



Review on Naphthenic Acids: An Important Environmental Pollutants Caused by Oil Extraction and Industries

Yaser Sotoudeh¹ | Mohammad Hossein Niksokhan^{2✉*} | Abdolreza Karbassi² | Mohammad Reza Sarafrazi³

1. PhD Candidate, Department of Environmental Engineering, University of Tehran, Iran
2. Department of Environmental Engineering, Faculty of Environment, University of Tehran, Iran
3. Connoisseur in charge of HSE petrochemical projects of National Iranian Petrochemical Company, Iran

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ABSTRACT

Naphthenic acids are a group of polar organic carboxylic acids that are present in crude oil naturally. They are cycloaliphatic carboxylic acids which have 10 to 16 carbons, which gained importance since the early twentieth century because of corrosion in oil refineries. Moreover, they are the most important environmental pollutants caused by oil extraction from oil sand reserves. Heavy crude oils which have high concentration of naphthenic acids are usually considered as poor-quality oil and sold at a lower price. Often, the high concentration of naphthenic acids in crude oil reduces the life of the equipment which are used in the exploration and refining process because of corrosion. Hence, researchers are increasingly interested in the chemical properties of naphthenic acids and the acidic components of the crude oils. The most popular methods for the identification and analysis of naphthenic acids are liquid and gas chromatography (GC), liquid-liquid extraction, Fourier transform infrared spectroscopy (FTIR), and solid-phase extraction (SPE). Naphthenic acids are the most important environmental pollutants caused by oil extraction from oil sand reserves. Previous studies have revealed that naphthenic acids can be absorbed by fish, but their distribution in different tissues of fish has not been specified. Experimental samples showed the highest toxicity to fish, while there was less toxicity to invertebrates and algae. Moreover, naphthenates have various industrial utilizations; they are used in synthetic detergents, corrosion inhibitors, lubricants, fuel and oil additives, wood preservatives, insecticides, fungicides, pesticides, wetting agents, napalm thickening agents, and oil desiccants that are utilized in painting and treating wood surfaces.

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INTRODUCTION

Naphthenic acids are polar organic carboxylic acids that are present in crude oil and have gained importance since the early twentieth century because of corrosion in oil refineries (Brown and Ulrich, 2015a). The researchers' findings show that crude oil resources in South America have the highest amount of acid-valued compounds in the world. Thus, this causes the oil acidity to have a special property resulting in improper use of this raw material for purification and recycle reuse (Pereira et al., 2012).

Acid studies have been around for more than a century and are found in various sources of

*Corresponding Author Email: niksokhan@ut.ac.ir

hydrocarbons including crude oil and oil sands. In 1883, Markonikov accepted the existence of acids in crude oils of Azerbaijan containing carboxylic groups related to carboxylic acids. Afterward, “naphthenic acid” has been used to describe all acidic materials which contain the carboxylic group in crude oils (Crawford et al., 2005).

According to Qian et al. (2001), naphthenic acids are carboxylic acids that exist in oil and make a fraction of thousands of various compounds, and are more found with monocarboxylic acids containing one or more twin cycloalkanes.

To be able to analyze this acid in the period that occurs, a method that examines its content by titration with potassium hydroxide (KOH) is used; hence, the number or index of naphthenic acid is produced. This index is applied to analyze the sample content; however, corrosion has no interference with the oil quality and the nature of the existing acids (Fields, 2005)

Therefore, to describe these acids, it is essential to extract and analyze them separately to evaluate the level of corrosion. This study was conducted to analyze the identification methods, damages of naphthenic acids, and their end applications.

Naphthenic acids have become high priority pollutants in the oil sands industry (Brown and Ulrich, 2015b). Due to water recycling efforts, actively used tailings ponds continue to show increasing concentrations of dissolved salts, minerals, trace metals, residual bitumen, and organic matter, including naphthenic acids (Allen, 2008).

Marsh (2006), suggested that naphthenic acids remaining in OSPW are resistant to biodegradation by indigenous microorganisms in tailings ponds after many years.

Naphthenic acids

Naphthenic acids are a combination of several cyclopentyl and cyclohexyl carboxylic acids and their molecular weight varies from 120 to more than 700 atomic mass units. Their major components are carboxylic acids which have a carbon backbone of 9-20 carbons. McKay et al. (1975), stated that “naphthenic acids are primarily cycloaliphatic carboxylic acids with 10 to 16 carbons”. Figure 1 illustrates image of naphthenic acid molecule.

The most common method for displaying naphthenic acids in crude oil is the following formula:



where n is the carbon number and Z is the hydrogen deficiency. Z values may be zero or a negative integer, which the value of Z indicates a hydrogen atom loss, occurring when a cycloaliphatic ring exists in the acidic structure. Therefore, Z = -2 is equal to one acid with one ring and Z = -4 is equal to one acid with two rings. More than one acid is naturally present for a Z value which allows the correct types of naphthenic acids to be identified; however, the molecular weight of crude oil naphthenic acids, on average, ranges between 200 and 700 Daltons (Oliveira et al., 2004).

The term “naphthenic acid” is derived from the ancient term “naphthene” (cycloaliphatic but non-aromatic) applied to categorize hydrocarbons. Initially, it was utilized to describe complex combinations of oil-based acids, and analytical methods which were present in the early 1900s could accurately identify a few parts of the naphthenic type. Today, naphthenic acid is used in a more general sense and refers to all carboxylic acids in oil, whether cyclic or non-cyclic, although commercial naphthenic acids are mostly cycloaliphatic acids. Some naphthenic acids contain more than 50% of mixed aliphatic and aromatic acids. Naphthenic acid salts which are called naphthenates, are used as hydrophobic sources of metal ions in various utilizations. During World War II, aluminum salts of naphthenic acid and palmitic acid were mixed for producing napalm (Clemente et al., 2005).

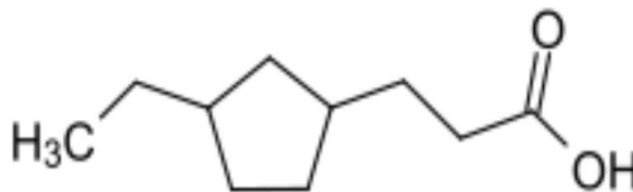


Fig. 1. Image of naphthenic acid molecule (Qian et al., 2001)

Properties of naphthenic acids

The American Petroleum Institute (API) defines naphthenic acids as structures with cyclopentane and cyclohexane rings that combine with several melted or simple structures with a carboxylic group joined to an aliphatic or cyclo-aliphatic side chain (Clemente et al., 2003).

Heavy crude oils which have high concentrations of naphthenic acids are categorized as poor-quality oil and sold at a lower price. The high concentration of naphthenic acids in crude oil reduces the life of the equipment which is utilized in the exploration and refining process because of corrosion. To increase the crude oil quality and save costs, it is very essential to eliminate naphthenic acid compounds from it (Adams et al., 2019).

Naphthenic acids have various properties in the examination and vary between dark colors; when they are in the distillation process, they are more inclined to light yellow and may even turn amber (Fields, 2005).

Naphthenic acids are sticky liquids containing phenolic and sulfur impurities that account for their distinctive odor. Their boiling point ranges widely from 250°-350° C. They can be completely solved in solvents and organic oils but are insoluble in water (> 50 mg/L). Naphthenic acids are weaker acids compared to carboxylic acids with low molecular weight such as acetic acid, but are stronger acids than phenol and cresylic acid. While naphthenic acids are mainly used in the production of metal salts, they can also react and make esters, amine salts, amides, imidazolines, and many other materials (Lochte et al., 1955).

Since naphthenic acids are impure chemicals, the melting point characteristics of these complex substances differ from their hydrocarbon composition. According to the information in the specifications of commercial product and material safety data sheets, the melting points of materials which are produced for commercial application have range from -35 to +2° C. Moreover, the boiling point properties of naphthenic acids and their salts differ based on the hydrocarbon composition of the complex materials found in them. According to data obtained from commercial product specifications and material safety data sheets, the boiling points of materials manufactured for commercial application are in the range of +140 to +370°C (US Environmental Protection Agency, 2012). In a study, Kinley (2015), stated the chemical and physical properties of Fluka naphthenic acids.

Naphthenic acids are a serious challenge for the oil industry because they tend to precipitate from solution in contact with water. Experiments which are designed to investigate the water shear effect, concentration of acid, concentration of brine, and brine pH on the amount of formed sediment show that the amount of sediment increases with increasing pH of brine and acid and calcium ions concentration (McKenzie et al., 2014).

Naphthenic acids are weak acids that their pKa content ranges from 5 to 6. Thus, alkaline solutions increase the solubility of naphthenic acid and acidic solutions decrease its solubility (Havre, 2002).

Here, naphthenic acids and their salts exist in considerable amounts in water and oil, and consequently, in the combination of colloidal solutions. However, water and oil emulsifier needs to be evaluated, which leads to changes and complexities in the tab input and output systems for evaluating compounds. Therefore, the decomposition of metal salts which are soluble in water, e.g., calcium and magnesium, causes the formation of nuclei and produces density of components, which account for the recurrent operational interruptions in the process of separation (John et al., 1998).

Application of naphthenic acids

Before use in large industries, this compound and various mixtures obtained, such as metal salts of naphthenic acids, are applied to assure that paint dryers, corrosion inhibitors, catalytic organic reactions, and lubricants are produced (Oliveira et al., 2004; Campos et al., 2006).

More than two-thirds of the produced naphthenic acid is applied for producing metal salts, and the largest volume is for copper naphthenate, which is used in the wood preserving industry. The naphthenic acid market is expanding in the field of wood and textile preserving. Copper and zinc naphthenates utilization is to inhibit dry rot and attacks of fungi and insects on wood. Zinc naphthenate is commonly utilized in the home wood industry because it creates a colorless layer on the wood. Another application of naphthenic acid is in tire industry, where cobalt naphthenate is applied as a bonding enhancer. Cobalt naphthenate increases the bonding of steel wires that are covered by brass to rubber. Simple esters are produced through the reaction of naphthenic acids with monohydric alcohols, olefins, or ethylene or propylene oxides. Naphthenic acid esters have often been mentioned as substitutes for phthalates as softeners for polyvinyl chloride (PVC) resins. Elsewhere in the market, lead naphthenate is used sparingly in high-pressure additives for oils and greases. Sodium and potassium naphthenates are applied in emulsified oils, because they have higher antiseptic properties than fatty acid soaps. Metal salts which are used as paint dryers constituted only 16% of the naphthenic acid market in 1993. In addition to the metal salt lubrication market, the miscellaneous market includes free acids which are used in concrete admixtures, engine lubricating oil, and asphalt coating applications (Brient et al., 1995).

Moreover, it can be used to extract copper along with the chief method of naphthenates for use in protection of environment, given that wood is utilized as an emulsifying agent in the manufacture of insecticides (Gruber et al., 2012).

Due to the polar compositions that are very important in oil, many geochemical studies have focused on the results of the biological, saturated, and aromatic parts, which led to analyses determining the source and maturity of oil (Galimberti et al., 2000).

Naphthenates have various industrial utilizations in synthetic detergents, lubricants, inhibitors of corrosion, additives of fuel and oil, preservatives of wood, insecticides, fungicides, pesticides, wetting agents, napalm thickening agents, and oil desiccants that are utilized in painting and treating wood surfaces. Beneficiary industrial naphthenates comprise aluminum, magnesium, calcium, barium, cobalt, copper, lead, manganese, nickel, vanadium, and zinc (Rogers et al., 2002a).

Release and damage of naphthenic acids

In an article, which is often cited, Rogers et al. (2002b), argued that “naphthenic acids are the most important environmental pollutants caused by oil extraction from oil sands sources”. They found that in the worst risky conditions, the wild mammals’ severe toxicity was unlikely, but repeated exposure to the naphthenic acids in the wetland might have harmful effects on health.

Samanipour et al. (2020), used liquid chromatography (LC) and mass spectrometry with Electrospray ionization (ESI) in the negative state to identify the complete chemical characteristics and the quantification of naphthenic acids in different water supply samples from

six oil platforms offshore Norway, which led to the identification of 55 unique naphthenic acid isomer groups from 181 homologous groups in all of the examined samples. The naphthenic acids total concentration was different between 6 and 56 mg/L in investigated platforms, while the single isomer groups' concentrations varied between 0.2 and 44 mg/L. Considering the concentration and distribution of naphthenic acids in samples, it seems that the $C_8H_{14}O_2$ isomer group was a significant index of the existence and concentration of total naphthenic acids in samples; the Pearson correlation coefficient was 0.89.

Extracting oil sand sources is done by a hot water extraction process. Alkaline pH causes naphthenic acids to release from oil sands and dissolve in water. These hydrous extracts include naphthenates extremely fatal for fish and other organisms living in water. Previous studies have revealed that naphthenic acids may be absorbed by fish, but their distribution in different tissues of fish has not been specified. In this study, in the laboratory, a rainbow trout was subjected to commercial naphthenic acids. After 10 days of being subjected to 3 mg/L naphthenic acids, the fish autopsy was carried out, and samples from heart, gills, liver, kidney, and muscle were extracted and analyzed using gas chromatography (GC) method - mass spectrometry (MS) - and free naphthenic acids. Each tissue had naphthenic acids and non-parametric statistical analysis demonstrated that the concentration in gills and liver was higher than the muscle, and liver concentration was more than the heart. Moreover, four different species of fish (two fish from each) were taken from the Athabasca River near two operational location of oil extraction and extraction of oil sands. Free naphthenic acid was not identified in muscle or liver of these fish (Young et al., 2011).

Naphthenic acids can cause many injuries in a combination with other compounds initially due to corrosion, and this was mainly presented in the purification equipment in 1920, because it indicates that naphthenic acids primarily account for materials' corrosion in the liquid phase in purification time (Zanin et al., 2002).

This combination is different from the combination of crude oil and conditions during refinement and oxidation. Sections that have high amount of naphthenic acids can lead to damage and corrosion to the equipment of oil refinery. Therefore, the corrosion of naphthenic acid is well investigated. Crude oil containing high amount of naphthenic acids is often known as crude oil with the total acid number or high acid crude oil. Naphthenic acids are the most important pollutants in water produced due to oil extraction from oil sands of Athabasca. They are acutely and chronically toxic to fish and other organisms (Rogers et al., 2002b). According to Zanin et al. (2002), corrosion due to naphthenic acids happens at 220° to 400° C, with increasing concentration of a substance.

Studies demonstrate that microbial organisms may utilize the commercial mixture of naphthenic acids as a source of energy, and these materials can be decomposed innately (Herman et al., 1993). Naphthenic acids are relatively soluble in water (50 mg/L). They are unlikely to remain in the water column for long, and a high percentage of them precipitate. They are suspected as endocrine disruptors, but are not mutagenic or carcinogenic. Recent studies have revealed that naphthenic acids are poorly absorbed to soil, and are vulnerable to aerobic degradation. A study consisting of three naphthenic acid models showed that among temperature, pH, and dissolved organic carbon (DOC), the most effective factor on microbial degradation was temperature (Headley et al., 2004). Swigert et al. (2015), conducted experiments on water samples polluted with naphthenic acids, which showed the highest toxicity to fish, while there was less toxicity to invertebrates and algae.

The naphthenic acids acute toxicity in experimental animals has been examined through oral and skin paths. In early studies (Rockhold, 1955) of acute oral poisoning, albino rats received a single dose of naphthenic acid preparation ranging from 0.036 to 10 g/l. All mice in the group of 10000 mg/L died and the symptoms of the effects on the central nervous system (CNS) were reported with doses of more than 5000 mg/L. In acute skin poisoning in rabbits, mild to

moderate symptoms of skin irritation were produced by naphthenic acid preparation in doses of more than 50 mg/L, but all animals under treatment survived.

Moreover, in acute poisoning, mice and guinea pigs were subjected to air saturated with naphthenic acid preparation for 6 hours, and all animals survived in the period of exposure. Exposure level was not analytically specified; however, the nominal concentration was calculated to be about 0.63 mg/L (60 ppm) (US Environmental Protection Agency, 2012).

Analyzing naphthenic acids in conventional crude oil is difficult. Woo et al. (2009), analyzed them by utilizing an activated carbon unit which was used as a guide for evaluating refined effluent in a refinery. These compounds have affirmed that these acids exist in the final wastewater treatment, but this behavior has also helped to reduce the aqueous environment.

Some organic molecules are applied as inhibitors of corrosion to decrease corrosion in the refining process units and their amount is dependent on the total acid number, because studies have shown that a protective layer on the pipes surface is formed by acid inhibitors, thus reducing the corrosion caused by naphthenic acids in crude oil (Chakravarthy et al., 2016).

Naphthenic acid toxicity is less to mammals but more to fish, bacteria, and wood insects. For humans, the fatal oral dose is 1 liter and for rats 3 to 5 grams per kilogram. Mortality appears to be due to gastrointestinal disorders. The International Agency for Research on Cancer, the US National Toxicology Program, or the US Occupational Safety and Health Act have not mentioned it as a carcinogen (Brient et al., 2000).

Pinzón-Espinosa et al. (2021), conducted further research to examine new generations of Fe-TAML activators to reduce hydrogen peroxide (H_2O_2) concentration and reaction time. Generally, their results show that Fe-TAML/ H_2O_2 systems are suitable candidates for decreasing the toxicity of effluents which contain naphthenic acid pollutants, and in the case of water stability of the petrochemical sector, this is a step forward.

Using industry and its compounds indicates the emergence of these materials in the environment, via the refinery waste disposal, and also in the disaster with oil spills. This is because at neutral or alkaline pH, naphthenic acids are soluble in water, as naphthenates, and have mobility in surface waters contaminated with oil (Woo et al., 2009).

The nature of the corrosion process of naphthenic acids depends on the location in the refining system. Furnace tubes, transmission lines, tower packed beds, pumps, valves, and clamps are all susceptible to this corrosion. Factors affecting the corrosion of naphthenic acids are sulfur compounds, operating temperature (corrosion increases with increasing temperature), fluid velocity, type of alloy, and type of naphthenic acid (Jalayer et al., 2013).

Naphthenic acids present in crude oil create corrosion problems, increase formation of emulsion, reduce the quality of oil, and deactivate the catalysts (Wu et al., 2019).

Merlin et al. (2007), in a study by sampling the Athabasca River from upstream and downstream and the oil development area found the concentrations of naphthenic acids in the river to be less than 1 mg/L and in the aquifers near the surface, less than 4 mg/L and in the base water table it was 55 mg/L and in waste ponds it was 110 mg/L on average.

The development of oil sands naphthenic acid resistance to biodegradation by indigenous microorganisms inhabiting tailings ponds has led to the exploration of more aggressive treatment regimens. Chemical oxidation with ozone to generate naphthenic acids against subsequent biodegradation has been shown to significantly improve treatment (Martin et al., 2010; Wang et al., 2013; Hwang et al., 2013).

Bovine bone activated charcoal is an attractive adsorbent with the potential to be used for naphthenic acid removal by petrochemical industries and fuel distribution companies and it is a viable, cheap in relation to its acquisition price and with possibility of regeneration option (Santos et al. 2020).

Balaberda et al. (2021), for the first time, a study was conducted to persulfate oxidation coupled to biodegradation for naphthenic acid remediation. This study has demonstrated the

potential of different doses of un-activated and activated persulfate coupled with biodegradation as an efficient treatment strategy to degrade Merichem naphthenic acids and reduce toxicity.

Identification of the naphthenic acid in oil

The components which form naphthenic acids were identified in 1955, and in this work, two acids with 10 carbon atoms other than fatty acids were identified (Clemente et al. 2004).

According to Clemente et al. (2004), other studies have revealed that in several samples of crude oil which were collected from around the world, there was up to 5% naphthenic acids. Besides, these studies established that concentrations and compounds of the naphthenic acid were originally related to the oil; therefore, low amount of naphthenic acids in oil makes it essential to utilize more steps before merging or extracting to eliminate adequate amounts for future analysis. At present, a method is available for identifying or determining the number of acids and analytical methods which are used counteract with acids, as a group or sub-groups, based on the N and Z distribution (number of carbon and ring).

Currently, most refineries use the total number of acids (TAN) as a criterion for crude measurement during the selection, evaluation, and processing of naphthenic acids (Chakravarthy et al., 2016).

Naphthenic acids are known as the most corrosive agents in acidic crude oil although they show less than 3% of the weight. Other methods have been suggested in the effort to eliminate naphthenic acids from oil; however, their utilization in the petrochemical industry is still a challenge (Dias et al., 2015).

Although naphthenic acid separation from hydrocarbon fractions is a rather simple process, crude oil extraction is impossible due to the low amount of acids in oil, the large volume of fluids used, and the frequency of other extracted caustic materials. The low solubility of naphthenate soaps with high molecular weight and the propensity of sodium naphthenate emulsion to direct retrieval of naphthenic acids from crude oil also cause difficulty. Although naphthenic acids can be eliminated from crude oil and heavy sectors through reaction with sodium hydroxide (NaOH) before and during distillation, these acids are probably unusable. Usually, naphthenic acids are acquired by caustic extraction of oil distillates with boiling temperature between 200° and 370° C. An ongoing process for the removal of naphthenic acids from refinery streams has been developed with caustic washing. The caustic extraction removes other acidic elements of the oil section as well, such as phenol and cresol (cresylic acid), mercaptans, and thiophenols. Besides decreasing corrosion in the refinery, to increase the quality of burning, stability of storage, and smell of white oil fuel and final diesel, caustic washing is essential (Brient et al., 2000).

It is reported that metallic oxides solutions, such as aluminum and magnesium oxides, have a high absorption capacity, and are able to eliminate more than 95% of sodium materials in a primary liquid hydrocarbon at 30-80 °C. Removing naphthenic acid from acidic solutions which are dissolved in dodecane by the use of decarboxylation process and calcined MgO as a catalyst led to 100% elimination of naphthenic acids from acidic solutions. Although it was a modeling work, it would be encouraging if we use it in the real system and the heavy crude oil (Adams et al., 2019).

According to Shah et al. (2014) a detailed de-acidification study at different temperatures and different ionic liquid/model oil was performed and the content of naphthenic acid before and after extraction was calculated (Figure 2).

In studies on refinery processes and corrosion related to naphthenic acids in heavy crude oil, various factors such as temperature, time, and pressure were investigated in experiments to observe their effect on reducing TAN in heavy crude oil. One of the important factors examined was temperature, the main factor in reducing TAN, because the increase from 300° to 400° C led to a reduction of TAN from 96.9 to 56. Other factors like pressure had a little effect on the

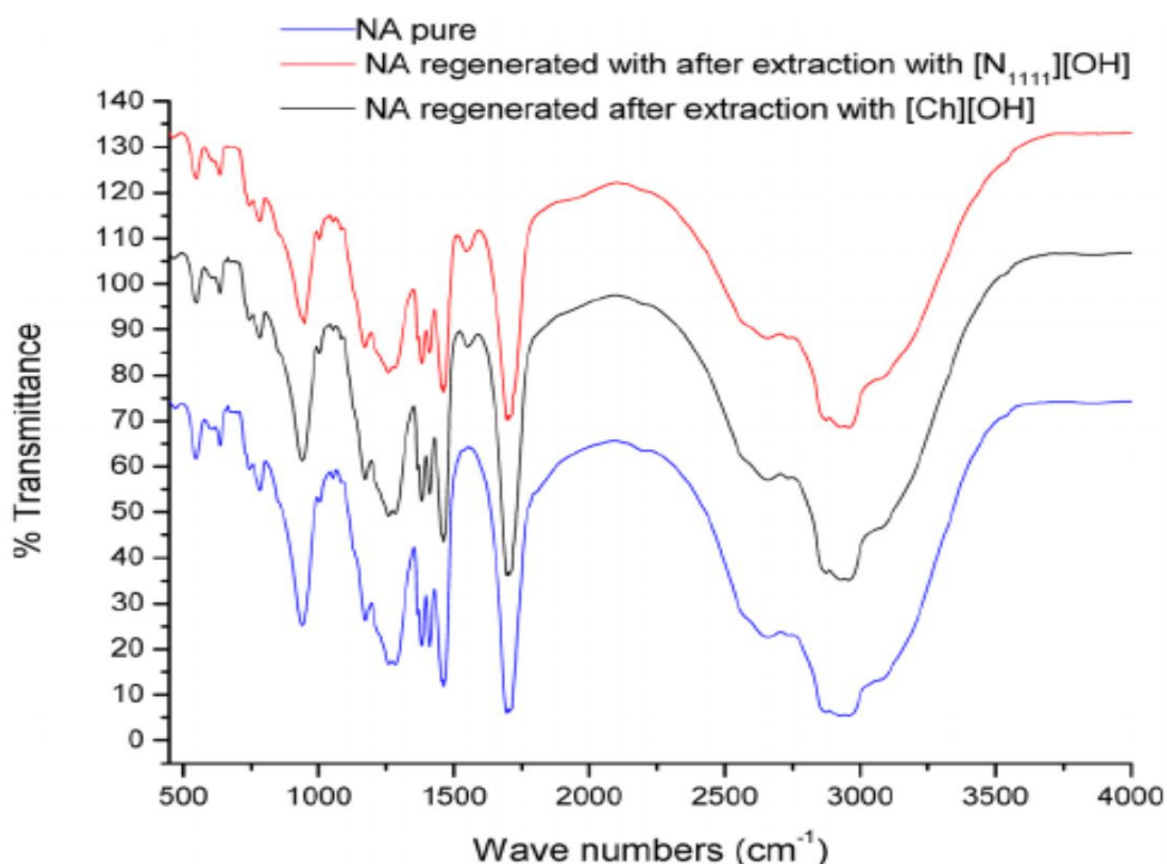


Fig. 2. FTIR spectra of pure and regenerated naphthenic acids after extraction (Shah et al., 2014).

reduction of TAN. The above-mentioned conditions are good, because they allow to perform the process designed for TAN-reduction operations with a low-cost budget (Khan et al., 2016).

Recently, nanotechnology is exposed as the most recent technology that can be used in decreasing TAN in the solutions. The synthesized nanoparticles, Se334, Fe₃O₄/SiO₂, Fe₃O₄/SiO₂ NH₂/C18, amino acid function type, Fourier transform infrared spectroscopy (FTIR) spectrum, and UV-visible spectrophotometer showed that no other crude oil component was removed. This study has obtained a significant success by achieving a 92% reduction in TAN (Simonsen et al., 2019).

In a test that was carried out on the naphthenic acid (CAS 1338-24-5), the parts of the naphthenic acid were dissolved in water and analyzed by the FTIR (Jivraj et al., 1991); then 100 mg/L loading solution of naphthenic acids was mixed and during 72 hours after solution was sampled. Solution concentration reached to 88.1 mg/L and the water pH was controlled at 7.5. The temperature was set at the laboratory environment condition (~20° C) (ABC Laboratories Inc., 2009).

Phagocyte-based multi-media modeling can provide initial data about the chemicals' relative distribution in selected environments (such as air, water, soil, sediment, and suspended sediment). Modeling findings demonstrate that when naphthenic acids release to environments connect to the soil and sediments, and negligible parts are divided into air, water, or habitat. However, all naphthenic acids are not made of the same chemical components, and naphthenic acid compounds with low molecular weight, if present, are expected to be partially divided into the water depending on their pKa and water pH (US Environmental Protection Agency, 2012).

According to Campos et al. (2006) and Seifert et al. (1969), extraction using alkaline solutions, free column chromatography, high-performance LC (HPLC) with modified ion chromatography, and chromatography are very important to reach to the oil and acid sector.

Recently, interest in the chemical properties of naphthenic acids and the acidic parts of crude oils has increased because of the problems imposed on oil refinery equipment by these components. Mainly, we can find naphthenic acids in low-maturity heavy crude oil. They can be acquired from crude oils via extraction methods including liquid-liquid extraction with alkaline solutions and solid-liquid extraction, or ion exchange chromatography (Colati et al., 2013).

The developed HF-LPME method was suitable for the extraction of polar compounds such as naphthenic acids from produced water. In addition, HF-LPME was shown to be more environmentally friendly by using less solvents and generating less waste compared to the standard LLE method. Low detection and quantitation limits were successfully attained, indicating that the HF-LPME and GC- FT-Orbitrap MS method can be used for simultaneous qualification and quantitation of complex samples in which the analytes are in low concentration (Aguiar Porto et al., 2021).

Methods for the analysis of naphthenic acids

Santesteavan et al. (2008), explain that petrochemical companies use hydrogen and carbon nuclear magnetic resonance spectroscopy (H-NMR and C-NMR), FTIR, and MS for the acid sectors.

Samanipour et al. (2019), in a study for partial retrieval and distribution of naphthenic acids in a sample of produced water used three methods of liquid-liquid extraction, solid-phase extraction (SPE) using hydrophilic lipophilic balanced (HLB) cartridges, and the combined method of ENV+ and C8 cartridges for evaluation. The results of statistical analysis indicated that the ENV method provided a perfect representation of the naphthenic acids' chemical diversity.

There is a wide range of methods for analyzing the total naphthenic acids. However, laboratory studies are necessary for comparing their accuracy and precision for normal analysis. Recent development in high and medium-resolution MS, with comprehensive MS techniques subsequent to a multi-dimensional chromatography or ion mobility spectrometry (IMS) led to the production of monocarboxylic naphthenic acids as well as a great range of other species including humics (Headley et al., 2013).

Wang and Kasperski (2010), in a paper presented a useful HPLC-MS method for the naphthenic acids analysis at pH of 8.1 in water. Inorganic salts were separated from the sample matrix using a direct HPLC column. They used FTIR and GC for ease of application of methods for the detection of naphthenic acid oil phase which are commonly used to detect naphthenic acids in tailings pond water. They have claimed that the FTIR usually overestimates the concentration of naphthenic acids.

Chakravarthy et al. (2016), provided a FTIR method to determine the naphthenic acids by utilizing a liquid cell in changing path length with calcium fluoride windows. Two-photon absorption band ranging from 1680 to 1800 CM^{-1} was seen during spectral measurement, and because of the production of monomer and dimer forms of carbonyl (CO) carboxylic acids, both are considered for determining the quantity. This method can even be used for volatile crude oil which cannot be measured. Thermal decomposition, an instance of non-transistor malicious methods, has demonstrated that the reduction of heavy crude oil acidity is ineffective. Often high temperature (above 400° C) is used. This heat crack creates heavy crude oil, which leads to the formation of coke.

It has been shown that thermal breakdown which is an instance of non-catalytic destructive techniques, is ineffective in reducing the acidity of heavy crude oil. Often, high temperature (>400°C) is applied which causes the thermal cracking of heavy crude oil, leading to production

of coke. As an option to this method, catalytic decarboxylation process has been applied to remove naphthenic acids from heavy crude oil. On the other hand, the polymeric compounds that show the fundamental features can be used to neutralize the naphthenic acids (Adams et al., 2019).

Tomczyk et al. (2001), identified 40% of acid compounds using the liquid-liquid technique, which only 10% of oxygen atoms present in the identified structure were ordinary carboxylic acids, and the results of this study showed that the acidic components of oil were revealed as a consequence of the biomass biodegradation by the microorganisms.

Researchers in the oil and gas industry have worked on various methods for removing naphthenic acids from crude oil. It is observed that from all the available physical and chemical methods, the methods based on catalyst are effective and their efficiency depends on the temperature of the catalyst calcination and also the catalyst level (Adams et al., 2019).

According to Qian et al. (2001), the MS method for evaluating the acidic sector obtained from the SPE of crude oil has identified the existence of acids which their N varies from 15 to 55 and Z from -2 to -12, as well as the existence of aromatic acids which have a maximum of 3 rings and structures which have more than two oxygen atoms, before it confirms the complexity degree of the acidic part of crude oil and reveals the phenols and other carboxylic acids prevalence.

The pKa of naphthenic acid from crude oil is 4.9. The partition coefficient logarithm changes linearly in comparison to the carbon number in molecules of naphthenic acid. Apparently, naphthenic acids with three rings are more hydrophilic than one or two-ring acids. We did not find any logical explanation for this. By calculating water dissociation and the separation of undissolved acid, a model was provided for the total concentration of acid in water. Experiments were performed with the help of GC-MS on synthetic naphthenic acids; the model showed and described the test points at low pH. There was a deviation between the model and the concentrations determined experimentally at higher pH. This has been suggested to be because of the formation of normal and inverse micelles (Havre et al., 2007).

GC specifically targets naphthenic acids and, together with MS, makes it possible to describe mixtures of naphthenic acids. Nevertheless, while low-resolution GC-MS is widely available and used in most cases, it must be acknowledged that this method is susceptible to incorrect classification and false-positive data (Brown and Ulrich., 2015a).

One of the important methods of refining crude oil is hydrogenation. It can saturate double bonds, increase hydrocarbon efficiency, reduce gas, bitumen, and gas formation, and decrease nitrogen and sulfur-containing compounds. Moreover, hydrogenation can remove compounds which contain oxygen such as naphthenic acids. Le Roy (1960). Asserted that the molybdenum oxide-silica alumina catalyst was effective in the naphthenic acids removal through hydrogenation (Wu et al., 2019).

Other analytical techniques have been developed for separation of naphthenic acids from oil, which, generally, can be evaluated in two ways. The first is the carboxyl group removal through esterification, hydrogenation, or thermal decomposition reactions, while the second includes the naphthenic acids removal from petroleum by liquid-liquid extraction (applying an alkaline solution with alcohol and ammonia), adsorption, separation of membrane, and electrostatic separation (Dias et al., 2015).

The naphthenic acid concentration in crude oil is usually calculated by titration with KOH for neutralization number by applying potentiometric (ASTM D664) or colorimetric (ASTM D974) methods. Similar methods are applied for measuring the number of crude or refined naphthenic acids after that were recovered from the oil sector. Naphthenic acids are a very complex combination of hundreds of compounds that is impossible to separate them as individual constituents, even with the use of high-resolution GC. Advances in gathering data on the naphthenic acids structure have lagged due to this complexity. In addition, infrared spectroscopy cannot clearly distinguish fatty acids from naphthenic acids (Brient et al., 2000).

According to Gruber et al. (2009), the most suitable method for gathering data about identification of the inorganic naphthenic acids structure is GC with MS (GC/MS), but this method has a drawback, because electronic ionization (EI) results in compounds' over-fragmentation which produces complex spectra that give little information about these acids' structure and molecular weight.

The most common and cost-effective way to separate naphthenic acids is to wash the diesel/kerosene sections by the use of alkali metals aqueous solution and then, acidification with mineral acids in order to retrieve naphthenic acid which is insoluble. Moreover, solvent adsorption and extraction have been utilized to reduce crude oils acidity (Shah et al., 2015).

The adsorption process to remove naphthenic acids from heavy crude oil can be applied at low temperatures for distillation sections. For the pretreatment of heavy oil before the adsorption process, strong bases including alkali metal hydroxides are often used. However, alkali metal hydroxides not only create an alkaline environment but also neutralize naphthenic acid compounds in heavy crude oil (Adams et al., 2019).

Photocatalysis provides a process to reduce the environmental hazards of naphthenic acids in refinery effluents. Photocatalytic degradation of naphthenic acids using the fixed-film TiO₂ under sunlight achieved an effective rate of removal of Fluka nanoparticles, which indicates the potential of using this technology to reduce the environmental hazards associated with naphthenic acids (McQueen et al., 2016).

Damasceno et al. (2014) analyzed a commercial sample of naphthenic acid purchased from Sigma Company using three methods: GC-MS, ESI-MS, and GC/time-of-flight (TOF)-MS. Due to fewer informative needs, ESI-MS is a suitable candidate for fast sample scanning that provides rapid analysis and can help control the quality of petrochemical samples.

A study was conducted on the concentration of acidity in Nowruz oil field sections, which currently has the highest acid number in Iran's oil fields, based on the carbon number. The results showed that further reduction of acid number in crude oil was not possible after separation of the aqueous phase, because the rest of the acidic compounds is related to naphthenic acids which are not easily separated by physical methods and are distributed in mid distillation and oil fractions (Pasban and Miran Beigi., 2012).

Simair et al. (2021), showed in a study that the treatment of oil sands water affected by process was possible by wetland treatment systems constructed and their design could be optimized to improve treatment. While all wetland treatment systems are built to improve water quality, oyster-shell-bedded wetlands have the best treatment, as the evidence shows. The design of each system with distinct operating conditions indicates that special factors of design, such as type of plant, pathway of flow, depth of water, and aeration can be changed, so that optimal conditions for the treatment of naphthenic acid compounds are facilitated.

To confirm that some of the compounds of specific naphthenic acids in wetlands are obtained from industrial or natural inputs, analysis of compounds by the conservative tracer (Hoeit et al., 2020) or the use of isotope geochemical methods (Ahad et al., 2020) will provide very useful information. Future studies may assess the time and seasonal dynamics of some of the naphthenic acid compounds in regional wetlands. These are dynamic ecosystems and abundant evidence exists about the effect of wetlands on some naphthenic acid compounds over time (Ajaro et al., 2018).

The presence of surfactants in water injected into oil reservoirs can change the mass transfer conditions of naphthenic acids. With the increase of divalent ions in the composition of water in contact with crude oil, especially sulfate ions, the dissolution of naphthenic acids in water increases as the pH decreases from 7.47 to 4.05. In fact, for the effectiveness of sulfate ions, the presence of a divalent cation such as magnesium is essential in the composition of water (Mokhtari and Ayatollahi., 2019).

An absolute analytical method for the determination of NA currently does not exist because

there is no method that can separate every NA compound (Scott et al., 2008).

Furthermore, measurements made even with the best available methods are not accurate, as commercial NA mixtures or individual compounds must be used for calibration. Therefore, the results should be considered semi-quantitative at best (Martin et al., 2008).

Scott et al. (2005) found that using a commercial mixture for calibration resulted in an unreliable measurement of a different commercial mixture, suggesting that significant differences exist even among commercially available NA mixtures (Hindle et al., 2013; Lu et al., 2013).

Strong alkaline imidazolium carbonate IL aqueous solution could effectively remove Naphthenic acid from high acid model oil. Temperature was an essential factor in the deacidification process, and the removal percentage of Naphthenic acid showed maximum with the increase of temperature (Geng et al., 2022).

CONCLUSION

Naphthenic acids are a group of polar organic carboxylic acids existing in crude oil in a natural way. They are cycloaliphatic carboxylic acids which have 10 to 16 carbons, which have gained importance since the early twentieth century because of corrosion in oil refineries. Naphthenic acids are the most important environmental pollutants caused by oil extraction from oil sands reserves. Heavy crude oil which has high concentration of naphthenic acids is categorized as oil with poor quality which is sold at lower prices. The high concentrations of naphthenic acids in crude oil reduces the life of the apparatus which is utilized in the exploration and refinement processes as a result of corrosion. Naphthenic acids are the main cause of high acidity of crude oil. In temperature higher than 230° C, the corrosion caused by naphthenic acids increases in distillation units.

Naphthenic acids are weaker acids compared to carboxylic acids with low molecular weight like acetic acid; however, they are stronger than phenol and cresylic acid. They are viscous liquids that are more likely to have a pale yellow color in the distillation process, and may even go to amber hue. They have boiling points ranging from +140° to 370° C. Naphthenic acids are considered weak acids with a pKa value of about 5 to 6. Therefore, alkaline solutions increase the solubility of naphthenic acids and acidic solutions reduce their solubility. Due to their desire to precipitate out of a water solution, they are a serious challenge for the oil industry. Experiments indicate that the amount of sediment formed increases by increasing the pH of salt water and the concentration of acid and calcium ions. More than two-thirds of the produced naphthenic acid is applied to produce metal salts; the largest part of it is used for copper naphthenate which is used in the wood preserving industry. The naphthenic acid market is expanding in the field of wood and textile preservatives. Another commercial use of naphthenic acid is in the tire industry, in which cobalt naphthenate is utilized as a bonding enhancer. Other applications of naphthenic acids are in concrete admixtures, engine lubricating oil, and asphalt coating. A study on three naphthenic acid models showed that from among pH, temperature, and DOC, the most effective factor on microbial degradation was temperature. Naphthenic acids are relatively soluble in water (50 mg/L). They are unlikely to remain in the water column for a long time, and a high percentage of them precipitate. They are suspected as endocrine disruptive materials, but are not mutagenic or carcinogenic.

Among the important factors examined, the temperature was the main cause of TAN decrease, because the increase from 300° to 400° C led to a decrease in TAN from 96.9 to 56. Other factors like pressure had little effect on TAN reduction. Naphthenic acids are mainly found in immature heavy crude oil. The most popular methods for the identification and analysis of naphthenic acids are LC, GC, liquid-liquid extraction, FTIR, and SPE. FTIR usually overestimates the concentration of naphthenic acids. Hydrogenation can remove compounds containing oxygen such as naphthenic acids. With the increase of divalent ions in the composition of water in

contact with crude oil, especially sulfate ions, the dissolution of naphthenic acids in water increases, reducing the pH from 7.47 to 4.05.

ESI-MS is a suitable candidate for fast scanning of sample that offers rapid analysis and can help control the quality of petrochemical samples. Researchers in the oil and gas industry have worked on a variety of methods to remove naphthenic acids from crude oil, and it has been observed that from the recent available physical and chemical techniques, methods based on catalyst are the most efficient methods.

Since the commercial market for naphthenic acids is growing and the technology of extracting it from oil is exclusive and confidential, in the future, we can focus on the techniques of extracting naphthenic acids for commercialization and also studies can be performed considering the problem of corrosion in transmission pipes caused by naphthenic acids, which is of great importance to refineries.

An important point to note is that naphthenic acids are mostly found in water produced from oil in the extraction stage and sometimes enter the oceans and nature directly, regardless of the specific conditions of purification and separation of naphthenic acids. Unfortunately, there is no study performed to determine the behavior of this substance in water, such as determining the diffusion and transfer coefficients, examining different models of diffusion and transfer in the seas and oceans, and determining its fate.

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