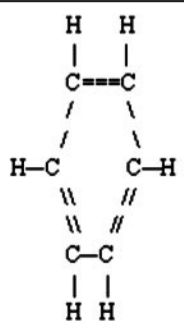
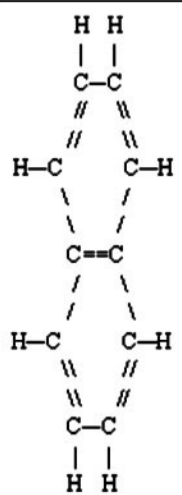


Example of simple aromatic compound:	Examples of simple double-ring aromatic compound:
BENZENE (C ₆ H ₆)	NAPHTHALENE (C ₁₀ H ₈)
	

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 occurring 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

$$\rho \text{ at } 20\text{C} = 0.0087 (\text{S}\%)^2 + 0.0607(\text{S}\%) + 0.7857$$

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.

Naphthenes

These are saturated ring compounds bearing the general formula C_nH_{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_6H_{12})
<pre> H H H-C-C-H / \ \ / V V H-C C \ / \ \ / H H-C-C-H H H </pre>	<pre> H H H-C-C-H \ / H \ \ \ \ H-C-C-H H H </pre>

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 burn 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 $80^\circ C$ 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.

Simplest Alkene (C ₂ H ₄):	Typical Alkenes with the same chemical formula (C ₄ H ₈) but different molecular structures:	
ETHYLENE (C ₂ H ₄)	1-BUTENE (C ₄ H ₈)	ISOBUTENE (C ₄ H ₈)
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{C} = \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \quad \\ \text{H} \quad \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H} - \text{C} = \text{C} - \text{C} - \text{H} \\ \quad \quad \quad \\ \quad \quad \text{H} - \text{C} - \text{H} \quad \text{H} \\ \quad \quad \\ \quad \quad \text{H} \end{array}$

Acetylenes and Properties (Alkynes)


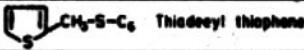


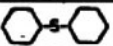

The general formula for this series is C_nH_{2n-2}. These are isomeric with diolefins. Acetylenes yield crystalline compounds with ammonia solution of copper salts and are attacked by sulfuric acid. Acetylenes can be readily hydrogenated to give stable compounds.

ACETYLENE (C _n H _{2n-2}) C≡C	
HC≡C-CH ₃	Methyl acetylene or Propyne-1 or Alkyne
CH ₃ -C≡C-CH ₃	Crotonylene or Butyne -2
C ₂ H ₅ -C≡C-CH ₃	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 ₂ H ₂):	Typical Diolefins with the same chemical formula (C ₄ H ₆) but different molecular structures:	
ACETYLENE (C ₂ H ₂)	1,2-BUTADIENE (C ₄ H ₆)	1,3-BUTADIENE (C ₄ H ₆)
$\text{H}-\text{C} \equiv \text{C}-\text{H}$	$\begin{array}{c} \text{H} \quad \quad \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{C} = \text{C} = \text{C} - \text{C} - \text{H} \\ \quad \quad \quad \\ \text{H} \quad \quad \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{C} = \text{C} - \text{C} = \text{C} \\ \quad \quad \quad \\ \text{H} \quad \quad \quad \text{H} \end{array}$

SULPHUR COMPOUNDS		
Mercaptans	$C_nH_{n+1}SH$	
	C_2H_5SH	Ethyl mercaptan
Sulphones	RSO_2	
	$C_7H_{15}SO_2$	Heptyl Sulphone
Sulphides	R_2S	
	$(CH_3)_2S$	Dimethyl sulphide
Di Sulphides	R_2S_2	
	$CH_3S-S-CH_3$	Dimethyl disulphide
Sulfoxides	R_2SO	
	CH_3CH_2SO	Dimethyl sulfoxide
Thiophenes		
		Thiocetyl thiophene
Thiophanes	$C_nH_{2n}S$	
		Butyl thiocyclohexane
Sulphates	$(C_nH_{2n+1})_2SO_4$ R_2SO_4	
		Thio benzol
Sulphonates	$C_6H_5SO_3$ $R SO_3$	
Carbonyl Sulphide	$CO S$	
		Cyclohexyl sulphide
		Thio cyclo heptane

Nitrogen

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 during petroleum formation; otherwise oxidation

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 compounds other than hydrogen sulfide and exceeding 0.5 % are denoted as high sulfur crudes.

Oxygen

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.

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Table 1: Petroleum classification according to chemical composition.

Class of petroleum	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,