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Reduction Of Total Acid Of Sudanese Crude Oils By Polar Solvent (Methanol)

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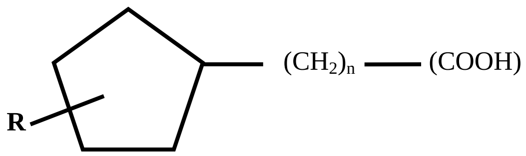
Abstract: This paper investigates the possibility of reduction of total acid for some Sudanese crude oils by using methanol as polar solvent in absent of a catalyst at @ 40 C° operation temperature for 16 hours. Two different types of crude oils were used one is high acid (heavy Fula), while other is low acid (Tharjas blend). The acid in heavy Fula blend after three extraction processes was reduced by (38%), and slight change has occurred in some properties of crude oil like density, pour point and kinematic viscosity. The acid in Tharjas blend after three extraction processes was reduced by (48%) and slight improvement has occurred in some properties of the oil.

Keywords: crude oil, naphthenic acid, total acid number (TAN), extraction, methanol.

I. INTRODUCTION

Petroleum (crude oil) is a complex mixture of thousands up to several of compounds, it's perhaps the most important substance consumed in whole society. It provides raw materials for fuel, industry, heating, transportation, plastics and other products. Although all crude oils contain the hydrocarbons composition, rarely to find two crude oils with the same characteristics and this is because every crude oil from whatever geographical source contains different quantities of the various compounds that makes up its composition [1], when refer to the type of fluid in the reservoir Crude oils produced in Nigeria for example would be high in cyclic paraffin content and have a relatively low specific gravity. On the other hand Crude oils are produced in some fields in Venezuela would have a very high gravity and a low content of material boiling below 350˚C [2]. A lot of researches and reviews have been reported in Sudanese crude oils that mentioned the Sudanese crude oils vary from heavy to light crude oil depending on the geological formation of the production area e.g. at block (6) we found two different types of crude light Fula crude oil and characterized by high API, low sulfur and acid content on the other hand heavy crude oil characteristic by high API and acid content.

The term naphthenic acid (NA), as commonly used in the petroleum industry, it refers to all carboxylic acids present in crude oil. Naphthenic acids are classified as monobasic carboxylic acids with the general formula RCOOH, where R represents the naphthene moiety consisting of cyclopentane and cyclohexane derivatives. Naphthenic acids are composed mainly of alkyl-substituted cycloaliphatic carboxylic acids, with smaller amounts of acyclic aliphatic (paraffinic or fatty) acids. Aromatic, olefinic, hydroxy, and dibasic acids are considered to be minor components. Commercial naphthenic acids also contain different amounts of unsaponifiable hydrocarbons, phenolic compounds, sulfur compounds, and water, with the general chemical formula $\mathbf{C_nH_{2n+Z}O_2}$, several studies were reported petroleum acids in crude oils from undetectable range to 3% by weight[3].



Naphthenic acid

The main problem of high acid crude oil is the high temperature naphthenic acid corrosion above 450 °F (232 °C) [4] .That appear clearly when naphthenic acid containing in crude oils are processed in refineries. Naphthenic acids present in crude oils are considered only to be a part of the problem and simple measures of corrosively based on the TAN are insufficient. The fundamental problem is the complexity of the factors affecting corrosiveness is crude oil composition, temperature, fluid velocity, turbulence, physical state (vapor or liquid), pressure and materials construction may also contribute to the extent of oxidation. Steel alloys that are resistant to corrosion by sulphide-containing compounds can be corroded by naphthenic acids. This "naphthenic acid corrosion" involves the reversible binding of the metal ion by the carboxylate (chelate) with the formation of hydrogen gas [5] as in equation (1) and when sulfur appear in crude oil react as in equation (2) &(3)below:

$$Fe + 2RCOOH \rightarrow Fe\,(RCOO)_2 + H_2 \quad (1)$$

$$Fe + H_2S \rightarrow FeS + H_2 \quad (2)$$

$$Fe\,(RCOO)_2 + H_2S \rightarrow FeS + 2RCOOH \quad (3)$$

In general, the features of high TAN crude are [6]:

- ✓ High acid number
- ✓ Low API number (or higher density, most of them higher than 930 kg/m3).
- ✓ High viscosity, high asphalt and gel content.
- ✓ Low solidification point.
- ✓ High nitrogen content.
- ✓ High content of heavy metals.
- ✓ Low yield of light distillates.

II. EXPERMENTAL

A. MATERIAL

- ✓ Two different crude oil samples were collected (from different field) one is heavy Fula crude oil from block (6) which characterized by low API, high acid content and low sulfur content. Other sample is Tharjas crude oil which is heavy crude, low sulfur and low acid when compare with Fula heavy crude oil.
- ✓ Methanol solvent for extraction process.
- ✓ Titration solvent (495 ml isopropanol, 500 ml toluene and 5 ml distil water in liter).

B. METHODS

- ✓ Extraction Process: 90 ml of crude oil was added to 10 ml of methanol and shaking well for 10 minutes .then it was kept at 40˚C for 16 hours.
- ✓ Total Acid Number (TAN) measurement: The total acid number was measured using an automatic potentiometer with solvetrode (Metrohm Titrino Plus model 848) following the ASTM D664 method [7], which known mass of oil was dissolved in 125 ml of titration solvent, the solution was titrated using 0.1N alcoholic KOH and total acid number (TAN) was calculated based on the following equation:

Acid number mg KOH/g = (A –B)*M * 56.1/W

Where

A = volume of alcoholic KOH solution used to titrate sample to end point

B = volume corresponding to A for blank titration, mL,

M = concentration of alcoholic KOH solution, mol/L,

W = sample, mass, g,

III. RESULT & DISCUSSION

A. HEAVY FULA BLEND CRUDE OIL TAN RESULTS DURING THREE EXTRACTIONS

NO	EXTRACTION	TAN mg KOH/g
1	Before extraction	7.69
2	First extraction	5.34
3	Second extraction	5.62
4	Third extraction	4.76

Table 1: Heavy Fula blend crude oil extracting results

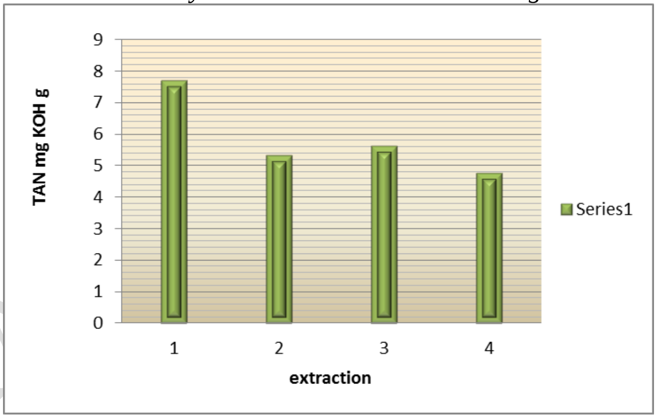


Figure 1: TAN during extraction processes

The total acid number of the Heavy Fula blend crude oil reduced from 7.69 mg KOH/g to 5.34 mgKOH/g in first extraction by ratio (30%) but this ratio decreased in the second extraction and this attributed to a rule that primary alcohols in fact can be oxidized first to aldehydes and then to carboxylic acid. And then the reduction increased slightly at third extraction to (11%) that indicates the first extraction is more effective one.

TEST	METHOD	UNIT	RESULTS BEFORE EXTRACTION	RESULTS AFTER EXTRACTION
Density at 15°C	ASTM D5002	g/cm³	0.9271	0.9127
Specific Gravity	ASTM D5002	Degree	0.9280	0.9136
API Gravity	ASTM D5002		20.99	23.39
Kinematic Viscosity @50°C	ASTM D445	mm²/s	326	1012
Pour Point	ASTM D5853	°C	+15	+12
Total Acid Number	ASTM D664	mg KOH/g	7.69	4.76

Table 2: Shows physical & chemical properties for heavy Fula blend before and after extraction

Slight change in density when compares the results the major improvement in pour point decrease by 3 ˚C but it still in the precision limit according to ASTM D5853. The kinematic viscosity had been raising to 1012 mm^2/sand this one of the flow problem that detected throw this method, the total acid number was reduced by ratio (38%) from its original value before process and its considerable reduction when compared with another methods.

B. THARJAS BLEND CRUDE OIL TAN RESULTS DURING THREE EXTRACTIONS

NO	EXTRACTION	TAN mg KOH/g
1	Before extraction	1.39
2	First extraction	1.10
3	Second extraction	0.91
4	Third extraction	0.72

Table 3: Tharjas blend crude oil results after three extractions processes

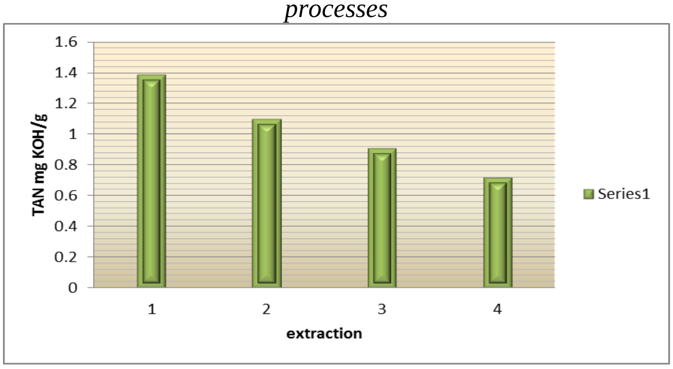


Figure 2: TAN during extraction processes

The total acid number of the Tharjas blend crude oil crude oil reduces from 1.39 mg KOH/g to 1.10 mg KOH/g in first extraction by ratio 20% but this ratio decreased in the second extraction to 17% and increased slightly at third extractionn to 21% that indicated all extraction process had same sequences.

TEST	METHOD	UNIT	RESULTS BEFORE EXTRACTION	RESULTS AFTER EXTRACTION
Density at 15°C	ASTM D5002	g/cm³	0.9295	0.9286
Specific Gravity	ASTM D5002	Degree	0.9303	0.9295
API Gravity	ASTM D5002		20.60	20.74
Kinematic Viscosity @50°C	ASTM D445	mm²/s	588.8	1000
Pour Point	ASTM D5853	°C	15	15
Total Acid Number	ASTM D664	mg KOH/g	1.39	0.72

Table 4: the physical properties for Tharjas blend crude oil before and after extractions

Table (4) shows the physical properties before and after extraction processes slight changed in density, API and pour point this indicate the extraction process could not effected on properties of crude oil. The kinematic viscosity raised to 1000mm^2/s and this one of the flow problem that detected throw this method, the total acid number was reduced by ratio(48%) from its original value before process and its considerable reduction when compared with another methods.

IV. CONCLUSION

The acid in heavy Fula blend after three extraction processes was reduced by (38%), and slight change has occurred in some properties of crude oil like density, pour point and kinematic viscosity. The acid in Tharjas blend after three extraction processes was reduced by (48%) and slight improvement has occurred in some properties of the oil.

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