to characterize naphthenic acids (Hindle *et al.*, 2013; Carpio *et al.*, 2014; Rowland *et al.*, 2014; Huang *et al.*, 2016; Amy *et al.*, 2018). Offshore production installations in Great Britain and Norway (North Sea), West Africa (Gulf of Guinea, Angular, Cameroon, Gabon, and Nigeria), the North West Shelf of Australia, South East Asia (South China Sea, Malaysia, Vietnam, Bohai Bay in China and Kutei Basin in Indonesia) and Gulf of Mexico have reported unprecedented deposition problem (Osuji and Anita, 2005; Priyanka *et al.*, 2015). In many oil producing regions of the world, the formation of calcium naphthenate deposits has resulted in problems such as blockage of surface equipment, extensive shutdown periods of offshore installations, increase in cationic content of crude oil and entrapped of oil in sludge (Patil, *et al.*, 2011; Paulo and Vanessa, 2012).

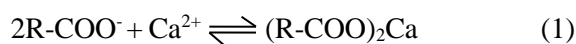
Crude oils generally contain a mixture of light and heavy hydrocarbons that can be classified as paraffin, naphthenic, and aromatics. The lighter parts of crude oils keep the heavier parts, which are wax and asphaltene, in the solution. The presence of light ends increases the solubility of wax in crude oils depending on the pressure, temperature, and composition of crude oils (Lutnaes *et al.*, 2007; Udemé, and Etim, 2012; Victor, *et al.*, 2015; Al-Kayiem, *et al.*, 2017). The polar fraction in petroleum liquids is the most problematic with respect to pollution, fouling of catalysts, corrosion, formation of deposits, and emulsions during production and processing (Yasin *et al.*, 2013; Putman and Marshall, 2016)

Naphthenate precipitation Formation

The primary condition for naphthenate soap precipitation is the presence of naphthenic acid in crude oil, which can react with the metal ions present in the formation water to form naphthenate soap (Lo, *et al.*, 2006; Patil, *et al.*, 2011; Victor, *et al.*, 2015) The acidity of crude oil reflected by the total acid number (TAN) measurement expressed in milligrams of KOH necessary to neutralize 1g of crude oil. Crude oils with acidity levels above 0.56 mg of KOH/g

are considered as potentially corrosive for refinery units (Dettman *et al.*, 2009; Alvisi and Lins, 2011; Priyanka *et al.*, 2015).

Two main types of naphthenates are known to form in production fluids: Calcium naphthenate solids that occur as sticky or harden deposits, and sodium naphthenates emulsion that can form tight emulsion as soaps or sludge (Mediaas, 2008; Mapolelo *et al.*, 2011). The cations present in the formation water react with the naphthenates to form metal soaps, generally calcium or sodium soaps, as calcium and sodium are among the most common cations present in the oilfield brine. The reaction between the $R-COO^-$ anion and the metal ion yields insoluble metal soaps. Because calcium is a divalent cation, the soap is formed by the reaction of calcium with two naphthenate anions.



In contrast, sodium is a monovalent cation, and therefore, the sodium naphthenate is formed according to:



The data presented in several literatures, indicates that metal soaps deposit at pH above 6.0 (Simon *et al.*, 2008; Headly *et al.*, 2016). When the pH of the water phase increases, the concentration of dissociated acids also increases, which in turn favour the formation of calcium naphthenate (Fafet *et al.*, 2008; Torleif *et al.*, 2013; Carpio *et al.*, 2014).

The aim of this research is to conduct a comprehensive investigation and optimization of the main factors that affect the precipitation behavior of naphthenic acids in an idealized system: Implication for naphthenic acid precipitation from crude oil with a view of minimizing the formation of naphthenate deposits and determine the optimal condition necessary for minimizing the precipitation of the naphthenic acids.

Origin and Structure of Naphthenic Acids

Kovalchik *et al.*, (2017) reported that naphthenic acids as a commercial derived from crude oil is a complex mixture of monocarboxylic acids containing one or more alkyl-substituted alicyclic rings (naphthenes) with lesser amount aliphatic carboxylic acids and naphthenic acids have long been important biomarkers and geochemical indicators for petroleum. Naphthenic acids comprise a complex mixture

of alkyl-substituted and cyclic aliphatic carboxylic acids, with general chemical formula $C_nH_{2n+Z}O_2$, where n indicates the carbon number and Z is zero or negative, even integer that specified the hydrogen deficiency resulting from ring formation. The rings may be fused or bridged, the acyclic compound are highly branched, unlike fatty acids (Scott *et al.*, 2008; Rowland *et al.*, 2014; Hughes *et al.*, 2017; Headly *et al.*, 2018).

.Fig 1 shows example of typical structures of naphthenic acids, the rings structures predominately contain 5- or 6-carbon atoms in various way combinations. Naphthenic acids with one ring belong to the $Z = -2$ family, those with two rings belong to the $Z = -4$ family and so on, naphthenic acids in the $Z = 0$ family are acyclic, but they are more likely to be branched rather than linear natural fatty acids. For example:

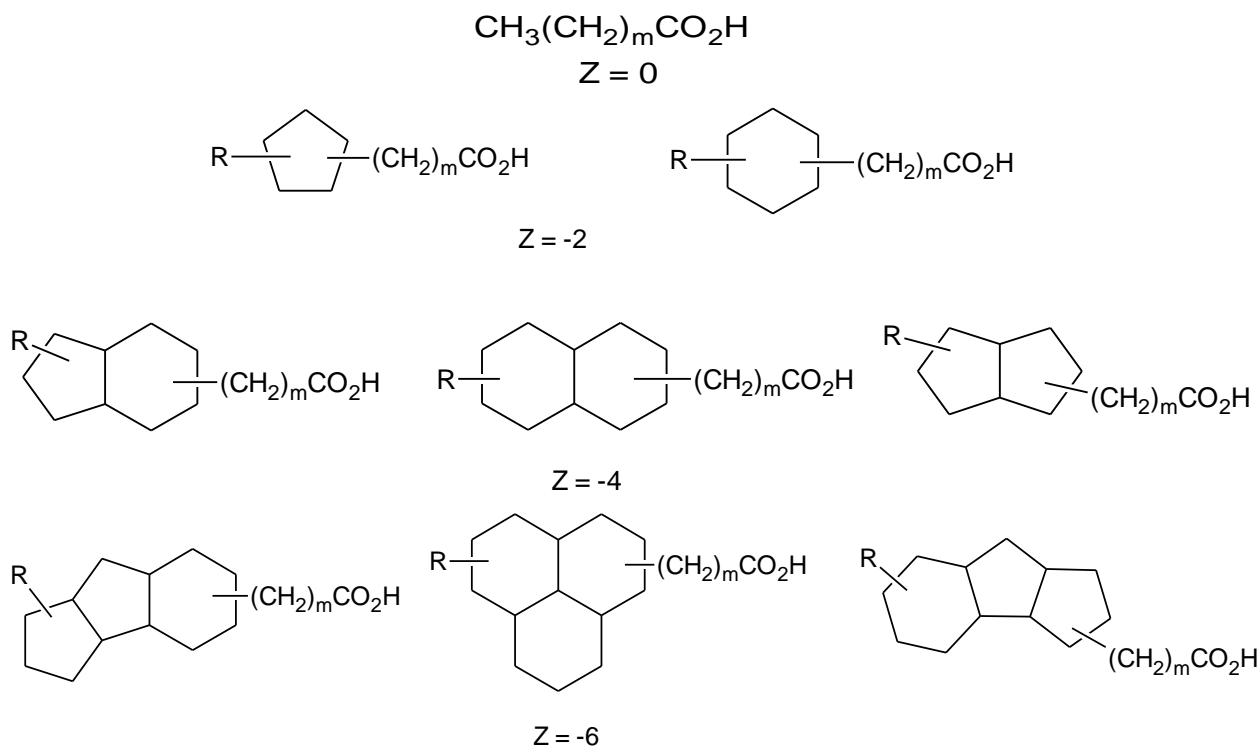


Figure 1: Scheme shows sample structures of naphthenic acid, where R is an alkyl group, Z described the hydrogen deficiency, and m is the number of CH_2 units and side chains (m)

METHODOLOGY

Chemical and Solvent

The solvent and chemical used include: Toluene, Naphthenic acid, Calcium chloride, Sodium chloride, and Magnesium chloride. The chemicals were analytical grade and were procured from Sigma-Aldrich and/or British Drug House (BDH) and used without further purification. Distilled water was used wherever needed. Routine glassware that were used was thoroughly cleaned with detergent, rinsed with copious amount of water and dried.

Sample Preparation

An accurately weighed amount of the relevant salt was dissolved in distilled water (50 to 100cm^3) and the solution was quantitatively

transferred into volumetric flask (1000cm^3) and dilute to the mark with distilled water (Mohammed and Sorbie, 2009).

Experimental Design

Response Surface (Box-Behnken) Statistical experimental design from MINITAB 17 statistical software were used to designed and analyzed the experiment. Four independent factors namely, naphthenic acid, calcium ion, pH and water cut were selected. The Table 1 shows the lower and upper levels of each factor was selected based on literature review (Ahmed *et al.*, 2014; Muhammad and Attahiru, 2017). Each run was set in duplicate and all the runs

were completely randomized to obtain a total of 54 runs (Appendix A and B)

Table 1: Independent factors investigate and their respective lower and upper levels

Factors	Code	Lower Levels	Upper Levels
Naphthenic acid concentration (mg/L)	n	2,000.00	20,000.00
Calcium ion concentration (mg/L)	c	5,000.00	120,000.00
pH	p	9.00	14.00
Water cut (%)	w	5.00	65.00

Description of the Experimental Runs

In each experimental run (Appendix A), the total volume of the oil phase and aqueous phase was kept at 150 cm³. The volume of aqueous phase (i.e water cut) needed for each run was been prepared by mixing one-fourth each of the water cut value of sodium, magnesium and calcium ions and Naphthenic acid solutions of respective concentration as given in the design matrix. The solutions were shaken vigorously and allowed to stay for 24 hours for proper dissolution, after

which the precipitate formed was filtered. The precipitate was washed with distilled water and toluene, dried at temperature of 60°C and finally weighed. The relative amount of precipitate obtained was used as response variable (Mohammed and Sorbie, 2010). The percentage of the precipitate yield relative to the total weight of the 2.032g, 1.910g and 1.694g precipitate obtained used for the percent runs (Appendix C) was calculated from Equation 3. (Ahmed *et al.*, 2014; Muhammad *et al.*, 2016, Kyari *et al.*, 2017)

$$\text{Naphthenate yield, } Y (\%) = \frac{\text{wt of the naphthenate obtained (g)} \times 100\%}{\text{Total wt of the naphthenate in the sample}} \dots\dots(3)$$

Data Analysis

The data obtained were analyzed using MINITAB 17 Statistical Software to estimate the main and interaction effects of the factors on the yield (y). The percentage naphthenate yield was fitted with full quadratic polynomial model equation using regression analysis (Equation 4) in order to correlate the yield with the operating factors.

$$y = \alpha_0 + \sum_{i=1}^4 \alpha_i x_i + \sum_{i=1}^4 \alpha_{ii} x_i^2 + \sum_{i=1}^4 \sum_{j=i+1}^4 \alpha_{ij} x_i x_j \quad (4)$$

Where $\alpha_0, \alpha_i, \alpha_{ii}, \alpha_{ij}$ are intercept, linear, quadratic and interaction coefficients, respectively, and the x_i and x_j are the independent variable. The effect of terms was evaluated using Analysis of Variance (ANOVA) at 95% level of confidence and the fitness of the model was evaluated by the coefficient of determination (R^2) (Tamilraesan *et al.*, 2012; Muhammad *et al.*, 2016; Kyari *et al.*, 2017). Contour plot was developed using the fitted quadratic polynomial equation, two of the independent factors were held at a constant value and changing the other variables. Optimizer on the Minitab 17 Statistical Software was used to optimize the factors and the optimal levels obtained were experimentally validated.

Optimization and Validation of the Naphthenate (%) Yields

Optimization of the Naphthenate yield was carried out using Surface Response Optimizer in Minitab 17 statistical software. The target was set to minimize the yield to zero. Table 6 shows the three solutions or mitigating strategies obtained from optimizer Response design.

Table 2: The design matrix and results of naphthenate precipitate (% yield) obtained for Idealized system

RunOrder	Ca (mg/L)	NAC Acid (mg/L)	pH	Watercut (%)	Nap.(g)	Nap. (%)
1	62500	2000	11.5	65	0.795	46.93
2	120000	11000	11.5	5	1.474	77.17
3	62500	11000	9	5	0.984	51.52

4	62500	11000	11.5	35	1.392	72.88
5	62500	20000	9	35	1.451	75.97
6	5000	11000	14	35	0.328	17.17
7	120000	2000	11.5	35	0.990	58.44
8	62500	11000	9	65	1.132	59.27
9	62500	20000	11.5	5	1.594	78.44
10	62500	2000	14	35	0.805	47.52
11	5000	11000	9	35	0.300	15.71
12	62500	11000	14	5	1.298	67.96
13	120000	11000	11.5	65	1.605	84.03
14	120000	20000	11.5	35	1.976	97.24
15	62500	11000	14	65	1.446	75.71
16	120000	11000	14	35	1.618	84.71
17	62500	11000	11.5	35	1.380	72.25
18	5000	11000	11.5	65	0.360	18.85
19	62500	11000	9	65	1.130	59.16
20	5000	2000	11.5	35	0.275	16.23
21	5000	11000	11.5	5	0.298	15.60
22	62500	20000	14	35	1.784	87.80
23	62500	11000	11.5	35	1.388	72.67
24	120000	20000	11.5	35	1.975	97.19
25	62500	11000	9	5	0.982	51.41
26	120000	11000	11.5	65	1.602	83.87
27	62500	2000	14	35	0.804	47.46
28	62500	11000	11.5	35	1.390	72.77
29	62500	2000	11.5	5	0.752	44.39
30	120000	11000	9	35	1.365	71.47
31	5000	11000	14	35	0.356	18.64
32	62500	2000	11.5	5	0.752	44.39
33	62500	2000	9	35	0.715	42.21
34	62500	2000	9	35	0.712	42.03
35	62500	20000	11.5	65	1.756	86.42
36	5000	11000	11.5	5	0.298	15.60
37	5000	20000	11.5	35	0.495	24.36
38	120000	11000	14	35	1.618	84.71
39	5000	20000	11.5	35	0.495	24.36
40	62500	20000	14	35	1.784	87.80
41	62500	20000	11.5	65	1.754	86.32
42	5000	2000	11.5	35	0.274	16.17
43	62500	11000	14	65	1.448	75.81
44	62500	2000	11.5	65	0.894	52.77
45	62500	20000	9	35	1.454	71.56
46	120000	11000	11.5	5	1.475	77.23
47	62500	11000	14	5	1.296	67.85
48	62500	20000	11.5	5	1.594	78.44
49	120000	11000	9	35	1.368	71.62

50	62500	11000	11.5	35	1.392	72.88
51	62500	11000	11.5	35	1.390	72.77
52	120000	2000	11.5	35	0.990	58.44
53	5000	11000	11.5	65	0.360	18.85
54	5000	11000	9	35	0.330	17.28

RESULTS

Table 3: Results of analysis of variance for the idealized system showing the significant and not significant terms

Source	Df	Adj- SS	Adj- MS	F-value	P-value	Significant
Model	14	33860.2	2418.6	260.46	0.000	S
Linear	4	29023.7	7255.9	781.41	0.000	S
c	1	22041.0	22041.0	2373.65	0.000	S
n	1	5981.8	5981.8	644.20	0.000	S
p	1	747.5	747.5	80.50	0.000	S
w	1	253.3	253.3	27.28	0.000	S
Squares	4	4251.8	1063.0	114.47	0.000	S
(c) ²	1	4126.8	4126.8	444.42	0.000	S
(n) ²	1	185.8	185.8	20.01	0.000	S
(p) ²	1	317.8	317.8	34.23	0.000	S
(w) ²	1	158.4	158.4	17.06	0.000	S
2-way interaction	6	584.6	97.4	10.49	0.000	S
c*n	1	468.9	468.9	50.49	0.000	S
c*p	1	69.1	69.1	7.44	0.010	S
c*w	1	6.2	6.2	0.66	0.421	NS
n*p	1	37.5	37.5	4.04	0.021	S
n*w	1	3.0	3.0	0.33	0.571	NS
p*w	1	0.0	0.0	0.00	0.981	NS
Error	39	362.1	9.3			
Lack- of- Fit	10	332.7	33.3	32.73	0.000	S
Pure Error	29	29.5	1.0			
Total	53	29794.4				

KEYS: c = Calcium ion conc. n = Naphthenic acid conc., p = pH, w = Water cut (%), S = statistically significant, NS = statistically not significant

S = 3.04725, R-sq = 98.94%, R²-sq (adj)= 98.56%, R²-sq (pred) = 97.89%

Table 4: Results of analysis of variance for the significant terms

Source	Df	Adj SS	Adj MS	F- Value	P- Value	Significance
Model	10	33813.5	3381.3	355.63	0.000	S
Linear	4	29023.7	7255.9	763.14	0.000	S
C	1	22041.0	22041.0	2318.15	0.040	S
N	1	5981.8	5981.8	629.14	0.000	S
P	1	747.5	747.5	78.62	0.000	S
W	1	253.3	253.3	26.64	0.000	S
Square	4	4251.8	1063.0	111.80	0.000	S
(c) ²	1	4126.8	4126.8	434.03	0.000	S
(n) ²	1	185.8	185.8	19.54	0.000	S
(p) ²	1	317.8	317.8	33.43	0.000	S
(w) ²	1	158.4	158.4	16.66	0.000	S
2-Way interaction	2	537.9	269.0	28.29	0.000	S
c*n	1	468.9	468.9	49.31	0.000	S
c*p	1	69.1	69.1	7.27	0.010	S
Error	43	408.8	9.5			
Lack- of- Fit	14	379.4	27.1	26.66	0.000	S
Pure Error	29	29.5	1.0			
Total	53	34222.3				

Model summary

S = 3.08351, R-sq = 98.81%, R²-sq (adj) = 98.67%, R²-sq (pred) = 97.94%, SS = Statistically Significant.

Table 5: Results of regression analysis showing the estimate of coded coefficients of the significant terms

Term	Effect	Coef	SE Coef	T- Value	P- Value	Significant
Constant		72.193	1.26	57.76	0.000	S
c.	60.609	30.305	0.629	48.15	0.000	S
n	31.575	15.787	0.629	25.08	0.000	S
p	11.162	5.581	0.629	8.87	0.000	S
w	6.498	3.249	0.629	5.16	0.000	S
(c) ²	-39.339	-19.669	0.944	-20.83	0.000	S
(n) ²	-8.347	-4.173	0.944	-4.42	0.000	S
(p) ²	10.918	-5.459	0.944	-5.78	0.000	S
(w) ²	-7.708	-3.854	0.944	-4.08	0.000	S
c*n	15.31	7.66	1.09	7.02	0.000	S
c*p	5.88	2.94	1.09	2.70	0.000	S

From regression analysis new model equation formed was given as follow:

$$\text{Naphthenate \% (Y)} = -134.4 + 0.000873c + 0.001963n + 21.04p + 0.4081w - 0.873pp - 0.00428ww + 0.000020cp \dots\dots\dots$$

3

Where Y is response variable (Amount of precipitate formed), c, n, p and w are the uncoded independent variable corresponding to Naphthenic acid concentration, Calcium ion concentration, pH and Water cut respectively.

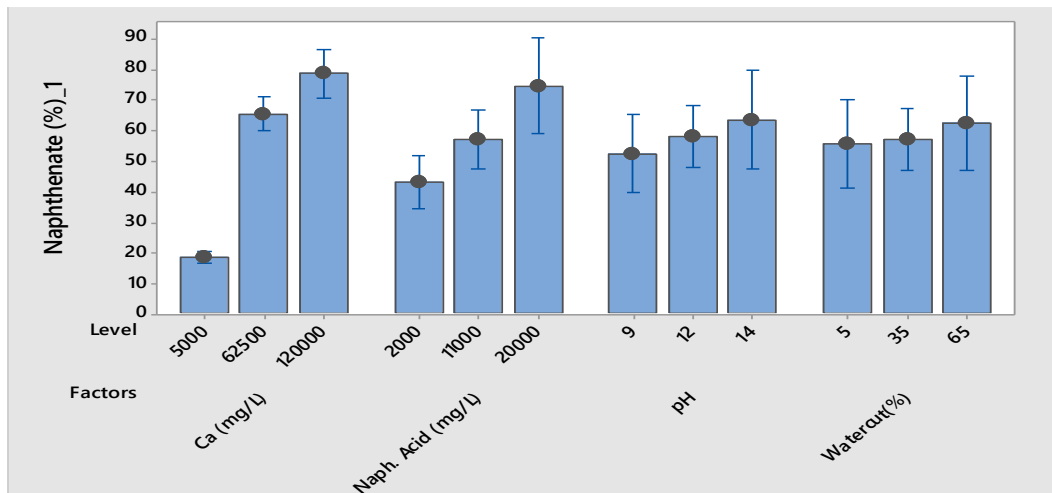


Figure 2: Bar chart showing summarized effect of the factors investigated on the relative amount of naphthenate precipitate for the idealized system

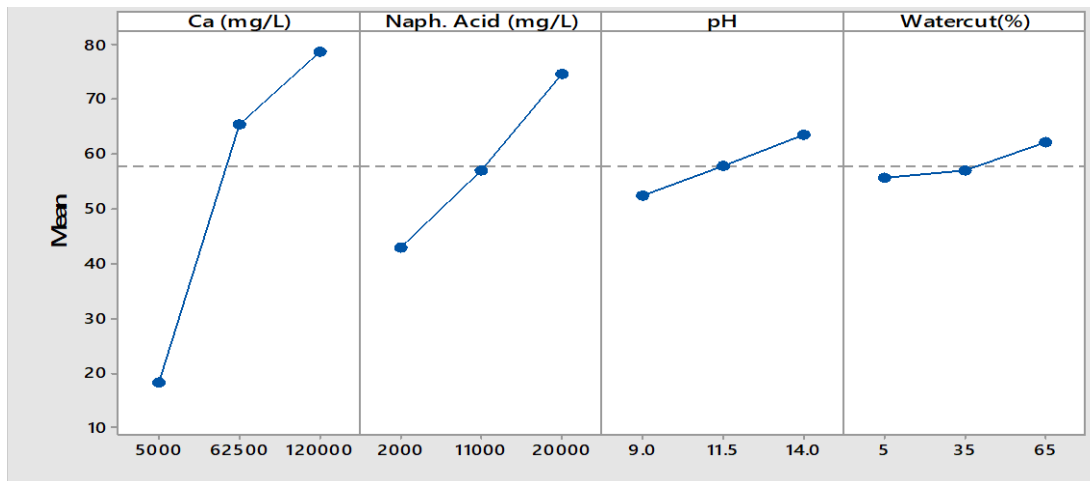


Figure 3: Main effect plot of the individual significant factors investigated

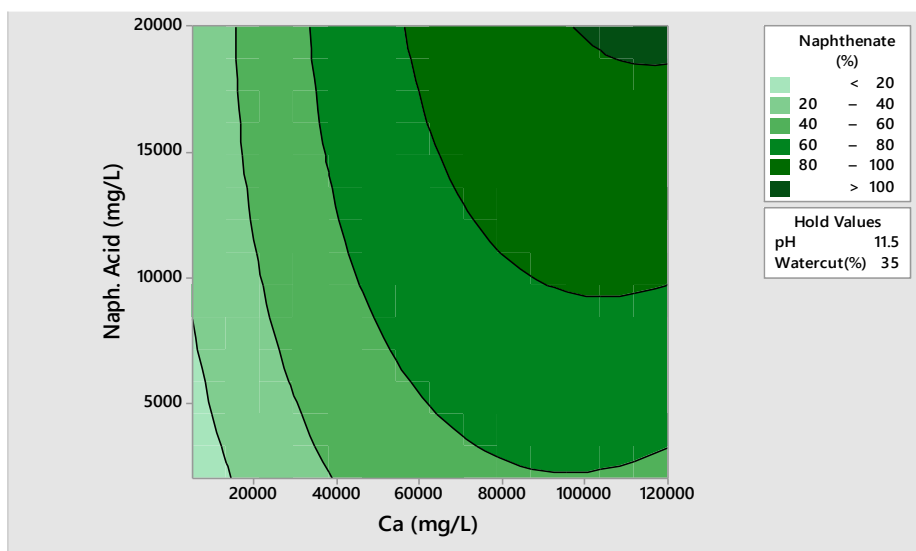


Figure 4: Contour Plot of effect of Naphthenic Acid versus Calcium ion Concentration on the amount of naphthenate Precipitate yield

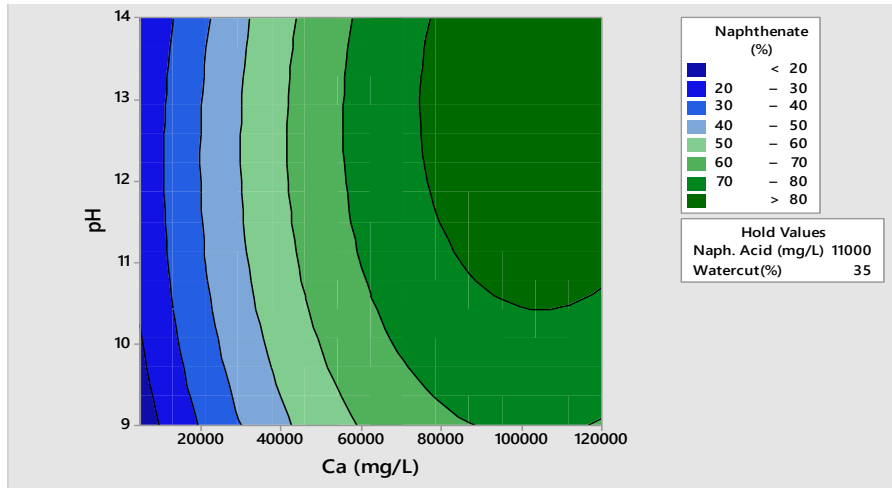


Figure 5: Contour Plot of the effect of pH versus Calcium ion Concentration on the amount of naphthenate precipitate yield

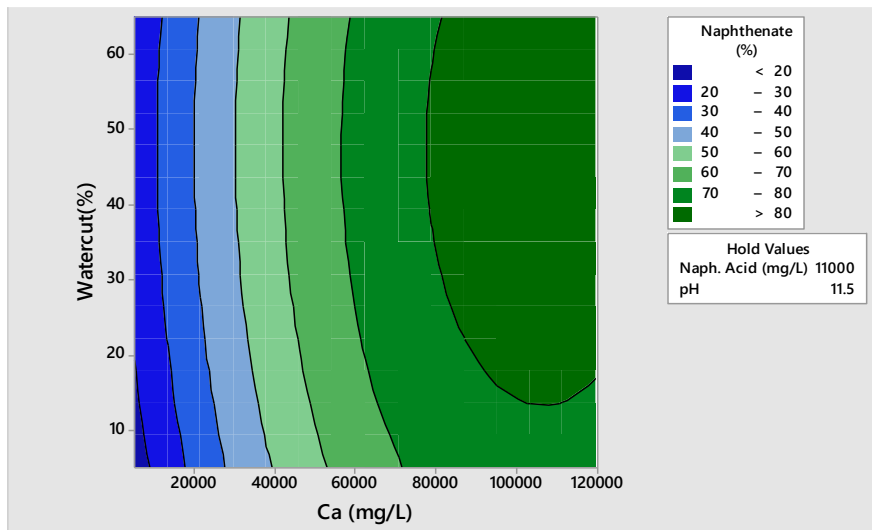


Figure 6: Contour Plot showing the effect of water cut versus Calcium ion Concentration on the amount naphthenate precipitate yield

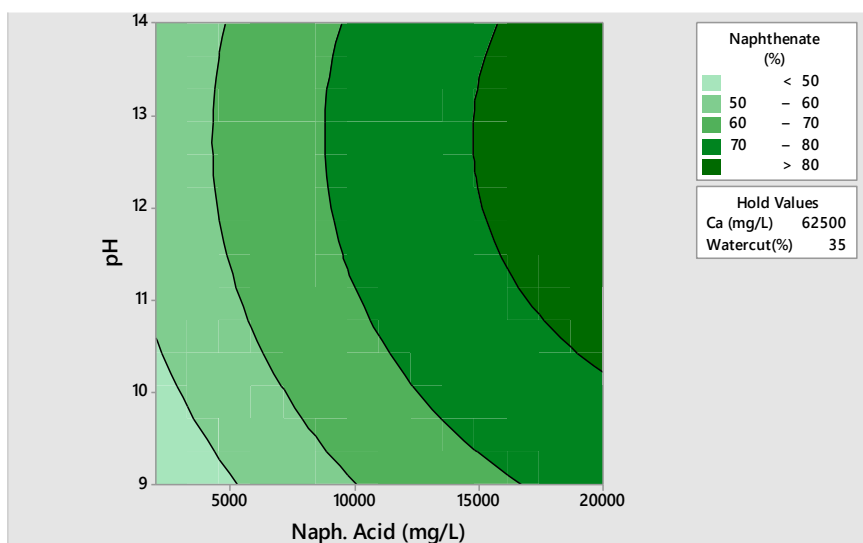


Figure 7: Contour Plot of showing the effect of pH versus Naphthenic acid Concentration on the amount of naphthenate precipitate yield for the idealized system

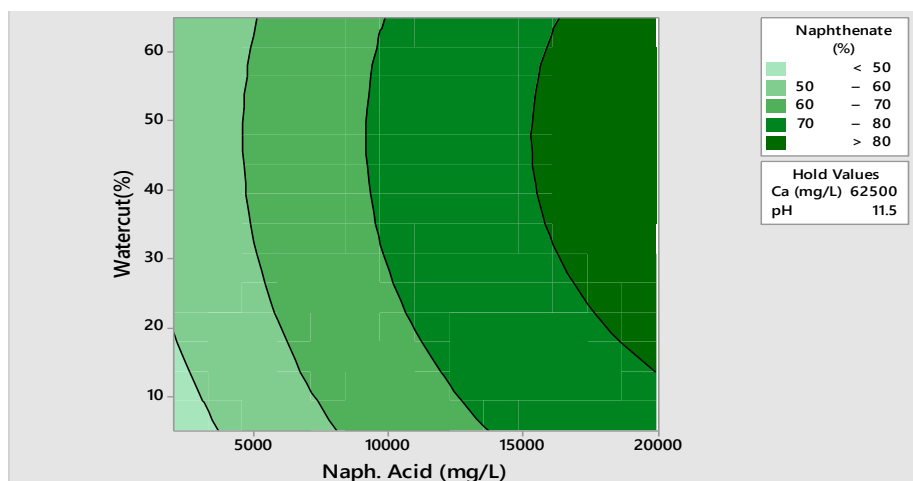


Figure 8: Contour Plot of showing effect of water cut versus naphthenic acid Concentration on the amount of naphthenate precipitate yield

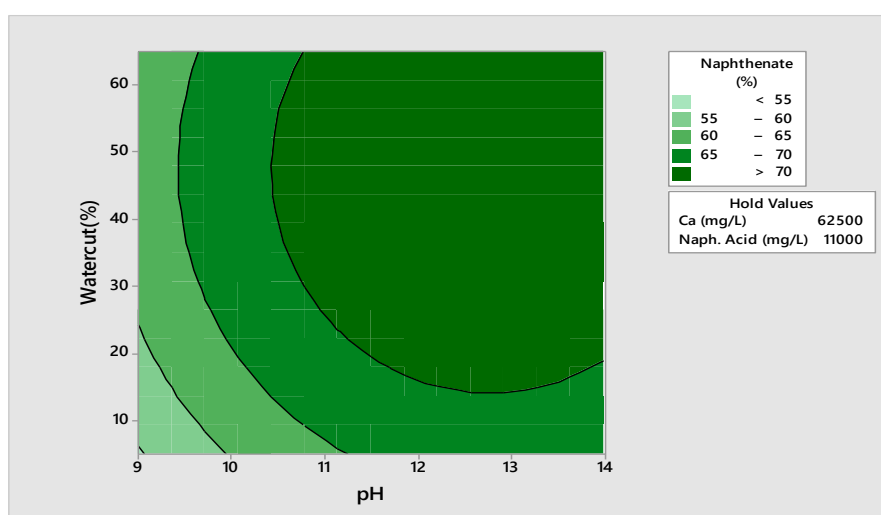


Figure 9: Contour Plot showing effect of water cut versus pH on the amount of naphthenate precipitate yield

Table 6: Result of the predicted yield and validation yield for the

Solution	Calcium ion (mg/L)	Naphthenic Acid (mg/L)	pH	Water cut (%)	Predicted Yield (%)	Experimental Yield (%)
1	5000	2000	9	5	1.62	2.05 ± 0.16
2	5000	2000	14	5	2.86	3.35 ± 0.24
3	5000	2000	9	65	7.94	8.80 ± 0.12

DISCUSSION

Results of analysis of variance for the statistically significant (SS) and not significant (NS) terms of the model developed for the idealized system (Table 3) revealed that the linear, square and interaction terms of the model

investigated on the amount of naphthenate yield were all statistically significant ($p < 0.05$) except those interactions involving calcium ion concentration versus water cut ($c*w$), naphthenic acid concentration versus water cut

(n^*w) and pH versus water cut (p^*w) that were statistically not significant ($p > 0.05$). The coefficient of determination (R^2) from the model summary shows that the model, including all the linear, square and some other two interaction terms account for about 98.94% of the experimental results obtained ($R^2 = 99.17\%$) with excellent prediction ability ($R^2(\text{pred}) = 97.89\%$) indicate that the model developed is well fitted to the experimental design and highly reliable. On eliminating the statistically not significant terms from the model (Table 4), from regression analysis new model equation (Eq. 4) based on the coded terms was obtained as follows:

$$\text{Naphthenate \% (Y)} = -134.4 + 0.000873c + 0.001963n + 21.04p + 0.4081w - 0.873pp - 0.00428ww + 0.000020cp \dots\dots\dots (4)$$

Figure 2 shows the result for the summarized effect of the four factors investigated on the relative amount of naphthenate produced. Increase in calcium ion and Naphthenic acid concentrations increases the amount of naphthenate formed, increase in each of those two factors shows sharp increase on the amount of naphthenate precipitate, on the other hand, pH of the formation water and water cut appear to show less significant effect on the naphthenate precipitation.

The optimization experiment in table 6 indicate that the predicted precipitate yield (%) grams should be 2.2808%, 4.0312% and 5.6574% respectively. In a quest to validate the optimal condition predicted by the optimizer, and also to confirm reliability of the model, a validation studies were collected empirically. The validated results were obtained empirically as follows 2.732 ± 0.651 , 3.4580 ± 0.173 and 4.8864 ± 1.412 , the solution 1 and 3 give the closest value to the predicted value of the optimizer, hence, are considered to be the best options

Conclusion

Comprehensive investigation of the factors that influence the precipitation formation of naphthenic acid from crude oil system was successful carried out. The result shows that factors such as Calcium ion concentration, Naphthenic acid concentration, pH and percent Water cut, were found to have significant effect on the precipitation of naphthenic acid from crude oil such that increase in the variables

results in higher yield of the naphthenate precipitate. However, calcium ion and naphthenic acid concentrations expressed stronger effects on the precipitation formation than the pH of the formation water and percent Water cut. Optimization and validation experiment of the factors investigated agree very closely to each others of less than 1% for all the solutions, this indicates that the empirical model from response surface design were well fitted to the model developed and it is highly reliable. In general, the observed effects of the factors suggest that precipitation of the naphthenic acid can be minimized with acidic formation water that contains relatively low concentration of calcium ions concentration particularly when the concentration of the naphthenic acid in the crude oil is as low as possible.

Naphthenate precipitation deposition could be reduced with slightly acidic pH and flooding the formation water containing salt and basic pH with fresh water which could dilute it to minimize the amount of naphthenate formation. Addition of acid will keep the pH low and thereby avoid naphthenate formation.

Recommendations

The extent of the work conducted is not sufficient to provide adequate information on the nature of acid in the naphthenate and other compounds present. Therefore, the need for instrumental analysis such as Thermogravimetric Analysis, Nuclear magnetic resonance (NMR) and Raman spectroscopy should be carried out on the nature and structure of the acid present. The effect of temperature and pressure should also be conducted on the amount of naphthenate produced during the experiment.

REFERENCES

- Ahmad, J., Bokhari, A., Yusuf, S. (2014). Optimization and parametric study of free fatty acid reduction from rubber seed oil by using response surface methodology. *Journal of Basic and Applied Science* 8: 299- 303.
- Amy C. Clingenpeel, Thomas R. Fredriksen, Kuangnan Qian, Michael R. Harper (2018). *Comprehensive Characterization of Petroleum Acids by Distillation, Solid Phase Extraction Separation, and Fourier*

- Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy and Fuels*.32 (9), 9271-9279.
- Anamet, I., (2013). Final Report: Metallurgical Evaluation of Samples from the Chevron U.S.A. Inc., Richmond # Crude Unit, Hayward, CA.
- Anon, (2014),. CSB Analysis of 2009 Silver Eagle Refinery Accident, Washington, D.C.
- Anon, (2013). Improving Public and Worker Safety at Oil Refineries:Draft Report of the Interagency Working Group on Refinery Safety, Sacramento, CA.
- Alvisi, P.P.; Lins, V.F.C. (2011). An overview of naphthenic acid corrosion in vacuum distillation plant. *Eng. Failure Anal.* **18**, 1403- 1406.
- Ahmad, J., Bokhari, A., Yusuf, S. (2014). Optimization and parametric study of free fatty acid reduction from rubber seed oil by using response surface methodology. *Journal of Basic and Applied Science* **8**: 299- 303.
- Arla, D., Siquin, A., Palemo, T., Hurtevent, C., Graciaa, A., Dicharry, C.(2007). Influence of ph and water content on the type and stability of acidic crude oil emulsions. *Energy and fuels***13**: 1337- 1342.
- Ashrafizadeh, S.N., Motae, E., and Hoshyargar, V. (2012). Emulsification of Heavy Crude Oil in Water by Natural surfactant, *Petroleum Science and Engineering*,**86-87**;137-143.
- Bataineh, M., Scott, A.C., Fedorak, P.M., Martin, J.W. (2006).Capillary HPLC / QTOF-MS for characterizing complex naphthenic mixtures and their microbial transformations. *Analytical. Chem.* **78**: 8354 – 8361.
- Brocart, B., Hurtevent, C.(2008). *J. Dispersion Sci. Technol.* **29**, 1496–1504.
- Carpio, E.O., Rodriguez, S., Rondon, M. and Brges, B. (2014). Stability of water-in-Boscan Crude Oil Emulsion: Effects of Salts, Alcohols and Glycol.*Journal of Petroleum Science and Engeering*, **122**.542-550.
- Civan, F., Alarcon, L. J., Campbell, S. E. 2004): “Laboratory Confirmation of New Emulsion Stability Model”, *Journal of Petroleum Science and Engineering*, vol. **43**: 25-34.
- Dettman, H.D.; Li, N.; Luo, J. (2009). Refinery corrosion organic acid structure and Athabasca bitumen. *CORROSION*, Atlanta, GA, 22-26.
- Fahim, M.A., Al-Sahhaf, T.A. & Elkilani, A.S., (2010). *Fundamentals of Petroleum Refining 1st ed., Oxford, U.K.: Elsevier.*
- Frank, R.A., R. Kavanagh, B.K. Burnison, G. Arsenault, J.V. Headley, K.M. Peru, G. Van Der Kraak, and K.R. Solomon. (2008). Toxicity assessment of collected fractions from an extracted naphthenic acid mixture. *Chemosphere* **72**:1309-1314.
- Gunstone, F. D., John, L. Harwood, and Albert J. Dijkstra (2007). *The Lipid Handbook with Cd-Rom*. 3rd ed. Boca Raton: CRC Press. ISBN 0849396883 | ISBN 978-0849396885.
- Grewre, D.M., Young R.F, Whittal R.M., Fedorak, P.M. (2010). Naphthenic acid and other acid extractable in water sample from Alberta: *Environ***408**: 5997- 6010.
- Headley, J.V., Peru, K.M., Barrow, M.P., 2016. Advances in mass spectrometric characterization of naphthenic acids fraction compounds in oil sands environmental samples and crude oil-A review. *Mass Spectrom. Rev.* **35** (2), 311- 328.
- Hindle, R., Noestheden, M., Peru, K., Headley, J. (2013). Quantitative analysis of naphthenic acids in water by liquid chromatography-accurate mass time-off light mass spectrometry. *Journal of Chromatography. A* **1286**: 166-174.
- Huang, R., McPhedran, K.N., Sun, N., Chelme-Ayala, P., Gamal El-Din, M., (2016). Investigation of the impact of organic solvent type and solution pH on the extraction efficiency of naphthenic acids from oil sands process-affected water. *Journal of Chemosphere.* **146**: 472 - 477.
- Huang, R., Chen, Y., Meshref, N.A.M., Chelme-Ayala, P., Dong, S., Ibrahim, D.M., Wang, C., Klammerth, N., Hughes, S.A., Headley, J.V., Peru, K.M., Brown, C., Mahaffey,

- A., Gamal El-Din, M., (2018). Characterization and determination of naphthenic acids species in oilsands process-affected water and groundwater from oil sands development area of Alberta, Canada. *Journal of Water*.
- Hughes, S.A., Mahaffey, A., Shore, B., Baker, J., Kilgour, B., Brown, C., Peru, K.M., Headley, J.V., Bailey, H.C., (2017). Using ultrahigh-resolution mass spectrometry and toxicity identification techniques to characterize the toxicity of oil sand sprocess-affected water: the case for classical naphthenic acids. *Environ. Toxicol. Chem.* <https://doi.org/10.1002/etc.3892>.
- Jorge A. Orrego-Ruiz, Andrea Gomez-Escudero, and Fernando A. Rojas-Ruiz (2016). Combination of Negative Electrospray Ionization and Positive Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry as a Quantitative Approach of Acid Species in Crude Oils. *Energy & Fuels*. **30** (10) , 8209-8215..
- Kovalchik, K.A., MacLennan, M.S., Peru, K.M., Headley, J.V., Chen, D.D.Y. (2017). Standard method design considerations for semi-quantification of total naphthenic acids in oil sands process affected water by mass spectrometry: a review. *Front. Chem. Sci. Eng.* **11** (3), 497- 507.
- Kruger, J., (2011). Cost of metallic corrosion. In R. W. Review, ed. *Uhlig's Corrosion Handbook*. New York, NY: Wiley, pp. 15–20.
- Kyari, M. Z., Danggoggo, S. M., Usman, B.B and Muhammad, A. B. (2017). Optimization of process variables in the Biodiesel production from *Lophira lanceolata* Seed Oil. *Nigeria Journal of Basic and Applied Science*. **25**(2): 75-86.
- Lengger, S.K., Scarlett, A.G., West, C.E., Frank, R.A., Hewitt, L.M., Milestone, C.B., Rowland, S.J. (2015). Use of the distributions of adamantane acids to profile short-term temporal and pond-scale spatial variations in the composition of oilsands process-affected waters. *Environ. Sci. Process. Impacts* **17**, 1415 -1423..
- Lochte, H.L. and Littmann, E.R. (2013). *The Petroleum Acids and Bases*. New York: Literacy licensing, LLC.
- Lo, C.C., Brownlee, B.G., Bunce, N.J. (2006). Mass spectrometric and toxicological assays of Athabasca oil sands naphthenic acids. *Water Resource*. **40**: 655- 664.
- Mediaas, H. (2008). Operational Challenges at HEIDRUN field. Calcium naphthanate deposition.in SPE Managing Napthenates and Soaps Emulsion. Pau.
- Mapolelo, M.M., Rodger, R.P., Blakney, G.T., Yen, A.T., Asmaning, A., Marshal, A.G. (2011). Characterization of naphthenic acids in crude oils and naphthenate by electrospray ionization FT – ICR mass spectrometry. *International Journal of mass spectrometry*. **300**, 149- 157
- Merlin, M., Guigard, S.E., Fedorak, P.M., (2007). Detecting naphthenic acids in waters by gas chromatography– mass spectrometry. *J. Chromatography*. **A1140**, 225–229.
- Muhammad, A.B. and Attahiru, A. (2017). Empirical Investigation of Hexadecanoic Acid from Toluene/Brine System; Implication to Acid Precipitation from Crude Oils. *Journal of Dispersion Science and Technology*, **38**, 545- 550
- Osuji, L.C and Anita B.S (2005). Geochemical implications of chemical fossil as oils for triterpanes. *Chem. Geol.*, **27**, 11 -28.
- Patil, P.D., Gude, V. G., Mannarswammy, A., Deng, Cooke, P., Muson-MacGee, S., Rhode, I., Lammers, P. and Nirmalakhandan, N. (2011). Optimization of Direct Conversion of Wet Algae to Biolodiesel under Supercritical Methanol Conditions. *B ioresource Technology*, **102**, 118-122.
- Priyanka Juyal, Mmiliki M. Mapolelo, Andrew Yen, Ryan P. Rodgers, and Stephan J. Allenson (2015). Identification of Calcium Naphthenate Deposition in South American Oil Fields. *Energy & Fuels* **29** (4) 2342-2350. .
- Putman J.C and Marshall A.G (2016). Screening Petroleum Crude Oils for ARN Tetraprotic Acids with Molecularly Imprinted

Polymers. Energy & Fuels. 30 (7) , 5651-5655.

Rowland S.M., Robbins W.K., Corilo Y.E., Marshall A.G. and Rodgers R.P. (2014). Solid-Phase Extraction Fractionation To Extend the Characterization of Naphthenic Acids in Crude Oil by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Energy and Fuels 28 (8) 5043-5048. .

Scott, A.C., Young, R.F., Fedorak, F.M. (2008). Comparison of GC-MS and FTIR for quantifying naphthenic acids in water sample. *Journal of Chemosphere* 73: 1258-1264.

Simon, S., Noidgard, E., Bruheim, P., Sjoblom, J. (2008). Determination of C8 tetra – acid content in calcium naphthenate deposit. *Journal of chromatography A*.

Torleif, H., Leif, O. J., and Kristian, S. (2013). Calcium Naphthenate Propagation during Flow in a Porous Medium. *Journal of Energy & Fuels*. 27 (11) 6440-6446.

Udeme, J.D., Etim, I.U. (2012). Physicochemical Studies of Nigeria's Crude Oil Blends, *Petroleum & Coal* 54 (3): 243-251.

Victor, A. A., Sunday, C. A., Eton, U.P., Duru , N., Adeyemi, A.(2015). Characterization of Nigerian Crude Oil Using ASTM86 TestMethod For Design Of MiniRefinery. *International Journal of ScientificResearch and EngineeringStudies* 2: 2349-8862.

Virmani, Y.P.(2013). The United States Cost of Corrosion Study. *NACE International*. Available at: <http://www.nace.org/Publications/Cost-of-Corrosion-Study/> [Accessed May 6, 2014].