Crude Oil

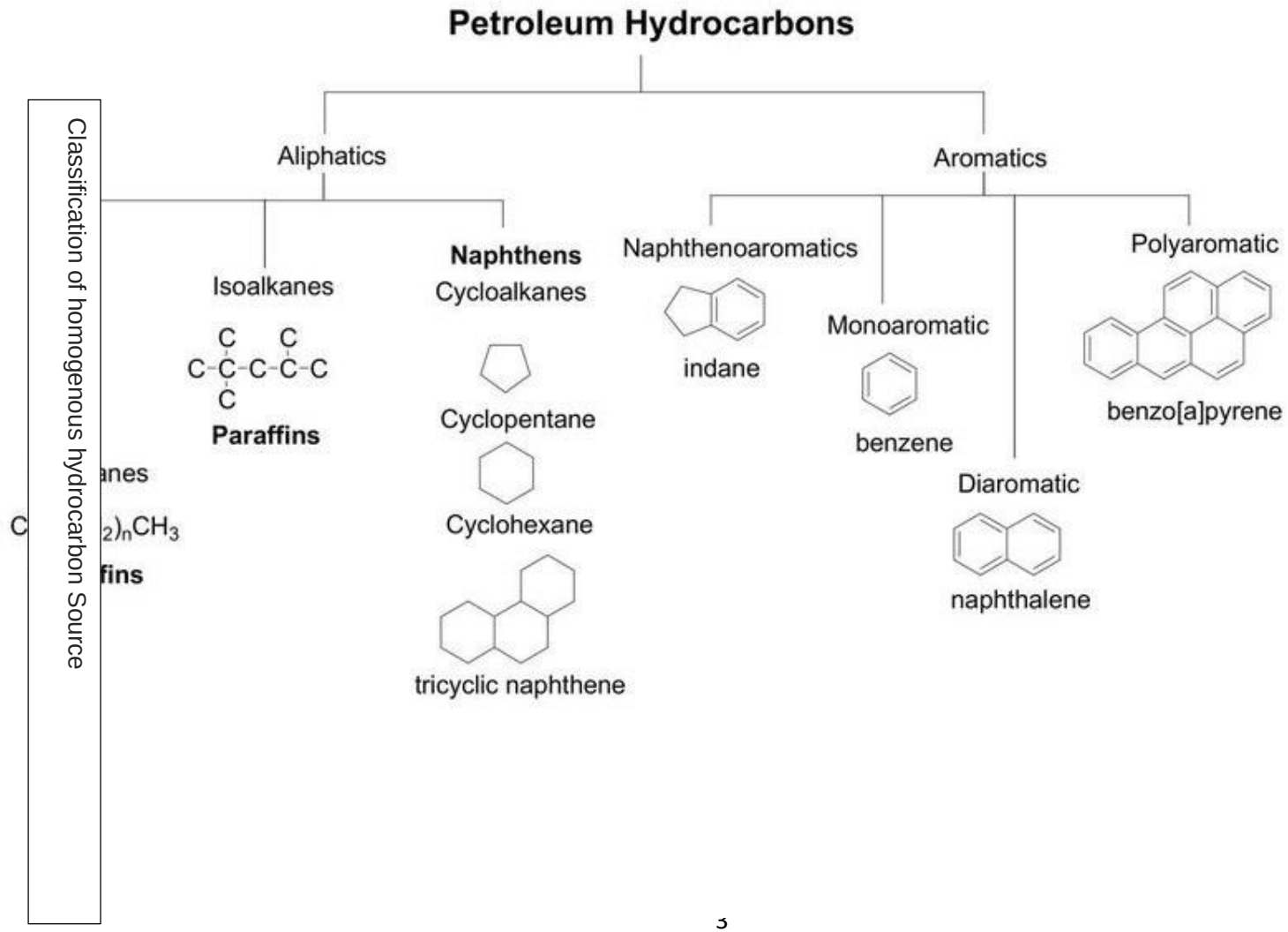
Crude oil, commonly known as petroleum, is a liquid found within the Earth comprised of hydrocarbons, organic compounds and small amounts of metal. While hydrocarbons are usually the primary component of crude oil, their composition can vary from 50%-97% depending on the type of crude oil and how it is extracted. Organic compounds like nitrogen, oxygen, and sulfur typically make-up between 6%-10% of crude oil while metals such as copper, arsenic, nickel, vanadium and iron account for less than 1% of the total composition.

Inorganic salts of magnesium chloride, sodium chlorides, and other mineral salts are also accompanied with crude oil from the well either because of water from formation or water and chemicals injected during drilling and production.

Only the simplest of these homologues can be isolated to some degree of purity on a commercial scale. Generally, in refining processes, isolation of relatively pure products is restricted to those compounds lighter than C7's. The majority of hydrocarbon compounds present in crude oil have been isolated however, but under delicate

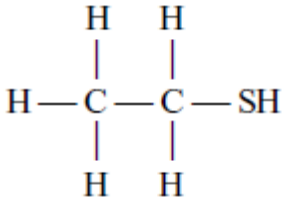
laboratory conditions. In refining processes the products are identified by groups of these hydrocarbons boiling between selective temperature ranges. Thus, for example a naphtha product would be labeled as a 90◦C to 140◦C cut.

Master 2024-2025 2nd. Semester
Petrochemicals
Dr. Raghed Y. Ghazal



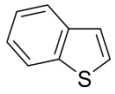
Heteroatom Compounds:

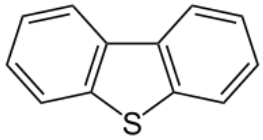
Not all compounds contained in crude oil are hydrocarbons. There are present also as impurities, small quantities of **sulfur, nitrogen, oxygen** and **metals**. By far the most important and the most common of these impurities is **sulfur**. This is present in the form of hydrogen sulfide and organic compounds of sulfur. These organic compounds are present through the whole boiling range of the hydrocarbons in the crude. They are similar in structure to the hydrocarbon families themselves, but with the addition of one or more sulfur atoms. The simplest of these is ethyl mercaptan which has a molecular structure as follows:



Ethyl Mercaptan

The higher carbon number ranges of these sulfur compounds are thiophenes which are found mostly in the heavy residuum range and disulfides found in the middle distillate range of the crude. The sulfur from these heavier sulfur products can only be removed by converting the sulfur to H_2S in a hydrotreating process operating under severe conditions of temperature and pressure and over a suitable catalyst. The lighter sulfur compounds are usually removed as mercaptans by extraction with caustic soda or other suitable proprietary solvents.

Thiophene


Benzothiophene


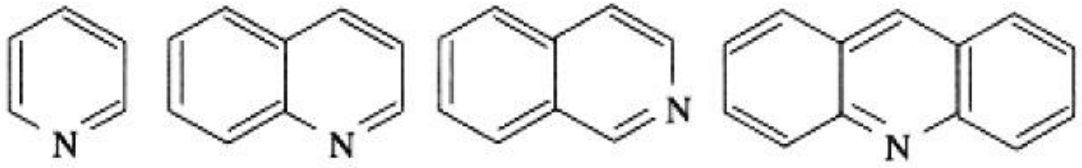
Dibenzothiophene

CH_3-S-CH_3 **CH3-S-S-CH3**

Dimethyl sulfide **Dimethyl disulfide** **cyclohexane thiol**

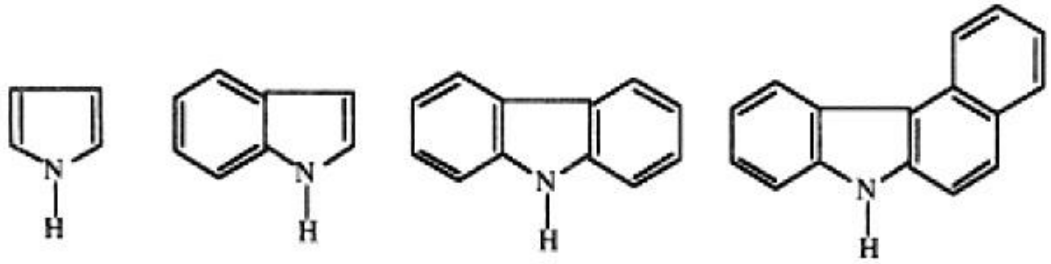
Nitrogen, the remaining impurity is usually found as dissolved gas in the crude or as amines or other nitrogen compounds in the heavier fractions. It is a problem only with certain processes in naphtha product range (such as catalytic reforming). It is removed with the sulfur compounds in this range by hydrotreating the feed to these processes.

Basic Nitrogen Compounds



Pyridine Quinoline Isoquinoline Acridine

Non-Basic Nitrogen Compounds



Pyrrole Indole Carbazole Benzocarbazole

Organic chlorides compounds are also present in crude oil in an amount not exceeding 0.0008-0.004%. These are not removed as such but metallic protection is applied against corrosion by HCl in the primary distillation

processes. This protection is in the form of monel lining in the sections of the process most vulnerable to chloride attack. Injection of ammonia is also applied to neutralize the HCl in these sections of the equipment.

Table (1) Organic chlorides in crude oil

Chemical compound's name	Formulation
Chloroform	CH_3-Cl
Carbon Tetra-chloride	C-Cl_4
Ethylene Tetra-chloro	C-Cl_2=C-Cl_2
Vinyl Chloride	C_2H_3-Cl
Chloro-Benzene	C_6-H_5-Cl
Fereon 113	C_2Cl_3
Chloro-perrine	CH_2=CClCH=CH_2
Di-chloride Propylene	$C_3H_6Cl_2$
Methane Di-chloro	CH_2Cl_2
Ethylene Tri-chloro	CHCl=CCl_2

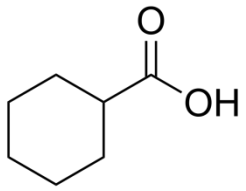
Metals in crude oil:

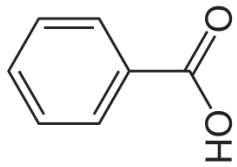
Some metals occur in crude oils. Some of the more considerable are, Fe, V, and Ni as well as Na, Mg, Ca and Al. They are present either as inorganic salts, such as Na and Mg chlorides, or in the form of organometallic compounds, such as those of Ni and V (as in porphyrins).

In spite of metals in crudes are found in trace amounts, their presence is harmful and should be removed. When crude oil is processed, Na and Mg chlorides produce hydrochloric acid, which is very corrosive. Desalting crude oils is a necessary step to reduce these salts.

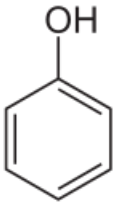
Oxygen compounds in crude oils are more complex than the sulfur types. However, their presence in petroleum streams is not poisonous to processing catalysts. Acidic oxygen compounds found in crude oils are weakly acidic such as carboxylic acids, cresylic acid, phenol, and naphthenic acid. Naphthenic acids are mainly cyclopentane and cyclohexane derivatives having a carboxyalkyl side chain. Naphthenic acids in the naphtha fraction have a special commercial importance and can be extracted by using dilute caustic solutions. The total acid content of most crude is generally low, but may reach as much as 3% as in some crudes.

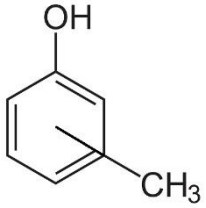
$CH_3(CH_2)_nCH_3COOH$

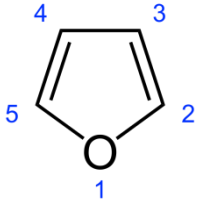


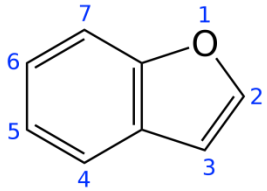


Aliphatic carboxylic Acids **Cyclohexane carboxylic acid** **Benzoic acid**

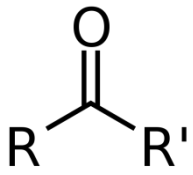




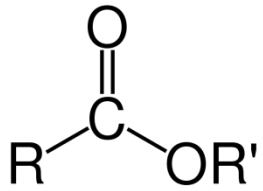




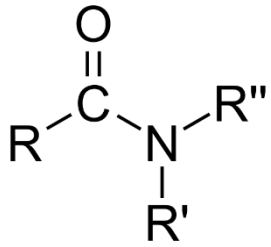
Phenol **cresylic acids** **Furan** **Benzofuran**



Ketones



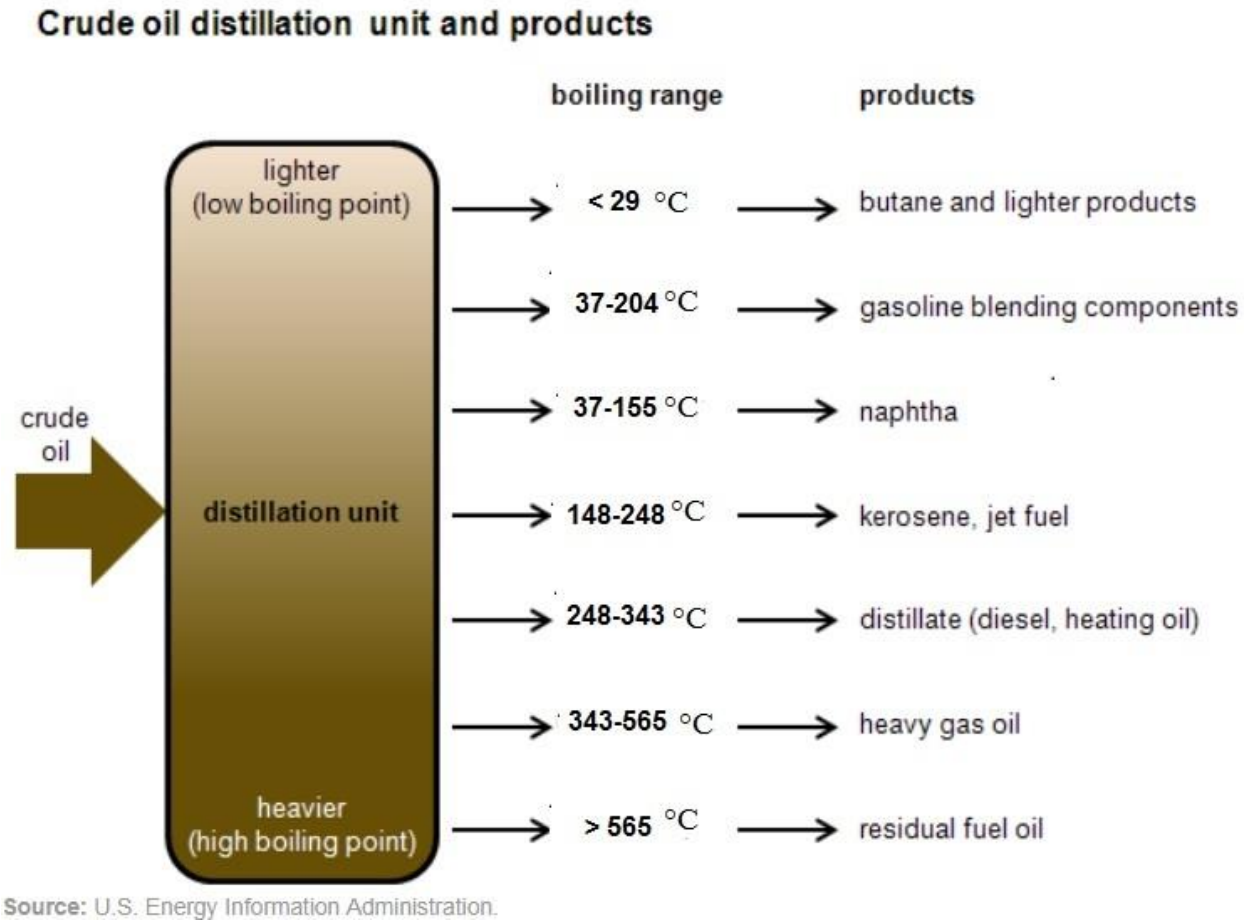
Esters



Amides

Petroleum Fractions

Petroleum can be separated into various types of fuel, by a process called **refining**, using **fractional distillation.**



1- Liquefied Petroleum Gas

Liquefied petroleum gas, commonly called LPG, is also known by the names of its principal generic components, propane and butane. The normal constituents of LPG are propane (C_3H_8), propylene (C_3H_6), butane (C_4H_{10}), and butylenes (C_4H_8),

Cis-2-Butene (C_4H_8), TransButene (C_4H_8) ,Isobutene (C_4H_8). These are commercial products and may contain other impurities such as smaller quantities of C5+ hydrocarbons. LPG as a liquid is colorless, and in vapor form it cannot be seen. Pure LPG has no smell.

LPG is the most versatile fuel used in domestic applications. It is used like natural gas and can do everything that natural gas can do. LPG is used for cooking, central heating, space heating, and hot water supply, as well as in a large number of appliances, such as ovens, stovetops, and

refrigerators in homes, hotels, and restaurants.

2-Naphtha

Naphtha is the lightest liquid distillate product of crude distillation consisting of C_5 toC_{10} hydrocarbons boiling in the 37 to 155°C range. It is produced from the atmospheric distillation of crude oil and from many secondary processing units in the refinery. Unlike other petroleum fuels such as kerosene, diesel, or fuel oil, naphtha is not a direct petroleum fuel but is used as a feedstock for the manufacture of plastics and polymers, synthetic fiber, petrochemicals, fertilizer, insecticides and pesticides, industrial solvents for making specialty solvents such as food grade hexane, dyes, and chemicals. In refineries, naphtha is one of the basic feedstocks for

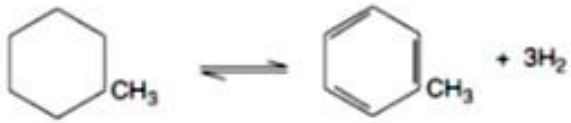
the manufacture of gasoline. At locations where natural gas is not available, naphtha is used as a feedstock for producing hydrogen required for hydroprocessing units in refineries. Naphtha is sometimes used as fuel in gas turbines or boilers for power generation units. The worldwide naphtha demand in 2006 was estimated at 900 million tons.

Catalytic reforming is an important refinery process for the manufacture of gasoline from naphtha. Straight run naphtha from crude oil distillation consists mainly of paraffins and naphthenes. It has a low octane number and cannot be used for gasoline blending.

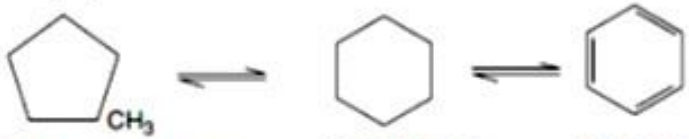
The catalytic reformer unit converts low-octane heavy naphtha to high-octane catalytic reformate. Reformate is used as a blend component for gasoline blending.

The manufacture of aromatics requires catalytic reforming units with continuous catalyst regeneration, operating in a higher severity RON range (100 to 102).

Dehydrogenation reactions

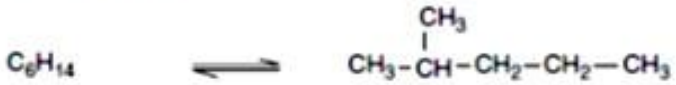


Methyl cyclohexane Toluene



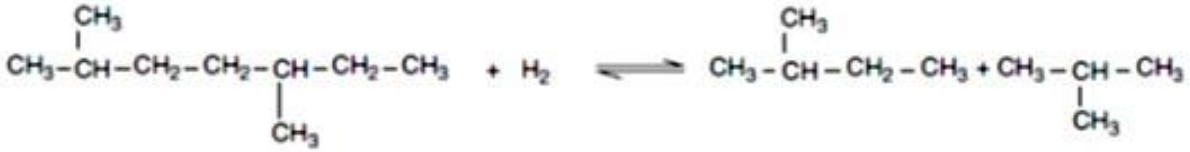
Methyl cyclopentane Cyclohexane Benzene

Isomerization reactions



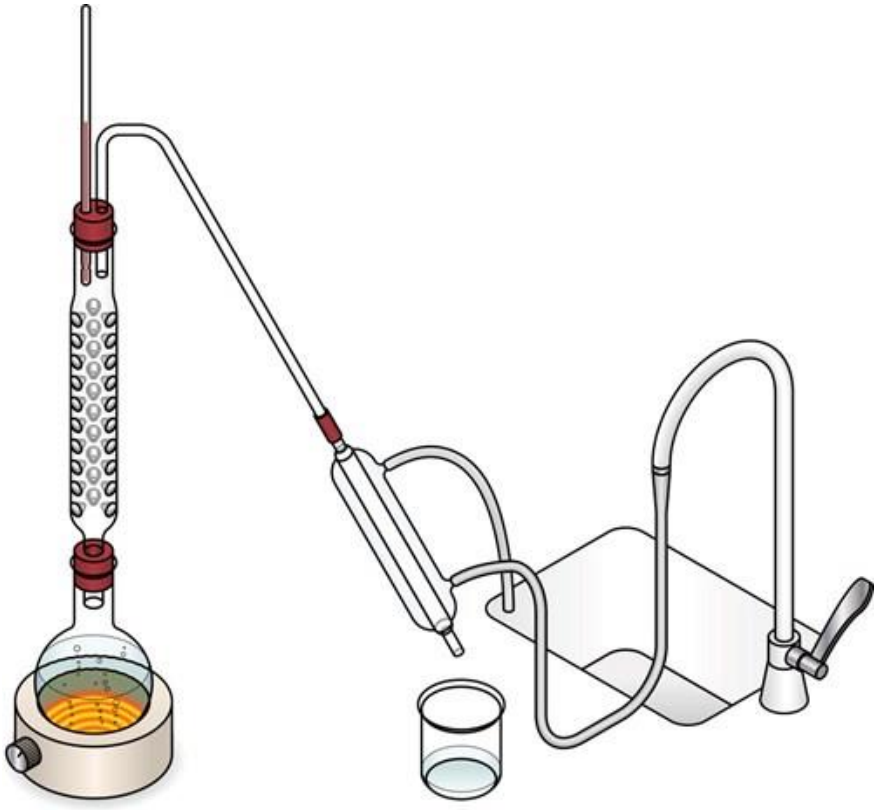
Paraffin dehydrocyclization

Hydrocracking reactions



Octane Number:

measure of the ability of a fuel to resist knocking when ignited in a mixture with air in the cylinder of an internal-combustion engine. The octane number is determined by comparing, under standard conditions, the knock intensity of the fuel with that of blends of two reference fuels: iso-octane, which resists knocking(O.N.=100), and n-heptane, which knocks readily(O.N.=0). The octane number is the percentage by volume of iso-octane in the iso-octane–heptane mixture that matches the fuel being tested in a standard test engine.



fractional distillation experiment

Types of Ocane Number :

There are two methods of measuring octane number of a fuel in the laboratory. The methods are known as motor octane number **(MON)** and research octane number **(RON)**.

The **motor octane number** is indicative of high-speed performance (900 rpm) and is measured under the conditions of heavy road use. The **research octane number** is indicative of normal road performance under low engine speed (600 rpm) city driving conditions. The third type of octane number is defined as posted octane number **(PON),** which is the arithmetic average of the MON and RON. Thus:

$$[PON=(MON+RON)/2]$$

Difference between **(MON) and (RON):**

(MON)	(RON)
1-determined at 900 rpm engine speed	**1-determined at 600 rpm engine speed**
2-The fuel is preheated before ignition	**2-Fuel is not heated**
3- (8 to 10) points lower than the RON	**3-(8 to 10) points higher than the RON**
4-input air at 20 to 52°C	**4-input air is maintained at 38°C**

2-Gasoline:

Gasoline may be defined as the fuel derived from crude oil, in the boiling range of 37 to 204°C, for use in spark-ignited internal combustion engines. Gasoline is one of the most important petroleum products. Most passenger cars use gasoline as fuel, and the demand for gasoline is directly linked to the growth of the automobile industry.

3- Kerosene

Kerosene is a distillate fraction of crude oil boiling between 140 and 240°C. It is heavier than naphtha and gasoline cut but lighter than diesel cut. The yield of kerosene from a medium gravity crude oil such as light Arabian is approximately 16 vol % (percentage by volume). Kerosene was one of the earliest petroleum products to be produced by refineries.

kerosene was used in lamps and lanterns for home and street lighting, replacing whale oil. Use of kerosene for lighting declined with the advent of electricity.

4-Diesel Fuel

The term *diesel* is used for motor vehicle fuel used in compression-ignited engines.The production of distillate fuels (480–650°F cut) is estimated at 23 million barrels per day. High-speed diesel engines (1200 r/min and greater) are used to power trucks,buses, tractors, farm machinery, railroad locomotives, passenger cars, yachts, pumps, compressors and small electric generators.

Natural Gas:

also called **methane gas** or **natural methane gas**, colourless highly flammable gaseous hydrocarbon consisting primarily of **methane** and **ethane**. It is a type of petroleum that commonly occurs in association with

crude oil. A natural resource and fossil fuel**, natural gas is used for** electricity generation, heating, and cooking and as a fuel for certain vehicles. It is important as a **chemical feedstock** in the manufacture of plastics and is necessary for a wide array of other chemical products, including fertilizers and dyes.

There are TWO types of natural gas **WET** gas that found with petroleum in the petroleum field and **DRY** gas found alone. The WET gas called **associated gas** and the DRY gas called **non associated gas.**

The mixture of natural gas also may contain other hydrocarbons, such as **propane, butane, pentane,** and **hexane**.

Oil and Gas Glossary and Definitions

Flash point: The lowest temperature to which the product must be heated under specified conditions to give off sufficient vapor to form a mixture with air that can be ignited momentarily by a lame.

Petroleum Fractions	Flash Point
Naphtha	-21°C
Kerosene	37-65°C
Gas Oil	52-96°C
Fuel Oil	61-115°C

Aniline point: The temperature, usually expressed in °F, above which equal volumes of a petroleum product are completely miscible; a qualitative indication of the relative proportions of parafins in a petroleum product that are miscible with aniline only at higher temperatures; a high aniline point indicates low aromatics.

API gravity: A measure of the lightness or heaviness of petroleum that is related to density and

specific gravity:

$$\text{°API} = (141.5/\text{sp gr @ } 60\text{°F}) - 131.5$$

Note: Light petroleum having an API gravity greater than 20°.

Petroleum Fractions	°API
Naphtha	~56
Kerosene	~44
Gas Oil	~23
Fuel Oil	~19

Acid number: A measure of the reactivity of petroleum with a caustic solution and given in terms of **milligrams** of potassium hydroxide (KOH) that are neutralized by **1 g** of petroleum.

Acid treating: A process in which unfinished petroleum products, such as gasoline, kerosene, and lubricating-oil stocks, are contacted with sulfuric acid to improve their color, odor, and other properties.

American Society for Testing and Materials (ASTM): The oficial organization in the United States for designing standard tests for petroleum and other industrial products.

Boiling range: The range of temperature, usually determined at atmospheric pressure in standard laboratory apparatus, over which the distillation of an oil commences, proceeds, and finishes.

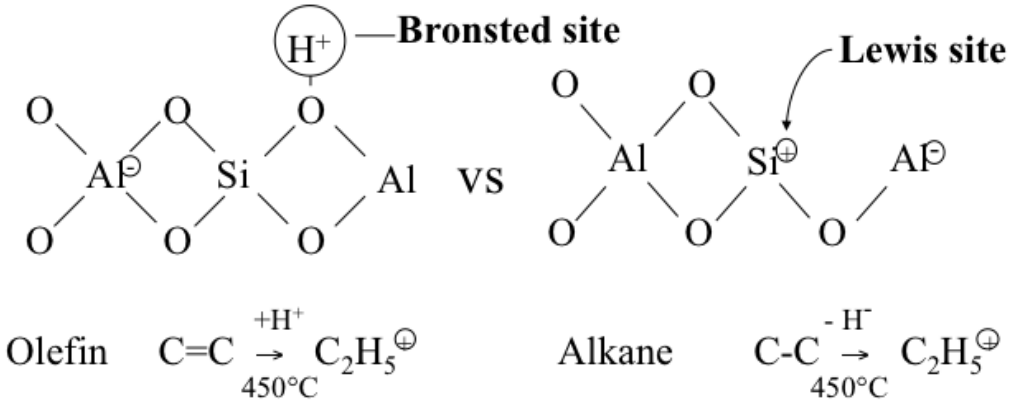
Brønsted acid: A chemical species that can act as a source of protons such as sulfuric acid and zeolite.

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{+2}$$

Formation of Carbocations on Acid Sites of Catalysts

Bronsted acid sites – donate protons

Lewis acid sites – accept electrons



Btu (British thermal unit): The energy required to raise the temperature of 1 lb. of water 1°F.

Calcining (Calcination): Heating a metal oxide or an ore to decompose carbonates, hydrates, or other compounds often in a controlled atmosphere.

Example for calcination:

$CaCO_3 \rightarrow CaO + CO_2$
Lime stone
$MgCO_3 \rightarrow MgO + CO_2$
Magnesite
$CuCO_3.Cu(OH)_2 \rightarrow 2CuO + H_2O + CO_2$
Malachite

Carbonization: The conversion of an organic compound into char or coke by heat in the substantial absence of air; often-used in reference to the destructive distillation (with simultaneous removal of distillate) of coal.

Cetane number: The Cetane number measures the ignition quality of a diesel fuel.

It is the percentage volume of Cetane (n-hexadecane, Cetane Number = 100) in alpha methylnaphthalene (Cetane Number = 0), that provides the specified standard of 13 degrees (crankshaft angle) ignition delay at the identical compression ratio to that of the fuel sample.

Types of Diesel	Cetane Numbers
Regular Diesel	**48**
Premium Diesel	55

Biodiesel (B100)	55
Biodiesel Blend (B20)	50

Distillation range: The difference between the temperature at the initial boiling point and at the end point, as obtained by the distillation test.

Doctor sweetening (Doctor Test): A process for sweetening gasoline, solvents, and kerosene by converting mercaptans to disulfides using sodium plumbite and sulfur.

Iodine number: A measure of the iodine absorption by oil under standard conditions; used to indicate the quantity of unsaturated compounds present

Leaded gasoline: Gasoline containing tetraethyl lead or other organometallic lead antiknock compounds.

Lewis acid: A chemical species that can accept an electron pair from a base.

PONA analysis: A method of analysis for paraffin (P), olefins (O), naphthenic (N), and aromatics (A).

PIONA analysis: A method of analysis for paraffin, iso-parafins, olefins, naphthenic, and aromatics.

Polymer gasoline: The product of polymerization of gaseous hydrocarbons to hydrocarbons boiling in the gasoline range.

Pour point: The lowest temperature at which oil will pour or low when it is chilled without disturbance under definite conditions.

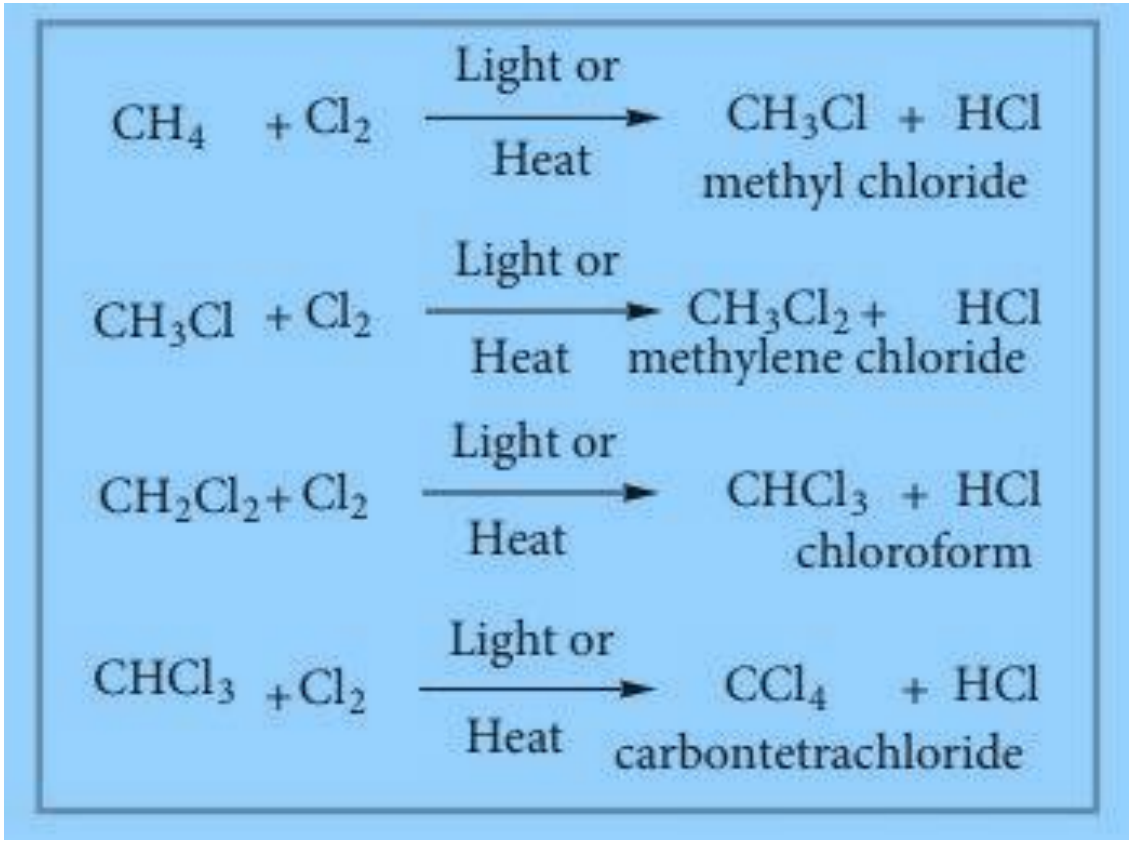
Reformed gasoline: Gasoline made by a reforming process.

Petrochemicals can be produced from Methane:

Methane (CH_4) is the major hydrocarbon component of **natural gas** and is also obtained in large quantities as a by product of petroleum refining.

1. Chlorinated products of methane:

Methane is chlorinated to get methyl chloride (CH_3CI), methylene chloride (CH_2CI_2), chloroform ($CHCI_3$) and carbon tetrachloride (CCI_4). Most of the chlorinated products of methane are used as a solvent.



2-Carbon black

Methane is converted into **carbon black** (a form of carbon) by pyrolysis (cracking) and hydrogen is obtained as a byproduct. Carbon black is any of a group of intensely black, finely divided forms of amorphous carbon,

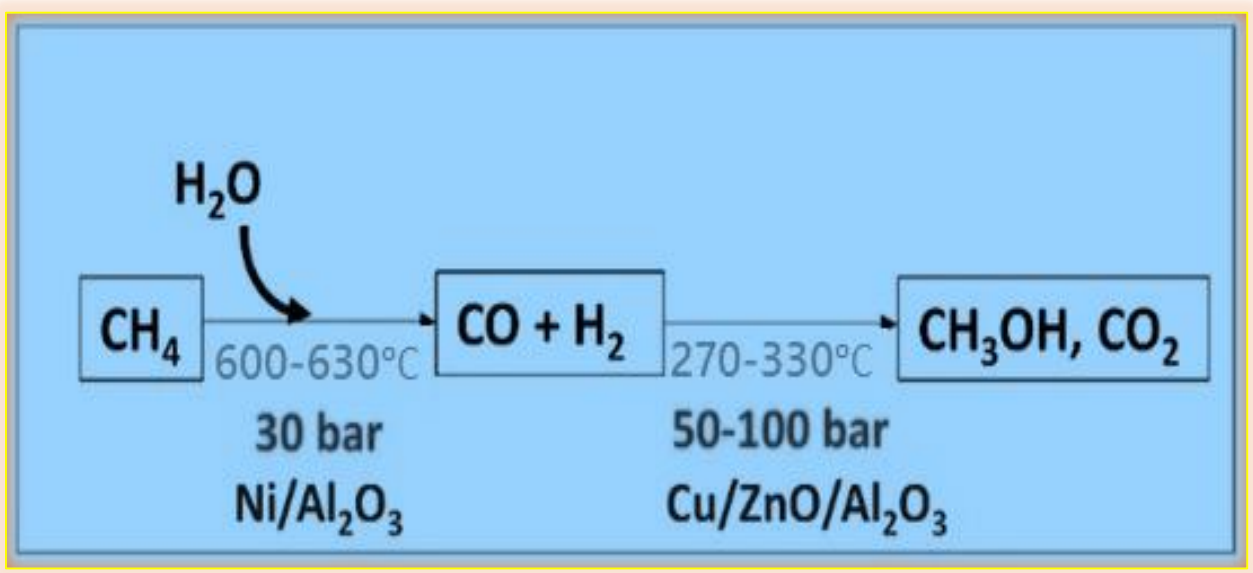
usually obtained as soot from the partial combustion of hydrocarbons, Used principally as **reinforcing agents** in automobile tires and other **rubber products** but also as extremely black **pigments** of high hiding power in printing ink, **paint**, And **carbon paper**. Carbon black is also used in **protective coatings**, **plastics**, and **resistors** for electronic circuits.

About one fourth of the weight of a standard automobile tire is carbon black.

$$CH_4 \longrightarrow C + 2H_2$$

3-Methyl alcohol

Methane is converted into methanol (methyl alcohol, CH_3OH) by catalytic oxidation.



Petrochemicals can be produce from ethylene :

Ethylene is obtained by pyrolysis of **natural gas** or from **naphtha** by cracking. Ethylene is an unsaturated hydrocarbon and has a carbon-carbon double bond. Therefore, ethylene is very reactive and can be converted to a variety of petrochemicals and useful end products.

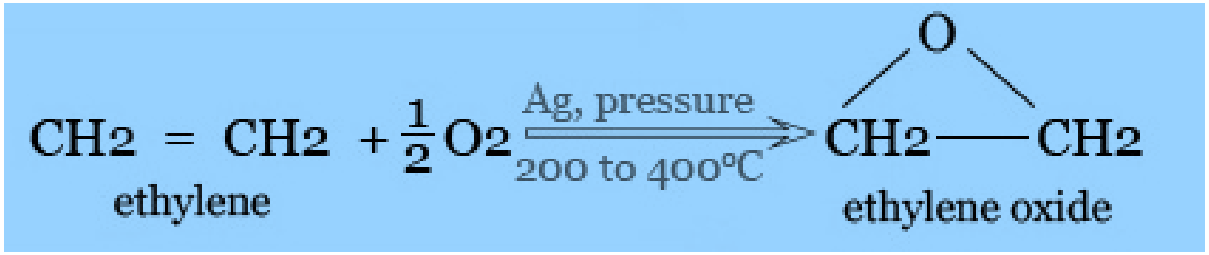
1.Ethyl Alcohol

Ethyl alcohol (ethanol) is made by hydration of ethylene. Ethyl alcohol is used as a solventand a raw material for the manufacture of acetic acid, ethyl acetate and a large number ofother useful products.

$$H_2C = CH_2 \xrightarrow{H_2O\ /H_2SO_4} CH_3CH_2OH$$

2. Ethylene Oxide

Ethylene is oxidized to ethylene oxide with air or oxygen in the presence of a catalyst. It isa raw material for the manufacture of ethylene glycol, which is a starting material for themanufacture of polyester.



Ethylene Glycol

Ethylene glycol (1,2-dihydroxyethane) is manufactured by starting with ethylene. Thereare several methods by which ethylene is converted to ethylene glycol.

Glycol is used as an anti-freeze in automobiles. Ethylene glycol is an important starting material for the manufacture of polyester.