

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# Recent Techniques for the Removal of Naphthenic Acid from Heavy Crude Oils

*Feyisayo Victoria Adams, Chikaodili E. Chukwuneke  
and Bolade O. Agboola*

## Abstract

Naphthenic acid (NA) is one of the components of heavy crude oil. It is composed of a carboxylic acid functional group attached to a hydrocarbon molecule. Heavy crude oils with high concentration of NA are usually classified as poor quality oil and are sold at cheaper price. The presence of high concentration of naphthenic acid in crude oil often result in limited life span of equipment used in exploration and refining processes due to corrosion. In order to improve the quality of such crude oil and to save cost, it becomes very important to remove NA compounds from it. Researchers, as well as the oil and gas industries, have been working on how to overcome this challenge, and several techniques have been developed for the removal of naphthenic acid from the crude oil. This study thus envisages to present the various recent techniques available for the removal of NA from heavy crude oil. It has been seen that of all the recent physical and chemical methods that are available, catalytic-based methods are effective and their effectiveness depend on the temperature at which the catalyst is calcined as well as the surface area of the catalyst.

**Keywords:** catalysts, extraction, heavy crude oil, naphthenic acids, petroleum refining

## 1. Introduction

Naphthenic acid (NA), which is a mixture of alicyclic carboxylic acid and saturated aliphatic acid, is a component of a heavy crude oil and it is responsible for the heavy crude oil's acidity [1]. The presence of NA in heavy crude oil poses great challenge in the exploration of the crude oil; this is due to the corrosiveness of the acid. The removal of NA compounds from crude oil is known as the most important process in upgrading heavy oil. Caustic washing and blending of heavy acidic crude oil with conventional crude oil are two conventional methods used in the removal of NAs from heavy crude oil. The disadvantage of blending method is in its low efficiency with removal of about 2–3% [2] and the NAs are often not completely removed from the blend as a result, it is often used as a corrosion mitigation tool. Meanwhile, the limitation of caustic washing method is in the large amount of wastewater which is usually produced during the process [2].

Several deacidification removal techniques have been reported in the literature. These include catalytic destructive methods, non-catalytic destructive methods, and non-catalytic non-destructive methods [3, 4]. Thermal decomposition, which is an example of non-catalytic destructive methods, has shown to be ineffective in the reduction of acidity in heavy crude oil [5]. High temperature, which is higher than 400°C, is often used. This offers thermal cracking of the heavy crude oil, which then resulted in coke formation [1]. Catalytic decarboxylation process [6] has been used as an alternative to the non-catalytic destructive methods for naphthenic acids (NAs) removal from heavy crude oil. Polymeric compounds exhibiting basicity characteristics, on the other hand, can be used to neutralize NAs. Although, expensive neutralizing agents, which are difficult to recover from deacidified products, are needed in this method.

Extractive separation is another method used in the removal of NAs from heavy crude oils. Using this method, valuable hydrocarbons are usually removed and this makes the process expensive. Extractive separation method requires multistage wash using different types of solvents. A single NA compound or their derivatives such as salt and water-oil emulsion can also be used [3]. It has been reported that solutions of metal oxides, such as those of aluminum and magnesium, exhibit high adsorption capacity and are able to remove more than 95% of the NAs present in a liquid hydrocarbon feedstock at temperatures between 30 and 80°C [4, 7].

Adsorption process of NA removal from heavy crude oil can be used under low temperature condition for distillate fractions. Strong bases, such as alkali metal hydroxides (MOH), are often used as pre-treatment of the heavy oil prior to the adsorption process. The MOH, however, does not only provide an alkaline environment, but it neutralizes the acidic components of NAs in the heavy crude oil. The major challenge associated with this technique is its environmental challenge as disposal of MOHs into the environment creates nuisance to the environment [7].

Esterification process has been used to remove NAs from heavy crude oils. The NAs reacts with alcohol with or without the addition of a catalyst to form ester [8]. Oxides and carboxylates of metals have been successfully applied in NAs removal from heavy crude oils [9–11] using the esterification method at reaction temperatures between 250 and 350°C [12].

Organic bases such as monoethanolamine, 2-(Dibutylamino) ethanol [13], glycolic solutions [11], or imidazole derivatives [14] as alcoholic solutions have been used as alternative method to dilute caustic wash in the NAs removal from heavy crude oil. However, the amount of organic bases needed for a successful extraction is usually in excess. This results in amine been left in the petroleum phase, thus creating problems in the downstream catalyst units which is used for oil upgrading. On the other hand, lysine-derived amino acid ionic liquids (AAILs) have shown better extraction efficiency compared to other AAILs, because lysine-derived AAILs contain two amino groups which can react with carboxylic acid group to form zwitterionic species [3].

Zeolites [3] and metal oxides [15] have been successfully applied in NAs removal from heavy crude oil. The limitations associated with this process, however, are the moderately high operating temperatures of 300–400°C and the use of hydrogen [5] to increase deacidification rate, because hydrogen is often not available for the process. The use of caustic soda (NaOH) is a known industrial method for the removal of NAs from the kerosene/diesel fractions. The NAs are usually separated from the oil fraction as sodium naphthenates and is dissolved in water to form soluble fraction. Thereafter, acidifying sodium naphthenates with a mineral acid, will result in the recovery of water insoluble NAs [3]. However, due to poor solubility of NAs, their removal becomes incomplete [3].

Reactive extraction method has gained wide interest in the removal of NAs from oil. This came in response to the extreme economic pressure NAs removal poses on industries. Due to the decrease in efficiency and limitations of well-known processes and the demand for inexpensive and environmentally safe and high purity products, it is imperative to consider new processes. Thus, this work is aimed at compiling recent techniques used in the removal of NAs from heavy crude oil. These techniques include the physical and chemical methods which are reactive extraction and adsorption of naphthenic acids (physical methods) and esterification of naphthenic acids, decarboxylation of naphthenic acids, and supercritical fluids (SCF) (chemical methods).

## 2. Physical methods

### 2.1 Reactive extraction of naphthenic acids

Reactive extraction is a separation process in which reactions between materials to be extracted and the extractants take place. This extraction process depends on degree of extraction and different parameters such as the loading ratio, complexation equilibrium constant, distribution coefficient, type of complexes, etc. The distribution coefficient and the degree of extraction are used to analyze the extraction process. Equation (1) is used in the calculation of the distribution coefficient,  $K_d$  [16].

$$K_d = \frac{C_{org}}{C_{aqu}} \quad (1)$$

where,  $C_{org}$  and  $C_{aqu}$  are the total concentration of carboxylic acid in organic phase and the total acid concentration (dissociated and un-dissociated) aqueous phase at equilibrium, respectively.

The degree of extraction is given as the ratio of acid concentration in the extracted phase to the initial acid concentration in aqueous solutions at equilibrium as shown in Eq. (2) [16].

$$E = \frac{K_d}{(1 + K_d)} \times 100 \quad (2)$$

Kumar et al. [16] determined equilibrium complexation constant, extraction mechanism, degree of extraction, and the distribution coefficients using varied concentration of extractant (hydroxides). In this process, NA was dissolved in 0.125–0.650 mol/L of kerosene at temperature range of 301–333 K and atmospheric pressure. The distribution coefficient ( $K_d$ ) of NA was found to be about—19.84 with degree of extraction of 56.48–95.16% at various temperature and concentration ranges. The highest degree of extraction (95.2%) was obtained at a concentration of 0.125 mol/L and at room temperature, while it decreased with increase in concentration. Meanwhile, the degree of extraction decreased as the temperature reached 60°C (333 K). It was observed that the degree of extraction increased with increase in the pH of the extractant [16].

Liquid-liquid extraction (LLE) has been found to be effective in the removal of NAs from heavy crude oils. However, the effectiveness of this process depends on the extractant and the experimental conditions such as temperature, contact time, and concentration. The use of ammonia or alcoholic alkaline solutions (such as potassium hydroxide (KOH) in alcohol) in the removal of NAs using LLE method is common and is effective. However, these extractants usually

form stable emulsions [17]. Due to this limitation, other extractants have been proposed by several researchers [9, 18]. Liquid alkanols, ammonia in varied ratio with water are examples of the proposed extractants. Pre-treatment of heavy crude oil before extraction using alkoxyated amine and water has also showed better results in the removal of NAs [19]. Also, a mixture of NaOH and ethanol with heavy crude oil with the reagent/oil ratio being 0.4:1 (w/w) at room temperature showed an optimal amount of NaOH in crude oil after extraction to be 3000  $\mu\text{g/g}$  under 5 min of extraction [14]. Liquid-liquid extraction (LLE) data were obtained for a ternary system of dodecane, naphthenic acid, and [DBU-Hex] [SCN] under atmospheric condition [20]. The solubility of NA was found to be higher in [DBU-Hex] [SCN] when compared to dodecane. Thus, [DBU-Hex] [SCN] was concluded to be better extractant for the removal of NA from heavy crude oil than dodecane.

Ionic liquids (ILs) have been considered as green solvents for extraction processes due to their unique properties [21, 22]. The physiochemical properties of ILs depend on the cations and anions of various ILs. The symmetry of the shape or/and alkyl chain in the cation could have effects on the viscosity, density, and surface tension of ILs, meanwhile ILs miscibility and their thermal stability could be affected by the anion [23]. The wide range of temperature for liquid phase and extremely low vapor pressure of ILs give them advantage over other solvents whether polar or non-polar organic solvents. Report has, however, showed that some ILs need large amount for effective extraction process for the removal of NAs. Also, the regeneration procedure for NA and ILs has been found to be complex [24, 25]. Low ILs/oil ratios of tetra-alkylphosphonium and tetra-alkylammonium hydroxide ILs were used in the removal of NA from a model acidic oil [26]. The results from the experiment showed tetra-alkylammonium-based ILs to be more efficient than tetra-alkylphosphonium-based ILs. It was observed that the longer the alkyl spacer length on the cation, the lower the extraction performance of the hydroxide-based ILs. The ILs used in the model acidic oil study showed a great reusability potential without losing its activity [26].

Neutralization method was used to remove NA from Doba crude oil using ILs ([N<sub>2221</sub>][MeCO<sub>3</sub>] Triethylmethylammonium methylcarbonate) at an optimum temperature of 338 K and a removal efficiency of 73.1% was achieved [12]. Under the same condition, an efficiency of 80.4 and 69.6% was achieved using [N<sub>2221</sub>] [HCO<sub>3</sub>] Triethylmethylammonium hydrogencarbonate and [N<sub>4441</sub>][MeCO<sub>3</sub>] Tributylmethylammonium methylcarbonate, respectively [12].

Crude oil containing dodecane and NA (TAN =  $1.44 \pm 0.01 \text{ mg KOH g}^{-1}$ ) was treated for NA removal using extraction method and 1-Decyl-3-ethylimidazolium phenolate.[C<sub>10mim</sub>][Phe] as extractant [27]. The optimum temperature, at which an efficiency removal of about 85.7% was achieved, was 320 K. On the other hand, when a crude oil having dodecane and NA (TAN =  $4.74 \pm 0.01 \text{ mg KOH g}^{-1}$ ) was treated, an efficiency of 83% was achieved at a temperature of 323.15 K [26]. Neutralization method was used in this case and Tetra methyl ammonium hydroxide, [N<sub>1111</sub>][OH] was used as the solvent. At a temperature of 323 K, a removal efficiency of 25% was obtained using extraction method with 1-ethyl-3-methylimidazolium ethyl sulfate [EMIM][EtSO<sub>4</sub>] as extractant [28].

Adsorption process was used for the removal of NA from crude oil containing white oil and NA (TAN =  $1.20 \text{ mg KOH g}^{-1}$ ) [29], dodecane and NA (TAN =  $3.46 \pm 0.01 \text{ mg KOH g}^{-1}$ ) [24] and dodecane and NA (TAN =  $2.93 \pm 0.01 \text{ mg KOH g}^{-1}$ ) [21] at temperatures of 313 K, 360.15 K and room temperature, respectively. A removal efficiency of 97.61, ~71.5, and 100% was achieved in the process using 1-methylimidazole acetate [Bmim][CH<sub>3</sub>COO] [29],

1-decyl-1,8-diazobicycloundec-7-enethiocyanate [DBU-Dec] [SCN] [24], and Butyl methyl imidazolium functionalized silica SilPrBmim [21] as ILs, respectively.

## 2.2 Adsorption of naphthenic acids

Adsorption process has recently been used for the removal of NAs from heavy crude oils. Example of these is the removal of NAs from Sudanese crude oil using zeolite and clay [30]. A study by Zhang et al. [31] showed that the use of a naturally occurring clay gave adsorption capacity for NAs as high as about 70 mg-NA/g clay. Though this process is effective and efficient, its limitation is in the disposal of the used clay.

Lately, nanotechnology has been brought to light as the latest technique that can be applied in reducing TAN present in solutions. Simonsen [32] synthesized amino-functionalized iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles which has a high selectivity for NA. Harnessing the magnetic properties of the nanoparticles, a magnetic field is applied to the mixture for the sequestration of the NA. Among the nanoparticles synthesized:  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ,  $\text{Fe}_3\text{O}_4/\text{SiO}_2 \text{NH}_2/\text{C}_{18}$ , the amino-functionalized type showed a high affinity for NA and spectra from FTIR and UV-Visible Spectrophotometer confirmed that no other crude oil components were eliminated. This study achieved a remarkable feat of attaining a TAN reduction of 92% with this novelty.

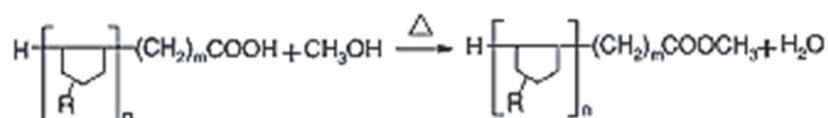
## 3. Chemical methods

### 3.1 Esterification of naphthenic acids

Esters are a byproduct of reacting  $\text{—COOH}$  with  $\text{—OH}$  and this reaction is useful for NAs removal from solutions, since the major functional group for organic acids are carboxyl groups. The general form of an esterification reaction of NA takes the form below (**Figure 1**).

In the absence of any catalyst, Khan et al. [2] optimized the removal of NA from heavy acid crude oil by varying the pressure, reaction time, crude concentration, and temperature. A mixture of HAC Laguna and Kuwait Crude with TAN value of 2.57 mg KOH/g was esterified with methanol in a batch reactor and under the enhanced conditions of 250°C, 6.4 MPa, and 33.3 wt% to yield low TAN crude of 0.08 mg KOH/g (96.9% removal).

Another example of this application is observed in the esterification of Colombian crude by Quiroga-Becerra et al. [34]. Temperature was varied to see its effect on shrinking the TAN content and also FTIR analysis was done on products at each temperature profile. At 250°C, the outcome of the study was impressive as the TAN value fell from 7.33 to 0.47 mg KOH/g. FTIR data also support the post reaction TAN results, as a shrinking in the carboxyl group wave number between 1705 and 1710  $\text{cm}^{-1}$  was observed. In addition, as a corollary to the esterification, a shift in the carbonyl group band to wave numbers 1730–1740  $\text{cm}^{-1}$ , indicated a reduction in acidity.



**Figure 1.**  
Esterification reaction of NA [33].



applications. In a study in which  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported 12-tungstophosphoric acid (TPA) catalyst was used in a fixed bed continuous flow reactor, factors such as increased methanol/crude oil ratio, temperature, and decreased liquid hourly space velocity (LHSV) downregulated the TAN value. Compared to other catalysts such as SnO/Al<sub>2</sub>O<sub>3</sub> [38] and Mg-Al Hydrotalcite [39], TPA/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has proven to enhance the transesterification of NAs at lesser temperature (250°C). The TPA/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst also decreased the Castilla crude oil TAN from 2 to <0.5 mg KOH/g with a methanol feedstock of 2 wt%. In addition, TPA/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can remain stable for up to 100 h of time-on-stream [40]. **Table 1** shows a compilation of scholarly works, where catalysts have been used for NA removal.

### 3.3 Supercritical fluids (SCF)

Improvements in chemical sciences and technology have impact in NA removal with the advent of employing SCF especially supercritical water (SCW) and supercritical methanol (SC-MeOH). The SCF by reason of definition are fluids that exist at temperatures and pressures beyond their critical points. They have been favored lately in NAs removal due to the global calls for greener processes that would mitigate environmentally toxic materials. The SC-MeOH has been reported to relieve refinery processes off the burden of corrosion issues associated with NAs in heavy crude oils. In conducted pilot experiments [45], various factors such as NA/SC-MeOH ratio, temperature, time, and pressure were studied to see their influence on TAN reduction in Laguna and Bachaquero-13 heavy crude oil. Among the process parameters studied, temperature was the key determinant on the TAN reduction as a rise from 300 to 400°C lead to a TAN decline from 56 to 96.9%. Other parameters such as pressure and NA/SC-MeOH ratio had little impact on TAN reduction. Hence, the use of the lowest test pressure of 10 MPa and highest NA/SC-MeOH ratio at 400°C. The aforementioned conditions are of a good report as it allows for the process designed to handle TAN reduction operation to be made on a low-cost budget.

Model oil	Catalyst	Reaction	Total acid conversion (%)	Reference
China crude	SnO—Al <sub>2</sub> O <sub>3</sub>	Esterification	82 (TAN before/after: 2.8/<0.5 mg KOH g <sup>-1</sup> )	[10]
Cyclo pentane carboxylic acid, cyclo hexane carboxylic acid, cyclo hexane propionic acid, and trans-4-pentyl cyclo hexane carboxylic acid dissolved in dodecane	MgO	Decarboxylation	~100	[41]
Bohai oil	NiAl-4-EG LDH	Esterification	~90	[42]
Bitumen derived heavy vacuum gas oil (HVGO)	ZnO	Decarboxylation	8.5	[43]
Heavy crude from petronas penapisan melaka	MgO	Neutralization	84.8	[44]

**Table 1.**  
 The model oil, catalyst type, reaction type, total acid conversion and the referenced work.

## 4. Conclusions

Selections of extractants and catalysts to be used for the removal of NAs from heavy crude oil whether they are to be used in the physical methods or the chemical methods are of utmost important. Calcination temperature, at which a catalyst is calcined, and the surface area of the catalyst were seen to have significant effects on its effectiveness in removing NAs from heavy crude oils. The higher the surface area of a catalyst, the more effective it is in its capacity to remove NAs from heavy crude oils. Also, catalysts, which are calcined at higher temperatures have been seen to exhibit high removal efficiency. A Cu/Ce (10:90)/Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 1000°C removed about 93% of NAs from Korean crude oil using catalytic deacidification method. Removal processes in which catalysts containing 10% Cu in them were used have been found to be effective in the removal of NAs from solutions. Metal oxides nanoparticles have also shown to be promising in the removal of NAs from solutions. Removal of NAs from acidic solutions dissolved in dodecane using decarboxylation process with calcined MgO as catalyst yielded about 100% removal of NAs from the acidic solutions. Although this was a modeled work, yet it looks promising if applied in real life system and heavy crude oils.

### Author details

Feyisayo Victoria Adams<sup>1,2\*</sup>, Chikaodili E. Chukwuneke<sup>1</sup> and Bolade O. Agboola<sup>1</sup>

<sup>1</sup> Department of Petroleum Chemistry, American University of Nigeria, Yola, Nigeria

<sup>2</sup> Faculty of Engineering and the Built Environment, Department of Metallurgy, School of Mining, Metallurgy and Chemical Engineering, University of Johannesburg, South Africa

\*Address all correspondence to: feyikayo@gmail.com

### IntechOpen

© 2019 The Author(s). Licensee IntechOpen. Distributed under the terms of the Creative Commons Attribution - NonCommercial 4.0 License (<https://creativecommons.org/licenses/by-nc/4.0/>), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited. 

## References

- [1] Mandal PC, Sasaki M. Total acid number reduction of naphthenic acids using supercritical fluid and ionic liquids. *Recent Insights in Petroleum Science and Engineering*. 2018:251-271. DOI: 10.5772/intechopen.71812. Available from: <https://www.intechopen.com/books/recent-insights-in-petroleum-science-and-engineering/total-acid-number-reduction-of-naphthenic-acids-using-supercritical-fluid-and-ionic-liquids>
- [2] Khan M, Riaz A, Yi M, Kim J. Removal of naphthenic acids from high acid crude via esterification with methanol. *Fuel Processing Technology*. 2017;**165**:123-130
- [3] Anderson K, Goodrich P, Hardacre C, Hussain A, Rooney DW. Removal of naphthenic acids from crude oil using amino acid ionic liquids. *Fuel*. 2013;**108**:715-722
- [4] Duncum S, Osborne CG. Process for deacidifying a crude oil system. US Patent 6 464,859. 2002
- [5] Blum S, Olmstead W, Bearden R. Thermal decomposition of naphthenic acids. US Patent 5 820,750. 1998
- [6] Takemura Y, Nakamura A, Taguchi H, Ouchi K. Catalytic decarboxylation of benzoic acid. *Industrial and Engineering Chemistry Product Research and Development*. 1985;**24**(2):213-215
- [7] Gillespie R, Arena BJ. Naphthenic acid removal as an adjunct to liquid hydrocarbon sweetening. US Patent 5 389,240. 1995
- [8] Yan-zhao H, Jian-hua Z, Yan-yan W, Ben-Cheng W. Removal of naphthenic acids from high acid crude oil through catalytic esterification on zinc-aluminum hydrotalcite-like compounds. *Journal of China University of Petroleum (Edition of Natural Science)*. 2010;**34**(6):147-156
- [9] Sartori G, Savage DW, Blum SC, Dalrymple DC, Wales WE. Metal compounds as accelerators for petroleum acid esterification. US Patent. 1999
- [10] Yan-zhen W, Jin-yun L, Xue-ying S, Hong-ling D, Chun-min S, Miao-miao Z. Removal of naphthenic acids from crude oils by fixed-bed catalytic esterification. *Fuel*. 2014;**116**:723-728
- [11] Wang YZ, Liu YP, Liu CG. Removal of naphthenic acids of a second vacuum fraction by catalytic esterification. *Petroleum Science and Technology*. 2008;**26**(12):1424-1432
- [12] Anderson K, Atkins MP, Goodrich P, Hardacre C, Hussain AS, Pilus R, et al. Naphthenic acid extraction and speciation from Doba crude oil using carbonate-based ionic liquids. *Fuel*. 2015;**146**:60-68
- [13] Lu R, Xu X, Yang J, Gao J. Reduction of total acid number of crude oil and distillate. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*. 2007;**29**(1):47-57
- [14] Shi LJ, Shen BX, Wang GQ. Removal of naphthenic acids from Beijiang crude oil by forming ionic liquids. *Energy & Fuels*. 2008;**22**(6):4177-4181
- [15] Zhang A, Ma Q, Wang K, Liu X, Shuler P, Tang Y. Naphthenic acid removal from crude oil through catalytic decarboxylation on magnesium oxide. *Applied Catalysis A: General*. 2006;**303**(1):103-109
- [16] Kumar RB, Shinde SN, Gaikwad SG. Reactive extraction of naphthenic acid by using sodium hydroxide as an extractant.

International Journal of Advanced Engineering Technology. 2014;5:103-106

[17] Gaikar VG, Maiti D. Adsorptive recovery of naphthenic acids using ion-exchange resins. *Reactive and Functional Polymers*. 1996;31(2):155-164

[18] Varadaraj R, Savage D, Wales WE. Removal of naphthenic acids in crude oils and distillates. US Patent 5 961,821. 1999

[19] Varadaraj R, Pugel T, Savage DW. Removal of naphthenic acids in crude oils and distillates. US Patent 6 096,196. 2000

[20] Najmuddin R, Mutalib M, Shah S, Suleman H, Lethesh K, Pilus R, et al. Liquid-liquid extraction of naphthenic acid using thiocyanate based ionic liquids. *Procedia Engineering*. 2016;148:662-670

[21] Shah SN, Pranesh M, Raj JJ, AbdulMutalib MI, Lethesh KC, Ghanem OB, et al. De-acidification of crude oil using supported ionic liquids phases. *Separation and Purification Technology*. 2018;196:96-105

[22] Ravilla UK, Banerjee T. Liquid-liquid equilibria of imidazolium based ionic liquid+ pyridine+ hydrocarbon at 298.15 K: Experiments and correlations. *Fluid Phase Equilibria*. 2012;324:17-27

[23] MacFarlane DR, Tachikawa N, Forsyth M, Pringle JM, Howlett PC, Elliott GD, Davis Jr. J.H, Watanabe M, Simon P, Angell C A. Energy applications of ionic liquids. *Energy & Environmental Science* 2014;7(1):232-250

[24] Shah SN, Ismail M, Ibrahim M, Mutalib A, Pilus RBM, Lethesh KC. Extraction and recovery of toxic acidic components from highly acidic oil using ionic liquids. *Fuel*. 2016;181:579-586

[25] Shah S, Lethesh KC, Mutalib MIA, Pilus RBM. Extraction and recovery of naphthenic acid from acidic oil using supported ionic liquid phases (SILPs). *Chemical Product and Process Modeling*. 2015;10(4):221-228

[26] Shah SN, Mutalib MIA, Pilus RBM, Lethesh KC. Extraction of naphthenic acid from highly acidic oil using hydroxide-based ionic liquids. *Energy & Fuels*. 2015;29(1):106-111

[27] Shah SN, Lethesh KC, Gonfa G, Ibrahim M, Mutalib A, Pilus RBM, et al. Extraction of naphthenic acid from highly acidic oil using phenolate based ionic liquids. *Chemical Engineering Journal*. 2016;284:487-493

[28] Coto B, Suárez I, Chirita M, Conde J, Giménez R, Rodríguez N, et al. Oil acidity reduction by extraction with [EMIM][EtSO<sub>4</sub>]: Experimental and model description. *Separation and Purification Technology*. 2019;223:234-242

[29] Shao X, Liu G, Yang J, Xu X. Research on the synthesis of ionic liquids/layered double hydroxides intercalation composites and their application on removal of naphthenic acid from oil research on the synthesis of ionic liquids/layered double hydroxides intercalation composites and their application on the removal of naphthenic acid from oil. *Energy & Fuels*. 2017;31(10):10718-10726

[30] Osman WSI, Dafaalla AA. Reduction total acid number (TAN) of some Sudanese crude oil by zeolite and clays. *International Journal of Chemical and Petroleum Sciences (IJCPS)*. 2015;1(1):8-16

[31] Zhang A, Ma Q, Tang Y. Catalytic decarboxylation for naphthenic acid removal from crude oils: A theoretical and experimental study. In: *Proceedings of the 227th ACS National Meeting*; March 28–April 1 2004; Anaheim, CA. 2004. PETR 98

- [32] Simonsen G, Strand M, Norrman J, Øye G. Amino-functionalized iron oxide nanoparticles designed for adsorption of naphthenic acids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2019;**568**:147-156
- [33] Wang Y, Liu Y, Liu C. Kinetics of the esterification of low-concentration naphthenic acids and methanol in oils with or without SnO as a catalyst. *Energy & Fuels*. 2008;**22**(4):2203-2206
- [34] Quiroga-Becerra H, Mejía-Miranda C, Laverde-Cataño D, Hernández-López M, Gómez-Sánchez M. A kinetic study of esterification of naphthenic acids from a Colombian heavy crude oil. *CT&F-Ciencia, Tecnología y Futuro*. 2012;**4**(5):21-31
- [35] Shohaimi NA, Azelee W, Bakar WA, Shukri NM, Shaidi AK. Extraction of naphthenic acids from acidic petroleum crude oil utilizing 2- methylimidazole with the aid of Ca/Al<sub>2</sub>O<sub>3</sub> AND Ce/Al<sub>2</sub>O<sub>3</sub> catalysts. e—Academia Special Issue TeMIC. 2019;**7**:47-57
- [36] Shohaimi NAM, Jaafar J, Bakar WAWAA. Chemical technique for the treatment of naphthenic acid in various crude oils. In: *Proceedings of the 24th Regional Symposium of Malaysia Analytical Sciences (SKAM 24)*; 21-23 November 2011; Langkawi, Kedah, Malaysia. p. 11
- [37] Shukri N, Bakar W, Jaafar J, Majid ZM. Removal of naphthenic acids from high acidity Korean crude oil utilizing catalytic deacidification method. *Journal of Industrial and Engineering Chemistry*. 2015;**28**:110-116
- [38] Wang YZ, Sun XY, Liu YP, Liu CG. Removal of naphthenic acids from a diesel fuel by esterification. *Energy & Fuels*. 2007;**21**(2):941-943
- [39] Li X, Zhu J, Liu Q, Bencheng W. The removal of naphthenic acids from dewaxed VGO via esterification catalyzed by Mg–Al hydrotalcite. *Fuel Processing Technology*. 2013;**111**:68-77
- [40] Rana B, Cho D, Cho K, Kim J-N. Total acid number (TAN) reduction of high acidic crude oil by catalytic esterification of naphthenic acids in fixed-bed continuous flow reactor. *Fuel*. 2018;**231**:271-280
- [41] Oh H, Park J, Rhee Y, Kim J. Decarboxylation of naphthenic acid using alkaline earth metal oxide. *Journal of Industrial and Engineering Chemistry*. 2011;**17**(4):788-793
- [42] Wang H, Liu X, Wu Y, Hou C, Qiu Y, Guo K. Microwave-assisted synthesis of ethylene glycol-intercalated NiAl LDHs and their application for intracrystalline catalytic esterification with naphthenic acids in crude oil. *Energy & Fuels*. 2017;**31**(9):9898-9904
- [43] Ding L, Rahimi P, Hawkins R, Bhatt S, Shi Y. General naphthenic acid removal from heavy oils on alkaline earth-metal oxides and ZnO catalysts. *Applied Catalysis A*. 2009;**371**:121-130
- [44] Akmar N, Shohaimi M, Azelee W, Abu W, Jaafar J, Shukri NM. Treatment of acidic petroleum crude oil utilizing catalytic neutralization technique of magnesium oxide catalyst. *Modern Chemistry & Applications*. 2013;**1**(3):1-5
- [45] Khan MK, Insyani R, Lee J, Yi M, Lee JW, Kim J. Non-catalytic, supercritical methanol route for effective de-acidification of naphthenic acids. *Fuel*. 2016;**182**:650-659