

Distribution of Acid in True Boiling Point (TBP) Distillation Cuts for High Acid Sudanese Crude Oil

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Abstract: The most important characterization properties for evaluation of the crude oil and its products in lab is the True boiling point distillation processes (TBP). Which consider as simulation distillation for atmospheric distillation unit (ADU) and vacuum (VDU) in refineries. This paper to study the distribution of acid contain in heavy crude oil samples during true boiling point distillation processes in distillates. From the results it can be clearly seen that in high acids crude oil samples HAC01 (TAN 7.56 mgKOH/g) and HAC02 (TAN 7.56 mgKOH/g) high amount of acid concentrated in vacuum gasoil cuts (VGO) and long residues while significant amount of acid concentrated in Atmospheric gasoil and slight amount of acids appeared in naphtha and kerosene cuts. In sample HAC03 (TAN 2.2 mgKOH/g) high amount of acid distributed in petroleum's high temperature cuts diesel and vacuum gasoil cuts while the amount of acid concentrated in short residue less than that in long residue. Processing of such crude oils may cause aggressive corrosive attack on the inside walls of equipment such as pipes, processing units and distillation towers specifically vacuum distillation unit which needs mitigation procedure to deal with high acid constituent, protecting distillation tower, storage tank, pipeline and other processing facilities.

Keywords: Crude oil, Distillation Process, True Boiling Point, Acids, Petroleum Cuts.

1. INTRODUCTION

Acidic crude oils are grades of crude oil that contain substantial amounts of organic acid like naphthenic acids (NAs) or other acidic compounds.

Scientist defined acidic crude oil as crude oil has acid number (TAN) more than 1 mg KOH/g at this level crude oils begin to be heavily discounted in value (1). In addition of acidity, there appear to be no other distinguishing properties that characterize these oils will be mention in this paper by details.

The ratio of these types of crude increased gradually in the world production from the early 1990s, the production of heavy crudes with a high acid content commenced and started to increase rapidly as new fields were developed the European refining industry has only limited capacity to process such crudes, and as a consequence some production had to be exported (2).

The main problem of high acidic crude oil is naphthenic acid corrosion which appear during production, processing, transportation and refining process. This corrosion tends to made fouling in these operating unit lead to increase the cost of process and militance.

In the early 19th century, the production of opportunity crude oil (heavy crudes with a high acid content, low API, high sulphur and high metal content) commenced and started to increase rapidly as new fields were developed in European area with low refinery capacity lead these country to export huge amount of their production to Asian as many African county do (3).

According to pervious study, acidic crudes are produced in every oil producing region incremental high acids crude production will rise by 1.8 million B/D in by 2010 and the output will continue to rise at least through 2015. China consider as dominate production, which is forecast to more than double from 2006 to 2015. Other locations historically noted for high acid crudes include Venezuela, India, Russia and some fields in California. Newer regions include the North Sea, West Africa, Mexico and offshore Brazil (5). Heavy, high-metal crudes produced from deeper wells and new extraction methods present technological challenges for refineries, including desalter upsets and other

hardware issues in systems that may have been designed for less demanding blend slates. e.g., DOBA crude produced in Chad, is a heavy, challenging crude contains between 250 and 350ppm calcium and high levels of naphthenic acids. In the general high-TAN crudes' gravities are often less than 29 API and often are low in sulfur (except for Venezuelan grades) and frequently produce high yields of gas oil. Acidic oils can vary widely in most other properties high acid crudes have the following properties (6).

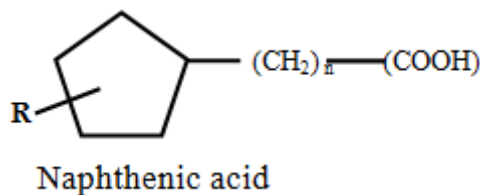
- High acid content.
- High density.
- Low viscosity.
- High ratio of asphalt content.
- High metals content.

Many chemical and physical techniques used to determine the quality of crude oil before refinery also to help in determine the price of the crude oil such as crude assay which contain true boiling point distillation, simulation distillation, water content, sulfur content, total acid number, etc...

Sudanese crude oil in Balila field also characteristic by heavy and high acidic crude in most production field with TAN value more than 10 mgKOH/g for some field. Like some well in Moga field.

2. HIGH ACID CRUDE AND NAPHTHENIC ACID RELATION

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 $C_nH_{2n+2}O_2$, several studies were reported petroleum acids in crude oils from undetectable range to 3% by weight (7).



Naphthenic acids are complex mixtures of linear, cyclic and aromatic acids that displays a wide range of molecular masses, typically the distribution of acid depend on the type of crude oil source we found that naphthenic acids ranging C10-C25 are present in diesel and naphtha fractions, but heavier C40-C50 acid compounds can be found in the parent crude oil⁽⁵⁾.

These acids include a broad range of compounds containing a carboxylic acid i.e., -COOH. depend on the hydrogen molecule to which these carboxylic group attach the organic acids can be broadly classified into:

- Aliphatic acids (Al-COOH) where the hydrocarbon molecule may be straight or branched hydrocarbon, e.g., acetic acid, propionic acid etc; where R is an aliphatic, aromatic, or naphthenic group. Depending on the type of organic acid the reaction product, $Fe(COOR)_2$, is soluble in crude oil in the aqueous phase. For this reason, corrosion by organic acids does not leave any product layers on the metal surface.



Corrosion by aliphatic acids normally occurs at temperature as low as 140 F (60°C) due to their low volatility. On the other hand, Corrosion by naphthenic acids normally occurs at temperatures above 430°F (~220°C); the corrosion rate increases with increase of temperature up to between

500 and 700°F (260-370°C) and drops above 700-750 F (370-400°C) due to the decomposition of the acids.

- Aromatic acids (AR. COOH) where the hydrocarbon molecule may be benzene or substituted benzene ring. Aromatic acids are not normally corrosive.
- Naphthenic acid (Nap. COOH) where the hydrocarbon molecule may be saturated cyclic ring e.g., cyclopentane, cyclohexane, etc. And this term usually uses in oil and gas industry refer to many organic acids presents in crude oil. Some crude oils contain naphthenic (organic) acids, which may become corrosive at temperatures above 430° F (220°C) during refinery process when the acid value of the crude is above a certain level (4).

3. HIGH ACID CRUDE REFINING

Refining acidic crude oils is of increasing interest due to their increased production and usually discounted value. Acids can be present in different cuts during the process like kerosene aviation turbine fuels because of acid treatment during refining. These trace acid quantities are undesirable because of the possibility of metal corrosion and impairment of the burning characteristics and other properties of the kerosene(5). acids are common concentrate in a high temperatures cuts like gas oil vacuum gas oils (VGO). And initially corrosive in the range of 180-220°C, then become increasingly corrosive, with a maximum between 280 and 385°C, and finally breakdown above 400°C. The acid breakdown above 400°C is due to thermal decarboxylation of the acid. The reason that naphthenic acids are problematic in refineries is that the distillation columns operate primarily between 250-400°C region to compound the problem, naphthenic acids volatilize along with the hydrocarbons in the CDU, and then either condense on the distillation column walls or on a narrow range of trays the condensation of naphthenic acids creates microenvironments in the refinery with much higher concentrations of naphthenic acids than the bulk crude. Previous study in Bohai crude oil showed that the carboxylic acids are mainly composed of naphthenic acids and branched chain fatty acids, found in high distillates cuts about 405°C and 505°C. With increase of boiling temperature of distillates, the content of naphthenic acids increases gradually (7).

Sudan heavy crude share represents 18% of the global production Fula heavy crude with high TAN and salt content affects the price and the environmental specifications, due to serious corrosion problems at the processing units of Khartoum refinery which process 40.000 bbl/day of High acid Fula crude oil as in table (1) below (8):

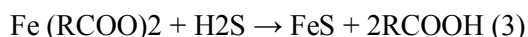
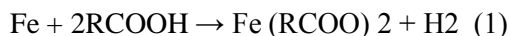
Table1. KRC Main Products

Production	Amounts kt/a
LPG	315
Gasoline	1,159
Diesel	1,837
Jet-A1	123
Heavy Coker diesel	364
Petroleum Coke	306

4. HIGH ACID CORROSION

It was reported that naphthenic acid corrosion in petroleum refineries usually occurs for petroleum cuts over the temperature range more than 200°C; however, at higher temperature more than 400°C the naphthenic acids decompose(9). The corrosivity of NAs is related to two main factor one of them is molecular weight (MW) and other is the total acid number. NAs can be further classified into α and β groups, α group corresponding to low molecular weight NAs (MW, ~125–425 amu, equivalent to ~C7 to C30 NAs) and exhibiting very high corrosivity and the latter having high MW (~325–900 amu) and low corrosivity (10,11). Generally, the main problem of high acid crude oil is the high temperature naphthenic acid corrosion above 450 °F (232 °C) ⁽⁴⁾. This temperature considers as operating temperatures relevant to crude oil refining, at this temperature acids in crude oil can be corrosive and the form of attack is appropriately called ‘naphthenic acid corrosion’. Crude oils are complex and sulphur species and chlorides may be present also which in different ways can influence the nature and extent of corrosion That appear clearly when naphthenic acid containing in crude oils are processed in refineries specially in distillation tower(8). Naphthenic acids present in crude oils are considered only to be a part of the problem and one of the constituents in the composition of

petroleum but simple measures of corrosivity based on the TAN are insufficient to produce relation between acidity or naphthenic acid and corrosion because may found other constituent of petroleum has the acidity properties like phenols, ketones and alcohol compounds. 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 (8) as in equation (1) and when sulfur appear in crude oil react as in equation (2) & (3) below:



corrosion can be classified into three general forms based on the type of damage that results and the three general forms are:

- uniform corrosion,
- localized corrosion
- stress corrosion

Typically found that naphthenic acids(organic acid), mineral acids such as hydrogen sulfide (H₂S), hydrogen cyanide (HCN), and carbon dioxide (CO₂) can be present in crude oil, all of these compound can contribute significantly to corrosion of equipment. Even materials suitable for sour service do not escape damage under such an onslaught of aggressive compounds. Irrespective of the type of corrosion that occurs, naphthenic acids in crude oil can cause corrosion which often occurs in the same places as high-temperature sulfur attack such as heater tube outlets, transfer lines, column flash zones, and pumps. Furthermore, naphthenic acids alone or in combination with other organic acids (such as phenols) can cause corrosion at temperatures as low as 65°C (150°F) up to 420°C (790°F) Crude oil with a total acid number (TAN) higher than 0.5 mg KOH per gram of crude oil and crude oil fractions are considered to be potentially corrosive between the temperature of 230-400°C (450-750°F), this type of attack is called “naphthenic acid corrosion”(13).

5. SAMPLE AND EXPERIMENTAL METHODS

5.1. Crude Oil Samples

For this study Heavy, high acid crude oil samples HAC01,HAC02 and HAC03were collected from different petroleum subfield in Sudan. The oil samples have different acidity HAC01 has high acid more than 7.00 mgKOH/g,HAC02 has acidity more 5.00 mg KOH/g and third sample hasacidity less than 3.00 mgKOH/g.

Some properties of samples were measured before TBP distillation to determine the main properties of crude oil like TAN, density, water content, sulfur and micro carbon residue

5.2. Method of Determination of Total Acid Number (TAN)

Total Acid Number (TAN) is amount of potassium hydroxide in milligrams that's needed to neutralize the acid in one gram of oil. Crude with TAN 1.0 mg KoH/g conventionally labeled as high TAN. Most high TAN oil tends to be heavy.

Test methods:

The sample was dissolved in a mixture of toluene and propan-2-ol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a reference electrode or a combination electrode. The meter readings are plotted manually or automatically against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve. When no definite inflections are obtained and for used oils, end points are taken at meter readings corresponding to those found for aqueous acidic and basic buffer solutions (16)

Total acid number was read for crude oil samples before (TBP) distillation process and for each cut after the distillation process as following: The sample is dissolved in a mixture of toluene and propan-

2-ol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using solvetrode. The meter readings are plotted manually or automatically against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve

5.3. True Boiling Point Distillation Process

This test method is one of a number of tests conducted on a crude oil to determine its value. It provides an estimate of the yields of fractions of various boiling ranges and is therefore valuable in technical discussions of a commercial nature. The sample container was heated to 50°C to facilitate easy transfer and homogenization. A small proportion of the sample was drawn prior to distillation process for the crude oil property analysis the distillation of the sample was carried out in accordance to ASTM D 2892 (15 Theoretical plate column) and ASTM D 5236 (Vacuum pot still) methods. The yield pattern of each fraction collected is tabulated in percentage weight and percentage volume as following (17)

6. RESULT

Physical and chemical properties of three crude oil samples were determining before true boiling point distillation analysis the result as following:

6.1.HAC01 Crude Properties

Test	Method	Unit	Results
Density at 15°C	ASTM D5002	g/cm ³	0.9271
Specific Gravity	ASTM D5002	Degree	0.9280
API Gravity	ASTM D5002		20.99
Gross Calorific Value	CALC	MJ/Kg	43.6939
Micro Carbon Residue	ASTM D	% wt	5.5
Water	ASTM D4006	% vol.	0.05
Total Acid Number	ASTM D664	mgKOH/kg	7.69
Total Sulphur	ASTM D	% wt	0.1097

6.2.HAC02 Crude Properties

Test Name	Test Method	Unit	Result
Density @15°C	ASTM D5002	g/cm3	0.9006
API	ASTM D5002		25.48
S.G	ASTM D5002		0.9014
Pour point	ASTM D5853	°C	0
Water content	ASTM D4006	V%	0.1
Asphaltene Content	IP143	Wt%	0.04
TAN	ASTM D664	mgKOH/g	5.3
Gross Calorific Value	Calc	MJ/Kg	43.927
Sulphur	ASTMD29	mg/kg	0.0326

6.3.HAC03 Crude Properties

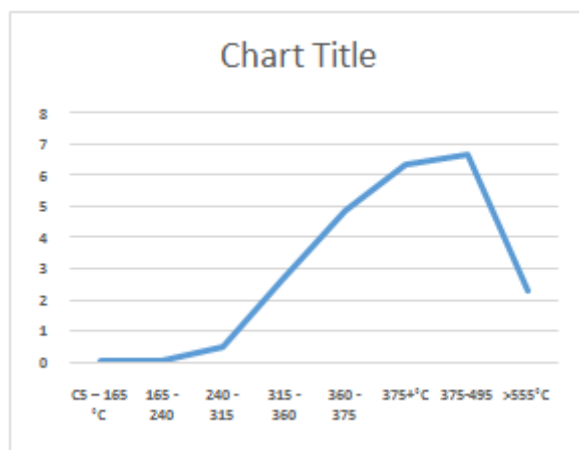
Test Name	Test Method	Unit	Result
Density @15°C	ASTM D5002	g/cm3	0.8743
API	ASTM D5002		30.2
S.G	ASTM D5002		0.875
Pour point	ASTM D5853	°C	33
Water content	ASTM D4006	V%	3
Asphaltene Content	IP143	Wt%	0.14
TAN	ASTM D664	mgKOH/g	2.2
Gross Calorific Value	Calc	MJ/Kg	44.157

6.4.HAC01 Acid Distribution

Material	TAN mgKOH/g
C5 – 165 °C	0.02
165 - 240	0.05
240 - 315	0.47

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315 - 360	2.66
360 - 375	4.88
375+°C	6.37
375-495	6.67
>555°C	2.28

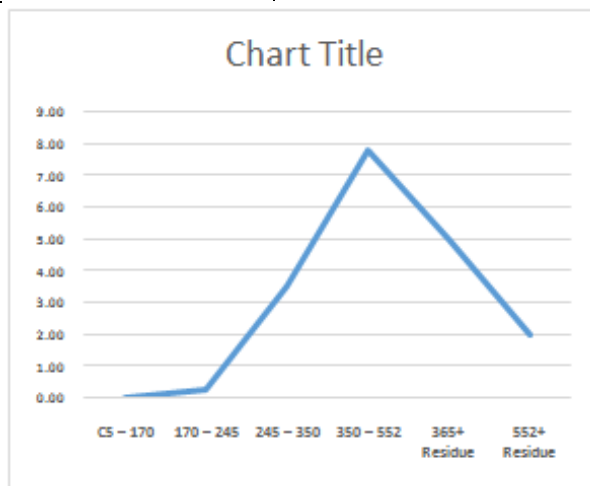


Graph1. HAC01 Acid Distribution in different range of temperature

As show in line graph and table above the acidic compounds concentrated in vacuum gasoil cut (VGO)375-495°C by high amount 6.67 mg KOH/g this concentration decreases more than 60% in short residue 2.28 mg KOH/g due to decompose the acidic compound as result of increasing the temperature of the distillation process. Acid was distributed in diesel cuts distilled under atmospheric pressure increased gradually with a temperature from 0.47 mg KOH/g at 240-315°C (light diesel), 2.66 mg KOH/gat 315-360°C (moderate diesel) to 4.88 mg KOH/gat 360-375°C (heavy diesel). The acid distributed in low temperature cuts naphtha and kerosene by low amount 0.02 and 0.05mgKOH/g respectively.

6.5.HAC02 Acids Distribution

Material	TAN
C5 – 170	0.00
170 – 245	0.27
245 – 350	3.50
350 – 552	7.80
365+ Residue	5.00
552+ Residue	2.00



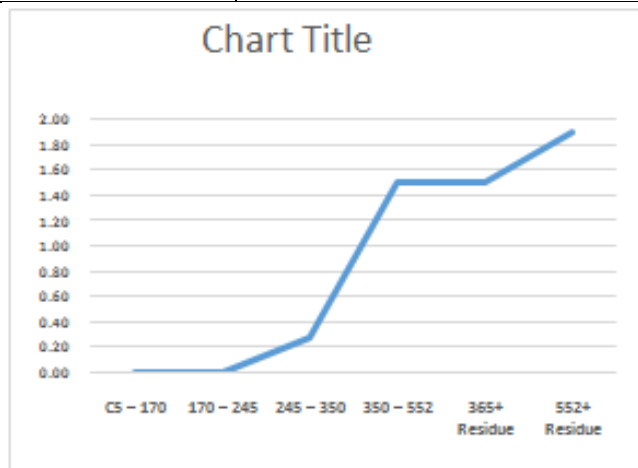
Graph2. HAC02 Acid Distribution in different range of temperature

The line graph and table above give information about distribution of acid in HAC02(TAN 5.3 mg KOH/g) in different cuts during true boiling point temperature distillation process as in HAC01high amount of this acid concentrated in vacuum gasoil cut (350-552°C) by 7.80 mg KOH/g, half of this

amount concentrated in atmospheric gasoil cut 3.50 mg KOH/g. less amount of acid concentrated in kerosene cut 0.27 mg KOH/g and no acid in naphtha cut, while the acid decomposed when temperature increased more than 552°C.

6.6. HAC03 Acid Distribution

Material	TAN
C5 – 170	0.00
170 – 245	0.00
245 – 350	0.28
350 – 552	1.50
365+ Residue	1.50
552+ Residue	1.90



Graph3. HAC03 Acid Distribution in different range of temperature

The line graph and table above give detail information about distribution of acid in different cuts during lab distillation process of HAC03 (TAN 2.2 mg KOH/g) this crude oil consider low acid crude when compare with HAC01 and HAC02 which has acid 7.56 and 5.3 mg KOH/g respectively but high TAN when consider has acid more than 1 mg KOH/g. high amount of acid remains in short residue 1.9 mg KOH/g other amount of acid distribute between atmospheric gasoil and vacuum gasoil.

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