## University of Technology Chemical Engineering Department Oil and Gas Refinery Eng Branch Second Year

# Properties of Petroleum Products Part (1)

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### What is Petroleum?

The word petroleum originated from the Latin words, Petra, meaning rock and oleum, meaning oil. Literally it means 'Rock Oil,' and can also be defined as a non-renewable fossil fuel or oil that is found underground. This is any naturally-occurring flammable mixture of hydrocarbons found in geological formations such as rock strata.

Technically, the term petroleum refers to describe any solid, liquid or gaseous hydrocarbons. It's also known as 'crude oil' or 'mineral oil.'

### Differences Between Crude Oil, Petroleum Products And Petroleum

Crude oil- Mixture of hydrocarbons existing as liquid in natural underground reservoirs and remain liquid during extraction.

Petroleum products- Produced from the processing of crude oil at petroleum refineries and extraction of liquid hydrocarbons at natural gas processing plants.

Petroleum- refers to the broad category that includes both crude oil and petroleum products.

### **Occurrence of Petroleum**

Petroleum occurs in the earth's crust, in all possible states and varies in color from light brown to dark brown or black, exhibiting luminescence in some cases. It is a mixture of various hydrocarbons, of homologous series namely paraffins, napthenes and aromatics.

The final result is a black viscous product of composition:

Carbon	80 to 89%
Hydrogen	12 to 14%
Nitrogen	0.3 to 1 %
Sulphur	0.3 to 3%
Oxygen	2 to 3%



### Petroleum Formation.

There are basically two theories explaining the origin of oil,

#### 1-Organic Theory (Biotic Theory)

- Oil developed millions of years from organic material remains of dead plants and animals (algae and planktons).
- The dead organisms sank to the bottom of water bodies (seas and lakes), where the environment tends to be anaerobic.
- They accumulated in the mud on the beds of the water bodies, partially decomposed.
- Sediment deposition on the bed of the water body, burying and compressing the organic matter under its weight.
- Increase in temperatures(100-160°c) and pressures resulted due to continued sediment deposition.
- With time the conditions broke down the organic compounds into shorter hydrocarbon chains, forming oil and natural gas.
- Oil and natural gas flowed from the source rock, accumulating in thicker more porous rock called a reservoir rock.
- Earth movements (faulting, folding) trapped the oil and natural gas in the reservoir rock between layers of impermeable rock or cap rock also called an oil trap.



#### Conditions necessary for biotic on formation.

- 1. Deep burial under sand and mud.
- 2. Pressure cooking.
- 3. Hydrocarbon migration from the source to the reservoir rock.
- 4. Impermeable rock to trap the oil.



#### 2- Inorganic Theory (Abiogenic/Abiotic Theory)

- This hypothesis of petroleum origin without biology was first proposed in 16<sup>th</sup> century by Georg Agricola, then in 19<sup>th</sup> century by Alexander (Prussian geographer), Dmitri (Russian chemist), Marceline (French chemist) and re-defined in 20<sup>th</sup> century by Cornell University physicist, Thomas Gold.
- Supporters of this hypothesis argued that hydrocarbons existed at the formation of the solar system and were abundant in other system and were abundant in other planets e.g. Saturn (زحل), Jupiter (کوکب المشتري),...
- The theory argued that petroleum originated from limitless pools of liquid primordial (الأساسي)hydrocarbons at great depths in the earth.
- These carbon-bearing fluids migrated upward from the mantle where they slowly replenish(نجديد) the reservoirs that conventional oil drillers tap.

Other hypothesis arose (نشأت) as a result of the Abiotic theory. These include,

i. <u>Deep seated terrestrial hypothesis</u>.

Proposed by Dmitri Mendeleev, he postulated that metallic carbides deep within the earth reacted with water at high temps, forming acetylene.

 $CaC_{2}(s)_{+}2H_{2}0 ----> Ca(OH)_{2}(s)+C_{2}H_{2}(g)$ 

ii. Extra terrestrial hypothesis.

Proposed by Sokoloff, he based a cosmic (الكون) origin to petroleum origin. He postulated that hydrocarbons precipitated as rain from original nebular matter from which the solar system formed.

### **Composition of Petroleum**

Petroleum occurs in nature in all three possible states solid, liquid and gas. The liquid petroleum is usually colored from dark brown to bluish black or black, exhibiting sometimes bloom or fluorescence. The semi-solid or solid petroleum is well known by the name pitch, usually black in color. Such kind of deposits ate assumed to form after the evaporation or migration of lighter fractions. The gaseous deposits of petroleum are known as natural gas deposits, where sometimes gasolines are also accompanied. Gas from condensate reservoirs contain a good portion of lighter fractions of a boiling point upto 30° C. Associated reservoirs contain gas mainly in dissolved form in liquid petroleum.

Although the composition of petroleum depends not, very much on the origin of formation, but certainly change with the time of formation, storage and different stratas (الطبقات) through which it migrated. It is a homogeneous mixture of various hydrocarbons of saturates and ring-structures. The average ultimate composition of petroleum is mainly given in terms of constituents of hydrocarbons, namely carbon and hydrogen as follows :

Carbon 84—86% Hydrogen 11—14%

The other major elements of importance are sulfur, oxygen and nitrogen. These elements in hydrocarbons are usually treated as impurities because of their inherent properties like odor, color corrosiveness etc. Generally these three elements combined, do not exceed 5% on an average.

The bulk of petroleum is made up of hydrocarbons, of saturated compounds like paraffins, naphthenes and unsaturated cyclic compounds mainly aromatics.

The highest carbon atom present in the crude is C70. Further, except first few hydrocarbons, all other hydrocarbons exhibit isomerism. The general properties of these homologous series are discussed below :

#### Paraffins :

 $C_nH_{2n+2}$  is the general formula of paraffins. First three compounds are gases while compounds upto  $C_{16}$  are liquids and beyond that, they assume semisolid consistency. Well beyond  $C_{30}$  assume shape of solid blocks, sometimes even crystalline forms. There are number of isomeric compounds for each compound, profoundly differing in properties. For example upto  $C_3$  no isomers are possible,  $C_4$  exhibits only two isomers, as shown here :

And  $C_5$  exhibits three isomers. The number of isomers increases as the number of carbon atoms increase  $C_{13}H_{28}$  exhibits 802 isomeric forms.

General properties of paraffins

Paraffins are stable, not attacked by sulfuric acid or other oxidizing agents. However, paraffins of higher order  $> C_{30}$  are prone to oxidation. Even usual oxidizing agents like potassium permanganate can cause good amount of oxidation. The aptitude to contribute the substituted products with halogens has magnified the petrochemical industry. Higher

paraffins are very much insoluble in water; though the lower ones are soluble in ethers and alcohols. Paraffins upto 3 carbon atoms have inclination to form hydrates such as  $[CH_4.7H_2O, C_2H_6. 7H_2O]$  and these hydrates offer clogging and corrosion difficulties. Hence drying is essential before usage.

Example of simplest HC molecule (CH <sub>4</sub> ):	Examples of straight chain paraffin molecule (Butane) and branched paraffin molecule (Isobutane) with same chemical formula $(C_4H_{10})$ :	
METHANE (CH <sub>4</sub> )	BUTANE ( $C_4H_{10}$ )	ISOBUTANE ( $C_4H_{10}$ )
H HCH H	Н Н Н Н         H-C-C-C-C-H         H Н Н Н	H H H       H-C-C-C-H       H H H H-C-H   H-C-H H

The specific gravity of the series increases with molecular weight, still paraffins have less specific gravity and boiling point than aromatics. Viscosity of paraffins is less but viscosity index is high in contrast to aromatics. The smoke point of the paraffins is very high, with poor illuminating characteristics. The pour point of paraffins is usually high; due to this paraffin rich crudes and products bring difficulties in transpiration and storage.

Isomers differ from n-paraffins by having slightly low boiling points, low pour points, high viscosity and viscosity index. Usually i-paraffins, are more reactive than n-paraffins.

High molecular compounds (>  $C_{20}$ ) may be of saturated or unsaturated nature, decompose if exposed to a temperature of above 370°C. Vacuum distillation is essential for distilling such boiling stocks to prevent them from thermal degradation.

#### Unsaturated (Olefins and Properties)

Olefins are represented by the general formula  $CnH_{2n}$ . The first four are gases and upto  $C_{15}$  are liquids and beyond  $C_{15}$  are solids. The boiling points of olefins are generally lower by few degrees than the saturated compounds of the same carbon number. Chemically these differ very much from paraffins. They are easily attacked by sulfuric acid and some of them even polymerize. Treatment with sulfuric acid and subsequent hydrolysis yields alcohols (e.g. isopropyl alcohol) and with permanganate oxidation, glycols are formed. Unsaturated compounds like olefins, diolefins, in general, do not appear in crudes to measurable quantities, however they are detected in some crudes. These unsaturated are mainly formed during cracking operations. The absence of unsaturates to a large extent can be best judged by the probable catalytic activity of the earth's crest in converting unsaturates to saturates and ring structures.

Simplest Alkene (C <sub>2</sub> H <sub>4</sub> ):	Typical Alkenes with the same chemical formula $(C_4H_8)$ but different molecular structures:	
ETHYLENE (C <sub>2</sub> H <sub>4</sub> )	1-BUTENE (C <sub>4</sub> H <sub>8</sub> )	ISOBUTENE (C4H8)
H H     C====C     H H	H H H H         C====C-C-C-H       H H H	H H H       H—C=====C C-H H—C-H H H H

#### Acetylenes and Properties (Alkynes)

The general formula for this series is  $CnH_{2n-2}$ . These are isomeric with diolefins. Acetylenes yield crystalline compounds with ammonia solution of copper salts and are attacked by sulfuric add. Acetylenes can be readily hydrogenated to give stable compounds.

ACETYLENE (C <sub>n</sub> H <sub>2n-2</sub> ) C=C		
HC ≡ C C H <sub>3</sub>	Methyl acetylene or Propyne-1 or Allyne	
CH₃-C≡C-CH₃ Crotonylene or Butyne -2		
C₂H₅~C≡C−CH₃	Ethyl methyl acetylene or Pentyne-2	

#### **Diolefins**

These are represented by the formula  $C_nH_2n_2$ . Like other unsaturates, these are produced during cracking reactions. These can be distinguished from acetylenes as they do not form salts with ammoniacal solutions of copper salts. But with mercuric chloride these form precipitates and sulfuric acid polymerises these unsaturates.

Simplest Alkyne: (C <sub>2</sub> H <sub>2</sub> ):	Typical Diolefins with the same chemical formula $(C_4H_6)$ but different molecular structures:		
ACETYLENE (C <sub>2</sub> H <sub>2</sub> )	1,2-BUTADIENE (C <sub>4</sub> H <sub>6</sub> )	1,3-BUTADIENE (C <sub>4</sub> H <sub>6</sub> )	
H-C==C-H	H H H       C=====C====CCH       H H H	H H H H         C=====C       H H	

#### **Naphthenes**

These are saturated ring compounds bearing the general formula  $CnH_{2n}$ . The prominence of ring structure starts with five carbon atoms. Although  $C_3$  and  $C_4$  ring structures, are in existence, their stability is decreased because of excessive strain (Bayer's Strain, Theory). Naphthenes are isomeric with olefins but differ profoundly in properties.. Naphthenes exhibit both the properties of saturated paraffins and unsaturated aromatics, the result of which, all the properties like sp. gravity, viscosity, pour point, thermal characteristics lie in between the two mentioned homologues. Usually, all the ring structures are having branched chains, where the isomeric character predominantly occurs, followed by positional isomerism in rings.

Example of typical single-ring naphthene:	Examples of naphthene with same chemical formula $(C_6H_{12})$ but different molecular structure:
CYCLOHEXANE ( $C_6H_{12}$ )	METHYL CYCLOPENTANE (C <sub>6</sub> H <sub>12</sub> )
H H     H-C-C-H H / \ H \ / \ H-C C \ /\ H-C-C-H     H H	H H     H-C-C-H   \ H   \ H   \     H-C-C-H   / H H-C-C-H     H H

#### Aromatics

The first and smallest of the aromatics is benzene; other simple aromatics to follow are toluene, xylene, cumene etc. Even though benzene is unsaturated, yet it follows the principles of substitution with halogens rather than addition. This is mainly due to symmetric grouping of closed ring structure and resonance.

Aromatics are usually having high boiling points, low pour points (freezing points), high octane numbers, high viscosity and low viscosity index and these bum characteristically with a red flame with much soot. As these behave like saturates, they resist oxidation. In petroleum fractions aromatics beyond 3-ring structure (Anthracenes) are probably non-existent. Aromatics usually extend their presence from a temperature of 80° C onwards and well dominate, in lower middle cuts and heavy cuts. Actually the light aromatics (BTX) do not exceed even 5% of crudes of general nature. Bulk of the aromatics are with side chains and naphthenes and exist in heavier portion of crudes.

Example of simple aromatic compound:	Examples of simple double-ring aromatic compound:
BENZENE (C <sub>6</sub> H <sub>6</sub> )	NAPTHALENE (C <sub>10</sub> H <sub>8</sub> )
H H     C===C / \ H-C C-H \ H-C C-H \ H H H H	H H     C-C // \ H-C C-H \/ / C==C / \ H-C C-H \/ \ H-C C-H \/ \ H-C C-H \/ \ H-H H H

#### **Inorganics**

Sulfur compounds: Sulfur is found in most of the crudes in variable amounts. Generally sulfur compounds are present in more quantities in higher molecular weight stocks. Usually the sulfur content does not exceed 5%, however rare exemptions are : Venezuela (5.25%), California (USA 5.21%), Qaiyarah (Iraq—7%) etc. crudes.

Sulfur in crude occurs in different forms (like free sulfur, hydrogen sulfide, mercaptans and thiophenes etc. These are frequently occuring compounds in almost all fractions of the crude though to a different degree. Heavier fractions contain sulfides, polysulfide, sulfonates and sulfates.

Sulfur occupies prominent position in refining due to its ominous problems of corrosion and odor. Pollution problems and following cost of waste treatment is punitive for all refiners with high sulfur-stocks. However, refiners habitually remove more detrimental sulfur compounds and leave the less harmful ones into the products, as seen in the case of sulfides converted to disulfides in gasolines. Some of the sulfonates are regarded as good emulsifiers and detergents, hence promptly extracted for use in cutting oils. Conspicuous effect of sulfur is reflected in increasing the density of crude.

A correlation presented by Obolentsev shows the influence of sulfur on gravity

 $\varrho$  at 20C = 0.0087 (S%)<sup>2</sup>+0.0607(S%)+0.7857

Different crudes are presented in following table. It clearly shows the effect of sulfur on API gravity of crude and pour point of crude. All sulfur crudes mysteriously exhibit low pour points.

Effect of Sulfur on Gravity and Pour Point.			
Crude	API	Pour Point oC	Sulfur %
Cyrus (Iran)	19	-23.3	3.48
Iranian Heavy	28.2	-34.4	2.84
Kuwait .	31.2	-17.8	2.5
North Slope (USA)	33.9	-17.9	2.45
Quatar Marine (Quatar)	33.9	15	2.05
Romashkinskaya (USSR)	33.4	-34.4	1.8
Bassdn (India)	32.6	-28.9	1.61
Nahorkatiya	30.8	-20.6	1.6
Ankleshwar	37	-3.9	1.5
Bombay High	26.8	-20.6	1.04
Arabian (Light) (S. Arabia)	31	30	0.16
Arabian (Heavy) (S. Arabia)	38.45	30	0.15
Arjuna (Indonesia)	37.7	26.7	0.12
Bu Attifcl (Libya)	46.6	39	0.1
Basrah (Iraq)	43	-20.6	0.08
Brass (Nigeria)	47	15	0.05
Darius (Iran)	38	30	0.001

Further, sulfur containing residuum when cracked leaves cross linked structures, resembling the phenomenon of vulcanization of rubber and offer perennial problems in desulfurization. Its presence in different fractions complicates the refining and treatment methods. Yet another problem is, it desists the effects of additives. Sulfur in gasoline inevitably depresses the effect of lead and demands more amount of additive. When crude contains more than 0.5% S, it is denoted as high sulfur crude. A terse distinction, at this juncture between sour crudes and sulfur crudes is desirable. Free hydrogen sulfide is available in some crudes, which naturally fosters corrosion. Such crudes are classified as sour crudes ; other sulfur bearing compounds are not taken into this account. The crudes containing sulfur crudes.

#### <u>Oxygen</u>

Oxygen and nitrogen do not occur in free state either in crudes or in fractions. Nitrogen presence in free form is well known in natural gas only. Oxygen occurs as oxygenated compounds like phenols, cresols, naphthenic acids, sulphonates, sulfates and sulfoxides.

_SULF	PHUR COMPOUNDS	
Mercaptans	CaHa++ SH	
-	C2H5 SH	Ethyl mercaptan
Sulphones	R SO 2	
	C7 HIS SO2	Heptyl Sulphone
Sulphides	R2S	
	(CH3)2S	Dimethyl sulphide
Di Sulphides	R2S2	
	CH3S.S CH3	Dimethyl disulphide
Sulfaxides	R>50	
	сн <sub>3</sub> >50 сн <sub>3</sub> >50	Dimethyl sulfoxide
Thiophenes		
	CH3-S-C	Thiadeey! thiophene
Thiophanes	C <sub>n</sub> H <sub>2n</sub> S	
· · · · ·	Q-c.	Butyl thiacyclohexane
Sulphates	(CnH2n+1)504 F	72504
	(),	Thio benzols
Sulphonates		5
Carbonyl Sulphide	CÓS	
	<b>○-</b> ₅-○	Cyclohexyl sulphide
	Q-°	Thio cyclo heptane

#### <u>Nitrogen</u>

Nitrogen exists in the form of indoles, pyridines, quinolines and amines, usually well below 2%. Nitrogen compounds exasperate problems in processing and stability of products. Catalyst deactivation or poisoning, gum formation are some of the offshoots of nitrogen. Nitrogen is present in two forms, basic and non-basic. Basic nitrogen is characterized by its titratability with perchloric acids, whereas nonbasic nitrogen is not titratable hence no possibility of extraction. Most of the nitrogen pigments impart color to crude and fractions. The most interesting compounds of nitrogen are porphyrins. These are obtained from living organisms and preserved in petroleum. It stands to reason that anaerobic conditions were prevailing durring petroleum formation; otherwise oxidation

would have destroyed them. Chlorophyll is also a complex of porphyrins, where central atom is magnesium instead of nickel or vanadium or iron. Iron porphyrins are also known as heme, the constituents of red cell in the blood.

Porphyrins pigments are usually associated in complex form with metals like, copper, iron, vanadium and nickel. The proper understanding of these pigments may augment the knowledge of origin and formation of petroleum. The following is an example of nitrogen complex :

Gravity API	38.8
Sulfur wt. %	02-0.0%
Vanadium ppm.	0.5—2.5
Nickel ppm.	1.0-170
Vanadyl porphyrins ppm.	0.7—1130

#### Asphalts, Resins and Bitumens

Asphalts are high molecular weight complex molecules, black in color, soluble preferably in aromatic solvents and carbon disulphide. Resins are mostly compounds of highly condensed ring structures, containing oxygen, sulfur and nitrogen, sometimes inorganic too. Though bitumen is a manufactured product, it is essentially made up of three components, asphalts, resins and mineral oil. These three components comprise a colloidal system; asphalts are suspended in oil and resins contribute to the stability of the system.

#### Less Inorganics

The other elements present are nickel, vanadium, iron, silica, sodium, magnesium, and halogens etc. Even though the analysis is not desirable as these metals hardly exceed 0.01%, yet may be analyzed for sensitive purposes. The ash formation is mainly due to these metals and inorganic. Sometimes organometallic compounds are available in colloidal form. Inorganic always leave a marked influence on fractions, for example halides may give off halogens during hydrolysis or thermal decomposition. Corrosion, pollution, ash etc. are mainly contributed by inorganic and the quality of crude and fractions are always debased by these small amounts.

### **Chemical Classification of Petroleum**

The chemical classification of petroleum that distinguishes between oils of a paraffin base from those of an asphaltene base was introduced into petroleum chemistry to distinguish the oils that separate paraffin on cooling from those that separate asphaltenes. The presence of paraffins is usually reflected in the paraffinic nature of the constituent fractions whereas a high asphaltic content corresponds with the naphthenic properties of the fractions. This could lead to the misconception that paraffin-base petroleum consists mainly of paraffins and that asphalt-base petroleum consists mainly of cyclic (or naphthenic) hydrocarbons. In

order to avoid confusion, a mixed base has been introduced for those oils that leave a mixture of asphaltic petroleum and paraffins as residue from nondestructive distillation. A fourth class has also been suggested, the hybrid base; it includes asphaltic oils that contain a small amount of paraffins. A simplified scheme has been figure below with paraffinic, naphthenic, aromatic, and asphaltic petroleums as extremes. It is indeed possible to characterize petroleum semi-quantitatively in this manner.

An attempt to give the classification system a quantitative basis suggested that petroleum should be called asphaltic if the distillation residue contained less than 2% of parafins and paraffinic if it contained more than 5%. A division according to the chemical composition of the 250 to 300°C fraction has also been suggested (Table 1) but the difficulty in using such a classification is that in the fractions boiling above 200°C, the molecules can no longer be placed in one group because most of them are typically of a mixed nature.



Purely naphthenic or aromatic molecules occur very seldom; cyclic compounds generally contain paraffinic side chains, and often even aromatic and naphthenic rings occur side by side. More direct chemical information is often desirable and can be supplied by means of the correlation index (Cl).

This index was developed by the U.S. Bureau of Mines. It is based on the plot of specific gravity at 48.64°C versus the reciprocal of the boiling point in degrees Kelvin (K = T°C + 273) for pure hydrocarbons for which the line described by the constants of the individual members of the normal paraffin series is given a value of CI = 0, and a parallel line passing through the point for the values of benzene is given as Cl = 100. The following empirical equation has been derived for estimating CI: CI=473.7d - 456.8 + 48.640/T

where T, in the case of a petroleum fraction, is the average boiling point, determined by the standard Bureau of Mines distillation method d is the specific gravity.

<b>Table 1:</b> Petroleum classification according to chemical composition.					
Class of petroleum	Compo	Composition of 250-300°C fraction, wt.%			
	Par.	Naphth.	Arom.	Wax	Asph.
Paraffinic	46-61	22-32	12-25	1.5-10	0-6
Paraffinic-naphthenic	42-45	38-39	16-20	1-6	-6
Naphthenic	15-26	61-76	8-13	trace	0-6
Paraffinic-naphthenic- aromatic	27-35	36-47	26-33	0.5-1	0-10
Aromatic	0-8	57-78	20-25	0-0.5	0-20

Thus, values for the index between 0 and 15 indicate a predominance of paraffinic hydrocarbons in the fraction; values from 15 to 50 indicate a predominance of either naphthenes or mixtures of paraffins, naphthenes, and aromatics; values above 50 indicate a predominant aromatic character. Although the correlation index yields useful information, it is in fact limited to distillable materials and, when many petroleum samples are to be compared, the analysis of results may be cumbersome.

It is also possible to describe a crude oil by an expression of its chemical composition on the basis of the correlation index figures for its middle portions.

#### **Classification by Density**

Density has been the principal and often the only specification of petroleum products and was taken as an index of the proportion of gasoline and kerosene present. As long as only one kind of petroleum is in use the relations are approximately true. However, since a wide variety of crude oils having various other properties occur in nature and have come into use, the significance of density measurements has disappeared. Nevertheless, petroleum samples having other properties that are similar can still be rated by gravity as can gasoline and naphtha within certain limits of other properties. The use of the density values has been advocated for quantitative application using a scheme of the American Petroleum Institute (API) based on the gravity of the 250 to 275°C (at the pressure 1 bar) and the 275 to 300°C (50 mbar) distillation fractions. Indeed, analysis of petroleum from different sources worldwide showed that 85% fell into one of the three classes: paraffin, intermediate, or naphthene base. It has also been proposed to classify heavy oils according to characterization gravity, defined as the arithmetic average of the instantaneous gravities of the distillates boiling at 177°C, 232°C and 288°C vapor line temperature at 33 mbar pressure in a true boiling point distillation.

In addition, a method of petroleum classification has been developed that is based on other properties as well as the density of selected fractions. The method consists of a preliminary examination of the aromatic content of the fraction boiling up to 145°C as well as that of the asphaltene content, followed by more detailed examination of the chemical composition of the naphtha (b.p. <200°C). For this examination, a graph (a composite of curves expressing the relation between percentage distillate from the naphtha, the aniline point,

refractive index, specific gravity, and the boiling point) is used. The aniline point after acid extraction is included in order to estimate the paraffin-naphthene ratio.

#### Characterization by Viscosity-Gravity Constant (vgc)

This parameter, along with the Universal Oil Products (UOP) characterization factor, has been used, to some extent, as a means of classifying crude oils. Both parameters are usually employed to give an indication of the paraffinicity of the petroleum. Both have been used, if a subtle differentiation can be made, as a means of petroleum characterization rather than for petroleum classification.

Nevertheless, the viscosity-gravity constant is one of the indexes proposed to characterize oil types. For heavy oils, the low-temperature viscosity is difficult to measure. The viscosity-gravity constant for such type of petroleum is calculated by the formula

#### VGS=d - 0. 24 - 0.022 log(v - 35.5)/0.755

where d is the specific gravity at 48.64°C v is the Saybolt viscosity at 99°C

The viscosity-gravity constant is of particular value in indicating petroleum of a predominantly paraffinic or cyclic composition. The lower the index number, the more paraffinic the stock; for example, naphthenic lubricating oil distillates.

have a vgc of 0.876 while the raffinate obtained by solvent extraction of lubricating oil distillate has a vgc of 0.840.

The UOP characterization factor is perhaps one of the more widely used of the derived characterization or classification factors and is defined by the formula  $K=T_B^{-1/3}/d$ 

where  $T_B$  is the average boiling point in degrees Rankine (degrees Fahrenheit + 460) and d is the specific gravity at 48.64°C.

This factor has been shown to be additive on a weight basis. It was originally devised to show the thermal cracking characteristics of heavy oils; thus, highly paraffinic oils have K of from 12.5 to 13.0 while naphthenic oils have K of from 10.5 to 12.5.

#### **Technological Classification of Petroleum**

According to technological petroleum classification, the oil can be classified

- low sulfur oil containing not more than 0.5% of the sulfur, whereby the gasoline fraction contains less than 0.1% sulfur and diesel fraction less than 0.2%.
- sulfur petroleum containing over 0.5% but under 2% of the sulfur, whereby the gasoline fraction contains less than 0.1% sulfur and the diesel fraction less than 1.0%.
- high sulfur petroleum containing over 2% of sulfur.
- low paraffinic petroleum containing under 1.5% of paraffins. This type of oil can be used for production of jet and winter diesel fuels without deparaffinization.

- medium paraffinic petroleum containing over 1.5% and under 6% of paraffins. This type of oil can be used for production of jet and summer diesel fuels without deparaffinization.
- high paraffinic petroleum containing over 6% of paraffins. This type of oil can be used for production of diesel and jet fuels only after deparaffinization.

### **Test Methods for Petroleum Products**

#### 1. Specific Gravity

This is the ratio of the density of a substance to that of water at the same temperature. The temperature usually specified is 15°C.

#### Specific-Gravity Bottle

The most accurate method of determining the specific gravity of an oil is to weigh a known volume in a specific-gravity bottle at 15°C. I fit is not convenient to carry out the determination at 15°C, a correction may be applied by measuring the specific gravity at some convenient temperature near 15°C and adding or subtracting 0.00063 per °C above or below 15°C. A convenient specific-gravity bottle for doing this, with ground-in thermometer for measuring temperature, is illustrated in Fig.



#### Hydrometer

The most rapid method is by means of a set of hydrometers. A hydrometer is placed in the oil sample at 15°C and allowed to come to rest. The specific gravity is shown on the scale at the point coincident with the surface of the oil.

#### A.P.l. Gravity

In the U.S., specific gravity of oil is often expressed as degrees A.P.l. (American Petroleum Institute).

A.P.I. gravity = 
$$\frac{141.5}{\text{Sp. gr. at } 60^{\circ}\text{F}} - 131.5$$

The specific gravity is an indication of the type of hydrocarbon present, being highest for aromatics and lowest for paraffins. The APl. gravity reverses this relationship.

#### 2. Viscosity

#### (a) Redwood Viscometer

The Redwood viscometer, illustrated in Fig., consists essentially of a standard cylindrical oil cup containing a standard agate orifice at the lower end, into which fits a spherical valve. The oil cup is surrounded by an oil-jacket containing a heater and stirring device. The oil in the outer bath is heated 2 or 3° above or below the required temperature of the determination, dependent upon the relative temperatures of the oil and the surrounding atmosphere. The oil sample, free from solid matter, is heated approximately to the desired temperature and poured into the oil cup up to a standard level. When equilibrium has been reached, i.e. when the oil in the inner cup remains steady at the desired temperature, the oil level is adjusted, the valve is opened and the time in seconds is taken for 50ml to run out. This time interval is recorded as the viscosity in Redwood Seconds at the specified temperature. The temperature must remain steady during the determination, within +0.25°C for temperatures below 70°C and within + 1°C for temperatures above 70°C.



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#### (g) U-tube Viscometer Principle of Method

U-tube glass viscometers allow an accurately reproducible volume of liquid to pass through a capillary at a constant temperature by the application of an accurately reproducible force. The time taken for a liquid to flow is proportional to the ratio of the dynamic viscosity to the density of the fluid, hence to its kinematic viscosity. The constant of proportionality for the instrument is obtained by carrying out a determination in the viscometer with a fluid of known viscosity.

The kinematic viscosity of a fluid of viscosity greater than 10 centistokes is given by the expression v = C t

where C is the viscometer constant, and t is the time of flow in seconds.

When the fluid has a viscosity of 10 centistokes, or less, a second coefficient is used to correct for changes in kinetic energy at the exit to the capillary. The expression then becomes

$$v = Ct - \frac{B}{t}$$

where B is the coefficient of kinetic energy, which may be determined experimentally, or eliminated by choosing long flow times.

The viscometer constant is determined by use of standard solutions of known kinematic viscosity, e.g. 40% sucrose: v = 4.39 cS at 25°C. Centistokes are still widely used.

#### Determination

A filtered sample of the oil under test is introduced into the viscometer by suction or by pipetting into the wide tube (DE in Fig.) so that air bubbles are absent and the level of oil stands a few millimetres above the level E. The viscometer is then placed in a thermostat, maintained at the required temperature, and adjusted so that it is exactly vertical. After a time, varying from 20min for temperatures near the normal to 30min at 100°C, the oil is blown or sucked into the tube A to a point 1 cm above the etched level B. The oil is then allowed to flow freely back down the capillary, taking the time of fall from the mark B to the mark C by means of an accurate stopwatch reading to 1/5 sec. The experiment is repeated until duplicate tests are repeatable within 0.2%.

#### (c) Viscosity Index (Saybolt)

The viscosity index is a number that expresses the temperature-viscosity relationship of an oil. Oils containing a high proportion of paraffins have relatively high viscosity indices (maximum value 100). Naphthenes have low V.I. (minimum 0).

The viscosity index of an oil is determined by measuring its viscosity at two temperatures and comparing the results with those for a standard oil of V.I. = 100 and for a standard oil of V.I. = 0.

Viscosity Index = 
$$\frac{L-U}{L-H} \times 100$$

where U =Saybolt viscosity of sample at 100°F,

L = Saybolt viscosity at 100°F of a standard oil (V.I. = 0) with the same viscosity at 210°F as the sample,

 $H = Saybolt viscosity at 100^{\circ}F$  of a standard oil (V.I. = 100) with the same viscosity at 210°F as the sample.

In practice Land H are obtained from tables, after the viscosity of the sample at 100°F has been determined.

The Say bolt viscometer is used in the U.S. in place of the Redwood instruments used in England. Results are expressed as "Saybolt Seconds Universal", at any given temperature, usually expressed in °F.



#### 3. Flash Point

The flash point is the temperature to which the oil must be heated, in a standard instrument, to give an inflammable mixture with air under the prescribed conditions. The Pensky-Marten apparatus is the British standard instrument for flash points above 50°C and the Abel apparatus is used for more volatile oils, with flash points below 50°C.

#### (a) Pensky Martin Closed-cup Test

The apparatus, illustrated in Fig. , consists of a brass cup, mounted in an air bath and heated by a gas flame. A propeller-type stirrer, operated by a flexible drive, extends from the centre of the cover into the cup. The cover has four openings: one for a thermometer, and the others fitted with sliding shutters for the introduction of a pilot flame and for ventilation. The temperature of the oil in the cup is raised at 5 to 6°C/min. The stirrer is rotated at ca. 60r.p.m. When the temperature has risen to ca. 15°C from the anticipated flash point, the pilot flame is dipped into the oil vapour for 2 sec every 1°C rise in temperature up to 105°C. Above 105°C, the flame is introduced every 2°C rise in temperature. The flash point is the temperature at which a distinct flash is observed when the pilot flame meets the vapour in the cup.

Open flash point. This may be determined after the closed flash point by removing the cover and continuing the heating until a distinct flash occurs across the open cup.



#### (b) Abel Closed-cup Test

The Abel apparatus consists of a brass cup sealed in a small water bath which is immersed in a second water bath. The cover of the brass cup is fitted in a manner similar to that in the Pensky-Marten apparatus. For oils with flash point  $<30^{\circ}$ C, the outer bath is filled with water at 55°C and is not heated further. The oil under test is then placed inside the cup. When the temperature reaches 19°C the pilot flame is introduced every \°C until a flash is obtained. For oils with flash points  $> 30^{\circ}$ C,  $<50^{\circ}$ C, the inner water bath is filled with cold water to a depth of 35 mm. The outer bath is filled with cold water and heated at a rate of 1°C/min. The flash point is obtained as before.

#### 4. Calorific Value

For non-volatile oils the same apparatus and procedure are used as for coal. Volatile oils may be considered to be gases and C.V. determined in gas calorimeters.

#### 5. Reid Vapour Pressure

This is a measure of the vapour pressure of an oil at 37.8°C expressed as millimetres of mercury.

The apparatus consists of a metal cylinder, or "bomb", fitted with an accurate dial pressure gauge, or a mercury manometer. The bomb consists of two parts: an upper expansion chamber and a lower liquid chamber. The oil is cooled and poured into the lower chamber until full. The temperature of the air in the upper chamber is taken and the two chambers are connected together in a gas-tight manner. The bomb is immersed upright in a water bath at 37.8°C and shaken repeatedly until a constant pressure reading is obtained. This is corrected, from tables, for initial air temperature and pressure.

#### 6. Cloud and Pour Points

The cloud point is the temperature at which a haze or cloud first appears in a sample of oil when cooled in a prescribed manner. The pour point is 2°C above the temperature at which the oil ceases to flow under the prescribed conditions. The oil is contained in a glass test tube fitted with a thermometer and immersed in one of three baths containing coolants, as shown in Fig. .

#### (a) Cloud Point

The oil sample is dehydrated and filtered at a temperature >25°C above the anticipated cloud point. It is then placed in a test tube and cooled progressively in coolants held at -1 to +2°C; -18 to -20°C and -35 to -32°C, respectively. The sample is inspected for cloudiness at temperature intervals of 1°C.



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#### (b) Pour Point

The sample is first heated to 46°C and cooled in air to 32°C before the tube is immersed in the same series of coolants. It is inspected at temperature intervals of 2°C by withdrawal and holding horizontal for 5 sec, until no flow is observed during this time interval.

#### 7. Aniline Point and Diesel Index

#### (a) Aniline Point

This is an approximate measure of the aromatic content of a mixture of hydrocarbons. It is defined as the lowest temperature at which an oil is completely miscible with an equal volume of aniline.

Since aromatics dissolve aniline (itself an aromatic substance) more readily than paraffins or iso-paraffins, the lower the aniline point the higher the proportion of aromatics in the oil. Since, also, the higher the aromatic content of an oil, the lower the cetane number (cf. Data Sheet No. 57) the aniline number can be used to indicate the probable behaviour of an oil in a diesel engine.

#### (b) Diesel Index

This is an expression developed to correlate aniline point and A.P.l. gravity (cf. Item 1, above) with cetane number.

Diesel Index =  $\frac{GA}{100}$ 

where G is the A.P.l. gravity of an oil, A is the aniline point of the oil.

#### Method of Test

Five millilitres each of a carefully dried sample of oil and aniline are placed in a test tube fitted with a thermometer and stirrer and enclosed in a larger tube to act as an air jacket. If, on stirring, the oil and aniline are completely miscible, the apparatus is cooled until the mixture is opaque. The temperature is then raised at l°C/min until the thermometer bulb is just visible. The temperature is then recorded as the aniline point.

If, at atmospheric temperature, the oil and aniline are not completely miscible, the temperature is raised until this occurs. The mixture is then cooled at l°C/min until the thermometer bulb is just obscured, when the temperature is recorded as the aniline point.

#### 8. Gum in Motor Fuel

#### (a) Existent Gum

Fifty millilitres of sample are evaporated in a glass dish of specified size on a steam bath for 1 hr, or until evaporation is complete, while heated air from a small jet impinges on the surface. The dish is transferred to a drying oven for 1 hr, and weighed after cooling. The weight in mg/100ml is reported as "Existent gum".

#### (b) Gum Stability

This is an approximate measure of the tendency to form gum during storage.

Fifty millilitres of the gasoline are placed in a glass dish inside a stainless-steel bomb, which is filled with oxygen at 690 kPa. The bomb assembly is placed in a boiling- water bath and connected to a sensitive pressure/time recorder. The time interval in minutes between placing the bomb in the water bath and recording a drop of 13.8 k Fa from the maximum pressure, is recorded as the induction period (oxygen stability).

#### 9. Sulphur

#### (a) Total

By combustion in a bomb calorimeter. This is best carried out in the bomb calorimeter in conjunction with the determination of calorific value (cf. Item 4, above).

The contents of the bomb are washed with distilled water into a beaker. Hydrochloric acid is added and the solution raised to boiling point. Barium chloride is added drop by drop to the boiling solution to precipitate the sulphuric acid as granular barium sulphate. After cooling, and standing for 24 hr, the precipitate is filtered off on an ashless paper, washed, ignited and weighed as barium sulphate.

% wt. of sulphur =  $\frac{Wt. \text{ of barium sulphate } \times 13.73}{Wt. \text{ of oil sample}}$ 

#### (b) Corrosion Sulphur—by copper strip test

A piece of mechanically cleaned pure sheet copper, 75 x 12 mm, is placed in a test tube with 40 ml of the sample, so that the copper is completely immersed. The tube is closed with a vented cork and heated in a boiling-water bath for 3 hr. The copper strip is then compared visually with a new strip of copper for signs of tarnish.

The results are recorded as:

No change	regult regative
Slight discoloration	result negative.
Brown shade	
Steel grey	
Black, not scaled	cult positive corrosive sulphur present
Black, scaled $\int_{-\infty}^{\infty}$	suit positive, corrosive suiphur present.

### 10. Water and Sediment

#### (a) Water

This is best determined by the Dean and Stark method. The apparatus consists of a roundbottom flask of capacity 50 ml connected to a Liebig condenser by a receiving tube of capacity 25 ml, graduated in 0.1 ml (Fig. 62.6). 100 ml of oil are placed in the flask with 25 ml of dry toluene. The flask is heated gently until the 25 ml of toluene have distilled into the graduated tube. The water, distilled with the toluene, separates to the bottom of the tube. Its volume is recorded as ml. or the weight as mg or per cent.

#### (b) Sediment

This is best carried out by solvent extraction in the apparatus shown as Fig. . Inside a 1 - liter Erlenmeyer flask is suspended a cold-finger condenser, which drops into a porous alumina thimble of dimensions 70 x 15 mm. The thimble is cleaned with benzene and dried before the test and 10 g of oil sample are introduced. Approximately 100 ml of benzene are placed in the flask, which is heated until the condensed benzene vapour, dripping from the cold finger through the thimble, has extracted all the oil. The thimble is then dried, reweighed, and the increase in weight recorded as per cent, or as mg sediment/100ml oil.



#### 11. Ash Content

This is the percentage by weight of inorganic residue obtained by the combustion of an oil in a porcelain, silica, or platinum dish The temperature of combustion is not specified, but the final temperature reached is preferably 800°C.

Twenty grammes of oil are placed in a clean, dry, weighed silica dish. This is placed inside a cold electric muffle furnace. The temperature is raised slowly until the oil burns when a flame is applied to the surface. When combustion is complete, the temperature of the muffle is raised to 800°C and kept at this temperature for a further hour. The crucible and ash are then cooled, reweighed and the weight of ash obtained by difference.

# 12. Carbon Residue(a) Conradson Carbon

This is the more usual test for measuring the "carbon" obtained by destructive distillation. The apparatus used is shown in Fig. and consists of a large porcelain crucible, placed inside two iron crucibles and heated by a Mckcr gas burner until all oil vapours arc driven off. A known weight of oil (e.g. 10 g) is placed inside the porcelain crucible and the apparatus assembled and heated at such a rate that the vapours start to burn in about 10min. The flame is then adjusted so that they burn at the top of the chimney for a further 21 to 23 min. The crucibles are then heated to a cherry-red heat for a further 7 to 8 min, giving a total time of 30 + 2 min. After cooling, the porcelain crucible is reweighed and the result recorded as %wt. Conradson carbon.



#### (b) Rams bottom Carbon Residue Test

In this test a known weight of oil (proportional to the anticipated weight of residue) is heated in a hemi-spherical glass bulb of standard dimensions by a bath of molten solder at 550°C for 20min. The residual carbon is weighed and recorded as %wt.. "Ramsbottom coke".

#### 13. Distillation

Distillation of oil is carried out in a standard round-bottom distillation flask of 250 ml capacity attached to a water-cooled condenser. The thermometer bulb is placed at the opening to the side arm of the flask.

One hundred millilitres of oil are placed in the flask and heated by a small gas flame so as to produce 10ml of distillate every 4 or 5min. The temperature of initial distillation is recorded; the temperature at which each further 10 ml distils and the final boiling point are also recorded.

### **Refinery Processes : Purpose And Definition**

Refineries are designed to manufacture marketable petroleum products from import streams of a variety of crude oils.

Refineries transform crude oil via an appropriate number of different processes into marketable petroleum products in programmed quantities and qualities for onward dispatch by sea, inland waterways, rail, road and product pipeline to the consuming markets.

The manufacturing of petroleum products entails a range of physical and chemical processes that are utilised to optimise yields of the most valuable products.

The Refinery Industry has two main tasks: -

■ Fractionating crude oils through distillation to separate them out into products of varying density and volatility.

■ Purifying and enhancing each fraction through physical and chemical treatment The refining industry continues in a constant state of flux with adaptions to satisfy changing product demand, competitive influences and refining margins.

The six basic refining processes are as follows; -

- 1. Separation: This is achieved by raising temperature of the input crude supply in pipes that pass through a furnace heated to circa 360°C. This vaporises individual fractions of the crude feed which then condense and separate out on trays within the column according to the varying boiling points and densities petroleum products. This process is known as simple distillation (topping and hydroskimming). In addition the application of a vacuum enables the products to vaporise at lower temperatures, which is known as vacuum distillation.
- 2. Reforming: This process changes the configuration of individual molecules as in catalytic reforming and isomerisation. This process is commonly used in the final stages of gasoline production.
- 3. Treating: This process uses catalysts, electrolysis and hydrogen to chemically remove contamination such as salts, nickel, vanadium, sulphur and nitrogen oxides. Examples of treatment processes include: hydrogenating, hydrofining, hydrofesulphurisation).
- 4. Cracking: This process breaks down large hydrocarbon molecules into smaller ones in the presence of a catalyst. A catalyst is used to speed up the rate of reaction. The catalysts (example: alumina) can be recycled numerous times. Chemical reactions utilising catalysts can be used in the presence of hydrogen or steam (examples: catalytic cracking, hydrocracking). Alternatively with the application of very high temperatures heat alone breaks down large hydrocarbon molecules. This process is known as thermal cracking. A common process used in European refineries is known as visbreaking.

- 5. Coking: Residues, the carbon-rich heavy ends of the refinery process are cooked' at high temperatures (600°C) to produce lighter products such as gasoil and naphtha.
- 6. Deep Conversion: Combines carbon extraction with the addition of hydrogen. This process is designed to convert the heaviest fractions (refinery residue or bottoms) into lighter and marketable products. Process includes coking, residue catalytic cracking and de-asphalting.



Figure 2-1 Processing Plan for Petroleum Refinery



	Carbon	Boiling	g Range <sup>O</sup> F
Refinery Process Stream	Numbe		
Straight Run Products of Atmospheric Distination of Crode On	4-12	<23	0 <446
Kappina	9-16	150-29	0 302-554
Niddle Distillate	11-20	205-34	5 401-653
Get Oil	11-25	206-40	<b>401-752</b>
*Atmospheric Tower Residuum	>20	> 350	>662
Products of Vacuum Distillation of Atmospheric Tower Residuum			
Vacuum Tower Condensate	11-25	205-40	0 401-752
Distillate	15-50		
Vacuum Gas Oil, Light	13-30	230-45	0 446-842
*Vacuum Gas Oil, Heavy	20-50	350-60	0 662-1112
Vacuum Residuum (Asphalt)	>34	>495	>923
Products of Cracking Processes (Catalytic Cracking, Thermal Cracking, Hydrocr	acking, Catalytic	Reformi	ng, etc.)
Naphtha	4-12	<230	<440
Distillate	0.00	150.40	0 202 752
Light	9-25	150-40	0 302-752
Intermediate	11-30	205-45	0 401-842
*Heavy (Catalytic, Thermal)	15-35	260-50	0 500-932
Hydrocracked	10-25	100-40	0 320-752
Residues		- 250	- (12)
*Catalytic Cracked Clarified Oil	>20	> 350	>002
*Catalytic Reformer Fractionator Residue	10-25	160-40	0 320-752
Hydrocracked Residuum	>20	> 330	>002
*Thermal Cracked Residuum	>20	>350	>662
Petroleum Coke			. 500
*Steam Cracked Residuum	>14	>260	> 500
Products of Extraction Processes (Solvent Refining, Deasphalting, Decarbonization,	Acid Treatment	<u>etc.</u>	
Raffinates	5.12	~ 230	< 446
Naphtha	9-20	150-345	302-653
Middle Distillate	11-25	205-400	401-752
	15-50		
Distillate Residual Oil Acobalt	>25	>400	> 752
Residual On, Asphan	_		
Exifacts	6-12	<220	<428
Prictillate (Light Heavy)	15-50		
Geo Oil	13-25	230-400	446-752
Residual Oil	>25		
Products of Hydrotreating Processes			
Naphtha	4-13	<2.30	<446
Distillate	9-50		
Paraffin Wax	20-50		
*Vacuum Gas Oil	13-50	230-600	446-1112
Residual Oil	>25	>400	>752

Table 2-1 Petroleum Rei	inery Process Streams
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\* Likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons. Source: U.S. Environmental Protection Agency, 1978.

### Fractionations of Crude oil

Petroleum is a complex mixture of various organic compounds. It consists of different hydrocarbons and heteroatomic compounds. It is technically impossibly to separate petroleum into individual compounds. In any case, it is unnecessary to separate the petroleum to the component level in order to obtain a technological or industrial classification.

A very important petroleum property is its fractional composition. This property is determined in the laboratory by slowly heating the oil and separating it into fractions having specified boiling ranges. Every fraction is characterized by the temperature at which boiling begins as well as the temperature boiling ends.

In the industrial method, fractionation is achieved by the method of rectification. Using this method, the fractions with boiling point up to 350°C are separated at atmospheric pressure. These are called the light fractions. Usually, during atmospheric rectification, the following individual fractions are obtained:

- Boiling begins -140°C gasoline fraction
- 140-180°C heavy naphtha
- 180 -240°C kerosene fraction
- 240-350°C diesel fraction

The residue after atmospheric distillation is called "atmospheric residue". This fraction, with a boiling point over 350°C, is usually distillated further at a low pressure or in a vacuum. This residue can be classified in two different ways depending on the intended application:

For further processing to fuel fractions:

- 350-500°C vacuum gas oil
- over 500°C vacuum residue

For further processing to lubricating oils:

- 300-400°C light oil fraction
- $400 450^{\circ}$ C medium oil fraction
- 450-490°C heavy oil fraction
- over 490°C vacuum residue

All the fractions obtained from atmospheric residue are called "heavy fractions". On the other hand, the products obtained after secondary processing of the heavy fractions are considered to be light fractions if boiling of the fraction ends at  $< 350^{\circ}$ C, and to be heavy fractions if boiling begins at  $> 350^{\circ}$ C.

The amount of light fractions can be very different for oils from different oil wells.

For example, it can be under 20% for some heavy oils from Alberta (Canada) and over 60% for some light oils form western Siberia (Russia). Typical analysis of a Canadian petroleum from oil wells in McMurray resulted in the following fractions:

- Gasoline and naphtha 2.8%
- Kerosene 0%
- Diesel- 19.0%
- Light oil 4.3%
- Medium oil 8.5%
- Heavy oil fraction 13.2%
- Vacuum residue 49.5%