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Total Acid Number Reduction of Naphthenic Acids Using Supercritical Fluid and Ionic Liquids

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Abstract

Naphthenic acids (NAs) are complex mixture of predominately alkyl-substituted cycloaliphatic carboxylic acids and small amount of acyclic acids present in crude oil, heavy oil and in oil sands bitumen. They are toxic components in refinery wastewater and in oil sand extraction water and lead to corrosion problems within the oil refineries. Therefore, the amount of NAs needs to suppress in petroleum oils and wastewater came from petroleum industry. This paper reviews the supercritical fluids (SCFs)- and ionic liquids (ILs)-based acidity reduction process from heavy oils by reviewing open literature. The potential benefits of SCFs- and ILs-based acidity reduction process of heavy oils are also explored. The reviewed articles reveal that total acid number (TAN) removal increase with increasing reaction time and temperature by the action of SCF. Supercritical methanol (SC-MeOH) has higher potentiality for removing acidity of NAs than supercritical water (SCW) without deposition of coke. TAN removal from NAs using SCF follows first order kinetics on TAN removal. ILs can reduce acidity of heavy oil either forming zwitterionic species or building cage structure around NAs through specific chemical bonds. Thus, non-catalytic SCF- and ILs-based TAN reduction process can open a new window to reduce acidity of heavy oils.

Keywords: supercritical fluid, naphthenic acid, total acid number, ionic liquid

1. Introduction

Heavy oil is a type of unconventional oil deposit (global estimated reserve of heavy oil and bitumen is 6.2 trillion barrels) all over the world. Such type of oil reservoirs are vastly undeveloped due to the difficulties of production, transportation and refining efficiently and inexpensively. Heavy oils contain significant quantity of metals, sulfur and nitrogen heteroatom-containing compounds and naphthenic acids (NAs) as contaminants. NAs are a mixture

of saturated aliphatic and alicyclic carboxylic acids. They are accountable for acidity of crude oils or heavy oils. NA content of heavy oil can be figured out in terms of total acid number (TAN), mg of KOH per g of oil. Crudes containing high TAN, specifically $\text{TAN} \geq 2$, have lower demand [1, 2]. Moreover, their existence in crude oil creates multiple problems: they are corrosive [3–6] in nature, lessen quality of product and make environmental disposal problems [7–9]. Therefore, their removal from heavy oils is considered as a pressing issue for petroleum industries.

A number of deacidification processes have been disclosed in open literature to deacidify acidic petroleum oil, such as non-catalytic non-destructive methods, non-catalytic destructive methods and catalytic destructive methods.

High TAN containing crudes are usually mixed off with low TAN containing crudes to eliminate excessive corrosion in refinery equipment. This process is obviously expensive and non-selective [7]. In a different way, polymeric compounds including adequate basicity may be used to entrap or neutralize NAs. This process, however, involves the use of costly neutralizing agents, which are difficult to recover from deacidified products. Another method, extractive separation, usually requires a multistage wash using various solvent to single NA compounds or their derivatives such as water-oil emulsion and salt [10–12]. But valuable hydrocarbon compounds are removed to do so making the process costly.

The metal oxide (such as magnesium oxide and aluminum oxide) solid solutions show high adsorption capacity and can readily remove at least 95% of the NAs present in a liquid hydrocarbon feedstock at temperatures of 30–80°C [12, 13]. Recent adsorption technology is only attainable for low temperature distillate fractions. The prior process requires a highly alkaline environment, a strong base such as alkali metal hydroxides (for example, caustic soda). Unfortunately, the caustic does not simply provide an alkaline environment but in time is neutralized by acidic components of the hydrocarbon stream. Therefore, this process requires its continuous replacement and replenishment. It is alarming that disposal of spent caustic solutions is itself an environmental problem [13].

Corrosion inhibitors such as organic poly sulfide or phosphites or phosphoric acid have been introduced to passivate metal surfaces by building a defensive layer on them. But, this process requires maintaining adequate thickness of the protective layer that enforces the costs of multiple inhibitor injections.

Esterification is a well-known process for removing NA compounds from petroleum oils. In this process, NAs reacts with alcohol in the presence or absence of catalyst to form ester [14]. Metal carboxylates [15] and metal oxides [16] are fruitfully applied in esterification at reaction temperatures of 250–350°C over enhanced reaction times [12].

Non-catalytic NA destruction methods, such as thermal decomposition [7, 17], have a limited success for acidity reduction of crude oil. High temperature, in excess of 400°C, is mostly required which can offer thermal cracking of the crude resulting coke formation [2]. In this regard, catalytic decarboxylation process [18] has come out as an alternative and economic process of NAs decomposition.

The success of zeolites [12] and metal oxides [19] for deacidification of crude oil is high. But the process still requires moderately high operating temperatures (300–400°C). Moreover, many of these applications require hydrogen [7] to increase deacidification rate. But, hydrogen is not usually available at a production site. Hydrotreating in the presence of alumina supported metal oxides such as cobalt, molybdenum or nickel oxides has been successfully used in this regard [20, 21]. Metal oxides saturated with copper [22] and nickels [23] in the liquid phase at moderate temperatures (greater than 200°C) have also been utilized for the decarboxylation of fatty acids. Catalytic process, however, would be less feasible in crude oil systems due to catalyst poisoning by aromatics compounds, nitrogen containing species, metals and sulfur containing species of crude oil.

Supported palladium and platinum catalysts are active to destruct NAs via decarboxylation [24] and decarbonylation [25] in the liquid or gas phase. It is seen that transition metals supported catalysts can efficiently decarboxylate a series of fatty acids at temperatures of 80–100°C even without hydrogen [26]. In addition, the same titania-based metal catalysts can resist sulfur significantly for fine chemical synthesis [27]. Though their activity and chemical stability is high, platinum group metal-based catalysts are cost-effective process for large scale operation.

A common industrial method of NAs removal from the kerosene/diesel fractions is a dilute caustic wash of them using alkali/alkaline earth metals. In this process, NAs is separated from oil fraction as calcium or sodium naphthenates, which is dissolved in water soluble fraction. Then, it is possible to recover the water insoluble NAs by acidifying calcium or sodium naphthenates with a mineral acid [12]. This process is an uneconomical one; as it is considered inexpensive, incomplete removal of all NAs due to its poor solubility coupled with the formation of emulsion [12]. Treating of petroleum products for removing of NAs via a dilute caustic wash is a common industrial method. As an alternative of this process, the researchers are using organic bases such as glycolic solutions [28], monoethanolamine or 2-(Dibutylamino) ethanol [29] or imidazole derivatives [30] as alcoholic solutions. However, excess amount of organic base is required to reach good extraction process. This large excess of base resulted in carryover of amine into the petroleum phase and can create problem in the downstream catalyst units used for upgrading the oil [31].

Recently, specific ionic liquids (ILs) have been used in different applications including acidity removal from petroleum industry. For example, sulfur-containing acids are successfully extracted from crude oil using ILs containing a cation with a connected amino group [32]. In addition, amino acid ionic liquids (AAILs) can neutralize NAs by the reaction where one amino group of the amino acid-anion can react with one carboxylic acid group to form zwitterionic species. In this regard, lysine-derived AAILs indicated higher extraction capability compared to other AAILs because AAILs derived from lysine contain two amino groups [12]. Mandal et al. [2, 33] have disclosed a new supercritical fluid-based deacidification process at high temperatures and pressures.

This review paper examines the open literatures of petroleum oil deacidification process using environmental benign solvent, supercritical fluids and ionic liquids.

2. Naphthenic acid

NAs are complex mixtures of alkyl-substituted acyclic and cycloaliphatic carboxylic acids found in hydrocarbon deposits (petroleum, oil sands bitumen and crude oils) [34–36]. They are originally come from aerobic microbial degradation of petroleum hydrocarbon [34]. They are described by the general chemical formula $C_nH_{2n+z}O_2$, where n indicates the number of carbon and z is either zero or a negative, even integer that secludes lack of hydrogen resulting from ring formation. The numbers of ring present in the compounds are obtained by dividing the absolute value of z by 2. The rings of NAs can be fused or bridged. **Figure 1** depicts examples of typical structures of NAs, which have a different number of rings [36].

NAs are non-volatile, chemically stable and perform as surfactants. The polarity and non-volatility of NAs increase with increasing molecular weight delivering specific compounds with different physical, chemical, and toxicological properties [34, 36–39]. NAs act as typical carboxylic acids having acid strength analogous with the higher fatty acids. NAs are little weaker acid than low molecular weight carboxylic acids like acetic acid [36, 40–42].

Commercial NAs, produced via extraction of petroleum distillates, have industrial applications as shown in **Table 1**. Sodium salt of NAs is soluble in water.

Steel alloys that can resist corrosion by sulfur-containing compounds can be suitable for corrosion by NAs [43, 44]. The process of NAs corrosion is obscure till now though it can chelate with the metal ion by the carboxylate forming hydrogen gas [45]. The amount of NA passing

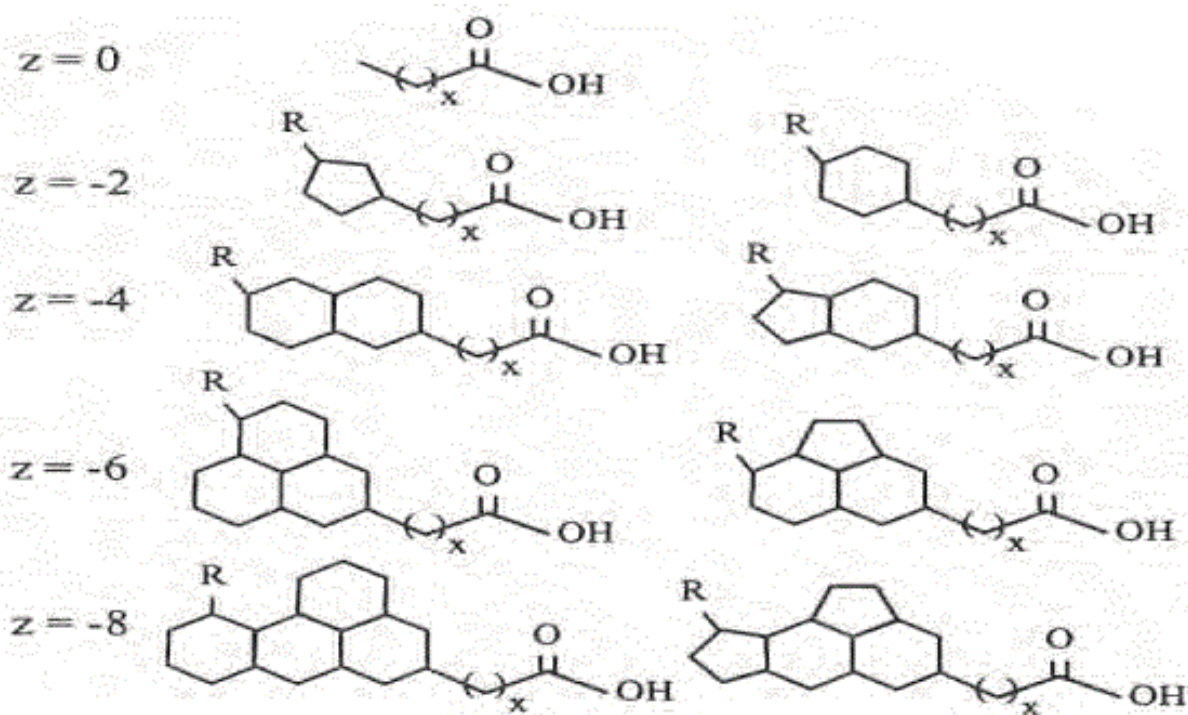


Figure 1. General structure of naphthenic acid.

NA metal salt	Industrial applications
Na salt	Emulsifying agent for agricultural insecticides Additive for cutting oils emulsion breaker in oil industry
Ca naphthenate	Additive for lubricating oil
Fe and Mn naphthenates	Fuel additives for improved combustion and reduced corrosion
Pb and Ba salts	Catalyst for oil-based paints
Cu and Zn naphthenate	Wood preservatives
Co naphthenate	Curing agent in rubbers and resins Adhesion promoter of steel cord to rubber
Mn, Pb, Co, and Ca soap	Oxidative catalysts

Table 1. Industrial usage of NAs [36].

through the system together with operating temperature of 220–400°C favor corrosion [43, 46]. NAs decompose at temperatures above 400°C creating a protective film over the alloy [43, 46]. Corrosivity increases with increasing total acid number (TAN) of crude oil. Yet, the spread of corrosion by NAs rely not only on TAN but also on the availability of the carboxylic acid group and the type of compounds [43, 44, 46].

Very few reports have been disclosed discussing NAs in refinery wastewater due to their analytical difficulties although discharged wastewater from petroleum refineries. Low molecular weight NAs (typically <500 Daltons) are readily dissolved as their carboxylates in water at neutral and alkaline pH [34]. Bitumen extraction from the Athabasca oil sands deposit in northeastern Alberta, Canada releases NAs into tailings pond water [44]. Holowenko et al. [47] discovered that tailings pond water contain 20–120 mg NAs per liter, which is sufficient to create environmental pollution. Dorn [48] concluded that NAs concentrations greater than 2.5–5 mg per liter in refinery effluent would be toxic to fish. Rogers et al. [49] supposed that the liver was the primary target of NAs toxicity. The low molecular weight NAs are more capable to biodegradation than the high molecular weight NAs [35, 44]. Scott et al. [35] disclosed that the commercial NAs are more readily biodegradable compounds than the NAs present in the oil sand tailings water.

3. History of SCF and IL

3.1. History of SCF

Baron Charles Cagniard de la Tour in 1822 revealed supercritical phenomena [50] while carrying out experiments in a sealed cannon barrel filled with various fluids at various temperatures. G. Gore in 1861 showed that camphor and naphthalene dissolved in liquid carbon dioxide, whereas many carboxylic acids did not dissolved in liquid carbon dioxide. The term, critical point, was eventually coined by Thomas Andrew in 1869 [50]

as the end of the vapor pressure curve in a phase diagram. The supercritical fluid (SCF) phenomena were first described by Hannay and Hogarth (1879) [50], who reported on the solubility of cobalt chloride in supercritical ethanol. Villard in 1896 [50] on his review of SCF solubility phenomena described the ability of methane, ethylene, carbon dioxide and nitrous oxide to dissolve a number of liquids and solid hydrocarbons such as carbon disulfide, camphor, stearic acid and paraffin wax. A few years later, E. H. Buchner (1906) [50] reviewed the literature and also made significant additions to the experimental database of high pressure SCF-solute mixtures. He became the first in a long line of researches to measure the solubility of a model compound, naphthalene, in supercritical carbon dioxide (sc-CO₂). Chemists continued to experiment with SCF for almost a century, although they remained something of a curiosity until the 1970s, when rising energy costs led chemists to consider SCF as a cheaper alternative to liquid extraction and distillation. Industrial use of SCFs as solvent began in 1950s. Nowadays the uses of supercritical fluid extraction (SFE) are largely apparent in the decaffeination of green coffee, food, nutraceuticals, perfumes and cosmetics, pharmaceuticals, textile, electronics, aerogels, ceramic and innovative materials, oil industry, laundry dry cleaning, analytical processes, like, supercritical fluid chromatography, nanoparticle and microparticle formation, generation of co-crystals in pharmaceutical processes, biodiesel production and several other new and upcoming applications [51].

Supercritical water (SCW) is water at a temperature and pressure above its critical points (374°C and 22.1 MPa). It is known as an environmentally benign solvent for a comprehensive variety of chemical reactions; it takes part in a reaction not only as a solvent but also as a reactant [52, 53]; thus, SCW is a logical choice to obstruct the precipitation of AS at the elevated cracking temperature beyond 400°C [54]. In addition, aromatic bonds—ethers and esters—and aliphatic bonds are freely broken in SCW [52, 55, 56]. Thermal reactions of heavy oil have been studied in SCW, showing that two major reactions occur under supercritical conditions: oxidation and hydrolysis [57–59]. These reactions allow tar to be decomposed successfully into useful chemical compounds in SCW [60, 61]. Hu et al. [62] treated oil shale using SCW showing a higher conversion and a larger oil recovery than toluene extraction process. SCW also delivered easier decomposition of the polar components in oil shale likened with supercritical toluene [63]. Park and Son [64] studied extraction of Athabasca oil sand bitumen in a microreactor using SCW, achieving a maximum 24% conversion at a temperature of 380°C, pressure of 30 MPa and a reaction time of 90 min. These results show that SCW can be used as an effective green solvent for the extraction and decomposition of heavy hydrocarbons.

Methanol's critical property data are $T_c = 239.63^\circ\text{C}$, $\rho_c = 277.49 \text{ kg/m}^3$ and $P_c = 8.08 \text{ MPa}$ [65], becoming supercritical with disappearing phase boundaries between liquid and gas at these conditions. Yadav and Chandra [66] discovered that the hydrogen bonding between methanol molecules decreases significantly with moving to the supercritical state from the ambient one. Supercritical methanol (SC-MeOH) can degrade polyethylene terephthalate (PET), which can be used for recycling waste plastics [67, 68]. SC-MeOH can also be used to produce biodiesel [69–70]. SC-MeOH can convert cellulose into methylated cellotriose, methylated

cellobiose, methyl α - and β -D-glucosides, levoglucosan and 5-hydroxymethylfurfural [71]. Wang et al. [72] have studied the kinetics of esterification reaction between low-concentration NAs and methanol with or without using catalyst at temperatures of 180–280°C in an autoclave reactor. Acidity reduction of NAs using SC-MeOH without the addition of catalyst has been disclosed in open literature by Mandal et al. [33]. They have proved that approximately 100% TAN was reduced at a temperature of 350°C, a methanol partial pressure (MPP) of 10 MPa and a reaction time of 60 min. In addition, TAN reduction kinetics were followed first-order kinetics with Arrhenius parameters of activation energy 5.78 kcal/mol and a pre-exponential factor 1.56 s⁻¹.

The SCF processes are the currently most interesting environmental benign process [73]. The sc-CO₂ and the SCW have proved to be very efficient as a green extracting agent [74] and they are efficiently replacing harmful organic solvents nowadays. In addition, recent scientific reports have utilized sc-CO₂ for the synthesis of graphene-related materials. Moreover, continuous hydrothermal systems offer the ability to carry out synthesis in a high-throughput mode, enabling the discovery of new materials [75]. Furthermore, SCW can remove heavy metals from metalloporphyrin compounds effectively and efficiently in an environmentally friendly way [76]. Thus, the sc-CO₂ and the SCW have attracted tremendous interest among academia and industry in this modern era as a green process.

3.2. Ionic liquid (IL) and its history

An ionic liquid (IL) is ionic, salt-like materials. The ions in ILs are poorly coordinated resulting low melting point (below 100°C, or even at room temperature). An IL contains charged cation, a bulk organic structure with low symmetry and anion held together by Coulombic interactions. It is hard to break these bonds and make ILs evaporate. The extensively used cations are based on ammonium, sulfonium, phosphonium, imidazolium, pyridinium, picolinium, pyrrolidinium, etc. with different substitutes. The anions of ILs may be halogen (first-generation ILs), organic ([CH₃COO]⁻, [CF₃CO₂]⁻, [PhCOO]⁻, etc.) or inorganic ([BF₄]⁻, [PF₆]⁻, [AlCl₄]⁻, etc.). The properties of ILs depend on mutual fit of cation and anion, size, geometry and charge distribution. Usually, the cation has an impact on the hydrophobicity or hydrogen bonding ability and the anion controls the water miscibility [77, 78]. The structures of some commonly used ionic liquid systems are tabulated in **Figure 2** [78, 79].

The field of ionic liquid (IL) is not new, but their application as solvents in chemical processes for synthesis and catalysis has recently become important. This interesting field began in 1914 after preparation of ethylammonium nitrate ([C₂H₅NH₃][NO₃]) with the melting point (mp) of 12°C by Paul Walden [78–80]. This compound is recognized as the first IL by many researchers [80] but due to its high reactivity has not really found a use. After two decades of silence, IL appears in an US patent no. 1943176 in 1934. The writer of this patent claimed that the cellulose has dissolved in halide salts of nitrogen-containing bases, such as 1-benzylpyridinium chloride, 1-ethylpyridinium chloride, etc. at the temperature above 100°C. After another declined phase in the history of IL, it re-emerged in the period just after World War II in 1948 as another US patent [79]. It was basically appeared in the open literature in 1951 [79] as the

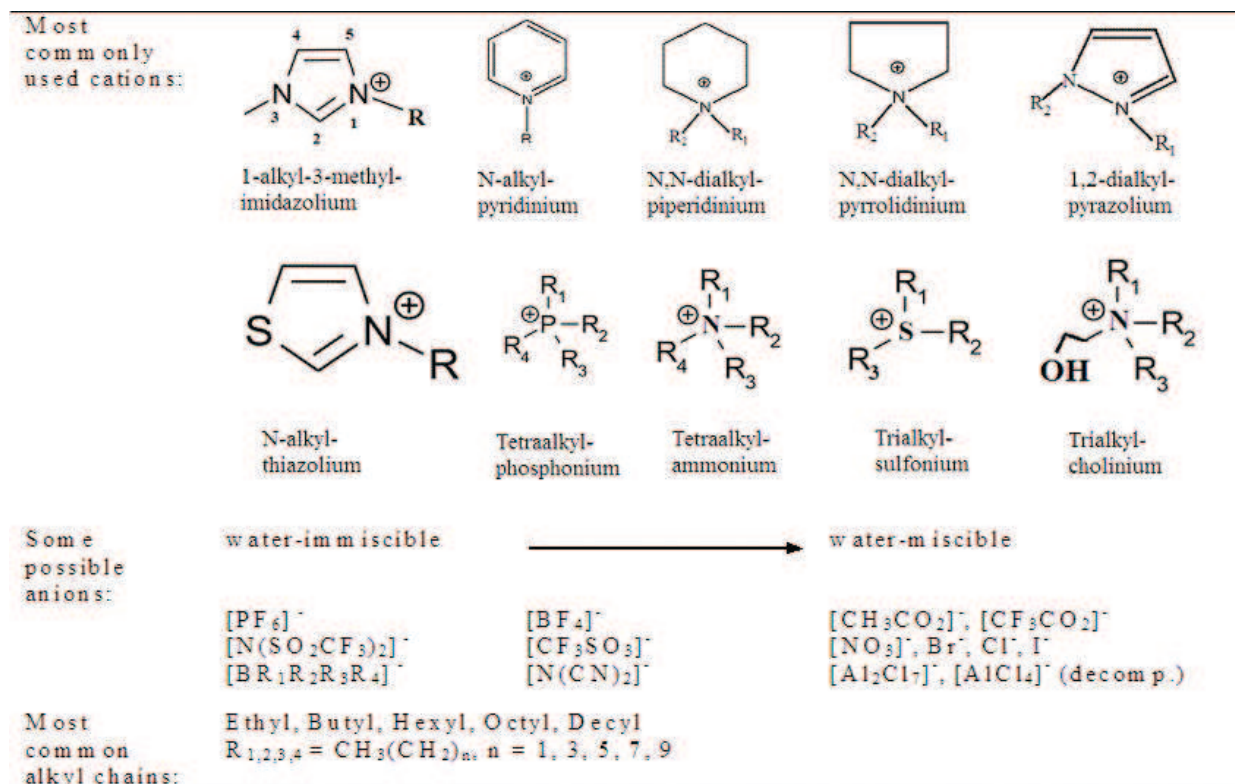


Figure 2. Some commonly used IL systems.

application of mixture of aluminum (III) chloride and 1-ethylpyridinium bromide to the electrodeposition of aluminum. But they have failed to investigate the IL at that time due to the complicated mixture of bromide and chloride salts. Later the physical and chemical properties of this IL were studied by Osteryoung group in 1975, aided by Bernard Gilbert [79]. The IL was created international attention in 1970s as aluminum chloride-based molten salts were utilized in 1940s for preparation of nuclear warheads batteries. Wilkes in 1970 attempted to develop better batteries for nuclear warheads and space probes that needed molten salts to operate [78]. The chemists of that period searched new salts that can remain liquid at lower temperatures as the molten salts were sufficiently hot to damage the neighboring materials. Wilkes and his co-workers carried on improving their ILs for using as battery electrolytes and in the long run they identified one low melting point IL [78]. Wilkes and Hussey discovered the $[C_2mim]Cl-AlCl_3$ IL system, liquid at room temperature, which was the first genuine example of IL system [79]. ILs became one of the most promising chemicals as solvents in the late 1990s.

ILs are versatile compounds due to their interesting properties. The properties of ILs are variable and can be in theory adjusted for any application, i.e., they are not all non-corrosive, but they can be designed to be non-corrosive. In general, they are characterized to have low vapor pressure, thermal and chemical stability and non-flammability. The research areas on ILs are growing very rapidly and it has numerous potential applications, such as, microwave-assisted organic synthesis, catalysis, biocatalysis, separation, extraction, electrochemistry, nanomaterials synthesis, polymerization reactions and corrosion inhibitors [81]. ILs can also

offer surprising efforts to reassess and optimize existing technologies and processes related to the petroleum industry. A large number of research studies on the assessment and utilization of ILs in pollutant removal including sulfur-, nitrogen- and flour-containing compounds; aromatics; naphthenic acids and asphaltene of refinery feeds are disclosed in open literature.

4. TAN removal using SCF

4.1. Effect of temperature on TAN reduction using SCF

The initial TAN of NA, used raw materials for potential experiments by Mandal et al. [2, 33], was 241.55 (mg of KOH/g of NA). TAN reduction takes place at high temperatures and pressures in the presence of SCW. But, SC-MeOH can reduce TAN at lower temperature and pressure than SCW. Temperature has a considerable effect on TAN reduction using SCF. For exploring temperature effect on TAN reduction using SCW, Mandal et al. [2] carried out a lot of experiments at temperatures of 400–490°C and water partial pressure (WPP) of 25–45 MPa. In addition, SC-MeOH effect on TAN reduction was explored at temperatures of 300–350°C and MPP of 10 MPa [33].

Figure 3 illustrates the high TAN removal which increased with increasing reaction time and temperature. Type of SCF was also an important factor on TAN reduction process. Mandal et al. [2] in 2012 disclosed that approximately 89% TAN is reduced at reaction temperature of 490°C and reaction time of 60 min in treatment without water depositing approximately 4.05% solid which was nothing but lean hydrogen content high molecular weight hydrocarbons. Solid formation is the indication of loss of valuable compounds and thus potential

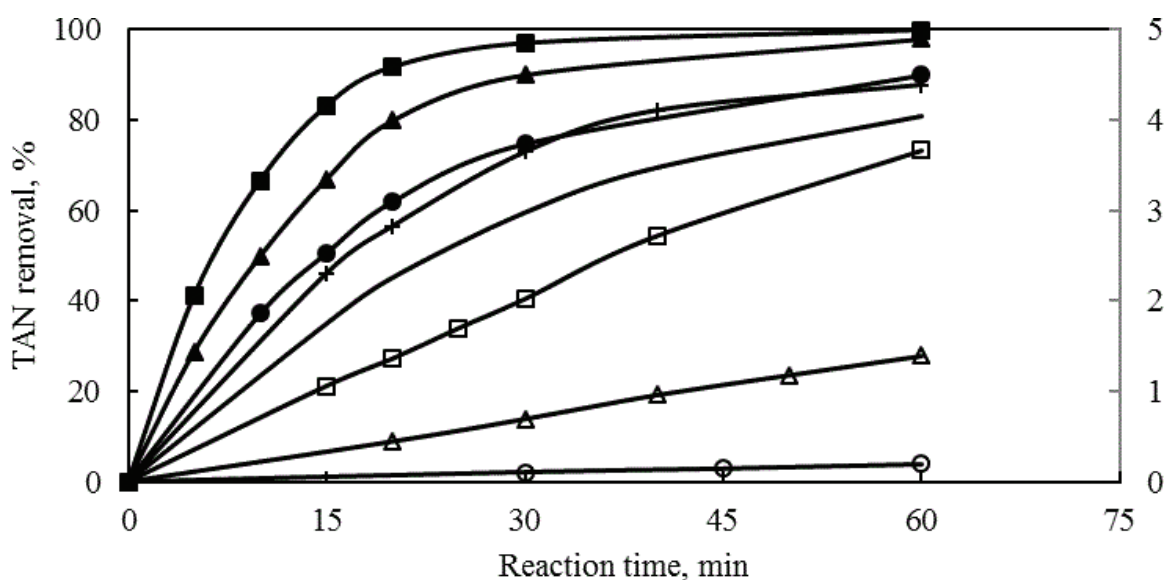


Figure 3. Variation of TAN as a function of reaction times, temperatures and water or methanol partial pressures (symbols: ○, 400°C, WPP of 45 MPa; △, 450°C, WPP of 45 MPa; □, 490°C, WPP of 45 MPa; +, 490°C, no water; -, 490°C, no water (solid); ●, 300°C, MPP of 10 MPa; ▲, 325°C, MPP of 10 MPa; ■, 350°C, MPP of 10 MPa).

revenue. Thus, it is desirable to reduce solid deposition from the economical point of view. SCW have the capability to reduce solid formation. Mandal et al. [2] do not observe solid deposition during their experiments using SCW at temperatures of 400–450°C. Solid deposition is detected at a temperature of 490°C, but depends on WPP and reaction time. The amount of solid deposition falls to 1.79 and 0.10% at WPPs of 30 and 45 MPa, respectively, indicating the drastic reduction of solid deposition at a WPP of 45 MPa. At extreme operating conditions (at temperature of 490°C, reaction time of 60 min and WPP of 45 MPa) of SCW treatment, the TAN reduction is reduced to approximately 73% which is less than the value (89%) obtained during pyrolysis without water.

4.2. Reaction kinetic study and mechanism

In 2012, Mandal et al. [2] conducted pioneering study on TAN removal using SCW. Their study revealed that TAN removed from NAs using SCW followed first-order kinetics. Mandal et al. [33] on another study showed that TAN removal from NAs using SC-MeOH also followed first-order kinetics. Wang et al. showed that the esterification reaction between NAs and subcritical methanol follows second-order kinetics with or without SnO catalyst in their study. The feedstock used by Wang et al. was the second vacuum fraction processed by a Chinese corporation having TAN content 3.69 (mg of KOH/g of feed stock), which was a mixture of NAs and higher hydrocarbons. The feedstock used by Mandal et al. [2, 33] was basically a blend of carboxylic acids having a TAN content 241.55 (mg of KOH/g of NA). The variation of properties of feed stock and reaction operating conditions were responsible for the variation of reaction order. **Figure 4** shows the Arrhenius type dependency of NAs removal rates on temperature. Based on such type of plot, Mandal et al. [2, 33] discovered the

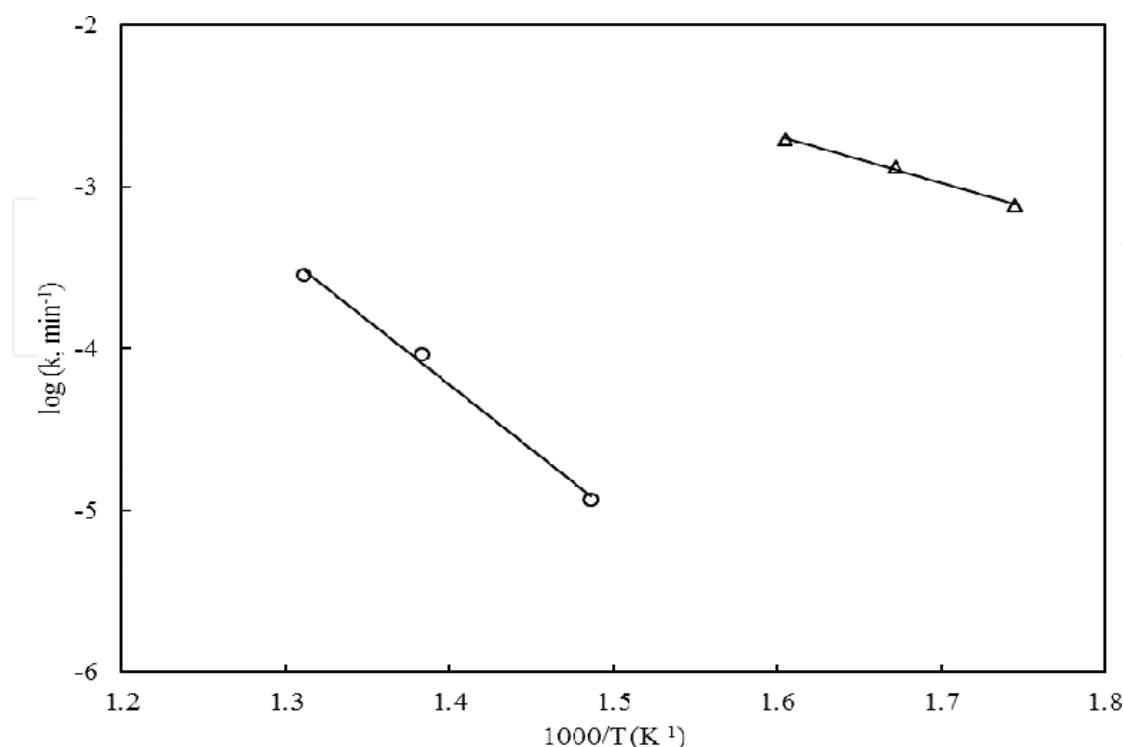


Figure 4. Arrhenius plot for reaction between NAs and SCF (symbols: ○, SCW; △, SC-MeOH).

activation energy and pre-exponential factor. Thus, the temperature-dependent rate constant can be expressed by the following Arrhenius equations:

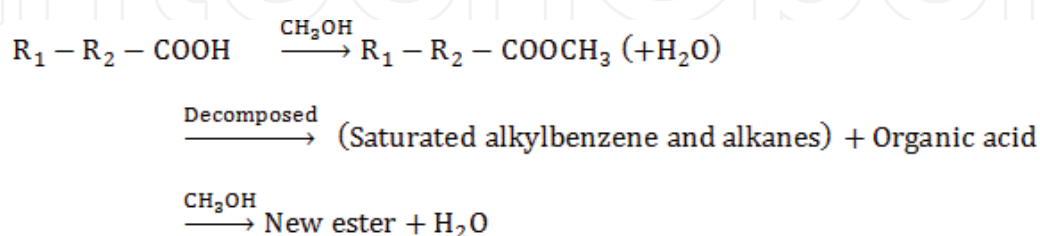
$$k_r(T) = 1.43 \times 10^5 e^{-\frac{66.24}{RT}}, \text{ for SCW} \quad (1)$$

$$k_r(T) = 1.56 e^{-\frac{5.78}{RT}}, \text{ for SC-MeOH} \quad (2)$$

The respective activation energies of the reaction of NAs with SCW and SC-MeOH are 66.24 and 5.78 kcal per mol. The activation energy of NAs for reacting with SCW is 91.27% higher than the activation energy of NAs for reacting with SC-MeOH at lower pressure. This indicates that 91.27% higher energy is required for the reaction of NAs with SCW.

According to the study of Mandal et al. [2, 33], SCW and SC-MeOH reduce acidity of NAs in different reactions and pathways (**Figure 5**). SCW acts as a hydrogen donor [82] and it can remove metal from metalloporphyrin where hydrogenation reaction is involved. NAs react with SCW to form stable compounds [2] and gaseous product (CO₂, CO, petroleum gas) where hydrogenation reaction is happening to occur. Based on the analysis using GC/MS and MALDI TOF/MS, Mandal et al. in 2012 [2] showed that hydrocarbons are formed through decarboxylation of NA followed by long-chain scission and formation of high molecular weight hydrocarbons. It is also observed that SCW can produce low molecular weight hydrocarbons suppressing char formation and production of high molecular weight hydrocarbons from alkylbenzene and NAs [2, 82]. NA is not hindered the quality of petroleum oil except corrosion problem.

On the other hand, SC-MeOH without a distinct catalyst can reduce acidity promptly by forming ester (like nonanoic acid, methyl ester; decanoic acid, methyl ester and so on), saturated alkylbenzene (like heptylbenzene) and alkane (like decosane). SC-MeOH as an excellent solvent can dissolve feedstock so that reactant molecules are in mutual close proximity to react readily. At the first step of reaction, SC-MeOH reacts with NAs to form ester and water. The thermal stability of ester depends on its carbon skeleton [33, 83]. Mandal et al. in 2013 [33] observed that concentration of saturated alkylbenzene and alkane is increasing with increasing reaction time. In the second step of reaction, the thermal effect of SC-MeOH can



Stable compounds (Saturated hydrocarbons; naphthalene, phenanthrene, anthracene, pyrene with their derivatives and so on) + Gaseous product (CO₂+ CO + petroleum gas)

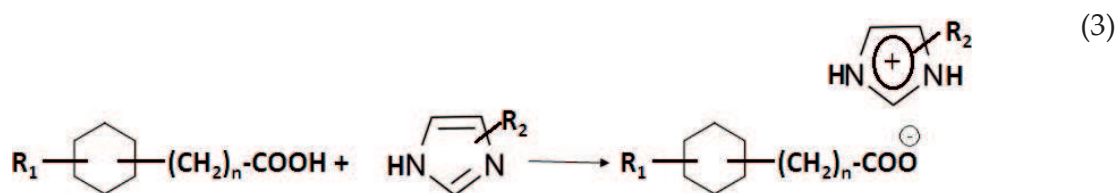
Figure 5. Reaction mechanism of NAs with SCF.

decompose unstable ester to form saturated alkylbenzene and alkane and produce new ester. In the third step of reaction, produced esters can react with SC-MeOH to form new ester and water.

5. TAN reduction using IL

Literature study revealed that NAs are successfully removed from crude fractions by aqueous base washing [84, 85]. But serious emulsion problems are experienced during operation.

Shi et al. [86] has proposed a fancy method to isolate NAs from highly acidic crude oils by forming ILs. In this method, the researchers prepared Brønsted ILs by acid-base reaction between basic imidazole and NAs to form naphthenates ILs according to the following reaction:



The acid removal rate has been affected by the 2-methylimidazole content, reagent/oil ratio, reaction time and reaction temperature. All of them had a positive effect on the acid removal rate except the reagent/oil ratio which had a negative effect on the oil yield rate. The same approach was employed by Baden Aniline and Sida Factory (BASF), the largest Ludwigshafen, Germany based chemical company in the world to develop the first successful large-scale industrial application of ILs in 2003 [81] through the process biphasic acid scavenging ILs (BASIL). In this process, they are using N-alkylimidazole derivative to scavenge acid that is formed in the alkoxyphenylphosphines production process as a by-product forming ILs. The reaction results in the formation of the IL N-alkylimidazolium chloride having a melting point of 75°C. The IL separates as a clear liquid phase from the pure product and is reused.

Crude oil can be deacidified with a basic IL [87]. The basic IL is a liquid salt having the general formula $[\text{C}^+][\text{A}^-]$, where C^+ is a cation having a basic moiety, preferably represented by a formula $[\text{Cat}^+(\text{Z-Bas})_n]$, and/or A^- is an anion having a basic moiety, preferably represented by $[\text{An}^-(\text{Z-Bas})]$. Here, Cat^+ is a positively charged moiety, An^- is an anionic moiety, Bas is a basic moiety, Z is a covalent bond joining Cat^+/An^- and Bas or is a divalent linking group and n is an integer from 1 to 3. The Cat^+ moiety comprises a heterocyclic ring structure selected from imidazolium, pyridinium, pyrazolium and so on. The An^- moiety comprises a CO_2^- or SO_3^- group. Base comprises at least one basic nitrogen, phosphorus, sulfur or oxygen atom and preferably selected from $-\text{N}(\text{R}_1)(\text{R}_2)$, $-\text{P}(\text{R}_1)(\text{R}_2)$, $-\text{S}(\text{R}_3)$, $-\text{O}(\text{R}_3)$, where R_1 and R_2 are independently selected from hydrogen, linear or branched alkyl, cycloalkyl, aryl and substituted ring and R_3 is selected from linear or branched alkyl, cycloalkyl, aryl

and substituted aryl. Z comprises divalent organic radical and preferably selected from a divalent alkylene radical, alkyleneoxyalkylene radical, polyoxyethylene radical and alkylenearylene or alkylenearylenealkylene radical.

Sun and Shi in 2012 [88] revealed that the ILs of imidazole anion having strong alkalinity had excellent performance on deacidification. They discovered that the lower the agent/oil mass ratio, the higher the NAs conversion and high temperature could decrease the reagent/oil ratio to achieve maximum deacidification rate with each IL. When [AMIm]Im is used, the performance of deacidification succeeded the order [OMIm]Im > [HMIm]Im > [BMIm]Im > [EMIm]Im. Duan et al. in 2013 [89] have studied on pyridinium, imidazolium and imidazolidine-based ILs at different alkalinity. They showed that the stronger alkalinity of ILs was, the higher deacidification would be and the deacidification succeeded the order [AMIm]Im > [AMIm]Br > [APy]Br. In addition, when the length of alkyl chain increased, each kind of ILs would have more excellent performance on deacidification.

Sun et al. [88, 89] explained NAs removal mechanism using ILs with the help of techniques proposed by Holbrey et al. [90]. Holbrey et al. [90] revealed that IL molecules themselves could form cage structure through specific chemical bonds. In this cage, the target molecules would be captured through the formation of liquid clathrate due to the π - π interaction between ILs and target molecules. This phenomenon would be helpful to explain the following facts: (1) the larger the π interaction between ILs and NAs, the stronger the IL alkalinity which means of great electron density, the better the effect of deacidification would be. (2) For the same anion containing ILs, the longer alkyl chain of ILs, the higher the deacidification activity as well as alkalinity, the more inclusive for NAs by increasing the space of the cage. Thus, NAs conversion increased with the larger of alkyl chain of the ILs. (3) Unregenerated ILs indicated good performance on deacidification in the following iterative reactions because each ILs molecules could adapt more than one NA molecules. The NAs could not be withdrawn completely from low NA containing oil as the surrounding alkane molecules made NA molecule difficult to penetrate into the clathrate structure of ILs. When fresh acidic oil added into this system, the surrounding alkane structure was broken and ILs showed good performance again. (4) The NA molecules could easily escape from the cage structure at high temperature due to unfavorable adsorption process at this condition. So, the reuse of IL would be decreased at such temperature condition.

Andersen et al. [12] have studied a number of tetraalkylammonium and tetraalkylphosphonium amino acid-based ILs to remove NAs from crude oil. A model oil having TAN 4.00 mg KOH g_{oil}⁻¹ has been charged in a glass vessel and heated the same at a temperature of 25°C for 1 h. An exact amount of ILs has then been mixed with the oil for reaction for 20 min. The percentage of NA removal obtained from the experiments is summarized in **Table 2**.

Table 2 revealed that all AAILs have showed excellent and swift acid removal after 20 min except [NTf₂]⁻-based ILs. The low extraction efficiency of [NTf₂]⁻-based ILs implies its weak interaction between the IL and the NA. There is a little effect of the cation type on acid removal

IL anion	NA Removal (%)	
	Tributylmethylammonium [N ₄₄₄₁] ⁺	Tetrabutylphosphonium [P ₄₄₄₄] ⁺
Bis (trifluoromethanesulfonyl)imide ([NTf ₂] ⁻)	2	3
Serinate ([Ser] ⁻)	31	32
Threonate ([Thr] ⁻)	35	37
Valinate ([Val] ⁻)	21	31
Cystinate ([Cys] ⁻)	26	27
Prolinate ([Pro] ⁻)	36	38
Lysinate ([Lys] ⁻)	46	41
Taurinate ([Tau] ⁻)	37	32

Table 2. Percentage of NA removal using a range of AAILs at a temperature of 25°C [12].

although [P₄₄₄₄]⁺ have the pioneering extraction efficiency due to their lower viscosity than the other. It is noticeable that [N₄₄₄₁] [Val] have the lowest acid removal capability than [P₄₄₄₄][Val] due to the highest melting point of [N₄₄₄₁] [Val] compared to [P₄₄₄₄][Val]. [Lys]⁻-based ILs have two amine groups per molecule of IL that can extend its acid removal capability. The other functional groups present on the anion such as hydroxyl group (-OH) in [Ser]⁻ and [Thr]⁻ and thiol (-SH) group in [Cys]⁻-based ILs have a little impact on the corresponding extraction efficiency.

The following two reactions are the possible reactions for removing NA using AAIL:



In the first reaction, the amino acid anion constructs IL-NA complex known as zwitterionic species by protonating the amino group and forming the carboxylate anion. In the second reaction, the protonation of amino acid anion and ion exchange with NA form the naphthenate salt releasing the amino acid. Andersen et al. [12] have confirmed based on infrared spectroscopy that the reaction mechanism involves a stoichiometric reaction between one amino group and one carboxylic acid group forming a zwitterionic species. Lysine anion contains two amino groups. Therefore, lysine-derived AAILs showed higher extraction capability compared to other AAILs.

Based on current studies, SCF process is more effective than IL-based process for reducing TAN of NAs. SC-MeOH without the addition of catalyst can reduce approximately 100% TAN at a temperature of 350°C, a methanol partial pressure (MPP) of 10 MPa and a reaction time of 60 min [33]. On the other hand, the IL, tributylmethylammonium lysinate, can reduce approximately 46% NA at a temperature of 25°C [12]. A lot of ILs are available in open market or possibility of production in laboratory that can be used to reduce TAN of NAs at room temperatures at high extent. The benefit of using ILs is needed room or low temperature to reduce TAN of NAs. In addition, it is possible to separate ILs after treatment reducing cost of process. Therefore, IL-based processes are attracting the researchers nowadays.

6. Conclusion

A number of TAN reduction methods have been developed for reducing the TAN content of crude oil to maintain TAN content of crude oil below the integer value 2. The SCF process and the IL-based process, known as environmental benign processes, are new processes in this area. SCF without the addition of catalyst can reduce TAN of NAs and substantial amounts of NAs are converted into non-acidic products. The reaction kinetics is consistent with first-order dependency on TAN removal. Like SCF, ILs can also reduce acidity of heavy oils either by forming zwitterionic species or creating cage structure around NAs through specific chemical bonds. In comparison, SCF process is more efficient than IL-based process for reducing TAN of NAs. Therefore, IL-based processes are attracting the researcher's attention due to their availability in laboratory or in open market and separability tendency after using.

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