

## **Introduction**

### **1.1 Crude oil**

Crude oil, more properly called petroleum, is a complex mixture of thousands of compounds. While most of these compounds are hydrocarbons, some contain oxygen, nitrogen, or sulfur, and there are trace amounts of metals, usually present in large molecules called a paraffins<sup>(1)</sup>. Crude petroleum varies in appearance from a yellow or green mobile liquid to darker and often almost black syrup fluids, sometimes solidifying to a black paste. This great variety in appearance is obviously caused by differences in composition. While some crude oils consist mainly of paraffin, others may be more cycloparaffinic (naphthenic) or aromatic in character. As for molecular size of the constituents, here again some oils may be particularly rich in hydrocarbons of low molecular weight, whereas others contain a high percentage of large, complicated molecule<sup>(2)</sup>

## 1.2 COMPOSITION OF PETROLEUM

Crude oils and high-boiling crude oil fractions are composed of many members of a relatively few homologous series of hydrocarbons. The composition of the total mixture, in terms of elementary composition, does not vary a great deal, but small differences in composition can greatly affect the physical properties and the processing required to produce salable products. Petroleum is essentially a mixture of hydrocarbons, and even the nonhydrocarbon elements are generally present as components of complex molecules, predominantly hydrocarbon in character, but containing small quantities of oxygen, sulfur, nitrogen, vanadium, nickel, and chromium 51. The hydrocarbons present in crude petroleum are classified into three general types: paraffins, naphthenes, and aromatics. In addition, there is a fourth type, olefins, that is formed during processing by the cracking or dehydrogenation of paraffins and naphthenes. There are no olefins in crude oils<sup>(3)</sup>.

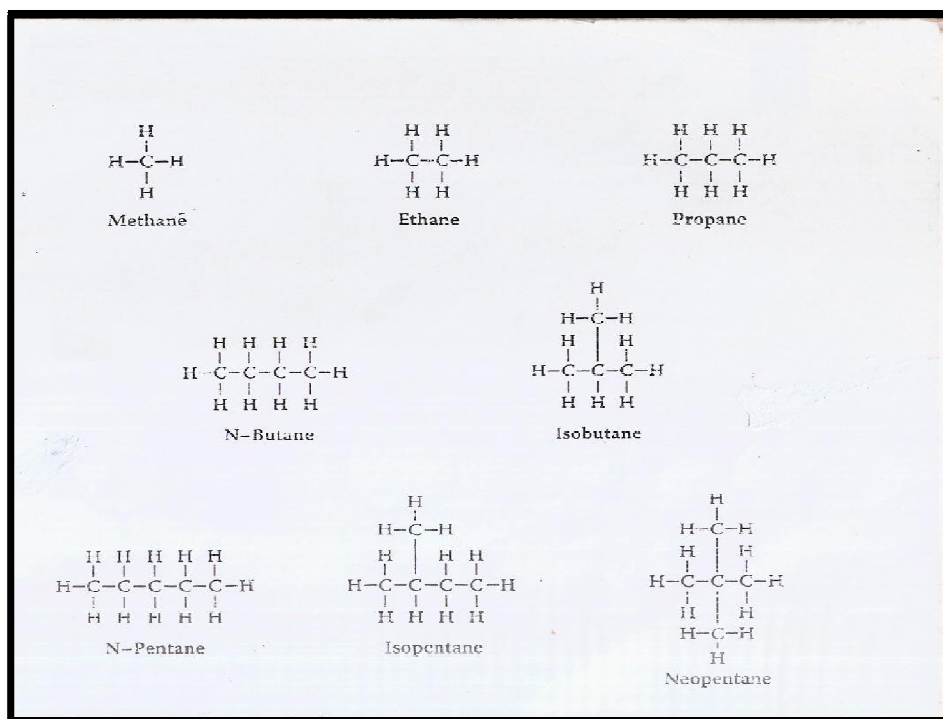
### 1.2.1 PARAFFINS

The paraffin series of hydrocarbons is characterized by the rule that the carbon atoms are connected by a single bond, and the other bonds are saturated with hydrogen atoms. The general formula for paraffins is  $C_nH_{2n+2}$ .

The simplest paraffin is methane,  $CH_4$ , followed by the homologous series of ethane, propane, normal and isobutene, and normal, iso-, and neopentane (Figure 1.1). When the number of carbon atoms in the molecule is greater than three, several hydrocarbons may exist that contain the same number of carbon and hydrogen atoms but have

different structures. This is because carbon is capable not only of chain formation, but also of forming single- or double-branched chains that give rise to isomers that have significantly different properties. For example, the motor octane number of n-octane is 17 and that of isooctane (2,2,4-Trimethyl pentane) is 100.

The number of possible isomers increases in geometric progression as the number of carbon atoms increases. There are 2 paraffin isomers of butane, 3 of pentane, and 17 structural isomers of octane, and by the time the number of carbon atoms has increased to 18, there are 60,533 isomers of cetane. Crude oil contains molecules with up to 70 carbon atoms, and hence the number of possible paraffinic hydrocarbons is very high<sup>(3)</sup>.



**Figure: 1.1 Paraffins in crude oil.**

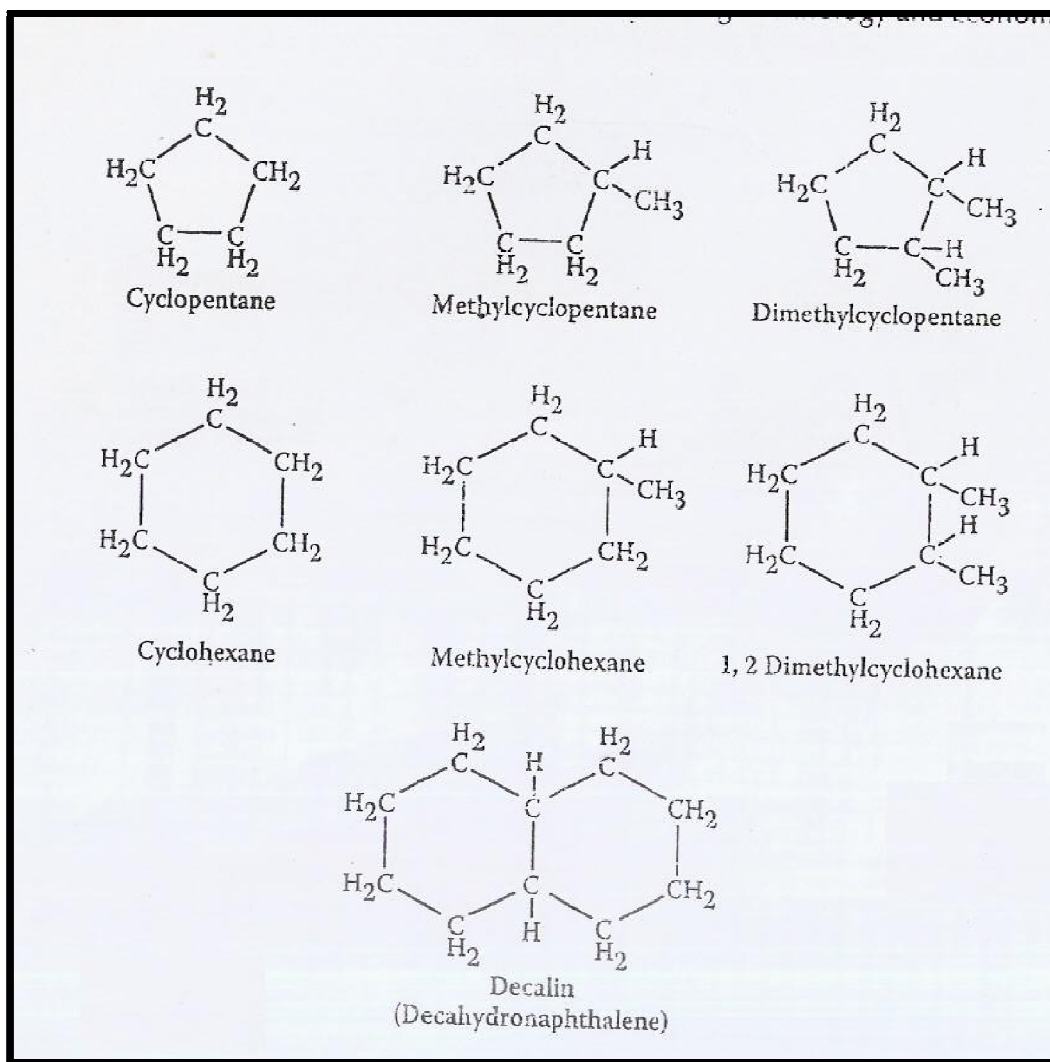
### 1.2.2 OLEFINS

Olefins do not naturally occur in crude oils but are formed during processing. They are very similar in structure to paraffins, but at least two of the carbon atoms are joined by double bonds. The general formula is  $C_nC_{2n}$ . Olefins are generally undesirable in finished products because the double bonds are reactive and the compounds are more easily oxidized and polymerized to form **gums** and **varnishes**. In gasoline boiling-range fractions, some olefins are desirable because olefins have higher octane numbers than paraffin compounds with the same number of carbon atoms. Olefins containing five carbon atoms have high reaction rates with compounds in the atmosphere that form pollutants and, even though they have high research octane numbers, are considered generally undesirable.

Some diolefins (containing two double bonds) are also formed during processing, but they react very rapidly with olefins to form high molecular weight polymers consisting of many simple unsaturated molecules joined together. Diolefins are very undesirable in products because they are so reactive they polymerize and form filter- and equipment plugging compounds<sup>(3)</sup>.

### 1.2.3 NAPHTHENES (CYCLOPARAFFINS)

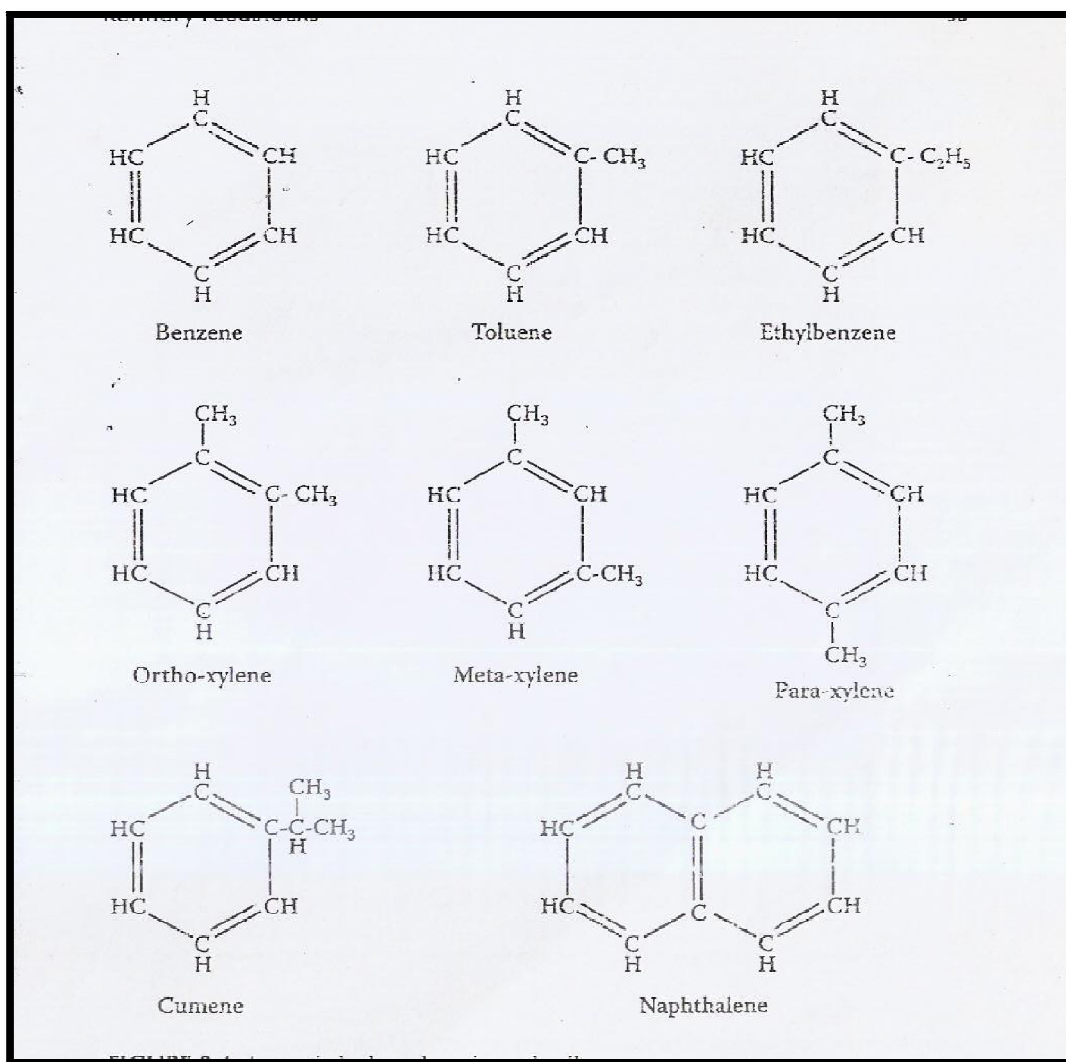
Cycloparaffin hydrocarbons in which all the available bonds of the carbon atoms are saturated with hydrogen are called naphthenes. There are many types of naphthenes present in crude oil, but, except for the lower-molecular-weight compounds such as cyclopentane and cyclohexane are generally not handled as individual compounds. They are classified according to boiling range and their properties determined with the help of correlation factors such as the  $K_w$  factor or CL. Some typical naphthenic compounds are shown in Figure 1.2.



**Figure: 1.2 Some Naphthenes which are present in crude Oil**

#### 1.2.4 AROMATICS

The aromatic series of hydrocarbons is chemically and physically very different from the paraffins and cycloparaffins (naphthenes). Aromatic hydrocarbons contain a benzene ring, which is unsaturated but very stable, and frequently behave as saturated compounds <sup>(5)</sup>.



**Figure: 1.3some Aromatics Hydrocarbon which are present in crude oil**

### 1.3 Crude Oil Classification

Crude oils are often classified by the group of hydrocarbon, which is considered to typify that crude. This does not mean, however, that the other groups of hydrocarbons are not represented in the oil. It may even be that, for instant, in the light fractions the aromatics predominate, while the normal paraffin are concentrated in the high-boiling ranges. A part from hydrocarbons which can be grouped in one of the main classes, paraffin, naphthene and aromatic, crude oils may also contain mixed – type hydrocarbon, such as naphthenes with paraffinic side – chains or aromatic nuclei with side – chains which cannot easily be classified in either of the main groups mentioned above. A rigid classification of crudes in paraffinic, naphthenic or mixed – type is therefore not possible. Nevertheless, many yardsticks have been proposed for the purpose of classifying crude oils, but none of them is truly successful in indicating chemical composition<sup>(4)</sup>.

The American Petroleum Institute (**API**) has developed a universal system for classifying crude oils based on their density. Rather than expressing the density in the traditional terms of weight per unit volume, the API gravity is described in degrees of the *empirical* API scale.

$$\text{API} = 141.5 / (\text{Spec. Gravity @ } 60^{\circ}\text{C}/60^{\circ}\text{F}) - 131.5$$

Petroleum characteristics as a function of API gravity are summarized in table 1.1.

**Table 1.1: API Crude Oil Classification**

<b>API Range (Degree 0)</b>	<b>Description</b>	<b>Rheology</b>	<b>Color</b>	<b>Main Components</b>
0.0 – 22.3	Heavy	Highly Viscous	Dark	Asphalt
22.3 – 31.3	Medium	Moderately Viscous	Brown	Gasoline & Diesels
31.3 - 47.0	Light	Very Fluid	Light Yellow	Condensate / Gasoline



## **1.4 Chemical and Physical properties:**

Crude oils appear as liquids of varying viscosities. Their color can range from green to dark brown. They can have an odor of hydrogen sulfide, turpentine or simply hydrocarbon. Their chemical compositions are very complex and depend essentially on their age, that is, the phase of development of the kerogene, regardless of the origin of the crude. Knowledge of a crude oil's overall physical and chemical characteristics will determine what kind of initial treatment- associated gas separation and stabilization at the field of production- transport, storage, and of course, price.

A detailed study of the properties of the potential products is of prime technical and economic importance, because it allows the refiner to have a choice in selecting feed stocks for his different units for separation, transformation and conversion, to set their operating conditions, in order to satisfy the needs of the marketplace in the best ways possible<sup>(5)</sup>.

### **1.4.1 Density:**

Density is defined as specific mass per unit volume under specified conditions of pressure and temperature. The density is usually determined at atmospheric pressure and at a temperature of 15 °C<sup>(5)</sup>.

### **1.4.2 API GRAVITY**

The density of petroleum oils is expressed in the United States in terms of API gravity rather than specific gravity: it is related to specific gravity in such a fashion that an increase in API gravity corresponds to a decrease in specific gravity. The units of API gravity are API° and can be calculated from specific gravity by equation 1.1:

$$\text{API} = \frac{141.5}{\text{Specific gravity}} - 1.1$$

In Equation (1.2), specific gravity and API gravity refer to the weight per unit volume at 60F (15.6°C) as compared to water at 60F. Crude oil gravity may range from less than 10API° to over 50API°, but most crudes fall in the 20 to 45API° range. API gravity always refers to the liquid sample at 60F (15.6°C). API gravities are not linear and, therefore, cannot be averaged. For example, a gallon of 30API° gravity hydrocarbons when mixed with a gallon of 40API° hydrocarbons will not yield 2 gal of 35API° hydrocarbons, but will give 2 gal of hydrocarbons with API gravity different from 35API°. Specific gravities can be averaged. In practice, however, API gravities are frequently averaged because the error is usually small<sup>(5)</sup>.

#### **1.4.3 Specific Gravity of Crude Oils**

Specific gravity is important commercially because the crude oil price depends partly on this property. The specific gravity is expressed most often in degrees API .

During loading and unloading of crude oil tankers, the specific gravity of the crude is measured to confirm that it meets the specifications for the case where payment is made on a barrel basis, or when the volume is converted into weight if the transaction is based on a price per ton.

Within the same geographical region, the crude specific gravity varies from one reservoir to another.

Within the same reservoir, we also observe variations of specific gravity from one well to another<sup>(5)</sup>.

Generally, the crude oils are classed according to specific gravity in four main categories:

- Light crudes                      sp. gr.  $d_4^{15} < 0.825$
- medium crudes     $0.825 < \text{sp. gr. } d_4^{15} < 0.875$
- Heavy crudes                       $0.875 < \text{sp. gr. } d_4^{15} < 1.000$
- Extra-heavy crudes      sp. gr.  $d_4^{15} > 1.000^{(5)}$ .

#### **1.4.4 Wax content:**

The behavior of oil may be influenced by wax content. Oils with wax contents greater than about 10% tend to have high pour points and if the ambient temperature is below this, the oil will be either a solid or a highly viscous liquid. High wax contents can also help to stabilize water-in-oil emulsions<sup>(5)</sup>.

#### **1.4.5 Crude Oil Pour Point**

When crude petroleum is cooled, there is no distinct change from liquid to solid as is the case for pure substances. First there is a more or less noticeable change in viscosity, then, if the temperature is lowered sufficiently, the crude oil ceases to be fluid, and approaches the solid state by thickening. This happens because crude oil is a complex mixture in which the majority of components do not generally crystallize; their transition to the solid state does not therefore occur at constant temperature, but rather along a temperature range, for which the parameters are a function of the crude oil's previous treatment. Knowledge of the crude's previous history is very important, Preheating to 45-65°C lowers the pour point because the crude petroleum contains seeds of paraffinic crystals, and these are destroyed during preheating. If the crude is preheated to a higher temperature (about 100°C), an increase

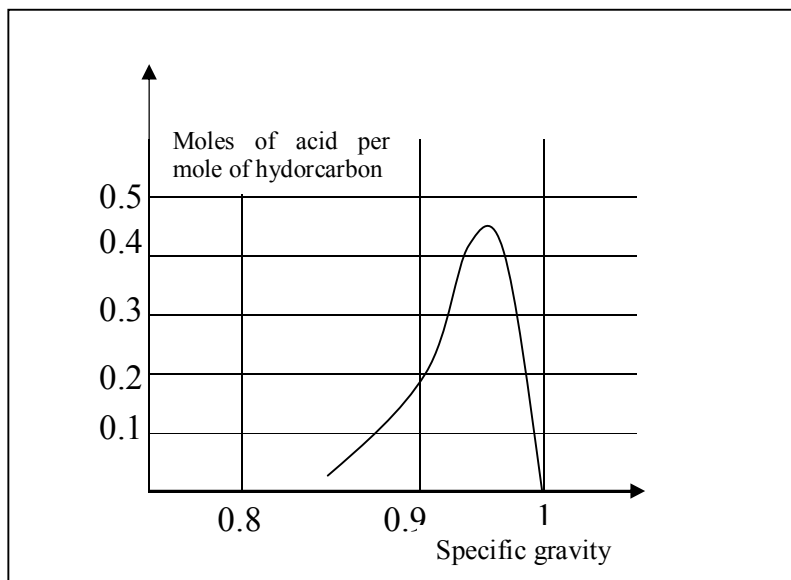
in pour point is observed which is due to the vaporization of light hydrocarbons; the crude has become heavier.

The pour point of crude oils is measured to give an approximate indication as to their “pumpability”. In fact, the agitation of the fluid brought on by pumping can stop, slow down or destroy the formation of crystals, conferring on the crude additional fluidity beyond that of the measured pour point temperature. The measurement of this temperature is defined by the standard NP 1’ 60-105 and by the standard ASTM D 97. Both test stipulate moreover preheating the sample to 45 to 48°C. Crude oil pour points usually are between —60°C and +30°C<sup>(5)</sup>.

#### **1.4.6 TAN: Acid Number**

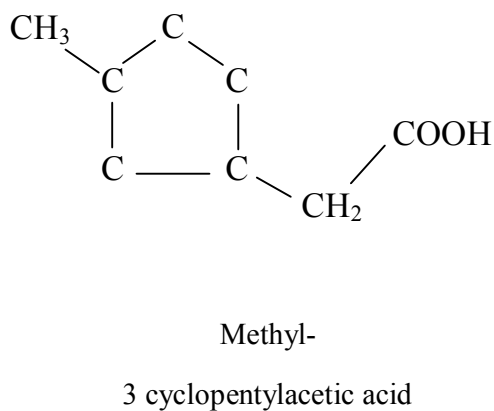
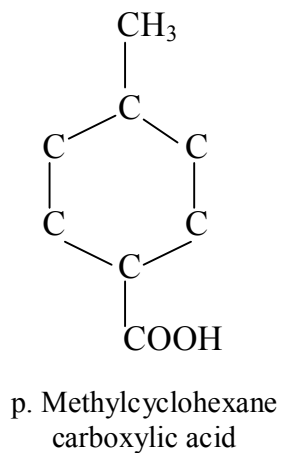
Crude oils contain carboxylic acids. These are analyzed by titration with potassium hydroxide and the result of the analysis is expressed in mg of KOH/g crude. It is worthwhile to mention that the distribution of naphthenic acids is not, uniform in a crude oil since a maximum value is observed in the fractions distilled between 400 and 450°C and whose average specific gravity is 0.950 (Figure 1.4).

In the light or medium cuts, the acids are linear as in Valeric acid  $\text{CH}_3 - (\text{CH}_2)_4 - \text{COOH}$  or stearic acid  $\text{CH}_3 (\text{CH}_2)_{16} - \text{COOH}$ <sup>(5)</sup>.



**Figure 1.4: Distribution of the acid content as a function of the specific of successive distillation fractions.**

The majority of acids contained in the diesel cuts are cyclic and come from cyclopentane or cyclohexane. They are better known as naphthenic acids.



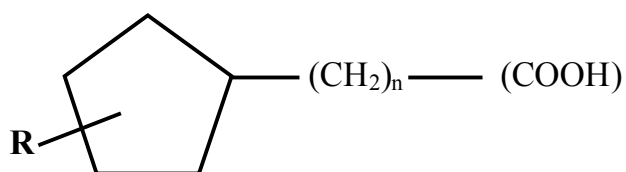
The presence of these acids in crude oils and petroleum cuts causes problems for the refiner because they form stable emulsions with caustic

solutions during desalting or in lubricating oil production; very corrosive at high temperatures (350-400°C), they attack ordinary carbon steel, which necessitates the use of alloy piping materials<sup>(7)</sup>.

#### 1.4.6.1 Naphthenic acid

Naphthenic acid is the name for unspecific mixture of several cyclopentyl carboxylic acids present in crude oils.

#### 1.4.6.2 Chemical formula:



R represents multiple alkyl groups or fused cycloaliphatic rings.

Naphthenic Acid is a:

- clear, amber colored liquid with a hydrocarbon odor.
- pH = 5.2 .
- Boiling point = 268 °C.
- Flash point = >149°C.
- Vapor density = 6.5 (air =1), much more dense than air.
- Not water soluble

Naphthenic acid is determined by ASTM D664 potentiometric titration method as Total Acid Number (TAN), which is the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil.

Crude with a Total Acid Number (TAN) >1.0mg KOH/g conventionally labeled as High TAN.

Most high TAN oil tends to be heavy<sup>(7)</sup>.

### **1.4.7 Water Content of Crude Oils**

In the crude, water is found partly in solution and partly in the form of more-or-less stable emulsion; this stability is due to the presence of asphaltenes or certain surfactant agents such as mercaptans or naphthenic acids.

The water content of crude oils is determined by a standardized method whose procedure is to cause the water to form an azeotrope with an aromatic (generally industrial xylene). Brought to ambient temperature, this azeotrope separates into two phases: water and xylene. The volume of water is then measured and compared with the total volume of treated crude<sup>(5)</sup>.

### **1.4.8 Sulfur Content of Crude Oils**

Crude oils contain organic sulfur compounds, dissolved hydrogen sulfide and sometimes even suspended sulfur. Generally speaking, the total sulfur content of crude is between 0.05 and 5% by weight. Crudes with greater than 5% sulfur generally require more extensive processing than those with lower sulfur content. Although the term “sourcrude” crude initially had reference to those crudes containing dissolved hydrogen sulfide independent of total sulfur content, it has come to mean any crude oil with a sulfur content high enough to require special processing. There is no sharp dividing line between sour and sweet crudes, but 0.5% sulfur content is frequently used as the criterion<sup>(5)</sup>.

#### **1.4.8.1 Origin of Sulfur:**

Sulfur comes mainly from the decomposition of organic matter, and one observes that with the passage of time and of gradual settling of material into strata, the crude oils lose their sulfur in the form of  $H_2S$  that appears

in the associated gas, a small portion stays with the liquid. Another possible origin of H<sub>2</sub>S is the reduction of sulfates by hydrogen by bacterial action of the type desulfotribiodesulfuricans (Equation 1.2):

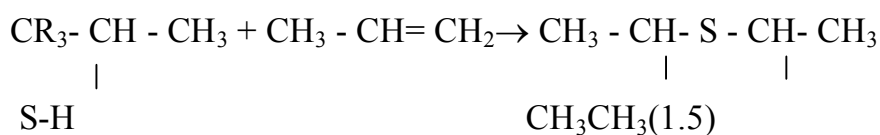
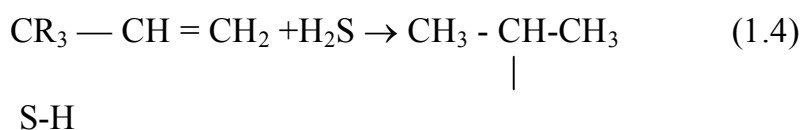


Hydrogen comes from the crude and the sulfate ions are held in the reservoir rock.

The H<sub>2</sub>S formed can react with the sulfates or rock to form sulfur (Equation 1.2) that remains in suspension as in the case of crude from Goldsmith, Texas, USA, or that, under the conditions of pressure, temperature and period of formation of the reservoir, can react with the hydrocarbons to give sulfur compounds:



H<sub>2</sub>S reacts in another way with the olefinic hydrocarbons producing thiols and sulfur compounds (Equation 1.4 and 1.5):



These reactions can explain the absence of olefins in crude oil, their presence being detected only in the erodes of low sulfur content. The sulfur content in crude from Bradford which is the one of the rare crudes containing olefins is about 0.4%.



Knowledge of the nature and quantity of sulfur compounds contained in crudes and petroleum cuts is of prime importance to the refiner, because it constitutes a constraint in the establishment of refinery flow sheets and the preparation of finished products. In fact a few of these products contain or entrain corrosive materials which, during refinery operations, reduce the service life of certain catalysts such as reforming catalysts, degrade the quality of finished products by changing their color and by giving them an Unpleasant odor, reduce the service life of lubricating oils, without mentioning atmospheric pollution from formation of  $\text{SO}_2$  and  $\text{SO}_3$  during the Combustion of petroleum fuels, and fires caused by contact between iron sulfide on the piping and air<sup>(5)</sup>.

#### **1.4.8.2 Nature of Sulfur Compounds Contained In Crude Oil**

Practically, one measures the quantity of total sulfur (in all its forms) contained in crude oil by analyzing the quantity of  $\text{SO}_2$  formed by the combustion of a sample of crude, and the result is taken into account when evaluating the crude oil price. When they are present, elementary sulfur and dissolved  $\text{H}_2\text{S}$  can also be analyzed. The sulfur compounds are classed in six chemical groups<sup>(5)</sup>.

##### **1.4.8.2.1 Free Elemental Sulfur S**

Free sulfur is rarely present in crude oils, but it can be found in suspension or dissolved in the liquid. The crude from Goldsmith (Texas, USA.) is richest in free sulfur (1% by weight for a total sulfur content of 2.17%). It could be produced by compounds in the reservoir rock by sulfate reduction (reaction 1.3).

#### **1.4.8.2.2 Hydrogen Sulfide H<sub>2</sub>S**

Hydrogen sulfide (H<sub>2</sub>) is found with the reservoir gas and dissolved in the crude (< 50 ppm by weight), but it is formed during refining operations such as catalytic cracking, hydrodesulphurization, and thermal cracking or by thermal decomposition of sulfur—containing hydrocarbons during distillation.

In the 1950's, crude oils were either corrosive (sour), or non-corrosive (sweet). Crudes containing more than 6 ppm of dissolved H<sub>2</sub>S were classed as sour because, beyond this limit, corrosion was observed on the walls at storage tanks by formation of scales of pyrophoric iron sulfides.

At this point in time, the total sulfur content of crudes was not taken into consideration, since most of them were produced and refined in the United-States and contained less than 1%, and only the gasoline coming from corrosive crudes needed sweetening (elimination of thiols) for them to meet the specifications then in force. Today all crudes containing more than one per cent sulfur are said to be “corrosive”.

#### **1.4.8.2.3 The Thiols**

Of the general formula, R — S — H, where R represents an aliphatic or cyclic radical, the thiols, also known as mercaptans, are acidic in behavior owing to their S - H functional group; they are corrosive and malodorous. Their concentration in crude oils is very low if not zero, but they are created from other sulfur compounds during refining operations and show up in the light cuts, as illustrated in Table 1.2<sup>(5)</sup>.

**Table 1.2 The light cuts as illustrated <sup>(5)</sup>**

Nature of cut (temperature interval, °C)	Mercaptan %	Total sulfur, %	% Mercaptan sulfur total sulfur
Crude petroleum	0.110	1.8	0.6
Butane	0.0228	0.0228	100
Light gasoline (20-70 °C)	0.0196	0.0240	82
Heavy gasoline( 70-150°C)	0.0162	0.026	62
Naphtha (150-190°C)	0.0084	0.059	14
Kerosene (190-250°C)	0.0015	0.17	0.9
Gas oil (250-370 °C)	0.0015	1.40	<0.1
Residue (370+ °C)	0	3.17	0

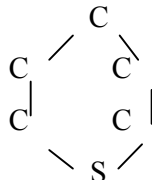
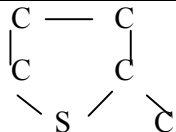
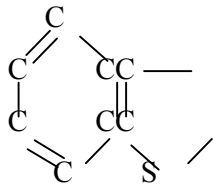
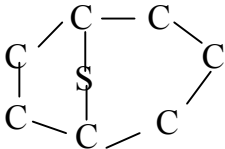
**Table 1.3 Mercaptans identified in crude oils <sup>(5)</sup>.**

Name	Chemical formula	Boiling point, °C	Cut
Methanethiol	CH <sub>3</sub> - SH	6	Butane Gasoline
Ethanethiol	CH <sub>3</sub> - CH <sub>2</sub> - SH	34	Gasoline
2 methylpropanthiol	$\begin{array}{c} \text{CH}_3\text{- CH-CH}_2\text{-SH} \\   \\ \text{CH}_3 \end{array}$	85	Gasoline
2 methylpropanthiol	$\begin{array}{c} \text{CH}_3\text{- CH-(CH}_2\text{)}_5\text{-SH} \\   \\ \text{CH}_3 \end{array}$	186	Kerosene
Cyclohexanethiol	$\begin{array}{c} \text{CH}_2 \\ / \quad \backslash \\ \text{CH}_2\text{CH}_2 \\   \quad \backslash \\ \text{CH}_2\text{CH}_2 \\   \quad \backslash \\ \text{CH} \\   \\ \text{S - H} \end{array}$	159	Gasoline

#### 1.4.8.2.4 The Sulfides

The sulfides are chemically neutral; they can have a linear or ring Structure. For molecules of equal carbon number, their boiling points are higher than those of mercaptans; they constitute the majority of sulfur containing hydrocarbons in the middle distillates kerosene and gas oil <sup>(5)</sup>.

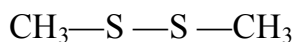
**Table 1.4 Sulfides identified in the oils <sup>(5)</sup>.**

Name	Chemical formula	Boiling point, °C	Cut
3 Thiapentane	$\text{CH}_3\text{-CH}_2\text{-S-CH}_2\text{-CH}_3$	92	Gasoline
2 Methyl-3 thiapentane	$\text{CH}_3\text{-CH}_2\text{-S-CH}_2\text{-CH}_3$ $\text{CH}_3$	108	Gasoline
Thiacyclohexane		85	Gasoline
2Methylthiacyclopentane		186	Gasoline
Thiaindane		159	Kerosene
Thiabicyclooctane		194.5	Kerosene and gas oil

#### 1.4.8.2.5 The Disulfides

These compounds are difficult to separate and, consequently, few have been identified:

- Dimethyl disulfide (2,3 dithiobutane)



- Diethyl disulfide (2,3 dithiohexane)

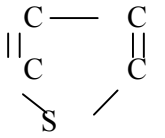
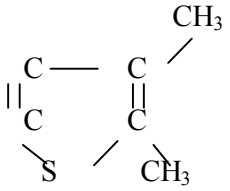
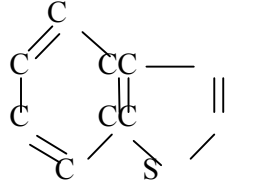
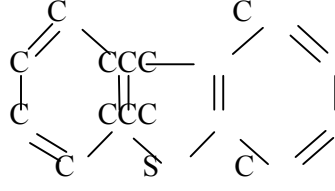


It is only recently that the more complex substances like trinaphtho-diphenyldisulfide have been able to be identified <sup>(5)</sup>.

#### 1.4.8.2.6 Thiophene and Derivatives

The presence of thiophene and its derivatives in crude oils was detected in 1899, but until 1953, the date at which the methyl-thiophenes were identified in kerosene from Agha Jan, Iran crude oil, it was believed that they came from the degradation of sulfides during refining operations. Finally, their presence was no longer doubted after the identification of benzothiophenes and their derivatives' (Table 1.5), and lately of naphthenobenzothiophenes in heavy cuts <sup>(5)</sup>.

**Table 1.5 Thiophene derivatives in crude oils <sup>(5)</sup>.**

Name	Chemical formula	Boiling point, °C	Cut
Thiophene		84	Gasoline
Dimethylthiophene		141.6	Gasoline and Kerosene
Bezothiophene		219.9	Kerosene
Dibenzothiophene		300	Gas oil

The major part of the sulfur contained in crude petroleum is distributed between the heavy cuts and residues (Table 1.6) in the form of sulfur compounds of the naphthenophenanthrene or naphthenoanthracene type, or in the form of benzothiophene's, that is, molecules having one or several naphthenic and aromatic rings that usually contain a single sulfur atom.

Note that the total sulfur levels are different from those appearing in Table 4 as a result of having different distillation ranges <sup>(5)</sup>.

**Table 1.6 Sulfur contained in crude distributed between heavy and cuts residues**

Cut	Light gasoline	Heavy gasoline	Kerosene	Gas oil	Residue	Curde
Temperature interval °C	20-70	70-180	180-260	260-370	370+	
Specific gravity $d_4^{15}$	0.648	0.741	0.801	0.856	0.957	
Average molecular weight	75	117	175	255	400	
Total sulfur ,weight %	0.024	0.032	0.202	1.436	3.167	1.80
Number of moles of sulfides	$\frac{1}{1800}$	$\frac{1}{855}$	$\frac{1}{90}$	$\frac{1}{9}$	$\frac{1}{2.5}$	
Total number of moles						

#### **1.4.9Viscosity of Crude Oils:**

The measurement of a crude oil's viscosity at different temperatures is particularly important for the calculation of pressure drop in pipelines and refinery piping systems, as well as for the specification of pumps and exchangers.

The exchange in viscosity with temperature is not the same for all crudes. The change in viscosity of a paraffinic crude increases rapidly with decreasing temperature; on the other hand, for the naphthenic crudes, the increase in viscosity is more gradual.

The viscosity is determined by measuring the time it takes for a crude to flow through a capillary tube of a given length at a precise temperature. This is called the kinematic viscosity, expressed in mm<sup>2</sup>/s. It is defined by the standards, NF T 60-100 or ASTM D 445. Viscosity can also be

determined by measuring the time it takes for the oil to flow through a calibrated orifice: standard ASTM D 88. It is expressed in Saybolt seconds (SSU) <sup>(5)</sup>.

#### **1.4.10 Asphaltene content:**

A good indication of how easily oil will form a water-in-oil emulsion is given by the asphaltene content. Oils with asphaltene contents greater than 0.5% tend to form stable emulsions. These emulsions can contain up to 80% water by volume and are generally extremely viscous. The rate at which emulsification takes place is primarily a function of sea state, although viscous oils tend to absorb water more slowly <sup>(5)</sup>.

#### **1.4.11 Nitrogen Content of Crude Oils**

Crude oils contain nitrogen compounds in the form of basic substances such as quinoline, isoquinoline, and pyridine, or neutral materials such as pyrrole, indole, and carbazole.

These compounds can be malodorous as in the case of quinoline, or they can have a pleasant odor as does indole. They decompose on heating to give organic bases or ammonia that reduce the acidity of refining catalysts in conversion units such as reformers or crackers, and initiate gum formation in distillates (kerosene, gas oil).

Table 1.7 gives some typical nitrogen and sulfur values.

Crude	%S	%N	N/S x 100
Kirkuk	2.0	0.10	5
Kuwait	2.5	0.15	6
Cash Saran	1.6	0.23	14



#### **1.4.12 Salt Content of Crude Oils**

Regardless of their presence in very small amounts, (Table 10), mineral salts cause serious problems during crude oil treatment. Chlorides of sodium, magnesium and calcium are almost always the prevailing compounds, along with gypsum and calcium carbonate.

The measurement of chlorides is standardized (NF M 07-023, ASTM 3230); the result of two measurements is expressed in mg of NaCl/kg of crude. Table 10 gives the salt contents of some crude oils; these values come from measurements taken in a refinery and thereby include the salts brought in by contamination.

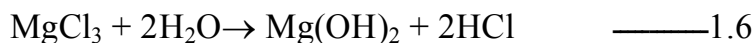
The presence of salts in crude oils has several disadvantages. During production; sodium chloride can deposit in layers on tubing walls after partial vaporization of the water due to the pressure drop between bottomhole and wellhead; when these deposits become important large enough, the diameter of the well tubing is reduced, which causes production loss. In order to reduce the impact of such incidents, freshwater is injected.

In the refinery; the salts deposit in the tubes of exchangers and reduce heat transfer, while in heater tubes, hot spots are created favoring cokeformation<sup>(5)</sup>.

**Table 1.8 Salt content of various crudes**

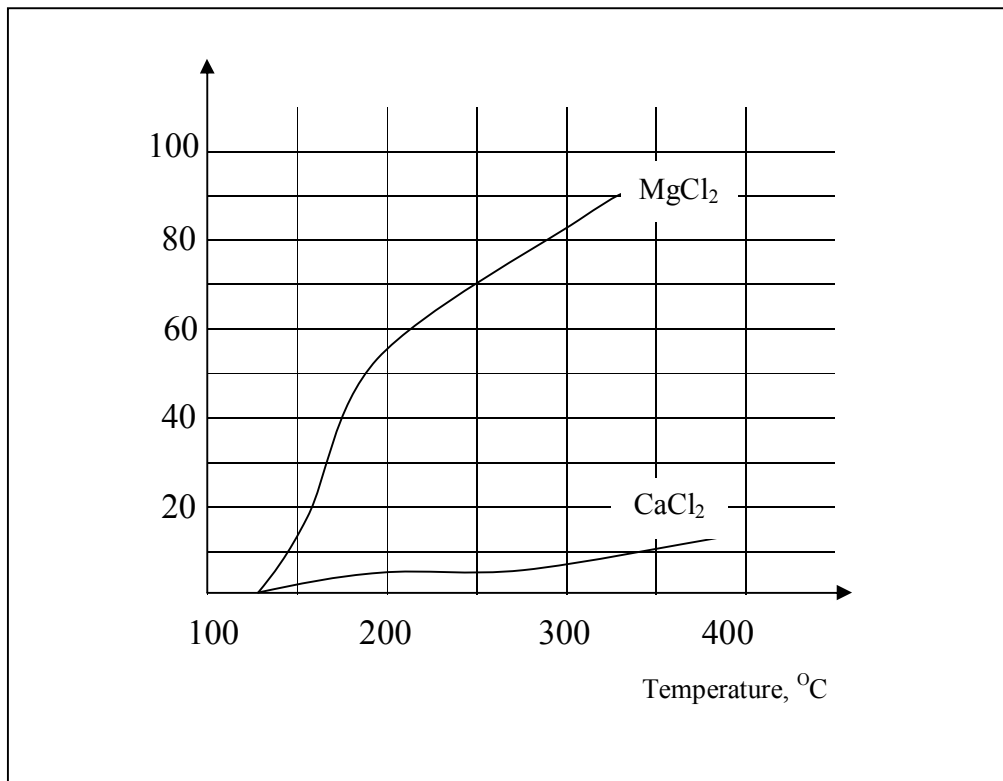
<b>Crude oil name</b>	<b>Country of origin</b>	<b>NaCl mg/kg (ppm weight)</b>
Arabian Light	Saudi Arabia	25
Agha Jari	Iran	25
HassiMessaoud	Algeria	30
Kuwait	Kuwait	35
Boscan	Venezuela	60
Bonny	Nigeria	135
Brega	Libya	153
Safaniyah	Saudi Arabia L	280
Sarir	Libya	345

The major portion of salt is found in residues; as these streams serve as the bases for fuels, or as feeds for asphalt and petroleum coke production, the presence of salt in these products causes fouling of burners, the alteration of asphalt emulsions, and the deterioration of coke quality. Furthermore, calcium and magnesium chlorides begin to hydrolyze at 120°C. This hydrolysis occurs rapidly as the temperature increases according to the reaction:



The hydrogen chloride released dissolves in water during condensation in the crude oil distillation column overhead or in the condenser, which cause corrosion of materials at these locations. The action of hydrochloric acid is favored and accelerated by the presence of hydrogen sulfide which results in the decomposition of sulfur-containing hydrocarbons; this forces the refiner to inject a basic material like ammonia at the point

where water condenses in the atmospheric distillation column. In addition, salts deactivate reforming and catalytic cracking catalysts. These hazards are reduced drastically by desalting crude oils, a process which consists of coalescing and decanting the fine water droplets in a vessel by using an electric field of 0.7 to 1 kV/cm.



#### 1.4.13 Vapor Pressure and Flash Point of Crude Oils

The measurement of the vapor pressure and flash point of crude oils enables the light hydrocarbon content to be estimated. The vapor pressure of a crude oil at the wellhead can reach 20 bar. If it were necessary to store and transport it under these conditions, heavy walled equipment would be required. For that, the pressure is reduced (<1 bar) by separating the high vapor pressure components using a series of pressure reductions (from one to four “flash” stages) in equipment called “separators”, which are in fact simple vessels that allow the separation of

the two liquid and vapor phases formed downstream of the pressure reduction point. The different components distribute themselves in the two phases in accordance with equilibrium relationships.

The resulting vapor phase is called “associated gas” and the liquid phase is said to be the crude oil. The production of gas is generally considered to be unavoidable because only a small portion is economically recoverable for sale, and yet the quantity produced is relatively high. The reservoirs in the Middle East are estimated to produce 0.14 ton of associated gas per ton of crude.

Safety standards govern the manipulation and storage of crude oil and petroleum products with regard to their flash points which are directly linked to vapor pressure. One generally observes that crude oils having a vapor pressure greater than 0.2 bar at 37.8°C (100°F), have a flash point less than 20°C.

During the course of operations such as filling and draining tanks and vessels, light hydrocarbons are lost. These losses are expressed as volume per cent of liquid. the Reid vapor pressure being expressed in psi, (pounds per square inch)\*. To reduce these losses, the crude oils are stored in floating roof tanks.

The measurement of vapor pressure is defined by the standards NF M 07-007 and ASTM D 323, flash points by the standards NF M 07-011 and ASTM D 56<sup>(5)</sup>.

#### **1.4.14 TBP Crude Oil Distillation:**

The TBP (True Boiling Point) distillation gives an almost exact picture of a crude petroleum by measuring the boiling points of the components making up the crude; whence its name. Crude petroleum is fractionated into around fifty cuts having a very narrow distillation intervals which allows them to be considered as fictitious pure hydrocarbons whose boiling points are equal to the arithmetic average of the initial and final boiling points,  $T_m = (T_1 + T_2)/2$ , the other physical characteristics being average properties measured for each cut<sup>(5)</sup>.

The different cuts obtained are collected; their initial and final distillation temperatures are recorded along with their weights and specific gravities. Other physical characteristics are measured: for the light fractions octane number, vapor pressure, molecular weight, PONA, weight per cent sulfur, el., and, for the heavy fractions, the aniline point, specific gravity, viscosity, sulfur content, and asphaltene content, etc.

The determination of properties for each cut enables curves to be obtained for yields and properties as well as curves for iso-properties that are useful in the economic analyses of crude oils.

It is possible to calculate the properties of wider cuts given the characteristics of the smaller fractions when these properties are additive in volume, weight or moles. Only the specific gravity, vapor pressure, sulfur content, and aromatics content give this advantage. All others, such as viscosity, flash point, pour point, need to be measured. In this case it is preferable to proceed with a TBP distillation of the wider cuts that correspond with those in an actual refinery whose properties have been measured.

The most commonly referenced so-called wide cuts are the following:

Gas	C3—C4
Light debutanized gasoline	$\left\{ \begin{array}{l} \text{C5— } 70^{\circ}\text{C} \\ \text{C5— } 80^{\circ}\text{C} \\ \text{C5 - } 100^{\circ}\text{C} \end{array} \right.$
Heavy gasoline 80 — 180°C 100 — 180°C	$\left\{ \begin{array}{l} 70— 140\text{ }^{\circ}\text{C} \end{array} \right.$
Kerosene 180—260°C	$\left\{ \begin{array}{l} 160 — 260^{\circ}\text{C} \end{array} \right.$
Gas oil 260 — 360°C 260 — 370°C 160— 360°C	$\left\{ \begin{array}{l} 260— 325^{\circ}\text{C} \end{array} \right.$
Residue T>360 °C T>370°C	$\left\{ \begin{array}{l} T>325^{\circ}\text{C} \end{array} \right.$

All the analytical results are represented as curves that enable easy and rational utilization.

In certain cases, the curves,  $T = f(\% \text{ distilled})$  or  $\text{specific gravity} = f(\% \text{ distilled})$ . Moving toward the heavy cuts, the curves become smoother because the number of isomers becomes very large and their boiling points and specific gravities are very close in value.

Certain curves,  $T = f(\% \text{ distilled})$ , level off at high temperatures due to the change in pressure and to the utilization of charts for converting temperatures under reduced pressure to equivalent temperatures under atmospheric pressure. Currently the charts used most often for this purpose are those published by the API.

#### **1.4.15 Sediments (Bottom Sediments)**

Solids materials that are insoluble in hydrocarbon or water can be entrained in the crude. These are called “bottom sediments” and comprise fine particles of sand, drilling mud, rock such as feldspar and gypsum, metals in the form of minerals or in their free state such as iron, copper, lead, nickel, and vanadium. The latter can come from pipeline erosion, storage tanks, valves and piping systems, etc.: whatever comes in contact with the crude oil. The presence of such substances in crude oil is highly undesirable because they can plug piping and contaminate the products.

During storage, sediments decant with the water phase and deposit along with paraffins and asphalts in the bottoms of storage tanks as thick sludges or slurries (BS&W). The interface between the water-sediment and the crude must be well monitored in order to avoid pumping the slurry into the refinery’s operating units where it can cause serious upsets.

To lessen the risk of pumping sludges or slurries into a unit, the practice is to leave a safety margin of 50 cm (heel) below the outlet nozzle or install a strainer on the pump suction line. The deposits accumulate with time and the tanks are periodically emptied and cleaned.

The water and sediment contents of crude oils is measured according to the standard methods NF M 07-020, ASTM D 96 and D 1796, which determine the volume of water and sediments separated from the crude by centrifuging in the presence of a solvent (toluene and of a demulsifying agent; Table 11 gives the bottom sediment and water content of a few crude oils<sup>(5)</sup>.

**Table 1.9 The bottom sediment and water content of some crude oils <sup>(5)</sup>.**

<b>Crude oil name</b>	<b>Water and sediment contents (BS&amp;W) in volume %</b>
Nigerian	0.1
Arabian light	0.1
Dahra	0.6
Mandgi	0.8
Bachaquero	2.0



### 1.5 Sudanese crude oil

According to the 2008 BP Statistical Energy Survey, Sudan had proved oil reserves of 6.614 billion barrels at the end of 2007 or 0.53 % of the world's reserves , and produced an average of 457 thousand barrels of crude oil per day in 2007(before the separation), 0.57% of the world total and a change of 38 % compared to 2006.

The Sudanese crude oil is waxy in character, has an average API degree of 32 and possesses no sulfur. <sup>(6)</sup>

Table (1) shows five oil samples selected from different oil fields in Muglad and Melut basins to present the wide spectrum of Sudanese crude oil properties, which range from heavy oil to light oil.

**Table 1.10 Sudanese crude Oil properties from test result<sup>(6)</sup>**

Property	UNITY-9	TALIH-2	TOMA SOUTH	ADAR
API	33.6	38.5	42.6	30
BS & W VOL	0	0	0	0
P. POINT FC	81 / 27	86 / 30	76 / 26.1	105 / 40.5
SALT CONT. lb/kib	22	2		
SULPHER WT. %	0.07	<0.05		
CST " 60 deg C	14.31	43.27	15.7	11.6 " 75.5 deg C
GAS/OIL RATIO	15.15	146.4		30
BPP	75	180		50

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## 1.6 Dar Blend

Petrodar Operating Company Ltd. is an operating company to carry out exploration, development and production of oil for Block 3E, 7E and 3D in Sudan.

The main objectives of Petrodar are to explore, develop and produce oil and gas in Blocks 3 and 7.

These blocks are situated in the south east of Sudan(before the separation in 2011), between longitude 31 and 34 and latitude 8 and 10 with a total area of about 72,000 Km<sup>2</sup>.

The majority of DAR blend is paraffinic, asphaltinic in nature. Its properties differ due to the various production fields. The main features of the blend mixture are, medium density, low sulphur content (sweet), high pour point (42°C), high TAN content and low metal content. The crude oil from the productive fields, Adar , Palouge, Gamary , and Moleeta are linked together Field Production Facilities (FPF) remove gas and water before pumping via Ps #1 to Central Processing Facilities (CPF) at Al-Jabalyn as further processing are conducted to meet the export quality.

The current production plan requires the pumped oil temperature shall be between (40-75°C), which may be exposed to low temperature, pressure, and change cooling temperature, pressure, and change cooling rate during the period between Central Processing Facilities (C.P.F) and Bashayer-2 Marine Terminal (B.2.M.T).

The production profile is up to 2025; with daily production rate about 35.000 barrels /d <sup>(7)</sup>.



Figure 1.5 Petrodar Facilities Overview

### 1.6.1 Pipeline

The pipeline split into two sections, the first section termed the field pipeline, links the FPF, at Paloug, to the CPF near Aljabalyen a distance of about 242km.

The second section, the export pipeline, links the CPF to the marine Terminal near Port Sudan, on the Red Sea Coast, The oil is transferred via a carbon steel pipeline, the overall length is estimated to be 1134 Km length and (32 inches diameter (812.8mm) with external coating (3 layer inches Polypropylene), and buried to minimum depth of 1m above pipeline surface.

The Crude is pumped via a series of 6 pumping stations and heaters stations to the marine terminal at Port Sudan.

The maximum design temperature, discharge pressure and Maximum flow rate for pipeline are 80°C, 98 bar and 500,000bbl/day respectively.(4)

**Table 1.11 Pipeline Data in Petrodar Crude**

Segment	Length (Km)	Nominal (OD)(mm)	Thickness (mm)	ID (mm)	Soil Thermal (W/MK)	Elevation Difference (m)	Ambient Temp (C)
PS#1-PS#2	242	812,8	13,71	789,38	0,65	1,3	33
PS#2-PS#3	247	812,8	11,71	789,38	1,3	-7	33
PS#3-PS#4	123	812,8	11,71	789,38	1,3	7	33
PS#4-PS#5	242	812,8	11,71	789,38	1,85	-27	34
PS#5-PS#6	237	812,8	11,71	789,38	0,56	120	35
PS#6-MT	282	812,8	11,71-11,71-18,91-23,4	789,38 787,58 774,98 766,00	0,56 0,56 1.85 1.85	-448,3	35



## **1.7 Objectives**

This study aims to evaluate Dar Blend in comparison with GNPOC or WNPOC and other crudes produced in Sudan using physic-chemical methods.

## **2.1 Collection of crude oil samples:**

Untreated crude oil samples were collected from FPF Fulla light, GNPOC, WNPOC and Star oil.

## **2.2 Methods:**

### **2.2.1 Determination of Density:**

This procedure was done according to ASTM D5002

Definition:

Density: mass per unit volume at a specified temperature.

Relative density: the ratio of the density of a material at a stated temperature to the density of water at a stated temperature.

Test Methods:

Approximately 0.7 mL of crude oil sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample.

Apparatus:

- Digital density analyzer.
- Circulating, constant, temperature bath.
- Syringe.
- Thermometer.

### **2.2.2 Determination of API:**

Definition:

A term used to express density petroleum instead of specific gravity in united state. <sup>(8)</sup>

The units of API gravity are API° and can be calculated from specific gravity by the following:

$$\text{API} = \frac{141.5}{\text{specific gravity}}$$

### 2.2.3 Determination of S.G:

This procedure was done according to ASTM D5002

The specific gravity is expressed most often in degrees API. Generally, the crude oils are classed according to specific gravity in four main categories

- Light crudes                      sp. gr.  $d_4^{15} < 0.825$
- medium crudes     $0.825 < \text{sp. gr. } d_4^{15} < 0.875$
- Heavy crudes                       $0.875 < \text{sp. gr. } d_4^{15} < 1.000$
- Extra-heavy crudes    sp. gr.  $d_4^{15} > 1.000$





**Figure 2.1 DMA 4500 Densitometer**

#### **2.2.4 Determination of Wax Content:**

**This procedure was done according to UOP46**

##### **Test methods:**

Light, clear oils are analyzed as received. Heavily colored oils and asphalts are clarified by treatment with Sulfuric acid. The asphalt-free sample is dissolved in warm ethylene chloride. This solution is chilled to 30 °C and filtered through a cold fritted glass filter. The wax collected on the filter is removed with hot hexane. The hexane is evaporated and the wax weighed.<sup>(9)</sup>

##### **Apparatus and reagent:**

- Balance.
- Crucibles, Goash 2A (2unit).
- Flask, Filtering, 500ml (3unit).
- Circulation, Water bath.
- Evaporator, Rota vapor.
- Water Suction pump.
- Flask, round bottom, 100 and 500cm.
- Asbestos wool, Glass wool, fuller, S earth.
- Petroleum naphtha, boiling arrange 40-60.
- Acetone.

##### **Calculation:**

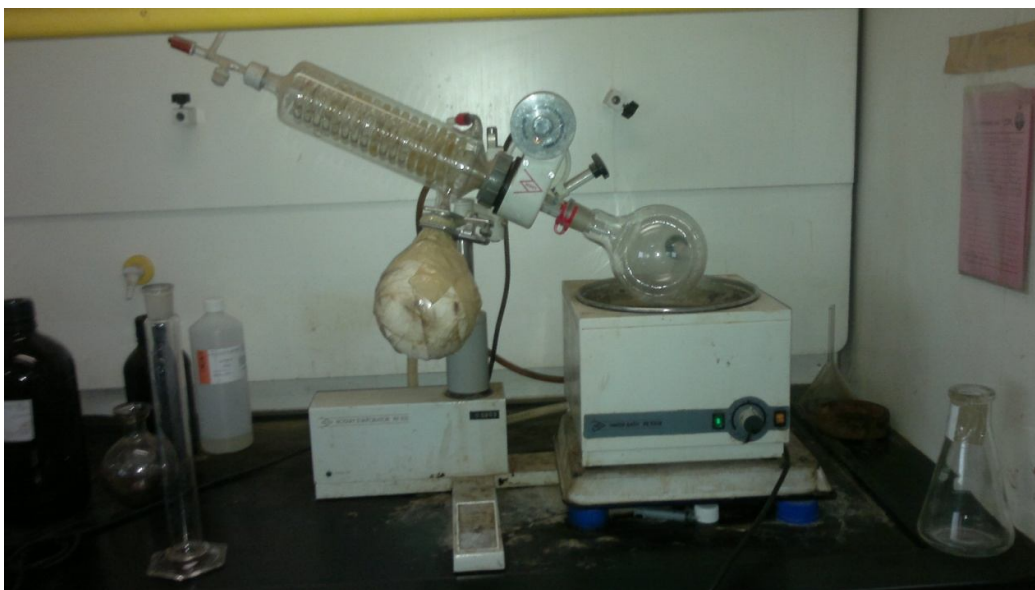
The wax content was calculated by the equation:

$$\text{Wax, wt\%} = (W2 - W1) / s * 100$$

Where W1= weight of round bottom flask in gram.

W2= weight of round bottom flask + wax in gram.

S = sample weight.



**Figure 2.2 Rotary Vacuum Evaporator**



**Figure 2.3 Cooling Instrument**

### **2.2.5 Determination of Pour Point:**

The pour point of crude oils is an important parameter from a processing point of view; its lowest temperature at which movement of specimen can be observed, essentially, define the temperature that is required to pump the crude. Since crude oil is a complex mixture of compounds, it does not congeal at specific temperature, but different compounds crystallize out of solution at different temperatures. Heating crude to 45-65 °C dissolves some of the paraffinic seed crystals, thereby lowering the pour point, while heating it to 100°C would again raise the pour point due to loss of light materials by evaporation. In practice pour point is determined after preheating to 45-48°C, as defined by the ASTM D97 method. Crude oil pour point usually range between -60 and +30°C.<sup>(10)</sup>

#### **Apparatus and reagent:**

- Teat Jar.
- Thermometer.
- Cork.
- Disk.
- Gasket.
- Bath.

#### **Procedures:**

The procedure of pour point determination described by ASTM D97-04. Result expressed by adding 3°C to the observed temperature and reported as pour point (ASTM D97)



**Figure 2.4 Cloud and Pour Test CABINET**

### **2.2.6 Determination of 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 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 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.<sup>(11)</sup>



**Figure 2.4 848 Titrino Plus**



### **2.2.7Determination of water content:**

Test methods:

The sample is heated under reflux conditions with a water immiscible solvent which co-distills with the water in the sample. Condensed solvent and water are continuously separated in a trap—the water settles in the graduated section of the trap, and the solvent returns to the distillation flask<sup>(12)</sup>.

#### **Apparatus:**

- glass distillation flask
- condenser
- graduated glass trap
- heater.



### 2.2.8 Determination of sulfur content:

The sample is placed in the beam emitted from an X-ray source. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration standards that bracket the sample concentration range of interest to obtain the sulfur concentration in mass %.

#### Apparatus and Reagents:

- X-ray Fluorescence Analyzer
- Purity of Reagents
- Di-n-Butyl Sulfide (DBS)
- Mineral Oil, White (MOW), ACS reagent grade or less than 2 mg/kg sulfur.

#### Calculation:

The concentration of sulfur in the sample is automatically Calculated from the calibration curve<sup>(13)</sup>



Figure 2.6 Oxford Instrument

### **2.2.2Determination of Kinematic viscosity:**

The viscosity of crude mainly influences pumping cost, because it determines the pressure drop in pipelines and refinery units. The viscosity temperature relationship depends on the crude composition, with paraffinic crudes showing a rapid increase in viscosity decrease temperature, while naphthenic crude have a more gradual decrease. Viscosity of crude oils varies over a wide range, having values of less than 10 to more 5000cSt.

#### **Apparatus**

- Viscometers

#### **Procedure:**

The crude oil was heated to 80C and kept in container for one hour in an oven. Then 8cm of sample were transferred on the brook field sample cell using plastic syringe after that the cell was connected to the device {viscometer} and began to record the viscosity reading<sup>(14)</sup>



**Figure 2.7 Viscometer –Water Path**

### **2.10.2 Determination of asphaltene content:**

Depositions of the heavy organics present in oil could happen due to various causes depending on their molecular nature. Resins are not known to deposit on their own, but they deposit with asphaltene. The reasons for asphaltene deposition can be due to many factor including variations of temperature, pressure, composition, flow regime, and wall and ellectrokintic effect. When various heavy organic compounds are present in a petroleum fluid their interactive effects must be also considered in order to understand the mechanisms of their collective deposition or lack of it. This is especially important when one of the interacting heavy organic compounds is asphaltene .

#### **Apparatus and Reagents:**

- Condencer.
- Reflux extractor.
- Conical flasks.
- Stopper.
- Evaporating dish.
- Filter funnel.
- Filter paper.
- Analytical balance.
- Forceps.
- Timing device.
- Oven.
- Graduated cylinder.
- String rods.
- Cooling vessel.
- Methyl benzene (toluene).
- Heptanes.

#### **Procedure:**

This method was done according to reference: IP143. Two g were weighted from the sample of residue which was obtained after distillation of crude at 250C°. Distillation was usually done if the API is above or equal 24,300cm normal heptane were added to sample in a flask then boiled under reflux for one hour. The solution was filtered through Whitman 42 filter paper. The filtrate was kept for analysis of resins and waxes. The residue was dissolved by addition of 200Cm of toluene and the completed dissolution was affected by using reflex extractor. Toluene

was removed by evaporation on a boiling water bath, and the asphaltenic residue was residue dried in an oven for 30 minutes and weighted.

### Calculation:

The asphaltene was calculated as follows:

$$\text{Asphaltene content } A\% = M/G * 100$$

Where:

M is the mass in g of asphaltene.

G is the mass in g of test portion. <sup>(15)</sup>



**Figure 2.8 Evapor Cooling**

### 3.1 Results and discussions:

**Table 3.1: Density of samples at 15 °C**

Sample type	Density @15°C
PDOC	0.9136
Fulla light	0.8813
WNPOC	0.9278
GNPOC	0.8784
Star oil	0.8363

The table notes that Dar Blend has high density 0.9136 compared with other oil comparisons, but the WNPOC scored the highest density of 0.9278 and Star oil which achieved less density of 0.8363. Results characterize Dar Blend as heavy crude as the density is higher than 0.875 according to the API. This is an indication of the lack of mild molecules in the crude which reduces the commercial value.

**Table 3.2 Measurements API for samples**

Sample type	API
PDOC	23.24
Fulla light	28.91
WNPOC	20.87
GNPOC	29.45
Star oil	37.55

Table 3.2 shows the results of measurements API for samples. The table notes that Dar Blend has a low API compared to other oils but WNPOC is of it, thus WNPOC has heavier materials in the table and Dar is also classified as heavy 23.24. Indicating the weight of Dar Blend as less than 25.

**Table 3.3 Specific Gravity of samples.**

Sample type	S.G
PDOC	0.9145
Fulla light	0.8821
WNPOC	0.9286
GNPOC	0.8729
Star oil	0.8369

**Table 3.4 Table Wax content for comparison crudes.**

Sample type	Wax content %
PDOC	19.28
Fulla light	21.68
WNPOC	20.99
GNPOC	29.95
Star oil	36.88

Table 3.4 shows Wax content for comparison crudes. Table notes that Dar Blendless wax percentage compared to other crudes. This explains the lack of the amount of crude paraffin thus facilitating the transfer process in the pipes. We also note that the star oil crude has the highest wax content in the table.

**Table 3.5 Result pour point of samples.**

Sample type	Pour point
PDOC	39
Fulla light	12
WNPOC	12
GNPOC	30
Star oil	42

Table 3.5 shows the result pour point of the crude comparison. Table notes that Dar Blend records a high pour point, but topped star oil as Fulla crude has a lower pour point. This indicates that the Dar Blend crude is heavy paraffinic.

**Table 3.6 Result of measuring TAN**

Sample type	TAN
PDOC	4.47
Fulla light	0.35
WNPOC	1.64
GNPOC	0.66
Star oil	0.12

Table 3.6 shows the result of measuring TAN crudes comparison. Table notes that Dar Blend log TAN is higher than other crudes comparison while star oil scored less TAN. This means the presence of naphthenic acids in crude. This requires the need to be treated.

**Table 3.7 The water content of the samples**

Sample type	Water content
PDOC	0.4
Fulla light	3.0
WNPOC	0.05
GNPOC	0.20
Star oil	2.8

Table 3.7 shows the water content of the crudes comparison. Table notes that the water content in Dar Blend is less than 5% and the average water content log for comparison crudes as WNPOC has less water content between crudes comparison.



**Table 3.8 The sulfur content of the samples.**

Sample type	sulfur content
PDOC	0.1272
Fulla light	0.0813
WNPOC	0.1227
GNPOC	0.0745
Star oil	0.0885

Table 3.8 shows the sulfur content of the crude comparison. Table note that Dar Blend scored the highest percentage of sulfur 0.1272 in comparison, while GNPOC crude least 0.0745. Although the proportion of high sulfur compared to other crudes, but we will classify as sweet crude.

**Table 3.9 The Kinematic viscosity of samples**

Sample type	k. Viscosity @50°C	k. Viscosity @60°C	k. Viscosity @70°C
PDOC	440.5	233.4	139,8
Fulla light	32,54	21,34	16.06
WNPOC	499.4	278.7	170.6
GNPOC	39.03	25.06	17.88
Star oil	12.97	7.761	6.696

Table 3.9 shows the Kinematic viscosity of crude comparison in different temperatures at a temperature of 50°C - 60°C - 70°C.

Table note that Kinematic viscosity less with increasing temperature in all crudes comparison.

Dar Blend record high Kinematic viscosity compared to other crudes and but WNPOC who recorded the highest score for the viscosity, while star oil less viscosity.

**Table 3.10 The Asphalten content of samples**

Sample type	Asphalten content
PDOC	0.12
Fulla light	0.1
WNPOC	0.08
GNPOC	0.14
Star oil	0.04

Table 3.10 shows the Asphaltene content of crude comparison

**Table 3.11 cationic composition of the crudes**

	Na	Mg	Ca	V	Fe	Ni	Cu	Al	As	Pb
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
PDOC	11,782	1,198	26,602	1,156	107,956	65,136	<0,1	0,86	<0,1	<0,1
Fulla light	27,564	0,926	10,112	0,581	21,533	7,642	<0,1	5,183	<0,1	<0,1
WNPOC	4,467	0,428	4,071	1,13	17,455	24,515	<0,1	1,506	<0,1	<0,1
GNPOC	4,666	0,435	4,927	0,609	3,424	7,611	<0,1	6,851	<0,1	<0,1
Star oil	50,995	0,55	6,124	0,365	26,328	2,34	<0,1	0,848	<0,1	<0,1

Results of Dar crude analysis are given in Tables , where density, API, Wax %, pour point, Total Acid Number (TAN) and water content are cited, in comparison with corresponding value of crude oils produced in adjacent oil fields namely Fulla light, WNPOC,GNPOC, and Star oil.

The density of the Dar blend was found to be 0. 9136 g/ml, which place it in the second high density value among the five crudes <sup>(16)</sup>. Consequently Dar crude is classified as heavy type according to API standard. Usually heavy crudes are of less commercial values compared to light ones if intended for fuel production, as it contains small fractions of low molecular weight component.

API values of Dar blend which was found to be 23. 2 also support the characterization of the crude as heavy type, according to the specification of American Petroleum Institute which sets limits of API value of 25 and

below as a measure of heavy crudes<sup>(16)</sup>. Heavy crudes are more valued in the petrochemical industries where more chemicals might be fractionated or synthesized from the crude. The wax % of Dar blend is low compared to other crudes cited in Table 4. This may be advantageous in transporting the crude through pipelines where heavy crudes with high wax contents tend to cause many problems in transportation and requires adjustment of viscosity and pumping pressure and maintaining the temperatures of the pipe lines.

The low API density reflects low of hydrogen/carbon ratio in the Dar blend, and consequently lack of light hydrocarbon fractions. The pour point of Dar blend ranked second among five crude oils produced in Sudan reaching 39° next only to the pour point of Star oil crude. It is interesting to note that the wax content of Star oil is 36.8% which justifies the high pour point. But the wax content of Dar blend is only 19.2%. Hence the high pour point is possibly due to the presence of mercaptants and other aromatic sulfur compounds of medium size. This view may be supported by the comparatively high level of sulfur in Dar blend compared to other crudes, as depicted in Tables.

Asphaltene content of Dar blend also ranked second among the five crudes investigated. It is shown in Table 10 along with the kinematic viscosities at different temperatures. The presence of asphaltene also contributes to the crystallization of high molecular weight molecules in the crude and, generally, enhances, crystallization of heavy waxes. This consequently raises the pour point. As Dar blend has a low wax content presence of Asphaltene would assist crystallization of aromatics and mercaptants hence raise the viscosity and ultimately the pour point Table 1 along with values of asphaltene content. The ratio of reduction of viscosity with increasing temperature by an increment of 10°C is almost equal in the five crudes. This would suggest a similar mechanism of aggregation of crude constituents the type of which shall be very decisive, and reflects in pour point and viscosity.

Table 22 shows the cationic content of the five crudes<sup>(17)</sup>. It is interesting to note the high content of Na in Star oil crude, and the high calcium content of Dar blend which was the lightest among all crudes. Presence of Ca usually results in formation of some sparingly soluble salts that tend to separate into the solid phase, which enhance the process of crystallization

of naphthenic fraction and sulfur containing aromatic fraction by providing seeding mechanism that accelerates the crystallization process.

The high value of Total Acid Number (TAN) in Dar blend constitutes its major disadvantage, which manifests itself in the corrosion problem that shall be associated with Dar blend processing. Presence of high sulfur content and sulfonic acid functions might be the reason for the high TAN value. Serious corrosion problems that result from high TAN may be mitigated by injection of basic sodium salts to neutralize the acidity and add to increasing the solubility of calcium compounds.

### Monthly OGMs Test Report:

**Table 3.12 Adar Oil Fields: 15/7/2011**

OGM	Water %	API	Density	Pour point	Viscosity @ 50°C	Viscosity @ 40°C	TAN	Wax content %	Asphaltene content %
1	72.0	30.79	0.8711	45	35.49	174.05	NA	NA	NA
2	86.0	28.20	0.8852	42	50.69	90.70	NA	NA	NA
3	18.0	30.45	0.8729	39	21.97	36.33	NA	NA	NA
4	1.4	30.11	0.8748	36	31.26	63.37	NA	NA	NA
5	30.0	24.37	0.9070	39	60.83	151.24	NA	NA	NA
6	23.0	23.09	0.9145	18	347.25	561.05	NA	NA	NA
7	16.0	18.94	0.9397	18	390.34	627.75	NA	NA	NA
8	1.8	19.90	0.9338	15	316.83	494.26	NA	NA	NA
9	50.0	31.83	0.8656	42	9.29	43.93	NA	NA	NA
10	86.0	26.37	0.8955	36	55.76	81.11	NA	NA	NA
11	63.0	35.76	0.8452	39	10.98	45.62	NA	NA	NA

**Table 3.13 Gumry Oil Field:15/7/2011**

OGM	Water %	API	Density	Pour point	Viscosity @ 50°C	Viscosity @ 40°C	TAN	Wax content %	Asphaltene content %
1	14.0	32.20	0.8636	42	19	42	NA	NA	NA
2	9.0	31.60	0.8668	42	29	117	NA	NA	NA
3	2.8	34.04	0.8540	42	19	130	NA	NA	NA
4	84.0	29.76	0.8767	42	22	61	NA	NA	NA
5	32.0	29.48	0.8782	45	41	154	NA	NA	NA
6	60.0	28.12	0.8854	42	42	0	NA	NA	NA

**Table 3.14 Palouge Oil Field:****30/5/2010**

Field	Water %	API	Density	Pour Point	Viscosity @ 50°C	Viscosity @ 40°C
Palouge	0.8	24.76	0.9048	39	204	354

**Table 3.15 Palouge OGMs**

OGM	Water %	API	Density	Pour point	Viscosity @ 50°C	Viscosity @ 40°C
1	67	29.87	0.8761	39	45	88
2	65	25.29	0.9017	39	276	300
3	41	22.89	0.9156	39	384	672
4	26	21.84	0.9219	36	504	800
5	35	19.82	0.9342	39	800	1536
6	75	25.65	0.8996	39	166	279
7	53	25.92	0.8981	42	336	588
8	35	18.68	0.9413	36	492	732
9	45	15.92	0.9590	30	5003	10654
10	9	18.86	0.9002	42	1176	2495
11	24	16.04	0.9582	30	3359	6671
12	37	17.5	0.9488	45	1200	2495
13	4.8	20.44	0.9305	39	648	1416
14	20	18.71	0.9488	36	1104	1845

**Table 3.16 Moleeta export crude:**

**30/5/2010**

Field	Water %	API	Density	Pour point	Viscosity @ 50C	Viscosity @ 40C
Moleeta	1.4	19.95	0.9335	36	888	1512

**Table 3.17 Moleeta OGMs:**

OGM	Water %	API	Density	Pour point	Viscosity @ 50C	Viscosity @ 40C
1	0.3	18.38	0.9432	30	1295	2735
2	20.0	19.95	0.9335	36	N/R	N/R
3	18.0	20.32	0.9312	39	440	827
4	35.0	20.81	0.9282	42	319	606
5	97.0	19.91	0.9337	39	N/A	N/A
6	40.0	17.07	0.9515	30	1763	3299
7	14.0	23.32	0.9132	33	1595	2639

### 3.2 Crude oil assays

A crude oil assay is essentially the chemical evaluation of crude oil feedstocks by petroleum testing laboratories. Each crude oil type has unique molecular, chemical characteristics.

No crude oil type is identical and there is crucial difference in crude oil quality.

Crude oil assay testing includes crude oil characterization of whole crude oils and the boiling -range fractions produced from physical distillation by various procedures is very important especially after new fields.

It has been known that heavy crude contains many impurities. Sulfur has been recognized as one of the major impurity, which affects the quality of the crude oil and processing cost.

Due to high concentration of these impurities, these crude are labeled as poor quality crude and have a lower price in the market. Crude Oil Quality at International Market. Crude price in international market is strongly Affected by the crude properties such as:

- water content
- TAN
- Sulfur
- API

API, TAN and sulphur are the main parameters determining the crude oil prices.

API gravity is the most frequently used measure to estimate the quality of a crude oil. It is one of the parameters focused for determining the price of crude oil. Generally, heavy crude oils have API gravity of 20 or less and light crude oils measure oils

34 or more units.

Heavy crude produce lower quantities of light and middle distillates and higher quantities of residue. Global demand patterns are moving towards an increasing requirement for light and middle distillate products.

Sulphur is the other parameter focused for determining the price of crude oil and determining factor in refinery processing cost, Increased sulfur levels in crude oils increases refining costs.

The most important question in the design, operation, handling crude is the crude oil properties, for that the crude analysis is very important for the pipeline, storage tanks, and the production facilities stage.

A modified ASTM Standard Test Method for, Density, API Gravity, Pour point,, Kinematics Viscosity, Water Content, Sulfur Content, Sediment, Carbon Residue Con., and T.A.N respectively were used to determine the properties of the crude oils.





### **3.3 Conclusion and Recommendations**

#### **3.3.1 Conclusion**

- Dar blend oil is a heavy crude based on API.
- Low asphalt content only 0.12%
- High TAN value about 4.47

#### **3.3.2 Recommendations**

- Optimizing the Dar blend by increasing the production from low TAN content fields (Gummry , Adar ) and decrease the production from high TAN content fields (Paluoge , moleeta )
- Dilution / blending after production from Gummry field start TAN decrease
- Corrective steps needs to proceed
- Corrosion monitoring program for power station engines and assess risk areas
- Corrosion inhibitors and programs reduce but does not eliminate corrosion

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