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REDUCTION OF THE TOTAL ACID NUMBER OF SUDANESEHEAVY CRUDE OIL

Ibrahim Mahmoud[1],* Ahmed Mahjub[2], Babiker Karama Abdalla[3], Gurashi Gasmel seed[4]
[1]Laboratory Supervisor, Petro-Energy E&P Co, LTD.
[2]Sabigat Industrial Complex,Sudan.
[3&4]KararyUniversity,College of Engineering,Khartoum, Sudan

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ABSTRACT

Sudanese heavy crude oils often exhibit high acidity, primarily due to significant concentrations of naphthenic acids (NAs), which are quantified by the Total Acid Number (TAN). Elevated TAN levels result in severe corrosion of refining and production equipment, storage tanks, and transport facilities, thereby increasing operational risks and lowering marketability due to reduced crude oil prices. This study investigates a method to reduce NAs in high-TAN crude oil using sodium hydroxide (NaOH) combined with a demulsifier under applied voltage. Experimental results demonstrate a significant reduction in TAN through this approach.

KEYWORDS: Sodium Hydroxide, Naphthenic Acid, Crude Oil, Total Acid Number, Demulsifier, Electrostatic Dehydration

1. INTRODUCTION

As global energy demand continues to rise and conventional crude oil reserves dwindle, high-acidity crude oil has emerged as an important feedstock due to its abundance and lower cost[1]. The decline in conventional oil supplies has compelled many nations to explore and utilize heavy and lower-quality crude oils to meet growing demand[2]. Naphthenic acids (NAs) are the primary contributors to the elevated acidity in these crude oils[3].The exhaustion of conventional oil reserves has amplified the significance of unconventional oils, including high-acid crudes (HACs) and heavy crudes, which are characterized by higher densities, viscosities, Total Acid Numbers (TANs), and carbon-to-hydrogen ratios[4].

The production of high-TAN crude oil has surged, and the increasing price of light, sweet crudes has motivated refineries to enhance sour crude oil processing to maximize profitability. Crude oil is a complex hydrocarbon mixture, also containing significant amounts of sulfur, chlorides, nitrogen, trace metals, and naphthenic acids[5]. The Total Acid Number (TAN) refers to the amount of potassium hydroxide (KOH) required to neutralize the acidity of one gram of oil, expressed in milligrams of KOH. While TAN is commonly used to measure oil acidity, its direct link to corrosive behavior remains debated[6]. Generally, oils with a TAN below 0.5 mg KOH/g are classified as low-acid, while those with a TAN above 1.0 mg KOH/g are considered high-acid. The petroleum industry faces major challenges in refining high-acid crude oils due to the corrosive nature of naphthenic acids, which can lead to equipment failures, increased maintenance costs, and environmental concerns[7].

Refinery corrosion linked to naphthenic acids has been a known issue since the early 20th century[8]. Naphthenic acids are a complex group of organic acids found naturally in crude oil, consisting of saturated acyclic, monocyclic, and polycyclic carboxylic acids with the formula $C_nH_{2n}+ZO_2$, where "n" is the carbon number, and "Z" accounts for the hydrogen atoms lost in ring formation[9]. Naphthenic acid content is typically measured via titration using potassium hydroxide (KOH), as described in ASTM methods D 974 and D 664. The result, commonly referred to as the Total Acid Number (TAN), represents the amount of KOH required to neutralize the

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acidic components in one gram of oil. Over time, technical studies have examined the relationship between TAN and corrosion, suggesting that corrosion risks can be predicted by TAN values[10]. Reducing crude oil acidity can help mitigate corrosion-related issues.

Several methods have been developed to reduce naphthenic acid content in crude oil, including catalytic decarboxylation[6]. Other strategies involve caustic addition, blending, neutralization, and the use of ionic liquids like ethanol[11]. Additionally, metal oxide or solid acid catalysts have been employed to lower crude oil acidity [12]. Addressing acidic crude oil is vital for improving production efficiency, and various treatment methods exist depending on the crude's properties. Naphthenic acids can be removed through dilution, caustic washing, or catalytic decarboxylation [11].

Zhang et al. studied the catalytic decarboxylation method, using commercially available MgO to remove naphthenic acids. The removal efficiency was evaluated by measuring acid conversion and CO_2 yield. Despite its effectiveness, catalytic decarboxylation is often considered destructive. An alternative method studied by Shi et al. involves forming ionic liquids to extract naphthenic acids, but it requires large solvent volumes, raising environmental concerns[6].

Bharat el al developed an effective and eco-friendly TPA-supported solid acid catalyst for the esterification of naphthenic acids in highly acidic crude oil. This process significantly reduces methanol consumption while lowering the Total Acid Number (TAN) of the crude oil to levels acceptable for refinery specifications.[10].

The objective of this study is to develop an effective method for reducing the naphthenic acid content in Sudanese heavy crude oil by utilizing a specific ratio of caustic soda, combined with electrostatic dehydration and the application of a demulsifier.

2. MATERIALS AND METHODS

A.Materials

The following materials were used in the experiments:

1. Heavy crude oil: Sample with a high Total Acid Number (TAN).
2. Sodium hydroxide (NaOH) solution: 4 wt% concentration.
3. Distilled water: For dilutions and cleaning.
4. Anhydrous 2-Propanol: 99.5% purity, with total impurities <0.003% and vapor pressure of 33 mm Hg.
5. Toluene: Analytical reagent grade.
6. Deionized water: Used in sample preparation.
7. Potassium hydroxide (KOH): Used for TAN titration.
8. Potassium hydrogen phthalate (KHP): Used for standardization in titration.
9. Demulsifier: Used at a dose of 50 ppm.

B. Equipment

The following equipment was employed for the experimental procedures:

1. Analytical balance: Capacity of 210 g with an accuracy of ±0.01 mg (Wagtech).
2. Shaker: Used to homogenize the crude oil samples before and during treatment.
3. Dehydration instrument: Utilized for separating water content from the crude oil after treatment.
4. Micropipette: For accurate measurement of small liquid volumes.
5. Bottle test glassware: Used to conduct bottle tests for evaluating the separation process.
6. Metrohm 877 Titrino Plus: Used for Total Acid Number (TAN) analysis through potentiometric titration(shown in Figure 1)

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Figure IMetrohm 877 Titrino Plus

C. Experimental Procedure

I. Crude Oil Characterization A sample of high-acidity Sudanese heavy crude oil was obtained. Initial crude oil properties, including TAN, API gravity, viscosity, and pour point, were measured. These properties are summarized in Table I and II , Figure IIAPI vs. TAN For All Fields and Figure IIIAPI vs. Pour point For All Fields illustrate the correlation between API gravity, Pour Point, and Total Acid Number (TAN) for the studied crude oil samples. As shown, there is a noticeable trend indicating that as the API gravity of the crude decreases, the TAN increases.

II. TAN Reduction Procedure The crude oil samples were treated with a 4 wt% NaOH solution to reduce TAN. The procedure involved the following steps:

a. Preheating: The crude oil sample was preheated to 70°C.

b. Mixing: The preheated oil sample was treated with varying ratios of NaOH solution. A demulsifier (50 ppm) was added, and the mixture was thoroughly homogenized using a shaker.

c. Electrostatic dehydration: The homogenized mixture was placed in test bottles fitted with electrodes, subjected to an electric field for 10 minutes to promote separation, and then left to settle for 15 minutes.

d. Water separation: After settlement, water was separated from the oil. If necessary, additional water washing was performed.

e. Stirring: The mixture was stirred at 1,200 rpm for 15 minutes to ensure complete water separation.

f. TAN analysis: The crude oil was analyzed for TAN after treatment, following ASTM D664 methodology.

III. Measurement of Total Acid Number (TAN) TAN was determined using the ASTM D664 method, which involves non-aqueous potentiometric titration. The following steps were carried out:[13]

a. Preparation of KHP standard solution: Potassium hydrogen phthalate (KHP) was heated at 80°C for 10 hours to remove moisture. The dried KHP was weighed accurately and dissolved in CO_2-free distilled water to prepare a standard solution.

b. Preparation of alcoholic KOH solution: 6 g of KOH was dissolved in approximately 1 liter of anhydrous 2-propanol, boiled gently for 30 minutes to increase solubility, and stored overnight. The solution was standardized using the KHP solution.

c. Sample preparation: Crude oil samples (1–5 g) were dissolved in a 125 ml solvent mixture (50% toluene, 49.5% anhydrous 2-propanol, 0.5% water), filtered, and transferred to a 250 ml titration vessel.

d. Titration: KOH solution was titrated into the oil sample until a constant potential was reached. The TAN was recorded from the titration curve. A blank titration of the solvent was also conducted for accuracy. The reduction in TAN was determined by comparing the untreated crude oil TAN with the post-treatment values.

Table IHigh TAN Heavy Crude properties

Sample Name	**Keyi Heavy Crude**	
Content	Water(v%)	5.6
	Sand(v%)	0
Density(g/cm3)	15.6℃	0.8937

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	50°C	0.8699
Pour Point	API 15°C	26.62
	(°C)	12
Viscosity (MPa.s)	29°C	364
	40°C	177
Acid Number	mg KOH/ g oil	4.7

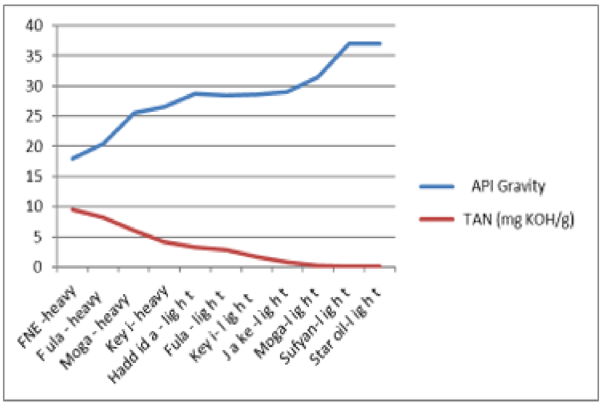

Figure IIAPI vs. TAN For All Fields

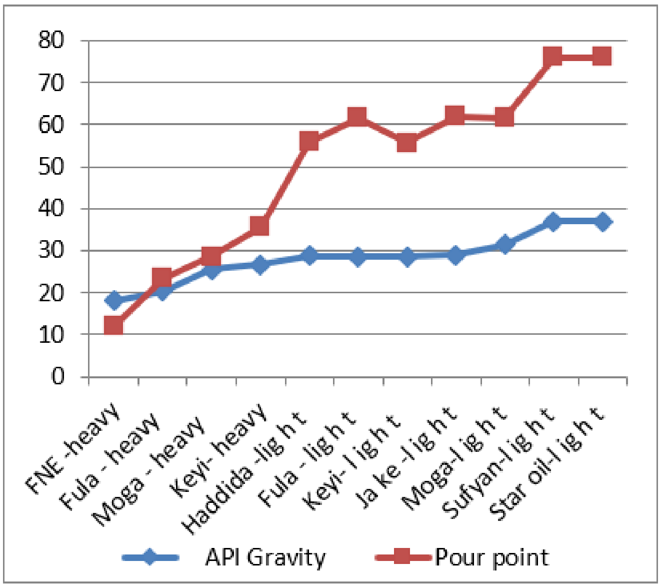

Figure IIIAPI vs. Pour point For All Fields

Table IICrude Oil Properties for All Fields

Crude Oil Name	API Gravity	TAN (mg KOH/g)	Pour point
FNE -heavy	18	9.5	-6
Fula -heavy	20.4	8.18	3
Moga -heavy	25.5	6.05	3
Keyi-heavy	26.6	4.07	9
Haddida-light	28.8	3.2	27

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Fula -light	28.5	2.8	33
Keyi-light	28.6	1.7	27
Jake -light	29	0.84	33
Moga-light	31.5	0.26	30
Sufyan-light	37	0.07	39
Star oil-light	37	0.05	39

Table IIICrude Oil Properties For Individual Well

Well Name	Test method	Sampling Position	Acid Number mg KOH/ g oil
Keyi -19	ASTM D 664	wellhead	3.67
Keyi-8	ASTM D 664	wellhead	3.20
Keyi S-2	ASTM D 664	wellhead	5.00
Keyi S-4	ASTM D 664	wellhead	5.30
Keyi -5	ASTM D 664	wellhead	6.10
Keyi -26	ASTM D 664	wellhead	5.90
Keyi -19	ASTM D 664	wellhead	3.67
Keyi-8	ASTM D 664	wellhead	3.20
Keyi S-2	ASTM D 664	wellhead	5.00
Keyi -5	ASTM D 664	wellhead	6.10
Keyi -26	ASTM D 664	wellhead	5.90
Keyi S-1	ASTM D 664	wellhead	5.00
Keyi -1	ASTM D 664	wellhead	0.06
Keyi-N-4	ASTM D 664	wellhead	2.00
Keyi S-1	ASTM D 664	wellhead	5.00
Keyi -1	ASTM D 664	wellhead	0.06
Keyi-N-4	ASTM D 664	wellhead	2.00

3. RESULTS AND DISCUSSIONS

1. TAN Reduction with Sodium Hydroxide Treatment

The effect of sodium hydroxide (NaOH) treatment on the Total Acid Number (TAN) of high-acidity Sudanese crude oil was investigated by varying the volume ratios of oil to NaOH solution. The results of TAN reduction at different oil-to-NaOH solution ratios are summarized in Table IV and Figure V (Acid number Curve vs Ratio of Basic Solution).

Table IVReduction of Total Acid Number (TAN)

Volume Ratio (Oil Solution)	Volume of Oil (ml)	Volume of Basic Solution (ml)	Dose of Demulsifier (ppm)	TAN of Untreated Crude Oil (mg KOH/g oil)	TAN of Treated Crude Oil (mg KOH/g oil)
100% : 0%	100.00	0.00	50.0	4.07	4.07
90% : 10%	90.00	10.00	50.0	4.07	3.20
80% : 20%	80.00	20.00	50.0	4.07	1.95
70% : 30%	70.00	30.00	50.0	4.07	1.37
60% : 40%	60.00	40.00	50.0	4.07	0.71
50% : 50%	50.00	50.00	50.0	4.07	0.35
40% : 60%	40.00	60.00	50.0	4.07	0.28
30% : 70%	30.00	70.00	50.0	4.07	0.12
20% : 80%	20.00	80.00	50.0	4.07	0.11
10% : 90%	10.00	90.00	50.0	4.07	0.10

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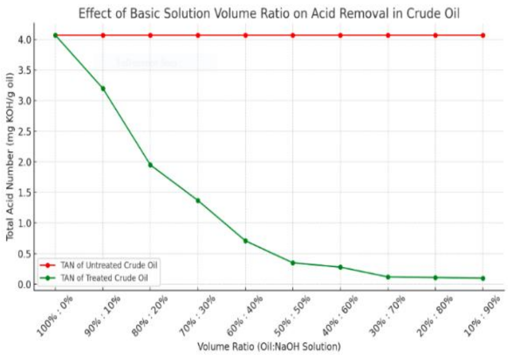

Figure IVAcid number Curve vs Ratio of Basic Solution

2. Analysis of Results

The untreated crude oil had a TAN of 4.07 mg KOH/g oil, indicating significant acidity due to the presence of naphthenic acids. The results clearly show a substantial reduction in TAN with increasing amounts of NaOH solution. The use of sodium hydroxide effectively neutralized the acidic components in the crude oil.

At a 90% oil-to-10% NaOH solution ratio, the TAN decreased to 3.20 mg KOH/g, which indicates a modest reduction in acidity. However, as the ratio of NaOH increased, more pronounced reductions were observed. At a 60:40 oil-to-solution ratio, the TAN dropped to 0.71 mg KOH/g, reflecting the strong neutralizing capacity of NaOH.
Further increasing the NaOH concentration (e.g., 40:60 and 30:70 ratios) led to even lower TAN values, with the lowest TAN recorded at 0.10 mg KOH/g for the 10% oil-to-90% NaOH solution ratio. This reduction achieved TAN levels that are acceptable for refinery processing, as oils with TAN below 1.0 mg KOH/g are generally considered low-acid crudes.

3. Impact of Demulsifier and Electrostatic Dehydration

The demulsifier was consistently dosed at 50 ppm across all experiments. Despite the TAN reduction, some challenges in demulsification were noted, particularly at higher NaOH concentrations. The formation of emulsions during treatment indicates the need for further optimization of the separation process. The electrostatic dehydration effectively aided in separating water from the treated crude oil, but higher doses of demulsifier or adjustments to the electrostatic field may improve overall phase separation.

4. TAN Reduction Efficiency

The NaOH treatment was highly effective in reducing the TAN of the crude oil samples, achieving reductions of up to 97.5% from the initial TAN of 4.07 mg KOH/g to 0.10 mg KOH/g at the 10% oil-to-90% NaOH ratio. This significant decrease in acidity demonstrates the potential of NaOH as a neutralizing agent for high-acidity crude oils.

5. Observations on NaOH Concentration

While higher concentrations of NaOH led to greater TAN reductions, the process of separating water and oil became more complex at elevated NaOH levels. This suggests that further fine-tuning of the NaOH concentration and demulsifier dosage is necessary to optimize both TAN reduction and phase separation efficiency.

4. CONCLUSION

This study demonstrates that sodium hydroxide (NaOH) is a highly effective agent for reducing the Total Acid Number (TAN) of high-acidity Sudanese crude oil. The TAN was reduced from an initial value of 4.07 mg KOH/g to as low as 0.10 mg KOH/g, achieving levels suitable for refinery processing. The reduction was achieved by using NaOH in combination with a demulsifier and electrostatic dehydration.

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The results highlight the strong neutralization capability of NaOH, particularly at higher concentrations, but also reveal challenges in the phase separation process due to the formation of emulsions. Future work should focus on optimizing the demulsification process and exploring different demulsifier concentrations to improve separation efficiency.

This method of TAN reduction offers a promising solution for refining high-acid crude oils, enhancing the marketability of such oils while minimizing corrosion risks and refining inefficiencies.

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