

الجامعة التكنولوجية

قسم الهندسة الكيميائية

المرحلة الثانية

تكنولوجيا الوقود

م. لمى حسين

INTRODUCTION

Fuel is a substance which, when burnt and react with oxygen or air, produces heat. The substances classified as fuel must necessarily contain one or several of the combustible elements : carbon, hydrogen, sulphur, etc. In the process of combustion, the chemical energy of fuel is converted into mechanical or electrical energy.

Fuels are classified mainly in four general classes namely:

- ☐ ***Fossil fuel***
- ☐ ***by-products fuel***
- ☐ ***chemical fuel***
- ☐ ***nuclear fuel.***

The first three release heat by combustion in presence of air or oxygen. Nuclear fuels release heat by nuclear fission or fusion by converting mass into energy.

☐ ***Fossil fuels*** are those which have been derived from fossil remains of plant and animal life and are found in the crust of the earth *e.g.* coal, petroleum, natural gas etc.

☐ ***By-product fuels*** are the co-product of some regular manufacturing process and are of a secondary nature. As for example, coke oven gas and blast furnace gas are the by-product fuels in the process of coke and ironmaking respectively.

☐ ***Chemical fuels*** are of an exotic nature and normally not used in conventional processes. Examples are hydrazine (a rocket fuel), ammonium nitrate, fluorine etc.

☐ ***Nuclear fuels*** which release heat by fission are uranium, plutonium etc. and those generating heat by fusion are deuterium and tritium (both are isotopes of hydrogen) etc. In both the situations, the mass is converted into energy.

Depending upon the state of occurrence, the fuels are classified as solid, liquid or gaseous. Fuels in each general division are further classified as (Table 1).

□ **Primary fuel** are those which occur in nature viz. coal, wood, petroleum, natural gas etc.

□ **Secondary fuels** are those which are derived from primary fuel *e.g.* fuel oil & kerosene (derived from petroleum), *Secondary fuels* are further classified into

a-manufactured and b-by-product fuels.

□ **Manufactured fuels** are those which are made for some specific purpose *e.g.*

coke (made for iron making), gasoline (made for internal combustion engines), producer gas (made for industrial heating) etc.

□ **By-product fuels** are those which are a co-product/side product (unavoidable product) of a regular manufacturing process *e.g.* bagasse, tar, refinery gas etc. By-product fuels help industries in conserving primary fuels.

Table 1.gives the classified list of important fuels (excluding chemical & nuclear fuel).

| General Division | Secondary Fuels | |
|------------------|-----------------|--|
| | Primary Fuels | Manufactured |
| Solid | Natural | |
| | Wood Coal | Semi-coke Coke Charcoal Briquettes Pulverised Coal |
| Liquid | | |
| | Petroleum | Petrol Kerosene Alcohol Colloidal fuels Fuel oil NaphthaVeget able Oil |
| Gaseous | | |
| | Natural gas | Producer gas Water gas Carburetted water gas Coal gas Oil gas Gober gas Reformed natural gas Butane Propane Acetylene nHydrogen LPG |
| | | Charcoal Wood refuse Bagasse Coke breeze Waste material from grain Tar Pitch Benzol Paper pulp mill waste Blast furnace gas Coke oven gas Oil refinery gas Sewage gas L.D. converter gas |

Nuclear fuels are of two-types:

☐ One type can release heat by its fission by neutron bombardment. Such fuels are called fissile fuel *e.g.* uranium-233, uranium-235, plutonium-239.

There are some nuclear fuels *e.g.* thorium-232 and uranium-238 which cannot be fission directly, but they can be converted into fissile material *e.g.* uranium-233 and plutonium-239 respectively. Such nuclear fuels are called fertile fuels.

☐ Another type of nuclear fuels release heat by fusion, *e.g.* deuterium & tritium (both are isotopes of hydrogen), hydrogen etc. But in both the cases whether the fuel undergoes fission or fusion, conversion of mass into energy takes place to release heat.

Depending upon the usage, fuels are classified as:

- ☐ *domestic fuel,*
- ☐ *illuminating fuel*
- ☐ *industrial fuel*
- ☐ *rocket fuel*

☐ **Domestic fuels** supply heat for cooking and space heating.

☐ **Illuminating fuels** *e.g.* kerosene, town gas etc. supply light in darkness.

☐ **Industrial fuels** supply heat for process heating, steam and electricity generation etc.

☐ **Rocket fuels** *e.g.* hydrazine are used for producing enormous thrust for the propulsion of rocket.

As per another general classification system, the fuels which generate heat by combustion are called '*Chemical Fuels*' and the fuels which generate heat by nuclear fission or fusion are **called** '*Nuclear Fuels*'.

FUELS AND THEIR CHARACTERISTICS

1- Solid Fuels

Solid fuels are mainly classified into two categories, i.e. natural fuels, such as wood, coal, etc. and manufactured fuels, such as charcoal, coke, briquettes, etc. (Table.1).

The various advantages and disadvantages of solid fuels are given below:

Advantages

- (a) They are easy to transport.
- (b) They are convenient to store without any risk of spontaneous explosion.

- (c) Their cost of production is low.
- (d) They possess moderate ignition temperature.

Disadvantages

- (a) Their ash content is high.
- (b) Their large proportion of heat is wasted.
- (c) They burn with clinker formation.
- (d) Their combustion operation cannot be controlled easily.
- (e) Their cost of handling is high.

2-LIQUID FUELS AND THEIR CHARACTERISTICS

The liquid fuels can be classified as follows:

- (a) Natural or crude oil, and
- (b) Artificial or manufactured oils.

The advantages and disadvantages of liquid fuels can be summarized as follows:

Advantages

- (a) They possess higher calorific value per unit mass than solid fuels.
- (b) They burn without dust, ash, clinkers, etc.
- (c) Their firing is easier and also fire can be extinguished easily by stopping liquid fuel supply.
- (d) They are easy to transport through pipes.
- (e) They can be stored indefinitely without any loss.
- (f) They are clean in use and economic to handle.
- (g) Loss of heat in chimney is very low due to greater cleanliness.
- (h) They require less excess air for complete combustion.
- (i) They require less furnace space for combustion.

Disadvantages

- (a) The cost of liquid fuel is relatively much higher as compared to solid fuel.
- (b) Costly special storage tanks are required for storing liquid fuels.
- (c) There is a greater risk of fire hazards, particularly, in case of highly inflammable and volatile liquid fuels.
- (d) They give bad odour.
- (e) For efficient burning of liquid fuels, specially constructed burners and spraying apparatus are required.

3-GASEOUS FUELS AND THEIR CHARACTERISTICS

Gaseous fuels occur in nature, besides being manufactured from solid and liquid fuels. The advantages and disadvantages of gaseous fuels are given below:

Advantages

Gaseous fuels due to ease and flexibility of their applications possess the following advantages over solid or liquid fuels:

- (a) They can be conveyed easily through pipelines to the actual place of need, thereby eliminating manual labour in transportation.
- (b) They can be lighted at ease.
- (c) They have high heat contents and hence help us in having higher temperatures.
- (d) They can be pre-heated by the heat of hot waste gases, thereby affecting economy in heat.
- (e) Their combustion can readily be controlled for change in demand like oxidizing or reducing atmosphere, length flame, temperature, etc.
- (f) They are clean in use.
- (g) They do not require any special burner.
- (h) They burn without any soot, or smoke and ashes.
- (i) They are free from impurities found in solid and liquid fuels.

Disadvantages

- (a) Very large storage tanks are needed.
- (b) They are highly inflammable, so chances of fire hazards in their use is high.

ORIGIN OF COAL

Coal is a complex mixture of plant substances altered in varying degree by physical and chemical processes. These processes which changed plant substances into coal has taken million of years and has been accomplished by bacteria, heat and pressure inside the earth's crust.

Different stages in the formation of coal from plant/vegetable debris (called peat to anthracite series) is as follows:

Plant/vegetable debris --> peat --> lignite --> sub-bituminous coal --> bituminous coal --> semi-anthracite --> coal anthracite --> coal graphite.

In this series from peat to anthracite; each member is more mature or *of* higher 'rank' than the one which precedes in the series. Thus anthracite coal is of higher rank than bituminous coal. Bituminous coal is of higher rank (i.e., more mature) than lignite. With the progress of coal forming reaction, moisture and oxygen content reduces and percentage of carbon increases.

Classification of Coal

Coals are classified based on various parameters like proximate analysis, maturity (rank), ultimate analysis, caking properties etc.

Their classification is only described in the following:

1- **Regnault's classification:** this was the first satisfactory classification given by Regnault in 1835 which is based **ultimate analysis of coal**.

2- Regnault Gruner s classification: was modified in 1874 by Gruner in which numerical limits were given for carbon, hydrogen and volatile matter to the higher rank coals defined by Regnault.

3- Brame s classification: it is modified and extended form of Gruner's classification which includes all the coals.

'Table Brame's Classification (i.e. Modified Gruner's Classification) of Coals

| No. of class | Name of Class | Carbon | Hydrogen | Oxygen | Volatile matter |
|--------------|------------------|--------|----------|--------|-----------------|
| I | Lignituous | 75-80 | 4.8-5.5 | 12-20 | 35-47 |
| II | Ligno-bituminous | 78-84 | 4.5-6 | 8-13.5 | 35-45 |
| III | Bituminous Coals | 82-86 | 5-6 | 6-12 | 30-40 |
| IV | | 82-86 | 4.5-5.5 | 5-9 | 30-40 |
| V | | 85-89 | 4.5-5.5 | 4-7.5 | 20-30 |
| VI | Semi-bituminous | 89-92 | 4-5 | 2-4.5 | 13-20 |
| VII | Semi-anthracite | 91-93 | 3-4.5 | 3-5 | 8-13 |
| VIII | Anthracite | > 92.5 | < 4 | < 3 | < 8 |

This classification system was further modified by Brame in 1925 to include other types of coals. There are dry coals with high oxygen content between the lignites and usual steam long flame coals which are termed as lignituous and lingo-bituminous.

4- Feazer` s classification: depending on the ratio of fixed carbon to volatile matter.

5- National Coal Borad (NCB) Classification: is based on two parameters:

- a- The percentage of volatile matter on the dry mineral matter free basis.
- b- The caking power of clean coal (containing < 10% ash) as indicated by Gray-King coke type.

Composition of Coals

Composition of coal is expressed in terms of its :

1-Proximate analysis

2-Ultimate analysis.

Proximate analysis of coal means determining the percentage of moisture, volatile matter, fixed carbon and ash. Proximate analysis with sulphur content and heating value of coal helps in deciding the mode of utilisation of a particular coal.

Ultimate analysis of coal: means determining of its total carbon, hydrogen, oxygen, nitrogen, sulphur and ash content. It gives analysis in terms of the elementary constituents and is helpful in combustion calculations for design of furnaces and its auxiliaries.

The changes in average composition from:

Wood → peat → lignite → bituminous coals → anthracite

Units Fundamentals, Definitions

1.Rank of coal (which is the most important variable in the nature of coal) is determined by volatile

calorific value and carbon content of coal, singly or in combination. This broadly into groups like lignite, bituminous and anthracite which is bituminous coals are subdivided into sub-classes based on their caking

capacity

2-Coalification (or metamorphism).

The process of conversion of lignite to anthracite is called coalification or metamorphism of coal.

3-Carbonisation of Coal.

Heating of coal in absence of air at high temperature to produce a residue coke, tar and gas is called its carbonization.

4-Gasification of Coal.

Heating of coal with insufficiently less quantity of air plus steam to produce a gas rich in CO and H₂ is called its gasification. This is done to produce gaseous fuel from solid and liquid fuel.

5-Combustion. It is an exothermic chemical reaction of a fuel with oxygen or air at high temperature to liberate heat.

6-Calorific value. The quantity of heat (kcal) liberated by the combustion of unit quantity of fuel is called its calorific value. Unit of calorific value is kcal/kg for solid and liquid fuels and kcal/Nm³ for gaseous fuels.

Calorific value or higher heating value at constant volume is the quantity of heat liberated by combusting the fuel at constant volume in oxygen saturated with water vapour, the original material and final products of combustion being at a reference temperature (25°C) and the water obtained from the fuel being in the liquid state.

Gross calorific value at constant pressure implies that the combustion takes place at constant pressure and not at constant volume. In the laboratory determinations, solid and liquid fuels are burnt at constant volume and gaseous fuels are burnt at constant pressure. In the ovens and furnaces, however, the combustion takes place at constant pressure.

The following formula is used in calculating the net calorific value from gross calorific value of solid and liquid fuels approximately:

$$C_N = C_G - 9H \dots \dots \dots (1)$$

Where C_N and C_G = net and gross calorific value in Kcal/Kg, respectively, and H = percentage of hydrogen of coal, including hydrogen of moisture and of water of hydrogen of minerals.

For gaseous fuel, the formula is:

$$C_N = C_G - 8.9V$$

Where C_N and C_G = net and gross calorific value in Kcal/Nm³, respectively, and V = volume percentage as H_2 of total hydrogen of gaseous fuel, including the hydrogen obtainable from other combustible components.

Coal Preparation:

There are four methods as following:

- 1- **Coal Preparation –Grading and Crushing:** the object of coal preparation is to provide each user with fuel of optimum specification for the appliance used.

Procedure:

Coal Preparation includes some or all of the following:

- Separation of coal types at the coal face e.g. into Hards and Brights.
- Screening or grading into fraction of different size.
- Hand- picking of large sizes to remove separate lumps of impurity.
- Crushing of larger sizes to provide the smaller size mostly required by industry.
- Cleaning to remove inorganic impurities when low- ash coal is required.
- Drying, when small- sized coals are washed to remove impurities.
- Blending to modify the properties of a coal.

2-Coal Preparation- Mechanical Cleaning Theory

To reduce the amount of ash formed from the coal in combustion appliance to an acceptable degree, in an economical manner.

3-Coal Preparation –Mechanical cleaning- Types of plants

- Dry- cleaning Processes.
- Wet - cleaning Processes.

Washing of coal

Most of the coals when mined contain impurities associated with which must be removed before the coal is used. Impurities are removed from coal by washing.

Coal contains two types of impurities:

-Fixed or inherent impurities: it is derived from coal forming plant and cannot be separation from coal by washing. A new process developed at central fuel research institute (CFRI), called oil agglomeration technique which consists mainly of leaching of coal impurities by petroleum oil can to some extent remove these impurities. Inherent mineral matter in coal is <3%.

- Free impurities: these are impurities adhering to the surface of the coal and comprise mainly of dirt band and rock particles which can be removal by washing of coal.

Nature of impurities present in coal are of the following: Residual inorganic matter of coal forming plants

- Mineral matter washed or blown into the coal forming mass during the period of its formation.
- Pyrites (FeS_2) formed by the reaction of iron sulphate with coal forming matter.

Objective of coal washing:

- 1- Reduces its ash content.
- 2- Reduces its sulphur and phosphorous contents which are detrimental particularly to metallurgical coals.
- 3- Increases its heating value.
- 4- Improves its coking properties.
- 5- Increases the fusion point of its ash by removing alkali chlorides (which is responsible for lowering the fusion point).
- 6- Reduces its clinkering tendency.
- 7- Increases its efficiency in use.

Advantage of Clean (Washed) Coal:

- Higher efficiency of utilisation.
- Less clinkering trouble in furnaces and gasifier.
- Lesser content of S, P, CI, and other harmful elements.
- improved coking properties.
- Economy of transport and stroage.
- reduces its ash content.

Types of Coal Washing Processes

They are of following three types:

1.Gravity Separation method:

- Wet processes.
- Dry processes.

2.Float and sink method

Fine solids and water floatation (Sand Magnetite and other materials)

3.Froth floatation method.

Modern Trendsin Coke Making

Modern trends in coke making aims it reducing specific heat consumption in coke making by way of fuel economy techniques and high productivity of the coke oven.

Some of the methods of economising fuel consumption in coke making are discussed below :

1-Washing of coal. Ash content in the coke can be reduced by suitably washing the coking coal.

2-Blending of coal. Highly coking coals are always blended *with* non-coking coal; anthracite, coke breeze, medium coking coal, fustian etc. to check its excessive swelling during carbonisation as it might damage the coke oven walls. Blending of coal improves the yield of uniform coke and its shatter index hence the yield of coke breeze will be low and that of the blast furnace grade will be high.

3-Preheating of coal charge. Coal charge of the coke oven can be preheated by the hot flue gas coming out of coke oven regenerators. Preheating of coal increases its bulk density resulting in increased productivity of the oven besides lowering the time of carbonisation and re-heat required for carbonisation.

Preheating of coal having high volatile matter and oxygen content results in the production of coke of improved quality, uniformity and stability.

4-Use of coal briquettes. Use of 30-50% of coal briquettes made with the help of a binder increases the charge density by 7-9% and improves the coking properties of the charge by expansion of briquettes during carbonisation. This allows the use of non-coking coals up to 10-20% in the coke oven.

5-Addition of coking agents. Low coking ability of some weakly coking coal can be improved by the addition of coking agent like asphalt, tar, pitch etc. but the presence of sulphur in the coking agent is detrimental. It permits the use of non-coking coals up to 5% and is suitable for existing ovens.

6-Formed coke. Formed coke is made from low rank, highly volatile non-coking coal with low swelling number. It is carbonised at a low temperature of 500°C to produce char either in a fluidised bed or in some retort where rapid heating of finely crushed charge is possible. The final product is called formed coke.

7-Dry-Quenching of coke. Dry quenching of coke aims at recovering the sensible heat of the hot coke.

Inert quenching is being used in many coke ovens abroad. It is used for the first time in India at Vizag Steel Plant.

8-Stamped charging of coal. Stamp charging is a means of increasing the bulk density of coal. Stamping enables the utilisation of larger proportion of substandard coking coal.

The Combustion of Coal

Due to spontaneous combustion, considerable amount of coal is lost. Higher atmospheric temperature promotes reaction of oxygen. Absorption of oxygen in coal begins as soon as it is broken out in the mine. Oxidation is most rapid in a freshly mined coal at higher temperatures. Some facts in this regard have been established and are given below:

- Oxidation of coal is a continuous process depending upon the time and conditions.

- The rate of oxidation increases with increasing temperature and decreasing size of coal particles.

- The external conditions which cause initial attainment of critical temperatures are:

- 1- External source of heat such as sun's rays, nearby steam pipes, furnace flues etc.

- 2- Fineness of size of coal which gives an increased surface area to come in contact with free air (Oxygen).

- 3-Coals with high textural moisture and high oxygen content have relatively low critical temperatures and are liable to ignite spontaneously.

Uses of Coal

Coal is used for:

- directly burning and getting heat.
- generating steam for producing electricity (nearly 0.5 kg of coal is burnt to generate 1 kWh of electricity).
- driving railway locomotives.
- manufacturing coke and coal gas (e.g. coke oven gas, producer gas, water gas etc.).
- manufacturing synthetic liquid fuels.
- gasification to produce nitrogenous fertiliser from synthesis gas.

Uses of Coal Chemicals

Coal chemical recovered from coke oven gas in by-product plant are subjected to various uses. Important uses of some of the chemicals are described below.

1.Clean Coke Oven Gas.

It is a fuel for steel plant furnaces mainly. Besides it is a source of H_2 for ammonia production.

2.Benzol.

It is used as a motor fuel blend *i.e.* blended with petrol up to 15-20% to give better anti-knock rating of the fuel. Also used for the manufacture of photographic material as solvent, for rubber manufacture. Benzol is also a source of benzene, toluene and xylene which are obtained by its distillation and are valuable chemicals.

3.Tar.

It is used

- for road making purposes
- as a fuel in furnaces
- for recovering various chemicals by its distillation.

4.Pitch.

It is used:

- as a fuel in furnaces.
- for making carbon electrodes.
- for road making purposes.

5.Creosote.

It is used as a fuel after mixing with pitch. The fuel is then called pitch-creosote mixture (PCM).

6.Phenol.

It is used

- for making the plastic, phenol-formaldehyde and is used as an electrical insulating material.
- for the manufacture of perfumes, plasticisers and detergents.
- for making medicines like aspirin.

7.Naphthalene.

It is used for manufacture of Beta-naphthol which is used for making dyes, pharmaceuticals and perfumes.

8.Pyridine. It is used for separation of various chemical products (as it forms azeotropes with water), for the manufacture of colouring substances and also for medicinal purposes.

9.Benzene. It is used for

- for making detergents.
- for making nylons.

10.Toluene. It is used

- for making dyes, plasticiser, pharmaceuticals, phenol, benzoic acid, benzene etc.
- as a solvent and diluent in coatings.
- for making the explosive 'Trinitrotoluene' (TNT).

11.Xylene.

It is used as a solvent for paints, pharmaceuticals etc.

Coal Tar Distillation

Coal tar is a black to brown oily and viscous fluid of characteristic odour produced during high or low temperature carbonisation of coal during coke manufacture.

Tar produced during low temperature carbonisation of coal (at 700 °C) is called low temperature tar whereas that produced during high temperature carbonisation (at 1100°C) is called high temperature tar.

-Low temperature tar Its yield is about 10% of dry coal. It is a brown colour oily liquid having very low viscosity, hence flows readily. It is paraffinic in nature. Its typical ultimate analysis is:

| | | |
|----------|--------|----------|
| C = 84% | H = 8% | N = 1% |
| S = 0.5% | | O = 6.5% |

It contains very less free carbon (about 3%).

-High temperature tar It is a thick, high viscosity, black coloured liquid with an aromatic nature. It contains more amount of useful aromatics like phenol, naphthalene, cresote, anthracene, benzol, pyridine etc. Its free carbon content is high (10%) and the yield is lower (3% dry coal) as compared to low temperature tar.

Typical analysis of H.T. tar is

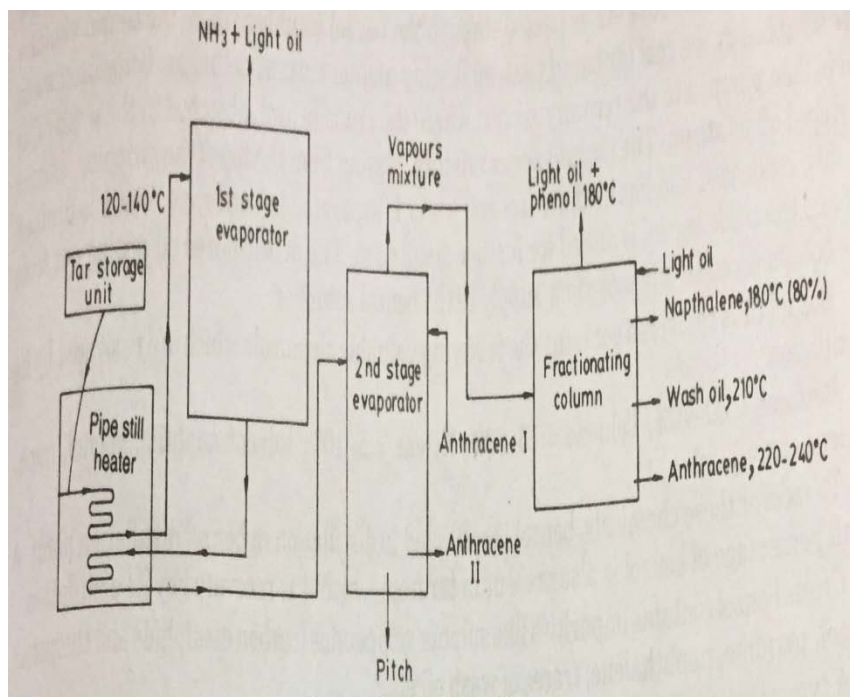
| | | |
|-----------|----------|----------|
| C = 90.5% | H = 5.5% | N = 0.9% |
| S = 0.8% | O = 2.3% | |

Distillation of Tar:

Tar contains around 300 identified chemicals. Hence, to recover economically some of these chemicals and to produce better fuel from tar, it is distilled. The main fraction of tar (which are recovered by distillation) their constituents, yield and boiling ranges are given in table:

Table Products of Tar Distillation

| Fractions | Boiling range , °C | Yield, weight% | Main constituents of the fractions |
|--------------------------|--------------------|----------------|--|
| Light oil | < 170 | 2-4 | Benzol, naphtha and phenol |
| Middle (or carbolic) oil | 170-230 | 5-7 | Phenol, tar acids, heavy naphtha, naphthalene and pyridine |
| Heavy (or creosote) oil | 230-270 | 15-25 | Impure naphthalene and creosote oil |
| Anthracene oil | 270-350 | 14-17 | Anthracene and wash oil |
| Pitch | Residue | 60-70 | — |



Flow Diagram of a typical tar distillation plant

Coal Gasification

Heating of coal with insufficiently less quantity of air plus steam to produce a gas rich in CO and H₂ is called its gasification. This is done to produce gaseous fuel from solid fuel.

The total coal gasification in single stage (using processes like Lurgi process, Winkler process) maximizes the conversion of coal into gaseous fuel and minimizes the tar formation. The gasification efficiency of these processes are very high and they are suitable for a wide range of feed material. The gases produced by the gasifier are mainly used as a fuel and a source of synthesis gas (hydrogen rich) for ammonia making in fertilizer plants.

Typical composition of Lurgi gas: cleaned and CO₂ free gas from oxygen and steam blown Lurgi generator is of following composition:

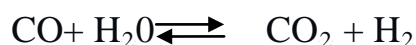
H₂=50%, CO=35%, CH₄=15%

Liquefaction of Coal (Fischer- Tropsch Process)

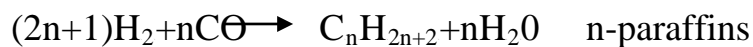
1.The raw material is the hard coke which is converted into a mixture of carbon monoxide and hydrogen by passing steam over red hot coke (water gas reaction):



2- Carbon monoxide is removed by converting it into carbon dioxide which is obtained by passing the water gas with extra steam over a promoted reduced iron oxide catalyst at 450°C .



3-The synthesis gas is passed at atmospheric pressure' over a cobalt-thorium oxide catalyst at $180\text{--}200^\circ\text{C}$. The reaction products are predominantly straight chain paraffins and olefins, the following equations:



4-The original catalysts for Fischer-Tropsch process was cobalt. Now cheaper iron-oxide catalysts are used. All the reactions are highly exothermic, hence control of reactor temperature is critical.

Operating Conditions of Fischer-Tropsch Reactors (High Pressure)

| Process | Temperature, $^\circ\text{C}$ | Pressure, atm | Catalyst |
|-----------------------|-------------------------------|---------------|---------------------------------|
| Arge fixed bed | Up to 270 | 25-30 | Precipitate Iron |
| Kellogg fluidized bed | 300-340 | 25-30 | Millscale or similar iron oxide |

Liquid Fuel/ Petroleum Petroleum Assay

Petroleum

Petroleum (or rock oil) is a naturally occurring brown to black oil comprising mainly of hydrocarbons found under the crust of the earth on shore or off shore.

It is obtained, from the ground either by natural seepage or by drilling wells to various depths. Either petroleum oil flows out itself due to underground gas pressure or these are mechanically pumped out.

Modern Theory. According to modern views, petroleum is believed to be formed by the decay and decomposition of:

- marine animals
- vegetable organism of the pre-historic forests, *i.e.* it is of animal as well as of plant origin.

It is thought that due to some upheavals or earthquakes, these prehistoric forests, and sea animals got buried under the crust of earth.

Due to action of prolonged action of high temperature and pressure in the interior of earth for ages, the biological matter decomposed into petroleum.

This modern theory explains

- the presence of brine
- coal in the vicinity of petroleum.
- Presence of brine is explained on the basis of animal origin while
- The presence of coal is explained by plant origin.

It also explains the presence of N and S compounds, chlorophyll and optically active compounds.

Difference Between Origins of Petroleum Oil and Coal

- Petroleum oil was formed mainly from sea plants and animals decaying under strongly reducing conditions while the coal was formed mainly from land plants decaying under mildly reducing conditions.
- Coal seams remained static where formed/deposited while oil can migrate under the effects of pressure and temperature so that the location of the existing deposits may not be the location of the initial accumulation of oil forming debris. The source rock is sedimentary and mainly or entirely of marine origin.

Composition of Petroleum.

Atypical composition (by weight %) of petroleum is given below

| | | |
|---------------------|-------------------|------------------|
| Carbon = 84-87% | Hydrogen = 11-15% | Sulphur = 0.1-3% |
| Nitrogen = 0.1-1.5% | Oxygen = 0.3-1.8% | |

The principal components of petroleum are hydrocarbons (paraffins, naphthenes, aromatics, olefins etc.), small amounts of sulphur, nitrogen & oxygen compounds as impurities and some inorganic compounds & metals (vanadium and platinum in traces).

Sulphur compounds found in petroleum are hydrogen sulphide, thiophenes, mercaptans. Oxygen occurs in combined form in alcohols, phenols, resins and organic acids present in petroleum. Nitrogen compound include pyridines, quinolines, pyroles etc. Inorganic compounds present in petroleum are salt, clay and sand etc.

Typical properties of crude oil:

Specific gravity = 0.80 - 0.95, viscosity at 37.8°C = 2.3 - 23 cst

carbon/hydrogen ratio = 6 - 8, pour point = 18 - 30°C ,

wax content = 6 -12%, flash point = 15 - 27°C

water content = 0.1 - 1.5% , Salt content = 1.5 - 8%,

Ash content = 0.004 - 0.006%.

PROduction of Petroleum

Petroleum almost always occurs along with gas called natural gas. After drilling in the crust of earth both natural gas and oil flow up through pipe under pressure initially. When the oil pressure decreases, then the residual oil is either sucked by a pump or pressure is created by injecting compressed gas or high pressure water through a pipe bored by the side of oil delivery pipe so that it can flow out.

When the oil well contains both oil and gas it is called (**wet well**) and if it contains only gas then it is called a (**dry well**).

A sketch of typical oil pool formation inside the crust of earth is given in Fig.1. Hard cap rock and hard rock at the bottom, both are impermeable to oil and gas. Geological studies indicates that petroleum was not formed in the pools where it is found today.

Deposits of crude petroleum were formed near seashores, but the action of the surrounding water gradually shifted the location of oil pool. After a period of many centuries, the oil was forced through layers of porous rock strata until it became trapped under a dome capped by hard rock. This makes it impossible for the gas or oil to escape and the water keeps the pool of water under pressure.

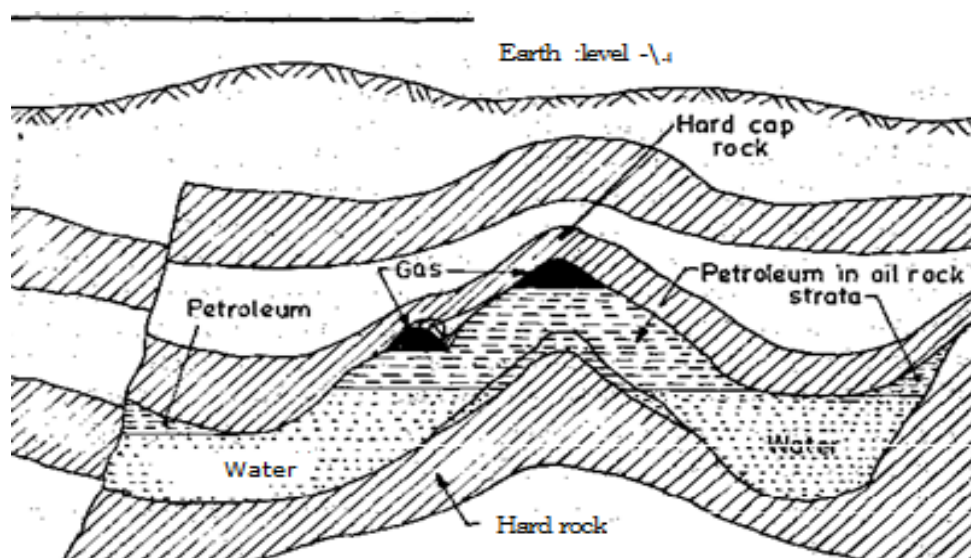


Fig.1. Typical oil-pool formations. In the centre, pool water has forced the petroleum and gas up into a dome, or anticline, in the porous oil rock layer. Hard cap rock prevents the escape of the oil. A fault, at the left, or a stratigraphic.

Pre-Treatment of Oil at Oil Field before Refining

Oil and gas when they come out of oil field are separated. The natural gas is compressed to liquify it which is used for heating of domestic and industrial ovens. Petroleum oil is made free of

- water,
- sediments and
- salts present in it.

It is then made free of some dissolved gases into it by the process called '*stabilisation*'. It is then sent to oil refineries _ for separation into various petroleum products by distillation mainly and auxiliary operations.

Crude oil as it comes out of well may contain up to (25%) water, salts (MgCl_2 , CaCl_2 , NaCl etc.) up to 2000-5000 (mg/litre) and sediments up to (1-1.5%).

For refining crude oil, the salt content in it should be < 50 mg/litre and Water $< 0.3\%$. Excessive water in crude requires extra heat for its distillation, increases its cost of transportation, forms emulsion which absorb materials like resin (hence emulsion breakers are to be used).

Salt in crude oil causes:

- scaling,
- corrosion and
- reduces heat transfer co-efficient during its processing.

Sediments present in crude causes:

- erosion and
- scaling.

In mechanical method of separation of impurities from crude oil, it is subjected to centrifuging, filtration and settling after heating it to $120-160^\circ\text{C}$ at 6-8 atm. pressure.

In physico-chemical method, emulsion breakers are added. But they are costly and cause corrosion & sludge formation.

Stabilisation of Crude Oil

Removal of dissolved gases from crude oil by heating it is called its stabilisation. Gas accompanied with crude oil must be removed to avoid breathing loss (loss of gasoline, if *gas* is not removed from oil during prerefining). Breathing loss occurs due to changes of humidity of ambient air and day and night temperature change also during emptying and filling of crude tanker. Breathing loss is about $0.4-0.75 \text{ kg/m}^3$ of tank volume per month.

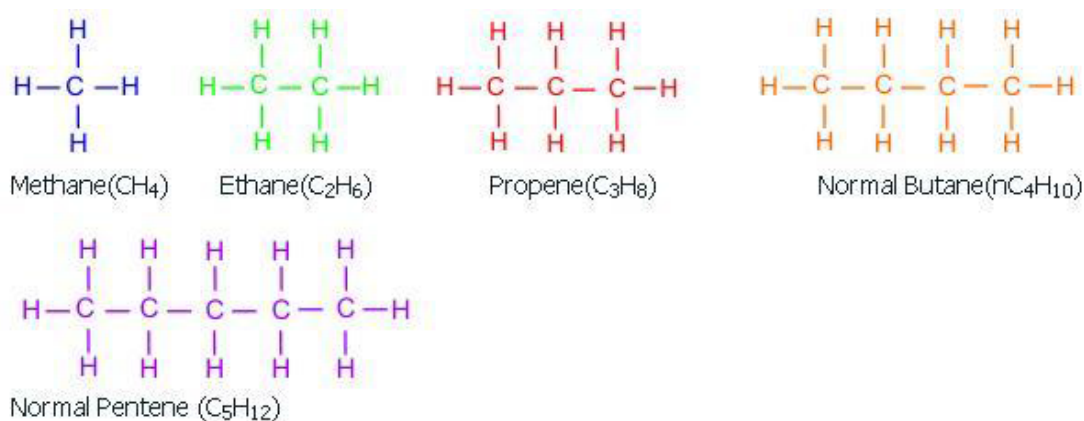
Classification of Petroleum

Depending on the nature of hydrocarbons present in it, crude petroleum oil is classified as

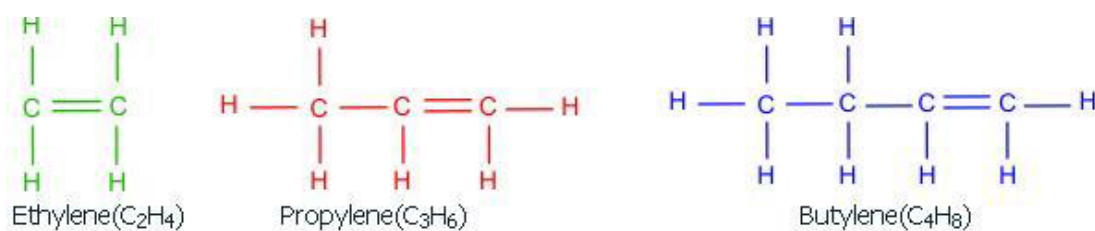
- ❖ paraffin base,
- ❖ naphthene base,
- ❖ asphalt base,
- ❖ or mixed base.

There are some crude oils which have up to 80% aromatic content, and these are known (as aromatic-base oil). Attempts have been made to define or classify petroleum based on various distillation properties when combined with another property such as density. It has been suggested that crude should be called asphaltic if the distillation residue contained less than 2% wax and paraffinic if it contained more than 5%.

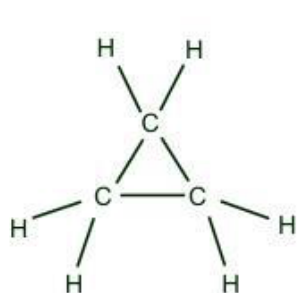
Paraffins: Paraffins refer to alkanes such as methane, ethane, propane, n and iso butane, n and iso pentane. These compounds are primarily obtained as a gas fraction from the crude distillation unit.



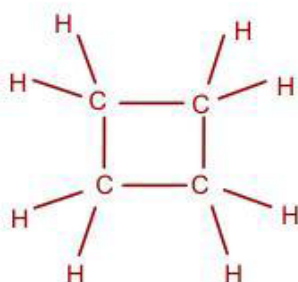
Olefins: Alkenes such as ethylene, propylene and butylenes are highly chemically reactive. They are not found in mentionable quantities in crude oil but are encountered in some refinery processes such as alkylation.



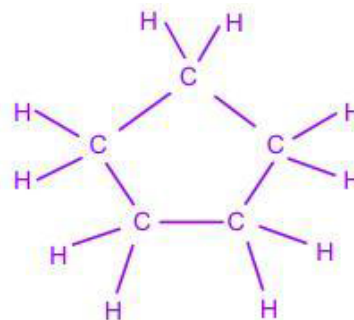
Naphthenes: Naphthenes or cycloalkanes such as cyclopropane, methyl cyclohexane are also present in the crude oil. These compounds are not aromatic and hence do not contribute much to the octane number. Therefore, in the reforming reaction, these compounds are targeted to generate aromatics which have higher octane numbers than the naphthenes.



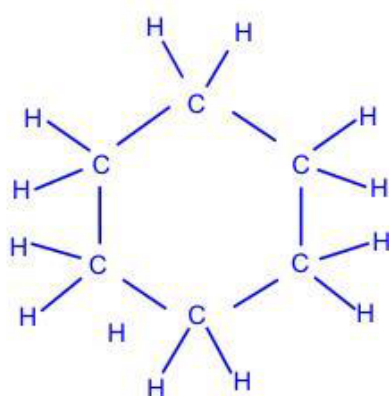
Cyclopropane(C_3H_6)



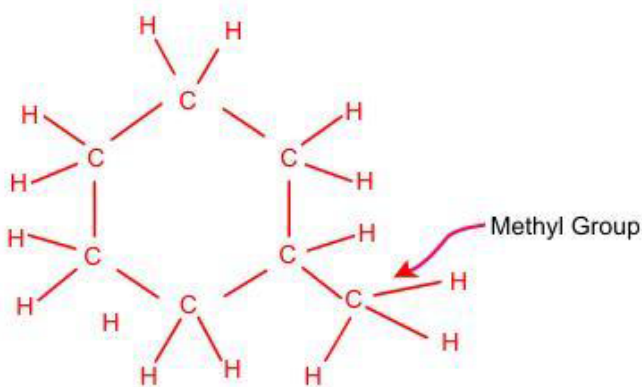
Cyclobutane(C_4H_8)



Cyclopentane(C_5H_{10})

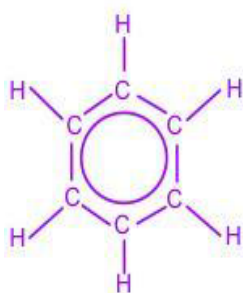


Cyclohexane(C_6H_{12})

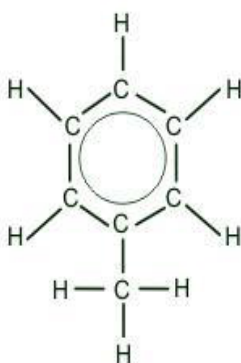


Methyl Cyclohexane(C_7H_{14})

Aromatics: Aromatics such as benzene, toluene o/m/p-xylene are also available in the crude oil. These contribute towards higher octane number products and the target is to maximize their quantity in a refinery process.



Benzene(C_6H_6)



Toluene(C_7H_8)



Para-X ylene(C_8H_{10})

Napthalenes: Polynuclear aromatics such as naphthalenes consist of two or three or more aromatic rings. Their molecular weight is usually between 150 – 500.



Naphthalenes

Organic sulphur compounds: Not all compounds in the crude are hydrocarbons consisting of hydrogen and carbon only. Organic sulphur compounds such as thiophene, pyridine also exist in the crude oil. The basic difficulty of these organic sulphur compounds is the additional hydrogen requirements in the hydrotreaters to meet the euro III standards. Therefore, the operating conditions of the hydrotreaters is significantly intense when compared to those that do not target the reduction in the concentration of these organic sulphur compounds. Therefore, ever growing environmental legislations indicate technology and process development/improvement on the processing of organic sulphur compounds.

Crude Oil Properties (Petroleum Assay)

Oxygen containing compounds: These compounds do not exist 2 % by weight in the crude oil. Typical examples are acetic and benzoic acids. These compounds cause corrosion and therefore needs to be effectively handled.

Resins: Resins are polynuclear aromatic structures supported with side chains of paraffins and small ring aromatics. Their molecular weights vary between 500 – 1500. These compounds also contain sulphur, nitrogen, oxygen, vanadium and nickel.

Asphaltenes: Asphaltenes are polynuclear aromatic structures consisting of 20 or more aromatic rings along with paraffinic and naphthenic chains. A crude with high quantities of resins and asphaltenes (heavy crude) is usually targeted for coke production.

Important Characterization Properties

Numerous important feed and product characterization properties in refinery engineering include

- API gravity
- Watson Characterization factor
- Viscosity
- Sulfur content
- True boiling point (TBP) curve
- Pour point
- Flash and fire point
- ASTM distillation curve
- Octane number

1.API gravity API gravity of petroleum fractions is a measure of density of the stream. Usually measured at 60 °F, the API gravity is expressed as:

$$\text{API}^\circ = 141.5/\text{specific gravity} - 131.5$$

where specific gravity is measured at 60 °F.

According to the above expression, 10 °API gravity indicates a specific gravity of 1 (equivalent to water specific gravity). In other words, higher values of API gravity indicate lower specific gravity and therefore lighter crude oils or refinery products and vice-versa. As far as crude oil is concerned, lighter API gravity value is desired as more amount of gas fraction, naphtha and gas oils can be produced from the lighter crude oil than with the heavier crude oil. Therefore, crude oil with high values of API gravity are expensive to procure due to their quality.

Table 2: Classification of crude oils

| Crude Category | Gravity |
|-------------------|----------------|
| Light crudes | API > 38 |
| Medium crudes | 38 > API > 29 |
| Heavy crudes | 29 > API > 8.5 |
| Very heavy crudes | API < 8.5 |

2. Watson characterization factor

The Watson characterization factor is usually expressed as $K = (TB)^{1/3} / \text{specific gravity}$

Where TB is the average boiling point in degrees R taken from five temperatures corresponding to 10, 30, 50, 70 and 90 volume % vaporized. Typically Watson characterization factor varies between 10.5 and 13 for various crude streams. A highly paraffinic crude typically possesses a K factor of 13. On the other hand, a highly naphthenic crude possesses a K factor of 10.5.

Therefore, Watson characterization factor can be used to judge upon the quality of the crude oil in terms of the dominance of the paraffinic or naphthenic components.

3. Sulfur content

Since crude oil is obtained from petroleum reservoirs, sulphur is present in the crude oil. Usually, crude oil has both organic and inorganic sulphur in which the inorganic sulphur dominates the composition. Typically, crude oils with high sulphur content are termed as sour crude. On the other hand, crude oils with low sulphur content are termed as sweet crude. Typically, crude oil sulphur content consists of 0.5 – 5 wt % of sulphur. Crudes with sulphur content lower than 0.5 wt % are termed as

sweet crudes. It is estimated that about 80 % of world crude oil reserves are sour.

4. Viscosity

Viscosity is a measure of the flow properties of the refinery stream. Typically in the refining industry, viscosity is measured in terms of centistokes (termed as cst) or saybolt seconds or redwood seconds. Usually, the viscosity measurements are carried out at 100 °F and 210 °F. Viscosity is a very important property for the heavy products obtained from the crude oil. The viscosity acts as an important characterization property in the blending units associated to heavy products such as bunker fuel. Typically, viscosity of these products is specified to be within a specified range and this is achieved by adjusting the viscosities of the streams entering the blending unit.

5. Flash and fire point

Flash and fire point are important properties that are relevant to the safety and transmission of refinery products. Flash point is the temperature above which the product flashes forming a mixture capable of inducing ignition with air. Fire point is the temperature well above the flash point where the product could catch fire. These two important properties are always taken care in the day to day operation of a refinery.

6. Pour point

When a petroleum product is cooled, first a cloudy appearance of the product occurs at a certain temperature. This temperature is termed as the cloud point. Upon further cooling, the product will cease to flow at a temperature. This temperature is termed as the pour point.

Both pour and cloud points are important properties of the product streams as far as heavier products are concerned. For heavier products, they are specified in a desired range and this is achieved by blending appropriate amounts of lighter intermediate products.

7. TBP/ASTM distillation curves

The most important characterization properties of the crude/intermediate/product streams are the TBP/ASTM distillation curves. Both these distillation curves are measured at 1 atm pressure. In both these cases, the boiling points of various volume fractions are being measured. However, the basic difference between TBP curve and ASTM distillation curve is that while TBP curve is measured using batch distillation apparatus consisting of no less than 100 trays and very high reflux ratio, the ASTM distillation is measured in a single stage apparatus without any reflux. Therefore, the ASTM does not indicate a good separation of various components and indicates the operation of the laboratory setup far away from the equilibrium

Crude Oil –Distillation

The process of distillation is the most common method adopted for separating the constituents of crude oil into compounds or groups of compounds having industrial uses.

Crude oil consists of a complex mixture of hydro-carbons widely differing in boiling points. Distillation is done to separate the crude oil into the basic fractions like motor gasoline kerosene, gas oil and fuel oil. The order in which these components emerge as crude oil is distilled is given in Table.1.

| | <i>Approximate Boiling</i> | <i>Uses</i> |
|---------------|----------------------------|---|
| Gases | -162 to -42 | Domestic cooking, Heating furnaces in |
| Gasoline/li | -1 to 150 | Motor Fuel. (straight run gasoline) |
| Heavy | 150-205 | Catalytic reformer feed, jet fuel, |
| Kerosine | 205-250 | Illuminant and fuel. |
| Light Gas Oil | 250-315 | High speed diesel oil, fuel oil, |
| Heavy Gas | 315-430 | Catalytic cracking feed. |
| Vacuum gas | 430-540 | Lubricating oil, catalytic cracking feed |
| Fuel | >595 | Fuel for furnaces, asphalt, bitumen, coke |

Various Crude Oil Distillation Systems

There are four ways in which the crude oil is distilled *i.e.*

- *Shell still distillation* (Obsolete).
- *Single stage distillation unit* (Atmospheric pressure).
- *Two-stage distillation unit* (Atmospheric and high pressure units).
- *Three-stage distillation unit* (High pressure, atmospheric, pressure and vacuum units).

Shell still distillation of crude oil.

It is the oldest and obsolete method of crude oil distillation which is accomplished in a battery of shell stills as shown in the Fig..1.

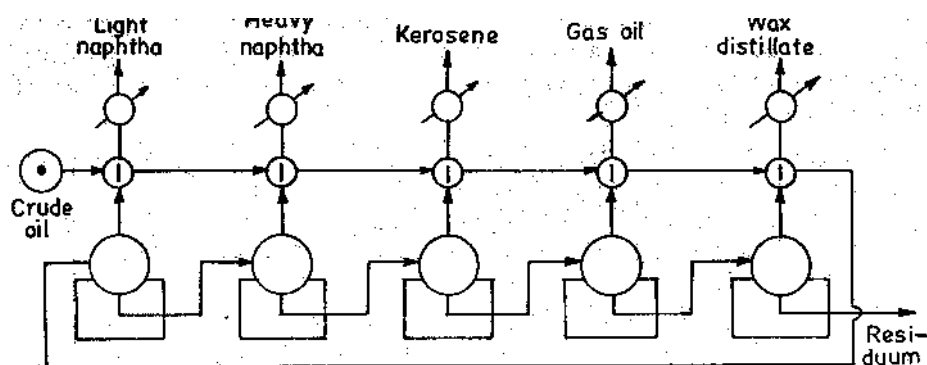


Fig.1:Battery of Shell Still

Preheated crude is charged continuously to horizontal, cylindrical stills which are externally fired. The lightest product (having lowest boiling point and molecular weight) is taken off at the first still (i.e. light naphtha) and the remaining liquid passes on to the following stills where the process is repeated, successively higher boiling point products being obtained in each still which is equipped with bubble cap columns to improve separation of products with overlapping boiling points.

Single stage atmospheric distillation unit.

A single-stage crude unit is shown in Fig.3. The crude feed is preheated by the outgoing streams and then enters a direct fired furnace-type heater (pipe still). The materials separate in the distillation column according to their boiling points, the lowest-boiling fraction leaving at the top of the column. Desired products may be withdrawn as side-streams at appropriate points on the column. The side-streams are further fractionated in small columns called strippers. Here, steam is used to free the cut from its more volatile components so that the initial boiling point of the products can be adjusted to its desired value. It is also called straight run distillation of crude oil.

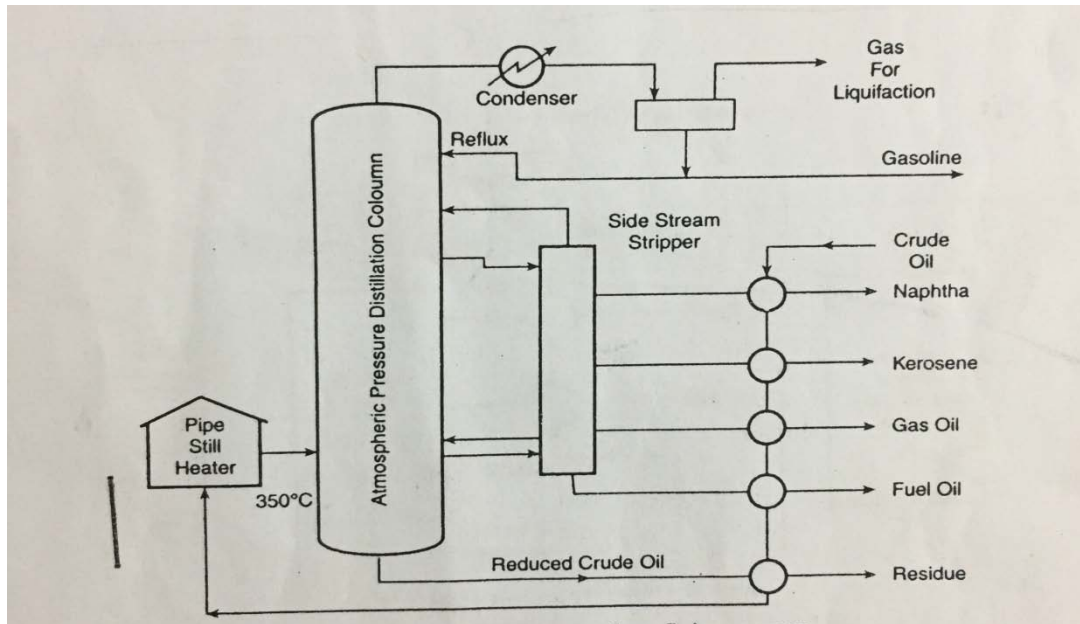


Fig 2: Single Stage Crude Refining Process

Typical yield (weight %) from atmospheric distillation of crude oil is :

- (gas + LPG + losses) = 2 to 3%,
- (gasoline + naphtha) C5 — 145°C = 8 to 15%,
- Kerosene (145 — 250°C) = 15 to 20%,
- High speed diesel oil (270 — 370°C) = 20 to 35%,
- Reduced crude (> 370°C) = 30 to 45%.

However capacity of single stage distillation unit for processing crude is limited which calls for addition of pressure units. Moreover, high boiling point products cannot be separated as operating it at higher temperature may result in cracking of products. Therefore vacuum units are added to get the high boiling point products vaporised and separated at lower temperature.

This is also called crude *topping* or **atmospheric distillation** of crude as the pressure in the distillation column is slightly above atmospheric.

Two stage distillation unit. This scheme of distillation includes a *primary tower* which operates at about 3-4 *atmospheric pressure* and a *secondary tower* operating at *atmospheric pressure* together with stabiliser. This scheme is used when crude is to be separated into six to ten narrow cuts (*i.e.* products with very close and overlapping boiling points). Two/three side streams (*e.g.* gasoline, naphtha) are withdrawn from primary tower while the overhead (gas) product becomes feed to stabiliser. Primary tower bottoms becomes the feed for secondary tower from which side-streams like kerosene, diesel, gas oil etc. are withdrawn at appropriate points after passing through strippers to remove the light components.

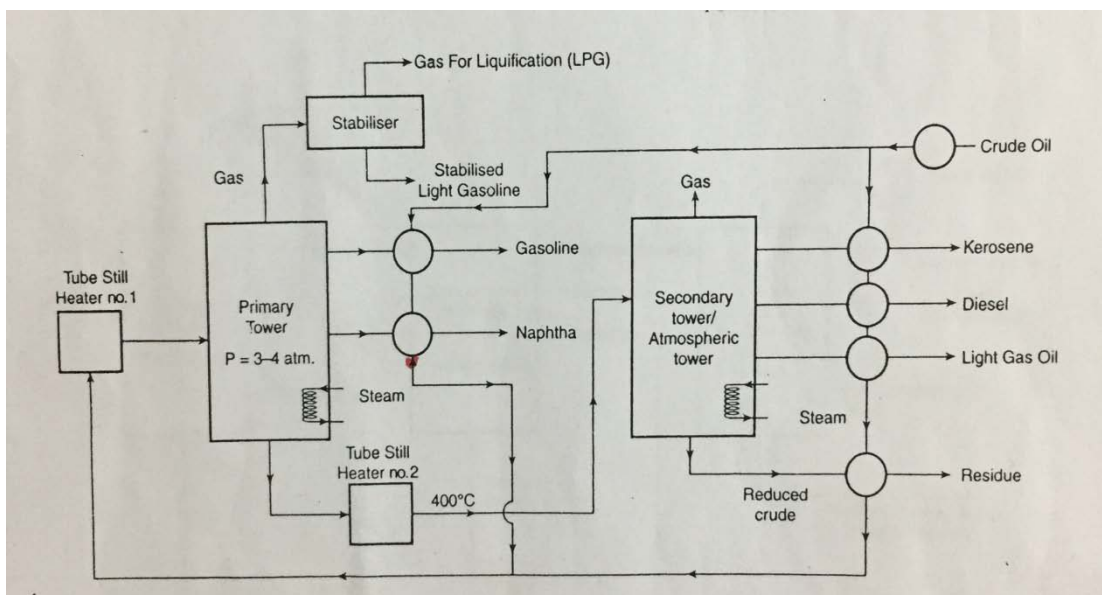


Fig 3:Two stage crude distillation

Three stage distillation unit. This system comprises of all the three *i.e.* pressure, atmosphere and vacuum tower. Because some products of crude are having very high boiling temperature or heat sensitive so that they cannot be distilled at atmospheric pressure. Since boiling point is reduced as the pressure is lowered (*i.e.* vacuum is created), such materials are distilled under vacuum. Vacuum distillation is used for the production of lubricating oils, asphalts and feed to catalytic cracking unit (*i.e.* heavy gas oil). Hence, a vacuum tower is added to a two stage distillation unit for the production of above products thus making it a three stage unit. Light vacuum gas oil (LVGO) is a blending component for light diesel oil (LDO) and a feedstock for catalytic cracker/hydrocracker. Heavy vacuum gas oil (HVGO) is a feedstock for visbreaker and catalytic cracker/hydrocracker. Vacuum residue is used for bitumen production as well as is a feed component for visbreaker.

The residue from the atmospheric tower is fed at about 425°C to the vacuum tower, where pressure is maintained at 80-110 mm Hg absolute. The overhead gas oil fraction is removed and the side streams are withdrawn through strippers. The bottom product is tar or asphalt.

Vacuum distillation units are similar to atmospheric crude distillation unit except that their diameter is larger due to larger crude vapor volumes at lower pressure (vacuum). 10 meter diameter vacuum columns are in operation, steam jet ejector or barometric condensers are used for maintaining desired vacuum in the vacuum tower.

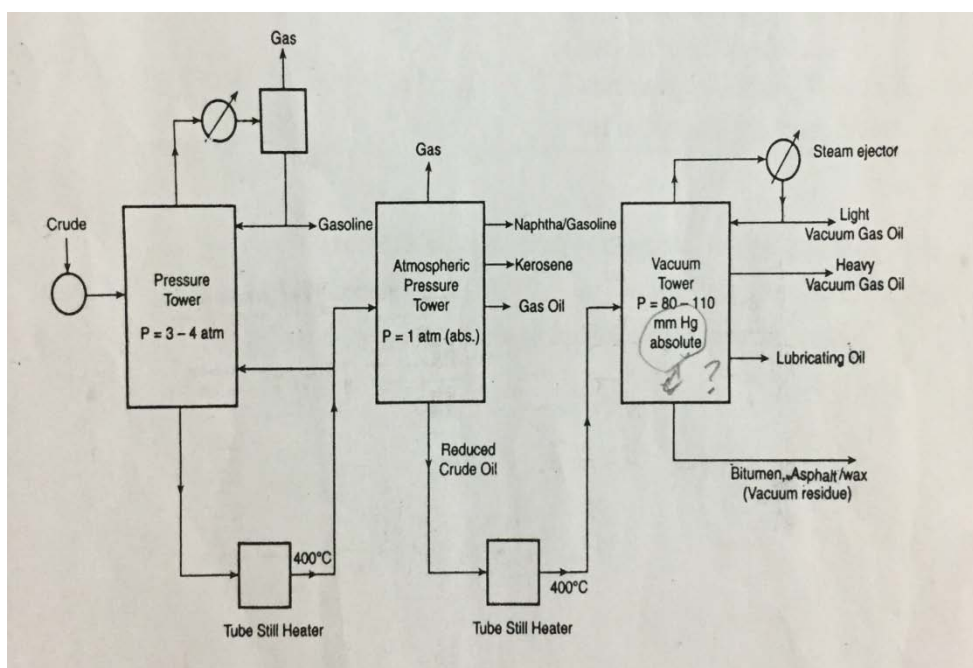
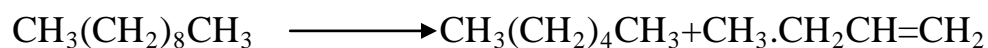


Fig. 4. A flow sheet of Three Stage Crude Distillation is Shown in

Cracking

Cracking means heating of higher boiling petroleum fractions like heavy fuel oil at high temperature (above decomposition temperature) and pressure to produce lower boiling lighter fractions. It is an endothermic reaction.

The main application of cracking is for production of gasoline from gas oil. It is also done to produce olefins (for petrochemicals production) from gas oil and naphtha, lower viscosity furnace oil (visbreaking) and coke. Important chemical reaction in thermal cracking (non catalytic) which is carried out at comparatively higher pressure (P) (1-7) atm and temperature (450-750) °C by heating the feed are decomposition, isomerisation and polymerization. First, the higher paraffin (n-decane) decomposes to lower paraffin and an olefin.



Types of Cracking:

There are two types of cracking:

1- Thermal cracking

When cracking (breaking larger molecules into smaller ones by heating) is done without any catalyst (which increases the rate of reaction, then it is called (**thermal cracking**).

There are various thermal cracking processes in which the product yields and characteristics are different some of them:

a- Low temperature and high pressure thermal cracking process:

Feed (residue from atmospheric distillation unit), **Products** (gas, fuel oil and gasoline) T and P 500 °C and 20 atm. This process is also called visbreaking when heavy fuel oil is thermally cracked to reduce its viscosity.

b- High temperature and high pressure process:

Feed (gas oil), **Product** (gas and gasoline), T and P 53 °C and 70 atm.

2-Catalytic Cracking

Cracking in presence of a catalyst is called (**catalytic cracking**).

The feed which may be (kerosene, fuel oil, gas oil, lubricating oil), atmospheric or vacuum and cracked residue etc .. is heated in presence of catalyst (like, platinum , nickel , iron silica-alumina etc..) at T (350-650) °C and P (1-15) atm to produce gas, petrol, diesel and residue (coke).

Higher temperature gives higher yield of gasoline, where as higher pressure reduce the octane number of gasoline.

Advantages of Catalytic Cracking Over Thermal Cracking:

- 1- Pressure and temperature required for catalytic cracking is lower.
- 2- Yield and octane number of petrol production is higher.
- 3- Petrol produced has less quantity of gum and gum forming material.
- 4- Sulphur content of the products is low.
- 5- Lead susceptibility of petrol produced is more.

Reforming

Reforming means rearrangement of molecules without much affecting the average molecular weight of feed which is generally naphtha of gasoline boiling rang. Reforming is carried out to produce high quality (octane number) gasoline by heating with or without catalyst the naphtha.

Feed for Reforming:

the feed is generally naphtha produced during straight run distillation of crude oil, catalytic cracking and coking process. The best result is obtained with naphtha (produced during straight run distillation) having high naphtha content.

Reforming Product:

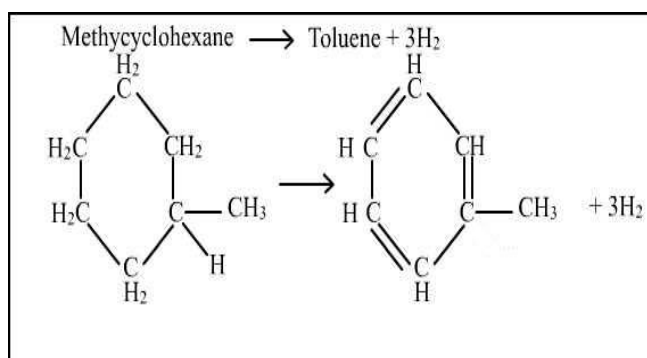
Besides the main product (reformate) or reformat gasoline, reforming also produces lighter hydrocarbons (gases), hydrogen and traces of very high boiling materials.

Chemical Reaction in Catalytic Reforming:

Octane number increases in the order:

paraffine→olefin→naphthene→ iso- paraffin→aromatic

The main reaction in the reforming process is dehydrogenation of naphthene to produce aromatics



Types of Reforming:

Reforming can be **thermal** or **catalytic** as in the case of cracking. Catalyst apart from accelerating the process also enhances the yield and quality (octane number) of gasoline. The gasoline produced by reforming is called reformed gasoline or reformate. Thermal reforming has been almost completely replaced by catalytic reforming.

- Thermal Reforming

This is carried out in absence of catalyst and its similar to high temperature, low pressure thermal cracking. Feed is usually Naphtha and the products are mainly gas (13 -14%) and gasoline (75 -80%) of octane number 81 -86, rest being polymer (unwanted gum) and losses.

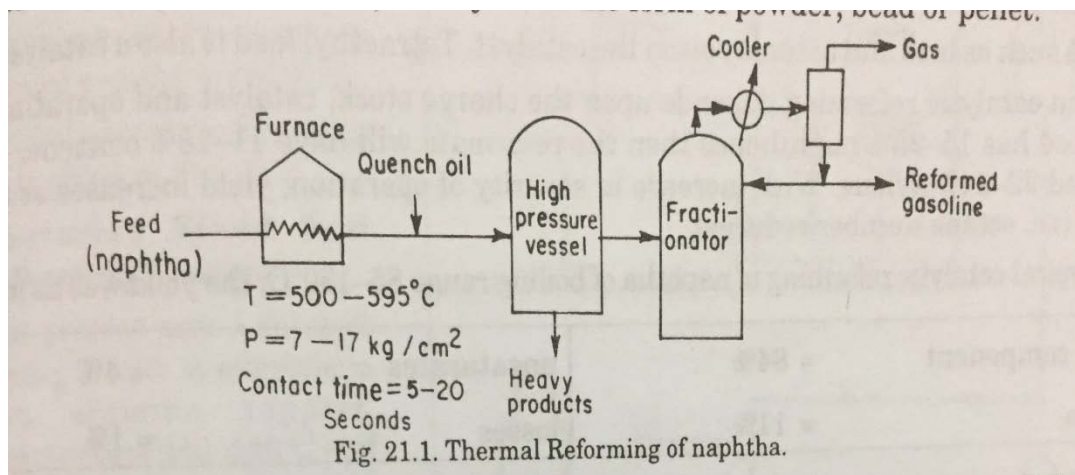


Figure: Thermal Reforming of Naphtha

-Catalytic Reforming

Reforming in the presence of a catalyst is called catalytic reforming.

There are two types of catalyst are used:

- Non- precious metal oxide type (e.g. molybdena or chromia supported on alumina base).
- Precious metal oxide type (e.g. platinum on a silica-alumina or alumina base).

Platinum is more active and selective catalyst.

Dewaxing:

Dewaxing is one of the most important and most difficult processes in lubricating oil manufacturing. There are two types of processes in use today. One uses refrigeration to crystallize the wax and solvent to dilute the oil portion sufficiently to permit rapid filtration to separate the wax from the oil. The other uses a selective hydrocracking process to crack the wax molecules to light hydrocarbons.

Solvent Deasphalting

- In this extraction process, which uses propane (or hexane) as a solvent, heavy oil fractions are separated to produce heavy lubricating oil, catalytic cracking feedstock, and asphalt.
- Feedstock and liquid propane are pumped to an extraction tower at precisely controlled mixtures, temperatures (150°-250° F), and pressures of 350-600 psi.
- Separation occurs in a rotating disc contactor, based on differences in solubility.
- The products are then evaporated and steam stripped to recover the propane, which is recycled.
- Deasphalting also removes some sulfur and nitrogen compounds, metals, carbon residues, and paraffins from the feedstock.

