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

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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 ([N₂₂₂₁][MeCO₃] 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 [N₂₂₂₁][HCO₃] Triethylmethylammonium hydrogencarbonate and [N₄₄₄₁][MeCO₃] Tributylmethylammonium methylcarbonate, respectively [12].

Crude oil containing dodecane and NA ($\text{TAN} = 1.44 \pm 0.01 \text{ mg KOH g}^{-1}$) was treated for NA removal using extraction method and 1-Decyl-3-ethylimidazolium phenolate.[C10mim][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 ($\text{TAN} = 4.74 \pm 0.01 \text{ mg KOH g}^{-1}$) 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, [N₁₁₁₁][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][EtSO₄] as extractant [28].

Adsorption process was used for the removal of NA from crude oil containing white oil and NA ($\text{TAN} = 1.20 \text{ mg KOH g}^{-1}$) [29], dodecane and NA ($\text{TAN} = 3.46 \pm 0.01 \text{ mg KOH g}^{-1}$) [24] and dodecane and NA ($\text{TAN} = 2.93 \pm 0.01 \text{ mg KOH g}^{-1}$) [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][CH₃COO] [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 (Fe_3O_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: Fe_3O_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 —COOH with —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 cm^{-1} was observed. In addition, as a corollary to the esterification, a shift in the carbonyl group band to wave numbers 1730–1740 cm^{-1} , indicated a reduction in acidity.

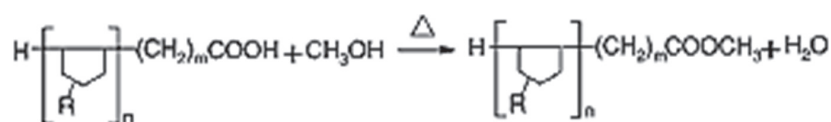


Figure 1.
 Esterification reaction of NA [33].

3.2 Decarboxylation of naphthenic acids

In catalytic decarboxylation, commercially available chemicals or self-prepared materials are usually used as catalysts to determine their suitability and effectiveness in removing NAs from heavy crude oils with model compound before using them in a real situation [31]. Metal oxide catalysts have been found to be very effective in NAs catalytic decarboxylation. The beauty of catalysis lies in its ubiquitous application as it cuts across many chemical methods of NA removal. Every chemical reaction can be encouraged to favor NA removal by the use of active catalyst that provides an alternative pathway that ensures the lowering of the activation energy for the reaction to occur (**Figure 2**).

A study carried out by Shohaimi et al. [35] has shown the use of monometallic alkaline earth metal oxides ($\text{Ca}/\text{Al}_2\text{O}_3$ and $\text{Ce}/\text{Al}_2\text{O}_3$) as catalysts for the removal of NAs from acidic Petronas Penapisan Melaka refinery heavy crude oil with TAN of 2.43 mg KOH/g to be successful. It was observed that the $\text{Ca}/\text{Al}_2\text{O}_3$ catalyst was more effective (83.5%) in removing the NAs from crude oil compared to $\text{Ce}/\text{Al}_2\text{O}_3$ catalyst (71.2%). In another study, other types of catalysts ($\text{Ni}/\text{Ca}/\text{Al}_2\text{O}_3$, $\text{Ni}/\text{Ba}/\text{Al}_2\text{O}_3$, $\text{Cu}/\text{Ca}/\text{Al}_2\text{O}_3$, and $\text{Cu}/\text{Ba}/\text{Al}_2\text{O}_3$) were studied in TANX 2000 (concentration range of 10–50 mg/L) and ammonia solution in ethylene glycol with a concentration range of 100–1000 mg/L to remove NAs from Petronas Penapisan Melaka refinery Heavy Crude (TAN of 2.43 mg KOH/g), Petronas Penapisan Melaka refinery Light Crude (TAN of 2.52 mg KOH/g) and Korean Crude oils. The highest concentrations of TANX 2000 solution and ammonium solution in ethylene glycol exhibited the best experimental conditions. The catalyst ($\text{Cu}/\text{Ca}(10:90)/\text{Al}_2\text{O}_3$) with calcination temperature of 1000°C gave the most effective results for all the three types of crude oil. With the use of catalysts, there was improvement in the removal of NAs from all the three crude oils that were studied [36].

With the goal of removing NAs at low temperatures and on an economy budget, rare earth metals known to possess great catalytic potential were explored by Shukri et al. [37]. These researchers tested the use of alumina supported CeO -, ZnO -, and SnO -based catalyst coupled with Cu, Co, Mn, and Ni as dopants to deacidify Korean crude oil. Results showed that the calcination temperature, base catalyst type with large surface area, and the base chemical agent do play a role in optimizing the reduction of NA in Korean crude. The results proved CeO to be the best catalyst and Cu ($\text{Cu}/\text{Ce}(10:90)/\text{Al}_2\text{O}_3$) as the most effective dopant, with an optimum deacidification achieved when the aforementioned was calcined at a temperature of 1000°C. A concentration of 1000 mg/L for 4% NH_3 -PEG gave the best acidity cutback for the basic chemical agent used, but it was only able to cut down the TAN from 8.32 to 3.65 mg KOH/g using the Ce oxide-based catalyst. However, after it was augmented with 1% of 10 M KOH, the TAN was reduced to 0.56 mg KOH/g thereby meeting acceptable industrial standards of crude oil acidity [37].

The limitations involved in extant NA removal techniques such as emulsion formations via neutralization, high cost from physical adsorption processes, and cost of hydrogen from catalytic hydrogenation have hampered their industrial

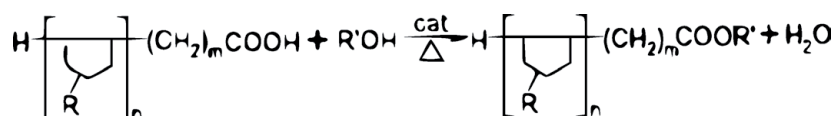


Figure 2.

A catalytic reaction for the removal of NA [10].

applications. In a study in which γ -Al₂O₃ 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/Al₂O₃ [38] and Mg-Al Hydrotalcite [39], TPA/ γ -Al₂O₃ has proven to enhance the transesterification of NAs at lesser temperature (250°C). The TPA/ γ -Al₂O₃ 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/ γ -Al₂O₃ 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 ₂ O ₃	Esterification	82 (TAN before/after: 2.8/<0.5 mg KOH g ⁻¹)	[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)/Al₂O₃ 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.

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