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Acidity removal of Iranian heavy crude oils by nanofluid demulsifier: An experimental investigation

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Abstract

The scope of this study is to propose a new and convenient method for reduction of acidity of heavy crude oils to less than 1 mg KOH/g of sample. For this purpose, acidity of several Iranian heavy crude oils has been investigated. Is this research, two precise methods were developed and the results compared for the acidity reduction of samples based on using nanofluid demulsifiers. In the first technique, after separating the formation water and salt of the samples, the acidity was determined potentiometrically on the treated samples by using trace quantities of a commercial polymer-based nanofluid demulsifier. In the second technique, distillation of crude samples was performed according to ASTM standard procedures and the related fractions were subsequently evaluated for acidity measurements. The results obtained from both separation techniques revealed that the formation water of crude samples is responsible for the presence of salt and some organic acids such as naphthenic acid and its derivatives. Here, the acidity removal techniques are ideally suited for heavy Iranian crude oils with water content between 0.05-20 vol.% and salt between 10-10000 pounds per thousand barrels (ptb).

Keywords: crude oil; nanofluid; demulsifier; acidity removal

1.Introduction

Regarding the difficulties assigned to the corrosion in wellhead, pumps and other process apparatuses, as well as oil pipes and refinery units, protection from corrosion of crude oil acidity is necessary. On the other hand, high acidity number results to inexpensive crude oil and has direct relation to income of oil companies.

The recognized acids in crude oil are including the naphthenic compounds, thiols, phenols, thiophenes and carboxylic acids. Total acid number (TAN) of crude oil obtains from these compounds except than hydrogen sulfide, and called them naphthenic acids. According to standard definition, the amount of potassium hydroxide in milligram that is needed to neutralize acidic compounds in a gram of sample crude is TAN [1-3].

Range of TAN for different crude oils could vary between 0.1 to 16.2 mgr of potassium hydroxide/ g of sample. Also, its concentration depends on the reservoir rocks and field that crude is produced. Crude oil with TAN between 0.6-1 is classified as medium, less than 0.6 as low and greater than 1 as high acid number [4].

Most of the refineries in the world are designed for the crude oils with total acid number less than 0.5. Only some of the refineries in north of US and China are able to process the oils with high acidity number. Production of crude oils with high acid number in north of US, north of Europe and east of Asia was about

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3955000 barrel per day in 2004.
Refiners have faced with the problem due to corrosion of naphthenic acids, since many years ago. Rate of naphthenic acids corrosion on process apparatus is varied at different temperatures. In addition, the type of corrosion varies by changing the concentration of naphthenic acid. Control of corrosion in refineries has been achieved by introducing anti-corrosion materials or by reinforcement of apparatuses to resist against corrosive materials. Corrosion due to naphthenic acid take place at 230-400 °C and their effects on process instrument are severe at 270-280 °C [5].
Acidity number could be reduced by neutralization of formation acids in crude oil with water- based alkaline solutions. This method results to reduction of sufficiency of desalting and dehydration systems in crude oil refining installation because of generation of stable emulsion between water and oil hydrocarbons.
Recent activities have been done for reduction of acid compounds in crude oil including cracking of acid molecules and chemical adsorption, but these solutions are not applicable in industry and remained in research scale. According to Eq. 1, catalytic cracking converts naphthenic acids to carbon dioxide and hydrocarbons [6-10]:

$$\mathrm{RCOOH} \rightarrow \mathrm{RH} + \mathrm{CO_2} \tag{1}$$

In this research, acidity number of different Iranian heavy crude oils has been studied. Higher distribution of acidity number for these crude oils indicates higher amount of soluble acids in their formation water. Acidity of studied crude oils was different, from 3.5 to 7.6 ml of potassium hydroxide in a gram of sample.

2. Material and Methods

2.1. Materials and Apparatuses

Centrifugal apparatus, rotary evaporator, distillation, potentiometer, memo titrator, de-oiling potstill, and mixer have been utilized in this study. Toluene (99.999%), Isopropanol (99.999%) and Hydrochloric acid (37 wt%), Potassium hydroxide, chloroform (99.999%) and Potassium hydrogen phthalate were obtained from Sigma-Aldrich.

2.2. Calculation Method

Acid number has been calculated according to Eq. 2:

$$\text{Acid Number}\ \left(\text{mg KOH / g Sample}\right) = \frac{(\mathrm{A}-\mathrm{B}) \times \mathrm{N} \times 56.1}{\mathrm{W}} \tag{2}$$

where A is the volume of KOH 0.1 N consumed by the sample, B is the volume of KOH 0.1 N consumed by control solvent, N is the molar concentration of KOH 0.1 N, and W is the weight of crude oil.

2.3. Procedure

Acid number of the crude oil was determined according to the UOP 565 standard [11, 12]. In this standard method, a part of sample is weighted and solved in a solvent such as Toluene, Isopropyl alcohol, or Chloroform. Then, acid number of sample was measured by a potentiometer apparatus that was equipped to glass electrode DG 112. Also, acid number of fractions were determined according to ASTM D664 standard test method that is specialized for determination of fraction's acid number. ASTM D664 is similar to UOP 565, only the titration solvent in ASTM method is 1% distilled water rather than Chloroform [13-15].

2.4. Separation of inorganic acids from heavy crude oils

In this research, formation water of crude oils was removed by evaporation with a rotary evaporator. In this method, crude oil in atmospheric pressure was heated to 130 °C and existing water in crude oils and light hydrocarbons was separated from crudes. Light hydrocarbons and water that was removed from crude oils, was transferred to the freezer for a day. By this method, water was separated from hydrocarbons in the ice crystal form and light hydrocarbons was added to the crude oil again. After that, it was observed that the acid number of crude oils has not been reduced; because dissolved acidic compounds in water has not been removed by evaporation method. In the other hand in this manner loss of light components was existed. So, another method for effective separation of dissolved components in water was designed.

2.5. Reduction of crudes acid number

Firstly, an aliquot of crude oil was weighted and then after addition of proper nano-demulsifier, it was carefully transferred to a medium pressure resistant vessel. Then the vessel was sealed and shaken for 0.5 hr in a shaker apparatus (supplied by Jank & Kunkel model VX8). Then the vessel was placed in a bath thermostated at 150 ^{0}C and for 1 hr. It was simultaneously removed and shaken again for more 0.5 hr and cooled down to the room temperature. 100 mL of crude sample was poured in the centrifuge conical vessel used in ASTM D4007 and the separation was completed by a centrifuge instrument (Hermle ZK446, Carlowitz, supplied by Germany) in different speeds. After separation of water and sediments, the total acid number of the samples was potentiometrically determined.

3. Results and Discussion

In this research different Iranian crude oils were selected to investigate their acid numbers. The main specifications of these crude oils are shown in Table 1. As can be seen in this table, the acid number of selected crude oils are in the range of high acid number.

Table 1: Specification of several Iranian crude oils.

Sample	API Gravity	Salt Content (ptb)	Water Content (Vol%)	Acid Number (mg KOH/g Oil)
Crude oil A	12.7	>7000	20	7.6
Crude oil B	24.8	5800	12	6.2
Crude oil C	27.1	3800	7	3.5
Crude oil D	18.74	4200	10	4.2

3.1. Selection of Demulsifier

In this research, different demulsifiers were selected based on the API gravity, asphaltene content and molecular weight of the crude oils. Best results were obtained from the new class of demulsifiers, Kemelix company. Inherent advantages of this material is low pour point temperature, BTX, chlorinated-free and a green additive. Table 2 shows typical physical properties of this additive. The studies revealed that the separation process carries out via formation of greater droplets of water from emulsioned water by its interaction with nano droplets of the Kemelix demulsifier.

Table 2: Physical properties of demulsifier.

Appearance	Viscouse liquid
Color	Cloudy
Odor	Not detected
Flash point, ^{o}C	120
pH	7-9
Density @ 25^{o}C, g/cm^3	1.049

3.2. Effective parameters in the reduction of acid number

Temperature is one of the most important parameter in the refining technology. The effect of increasing temperature from 25 to 120 ^{0}C on the reduction of dissolved acids in formation water of crude oils was investigated and results have been shown in Figure 1. Acid number of crude oils was decreased by increasing the temperature, as shown in figure 1. The viscosity of crudes decreased at higher temperature and as a result, separation of inorganic and aqueous phases has been facilitated. By increasing the temperature from 100 ^{0}C, the acid number of crudes remain constant and further increase in temperature has no significant effect on the reduction of acid number. The effect of temperature on the acid number of crude oils A and B was more than others.

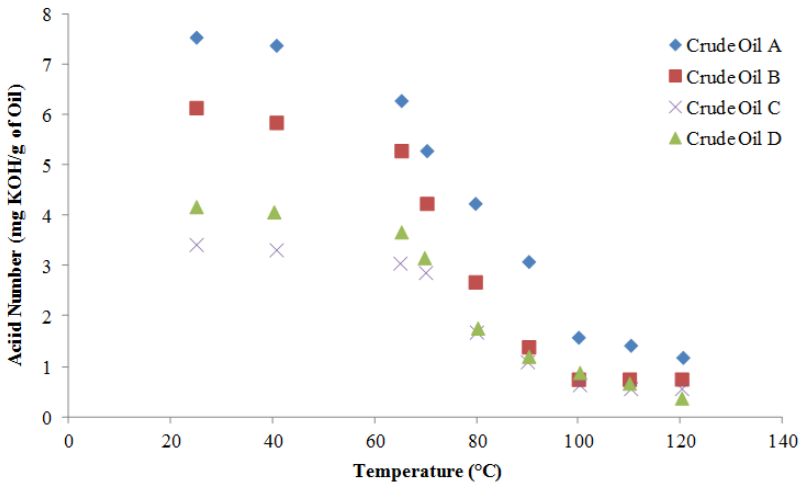

Figure 1: Variations of acidity of Iranian heavy crude oils vs. temperature.

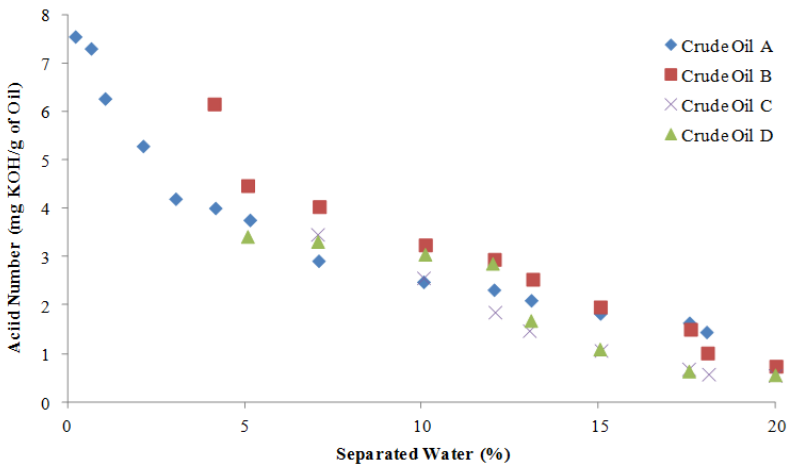

Figure 2: Variations of acidity of Iranian heavy crude oils with separation of formation water.

3.3. Effect of formation water in crude oils

Unlike the first method that formation water was removed in it by a rotary dryer and had no significant effect on the reduction of acid number of crudes, in second method the acid number of hydrocarbon phase was measured and the water content was determined. The results on the studied crudes have been shown in figure 2.

As shown in figure 2, acid number of crudes A and B has been reduced better by reducing the formation water of crudes. The acid number of crude D has been decreased from 4.2 to 0.4 mg KOH/g of sample that is about 10% of before processing. Also, the crude was upgraded from high acid number to low acid number category (figure 2).

3.4. Effect of centrifugation speed on reduction of acid number

In this study the effect of centrifugation speed was investigated further than appropriate demulsifier and selection of temperature. The effect of centrifugation speed on the phase separation and reduction of inorganic acids in hydrocarbon phase has been demonstrated in Figure 3. According to this figure, acid number has been decreased by increasing the centrifugal force (speed) for all of the studied crudes. The results implied that in the speeds above 2500 rpm, the acid number remains constant. Centrifugation speed had linear effect on the acid number of crudes. So, it can be resulted that 2500 rpm is the optimum centrifugation speed for decreasing of crud's acid number.

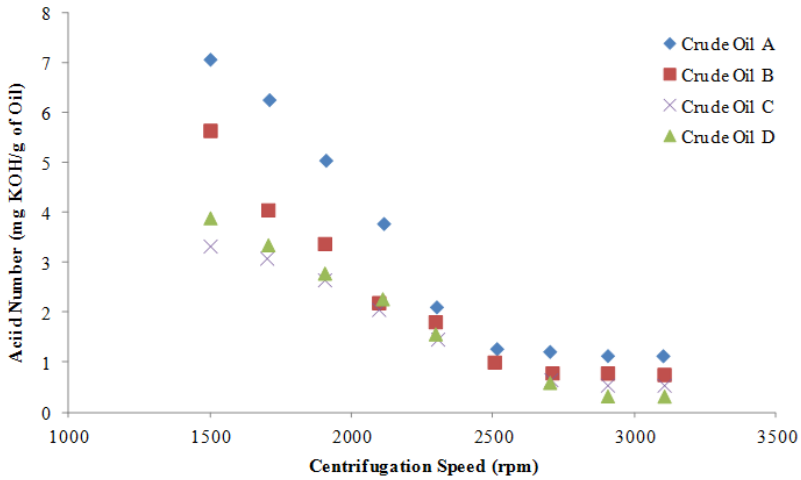

Figure 3: Variations of acidity of Iranian heavy crude oils vs. centrifugation speed.

3.5. Verification of method

The results implied that about 80 to 90% of acidic materials are soluble in formation water of crude oil and were removed from hydrocarbon phase by the method that has been used in this study.

For verification of the mentioned claim, it was assumed that acid number of crude oil became constant due to naphthenic acids in hydrocarbon phase that is not soluble in formation water and cannot be removed by physical method.

By studying figures 1 to 3, it was demonstrated that crude A with acid number of 1.2 after processing had the highest acid number between four crudes. So, crude A was selected for verification of the method.

Firstly, fractions of the crude A were obtained from distillation and separation was performed based on the carbon number. Results have been shown in Table 3. Also, acid number distribution of the fractions has been demonstrated in figure 4.

Table 3: Compositional analysis of crude A.

Carbon No.	Boiling Range of fractions@ 760 mmHg	wt%	Cuml. wt%	Sp.Gr@ 15.56°C/15.56°C	vol%	Cuml. vol%
C2	-----	0.07	0.07	0.3740	0.17	0.17
C3	-----	0.41	0.48	0.5080	0.75	0.93
iC4	-----	0.22	0.70	0.5630	0.36	1.29
nC4	-----	0.16	0.86	0.5878	0.25	1.54
iC5	-----	0.04	0.90	0.6284	0.06	1.60
nC5	15-36.1	0.75	1.65	0.6344	1.10	2.70
C6	36.1-68.7	1.44	3.09	0.6557	2.05	4.75
C7	68.7-98.4	2.30	5.39	0.7175	2.99	7.74
C8	98.4-125.7	2.10	7.49	0.7304	2.68	10.42
C9	125.7-150.8	2.10	9.59	0.7529	2.60	13.02
C10	150.8-174.1	2.20	11.79	0.7731	2.65	15.67
C11	174.1-195.9	2.60	14.39	0.7923	3.06	18.73
C12	195.9-216.3	2.00	16.39	0.7972	2.34	21.07
C13	216.3-235.4	2.00	18.39	0.8072	2.31	23.38
C14	235.4-253.5	1.66	20.05	0.8198	1.89	25.27
C15	253.5-270.6	1.84	21.89	0.8337	2.06	27.33
C16	270.6-286.8	1.89	23.78	0.8465	2.08	29.41
C17	286.8-302.2	1.31	25.09	0.8528	1.43	30.84
C18	302.2-316.7	1.70	26.79	0.8630	1.83	32.67
C19	316.7-330.6	2.10	28.89	0.8701	2.25	34.92
C20+	>343.8	71.11	100	0.9921	63.16	100

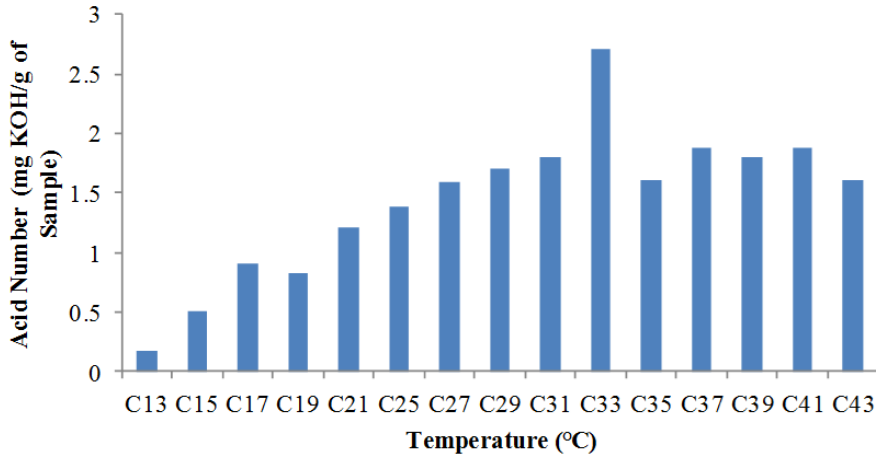

Figure 4: Distribution on acidity of crude A fractions.

The lightest hydrocarbon in crude A was ethane. The separation was continued until carbon number 44 that is equivalent to temperature end in the distillation of crudes (545 °C). Also, weight and mole percent, molecular weight and specific gravity of each fraction was obtained and presented in table 3. After separation of fractions, acid number of them were measured according to ASTM D664.

As shown in figure 4, acid number were increased to higher than 0.5 mg KOH/g of sample for fractions with 15 carbon number and greater, and increasing was continued to higher than 1 for fraction with carbon number greater than 19. The highest acid number was 2.7 for fraction with 33 carbon number. After that, acid number was decreased but it was between 1 and 2 until fraction with 44 carbon number. These results implied that naphthenic acids are available in mid distillation and oil fractions of crude A and could not be separated.

Since the acid number of crudes and fractions are a linear property, summation of product of fraction's acid number with weight percent of them should be in compliance with total acid number of a crude free of water. So, according to table 3 and figure 1, about 85% of crude A with acid number of 1.2 are available in fractions and about 15% of its acid number are in heavy residue. The results verified the claim that most of the acids in heavy crudes are soluble in water.

3. Conclusion

In this research, the acid number, formation water and API gravity of different Iranian crude oils have been investigated. The studies showed that the exited formation water was a major reason for increasing the total acid number of the crude oils. For this purpose, a new technique was developed to solve the problem of separation of formation water and its unfavorable effects on the samples. The results revealed under the optimal conditions such as temperature above 100 °C and centrifugation speed above 2500 rpm the best separation of formation water and salt was quantitatively performed. In this method, after treatment of crude oils by trace quantities of the polymer base demulsifier, the final concentration of acids in crude oil have been reported. The result showed that acid number of heavy crude oils would decrease down to 80% by removing the formation water of the crudes.

In addition, distribution of acid number in fractions of the heavy crude oil based on the carbon number was also investigated. The results demonstrated that further reduction in acidity of crude oil after separating the formation water is not possible, owning to other acidic compounds in crude samples are organic soluble naphthenic acids that could not be remove by physical methods and therefore are distributed in mid distillation and oil fraction of crudes.

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