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Determination of Naphthenic Acids Concentration and Total Acidity and Investigation of the Impact of Their Nanoemulsions Structure on the Design of Oil Refinery

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Abstract

Naphthenic acids and TAN are one of the ever-increasing crucial problems in oil, shale oil and sand oil industry and also environment protection. Furtherer, they increases the corrosion of some parts of a refinery and transport pipelines and also can create nanoemulsions and make complicated the refining process especially in desalters. To prevent these problems it is important to first obtain a basic knowledge about the distribution/structure of Naphthenic acids and their relationship with TAN. This might be useful for troubleshooting of probable problems when the feed of refinery changes. In the present work, two fractions of Soroush-Norowz blend crude oil were analyzed to obtain their naphthenic acids concentration and TAN. At the second step, these two fractions were physically to sub-fractions by 25 °C intervals. After that, their naphthenic acids concentration and TAN was determined to obtain a detailed view about the distribution of naphthenic acids and TAN of each sub-fraction. In addition, the obtained results gave us a view point about the overall molecular structure of naphthenic acids presents in the Soroush-Norowz blend crude oil and can guide us toward better understanding of chemical structure of mentioned crude oil and consequently better designing of oil refinery in order to minimize the corrosion and also upper the performance of some special units such as desalters.

Keywords: Nanoemulsion; Naphthenic Acids; Crude Oil; Total Acid Number

1. Introduction

Naphthenic acids are one of the most important environmental pollutants releases from oil industry and specially refining of oil sand, bitumen and shale oil. Among receptors in the nature, i.e. air, soil and water, the last one is the most vulnerable part which can pollute by naphthenic acids [1-3]. From pure chemistry point of view, naphthenic acids are alkyl-substituted cycloaliphatic carboxylic acids, containing

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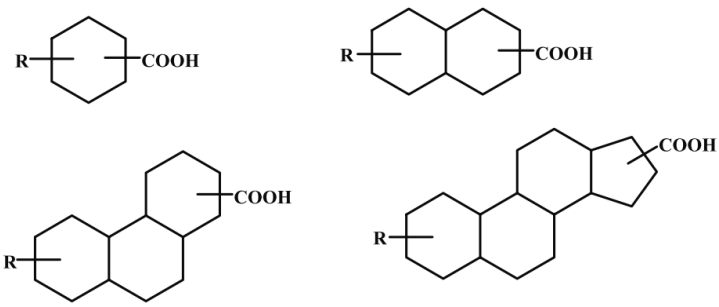
cyclopentane and cyclohexane rings and small amounts of acyclic acids and aromatic acids. They can be describe by a general formula of $C_nH_{(2n+Z)}O_2$, where n indicates the carbon number and Z is zero or a negative, even integer that specifies the hydrogen deficiency resulting from ring formation.



These compounds, Naphthenic acids (NAs), are also thought to have originated from aerobic microbial biodegradation of petroleum hydrocarbons in reservoir (i.e., in situ) (Meredith et al. 2000) and they are found everywhere in petroleum deposits [4-6]. These compounds can enter surface waters through natural discharge of groundwater and erosion of riverbank oil deposits and also release of reclaimed oil sands pit lake water. Accepted quantification methods include Fourier transform infrared (FTIR) spectroscopy and high-performance liquid chromatography (HPLC) [5-7]. Characterization of NAs by mass spectrometry (MS) and gas chromatography-electron impact mass spectrometry (GC-MS) can provide qualitative data useful for comparing NAs from different sources. However, from industry point of view, these compounds distributed through all the fractions of distillation column in oil refinery and can make a severe corrosion in pipelines, towers and storage tanks during high temperature operations in petroleum refinery including the lube plant and desulphurization units. Furthermore, formic, acetic, propionic and butyric, which are formed by the thermal degradation of naphthenic acids, attack the process equipment [1, 8-10]. Severe naphthenic acid corrosion was seen in atmospheric and vacuum towers of distillation column at temperature 230°C to 450°C and the damage was in the form of pitting in furnace tubes and transfer lines, Side cut piping, Exchangers [7-10]. Operation conditions such as high velocity, high TAN, physical state of feed, can also increase corrosion by naphthenic acids. There are several pathways to mitigate naphthenic acid corrosion, such as persistent materials for equipment, blending, topping, neutralization and chemical treatment using corrosion inhibitors. However, they can be removed at the source of crude oil via decarboxilation, extraction and adsorption. These methods were developed by many famous oil companies such as ExxonMobil, BP and UOP in order to prevent discount of oil price originated from naphthenic acid concentration [1-3,4-7].

Naphthenic acid content in the different crude oils may vary in the range of 0-4%. Earlier naphthenic acids were readily accepted chiefly in the form of metal soaps, for use as driers, lubricant additives and fungicides [10-11]. Iran is one of the main oil production countries. The crude oils of Iran are almost sour and acidity of some of them is higher than the traditional limitations in the market. One of the high TAN crude oils is Soroush-Norowz blend oil field. In order to evaluate the corrosion of this crude oil in the industry, it is vital to obtain appropriate information about distribution of naphthenic acids in the distillation tower.

2. Experimental

All chemicals were purchased from Merck and used as received without further purification. In order to obtain oil fractions, crude oil was distilled via modified ASTM 2789 (TBP distillation) and fractions were collected in 25 °C intervals. Then, fractions from 125 °C up to 385 °C were conducted to proper analytical technique, i.e. potentiometric titration via UOP-565 method.

Sodium hydroxide (analytical grade) was weighed and solved in isopropanol (99.9 %) to obtain 0.01 normal titration solvent. The true normality of this titrant was obtained by potassium hydrogen phthalate solution of known concentration. 150 grams and 95 grams of sodium chloride and cooper sulfate, respectively, was prepared and used as oxidant of thiols. 100 mL of this solution and 70 mL of petroleum

fraction were added together and stirred vigorously for 30 minutes. Then the upper part (petroleum fraction) was decanted and filtered through a whatman No. 4 filter paper to obtain a clear solution. After that, this solution was titrated by standardized sodium hydroxide solution to obtain the concentration of naphthenic acids in the corresponding fraction.

3. Results and Discussion

At first step both of kerosene and diesel fractions of Sorush-Norouz blend crude oil were analyzed. The results were given in Table 1.

Table 1. Naphthenic acid and TAN of Sorush-Norouz blend crude oil in mg KOH/gr Sample and ppmw.

Fraction type	Total Acidity (mg KOH/gr Sample)	Naphthenic acids (mg KOH/gr Sample)	Naphthenic acids (ppmw)
Kerosene	0.126	0.137	**380**
Diesel	0.451	0.385	**2050**

As can be seen, the concentration of naphthenic acid and TAN in kerosene is very lower than diesel. It is generally known that naphthenic acid and TAN is higher in kerosene fraction than diesel fraction. In order to clear this phenomenon it was decided to obtain sub-fractions (cut points) via 25 °C intervals to analyze them in term of naphthenic acid and TAN.

All the obtained sub- fractions of Soroush-Norouz crude oil were titrated and both their naphthenic acids (NAs) concentration and total acid Number (TAN) were measured by titration. The results were given in Table 2. The graphical depiction of these results was also displayed in Figure 1 (Naphthenic acid) and Figure 2 (TAN).

It can be seen that as the cut point increases naphthenic acid and TAN remains almost constant. This trend is seen up to 250 °C. But after this cut point concentration of naphthenic acid and TAN suddenly increases. Despite its name, kerosene fraction has very low concentrations of both naphthenic acid and TAN in comparison with Diesel fraction.

On the other hand, naphthenic acid concentration is almost equal with TAN. Once can suggests that the major molecular structure of carboxylic acids have not long chain structure but instead they have formed from fused and/or branched aromatic/cyclic rings. This suggestion comes from the fact that if the long chain structure presence in each sub fraction, they can form reverse nano-reversemicelles and entrap the water/inorganic acids in their interior hydrophilic core and the difference between the naphthenic acid concentration and TAN is not negligible.

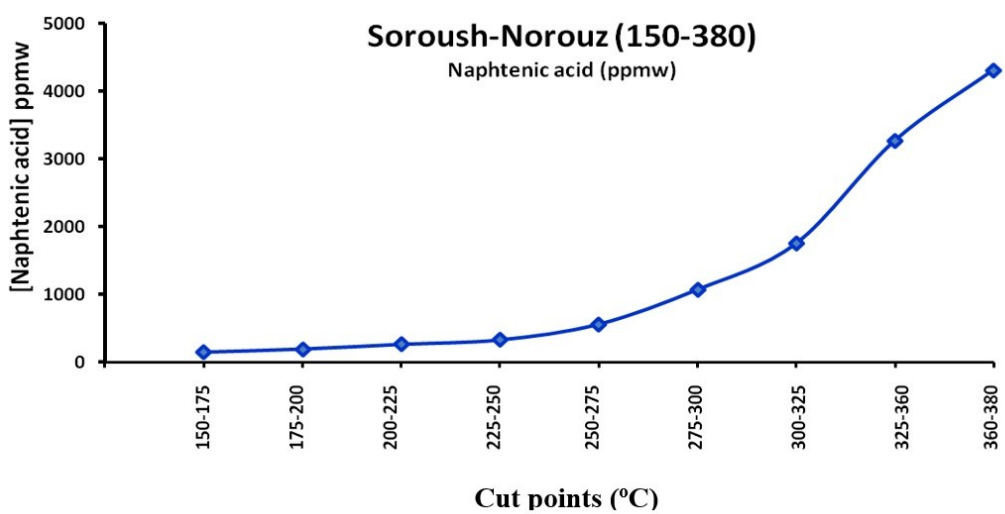


Figure 1. Naphthenic acid concentration of Soroush-Norouz blend cut points via 25 °C intervals.

Table 2. Naphthenic acids concentration and TAN of cut points of Soroush-Norouz crude oil in *mg KOH/g sample* and *ppmw*.

Sub-fraction cut point (°C)	Naphthenic acids (mg KOH/g sample)	Naphthenic acids (ppmw)
150-175	0.054	151
175-200	0.075	197
200-225	0.099	266
225-250	0.112	332
250-275	0.165	563
275-300	0.277	1075
300-325	0.359	1756
325-360	0.455	3275
360-380	0.60	4318

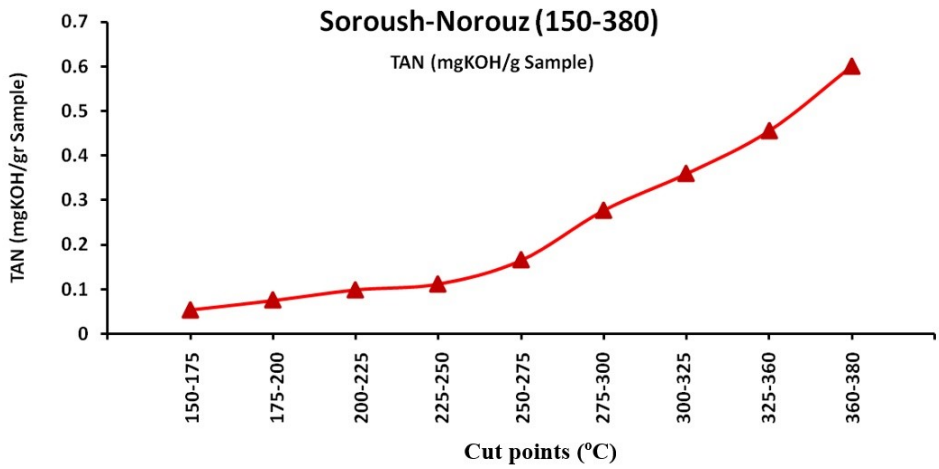


Figure 2. TAN of Soroush-Norouz blend cut points via 25 °C intervals.

Furthermore, from engineering point of view, the micellar (nanoemulsion) structure of long chain naphthenic acids can cause difficulties for refineries and surface overhead facility systems, namely desalters and coalescers for the reason that it is more hard to extract (breaking of emulsions) the water from the well-structured nanomicelles of long chain naphthenic acids rather than weekly-formed nanomicelles of cyclic/short chain naphthenic acids. Presence of water in kerosene is very important, because it is the main source of variety jet fuels such as 100LL, ATK, JET-A1, JP4 and JP10 for use in commercial and fighter aircrafts.

4. Conclusion

From this work, ones can provide a measure of concentration of naphthenic acids and TAN of sub-fractions of a crude oil to be exported and/or refined from economic view point. Additionally, they can obtain a view from the overall molecular structure of naphthenic acids and the nanomicelles (nanoemulsions) that might present in the oil. On the other hand, chemical engineers can estimate the simplicity or hardness of the entrapped water and subsequently acidity and salt content of a crude oil to evaluate the performance of designed desalters and so redesigned or optimize its structure. More ever, refineries can troubleshoot the high concentration of naphthenic acids and TAN in case of probable change of feed stream in special cases such as when some oil suppliers cannot provide the specific crude oil for which the refinery is first and foremost designed. Finally, presence of naphthenic acids causes adsorption/entrapment of water, inorganic and ionic pollutants/additives within their performed nanoemulsion structure in the fuel. This phenomenon is crucial in the production, storage and performance of commercial and military grade jet fuels.

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