Chapter One

Introduction

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1.1. Introduction:

Gasoline (also referred to as *motor gasoline, petrol* in Britain, *benzene* in Europe) is a mixture of volatile, flammable liquid hydrocarbons derived from petroleum that is used as fuel for internal combustion engines such as occur in motor vehicles, excluding aircraft. The boiling range of motor gasoline falls between –1°C (30°F) and 216°C (421°F) and has the potential to contain several hundred isomers of the various hydrocarbons.

The hydrocarbon constituents in this boiling range are those that have 4–12carbon atoms in their molecular structure and fall into three general types:

(1) paraffins (including the cycloparaffins and branched materials).

(2) Olefins.

(3) Aromatics.

Gasoline boils at about the same range as naphtha (a precursor to gasoline) but below kerosene .The various test methods dedicated to the determination of the amounts of carbon, hydrogen, and nitrogen (ASTM D-5291) as well as the determination of oxygen, sulfur, metals, and chlorine (ASTM D-808) are not included in this discussion**.** [1]

1.2. Historical background:

The history of gasoline begins with the first oil well in 1859.The petroleum was used to produce kerosene for lighting. In 1892, the invention of the automobile prompted an interest in gasoline as a fuel. By 1920, 9 million automobiles were on the roads, so service stations began showing up everywhere. By 1950, cars were becoming more complex, so octane levels were increased and lead was added to the gas to improve the performance of the engine. However, leads to health issues, so the 1970 saw the removal of lead from gasoline. We all know that gasoline comes from crude oil. The media is always reminding us of how much it costs per barrel. But what is gasoline chemistry? What is done to crude oil that turns it into gasoline?

Below is a list of the chemicals you will find in your car's gasoline:

1. Hydrocarbon Octane, which has an engine cleaning effect
2. Aromatic hydrocarbons such as Benzene and Toluene
3. Paraffin's
4. Cyclic alkaline
5. Alkenes and Polyenes
6. Alkyl sophists that prevent engine filters from becoming clogged.[2]

1.3. Chemical and physical properties:

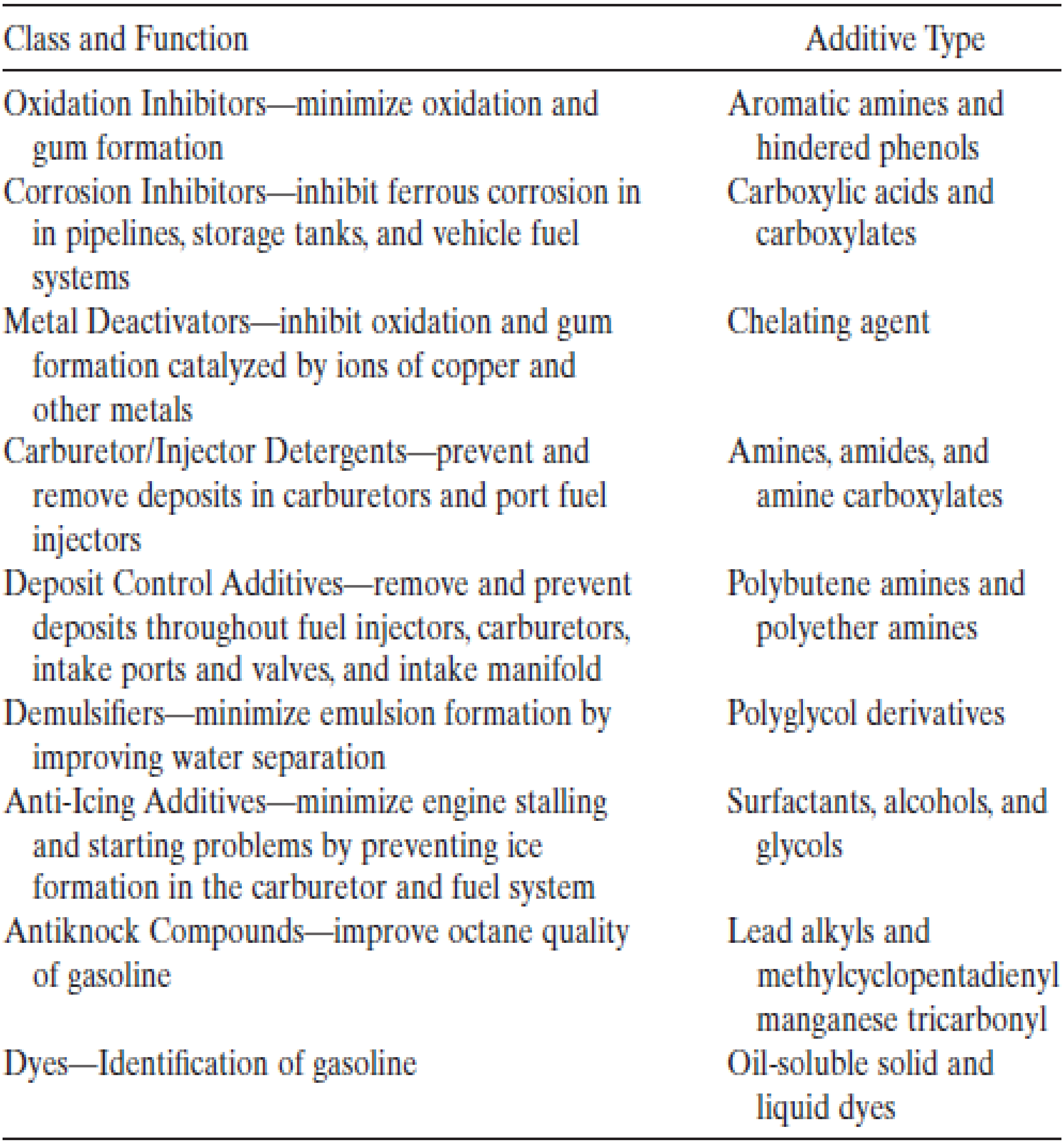
Property	Information	Reference
Molecular weight	108[a]	Anonymous 1989
Color	Colorless to pale brown or pink	Sax and Lewis 1989; Weiss 1986
Physical state	Liquid	Sax and Lewis 1989
Melting point	No data	
Boiling point	Initially, 39°C After 10% distilled, 60°C After 50% distilled, 110°C After 90% distilled, 170°C Final boiling point, 204°C	Budavari et al. 1989; OHM/TADS 1991; Sax and Lewis 1989
Density	0.7-0.8 g/cm^{3}[b]	IARC 1989
Odor	Gasoline odor	Weiss 1986
Odor threshold	0.025 ppm[c]	Weiss 1986
Solubility:		
Water at 20°C	Insoluble	OHM/TADS 1991; Sax and Lewis 1989
Organic solvent(s)	Absolute alcohol, ether, chloroform, benzene	Budavari et al. 1989; Sax and Lewis 1989
Partition coefficients:		
Log K_{ow}	2.13-4.87[d]	Air Force 1989
Log K_{oc}	1.81-4.56[d]	Air Force 1989
Vapor pressure[e]		ASTM 1989
at 60°C	465 mmHg	
at 56°C	518 mmHg	
at 51°C	593 mmHg	
at 47°C	698 mmHg	
at 41°C	773 mmHg	
Henry's law constant:		
at 20°C	4.8×10^{-4}-3.3 m^{3}/mol[d]	Air Force 1989
Autoignition temperature	280-486°C	NEPA 1986; Sax and Lewis 1989; Weiss 1986
Flashpoint	-46°C	Sax and Lewis 1989
Flammability limits	1.4-7.4%	Weiss 1986

1.4. Test methods of gasoline:

The test protocols used for gasoline are similar to the protocols used for naphtha .The similarity of the two liquids requires the application of similar test methods. However, knocking properties are emphasized for gasoline and there are several other differences that must be recognized. But, all in all, consultation of the test methods used for the analysis of naphtha can assist in developing protocols for gasoline. The properties of gasoline are quite diverse, and the principal properties affecting the performance of gasoline are volatility and combustion characteristics. These properties are adjusted according to the topography and climate of the country in which the gasoline is to be used. For example, mountainous regions will require gasoline with volatility and knock characteristics somewhat different from those that are satisfactory in flat or undulating country only a little above sea level. Similarly, areas that exhibit extremes of climatic temperature .Because of the high standards set for gasoline, as with naphtha, it is essential to use the correct techniques when taking samples for testing (ASTM D-270, ASTM D-4057, and IP 51). Mishandling, or the slightest trace of contaminant, can give rise to misleading results. Special care is necessary to ensure that containers are scrupulously clean and free from odor. Samples should be taken with the minimum of disturbance so as to avoid loss of volatile components; in the case of the lightest solvents it may be necessary to chill the sample. While awaiting examination, samples should be kept in a cool dark place so as to ensure that they do not discolor or develop odors**.** [1]

1.4.1. Additives:

Additives are chemical compounds intended to improve some specific properties of gasoline or other petroleum products and can be mono functional or multifunctional (Table 1.1; ASTM D-2669). Different additives, even when added for identical purposes, may be incompatible with each other and may, for example, react and form new compounds. Consequently, a blend of two or more gasoline, containing different additives, may form a system in which the additives react with each other and so deprive the blend of their beneficial effect. Thus certain substances added to gasoline, notably the lead alkyls, have a profound effect on antiknock properties and inhibit the pre combustion oxidation chain that is known to promote knocking.



Class and Function	Additive Type
Oxidation Inhibitors—minimize oxidation and gum formation	Aromatic amines and hindered phenols
Corrosion Inhibitors—inhibit ferrous corrosion in in pipelines, storage tanks, and vehicle fuel systems	Carboxylic acids and carboxylates
Metal Deactivators—inhibit oxidation and gum formation catalyzed by ions of copper and other metals	Chelating agent
Carburetor/Injector Detergents—prevent and remove deposits in carburetors and port fuel injectors	Amines, amides, and amine carboxylates
Deposit Control Additives—remove and prevent deposits throughout fuel injectors, carburetors, intake ports and valves, and intake manifold	Polybutene amines and polyether amines
Demulsifiers—minimize emulsion formation by improving water separation	Polyglycol derivatives
Anti-Icing Additives—minimize engine stalling and starting problems by preventing ice formation in the carburetor and fuel system	Surfactants, alcohols, and glycols
Antiknock Compounds—improve octane quality of gasoline	Lead alkyls and methylcyclopentadienyl manganese tricarbonyl
Dyes—Identification of gasoline	Oil-soluble solid and liquid dyes

tetraethyl lead (TEL) was the preferred compound, but more recently tetra methyl lead (TML) has been shown to have advantages with certain modern types of gasoline because of its lower boiling point (110°C/230°F as against 200°C/392°F for tetraethyl lead) and therefore its higher vapor pressure, which enables it to be more evenly distributed among the engine cylinders with the more volatile components of the gasoline.

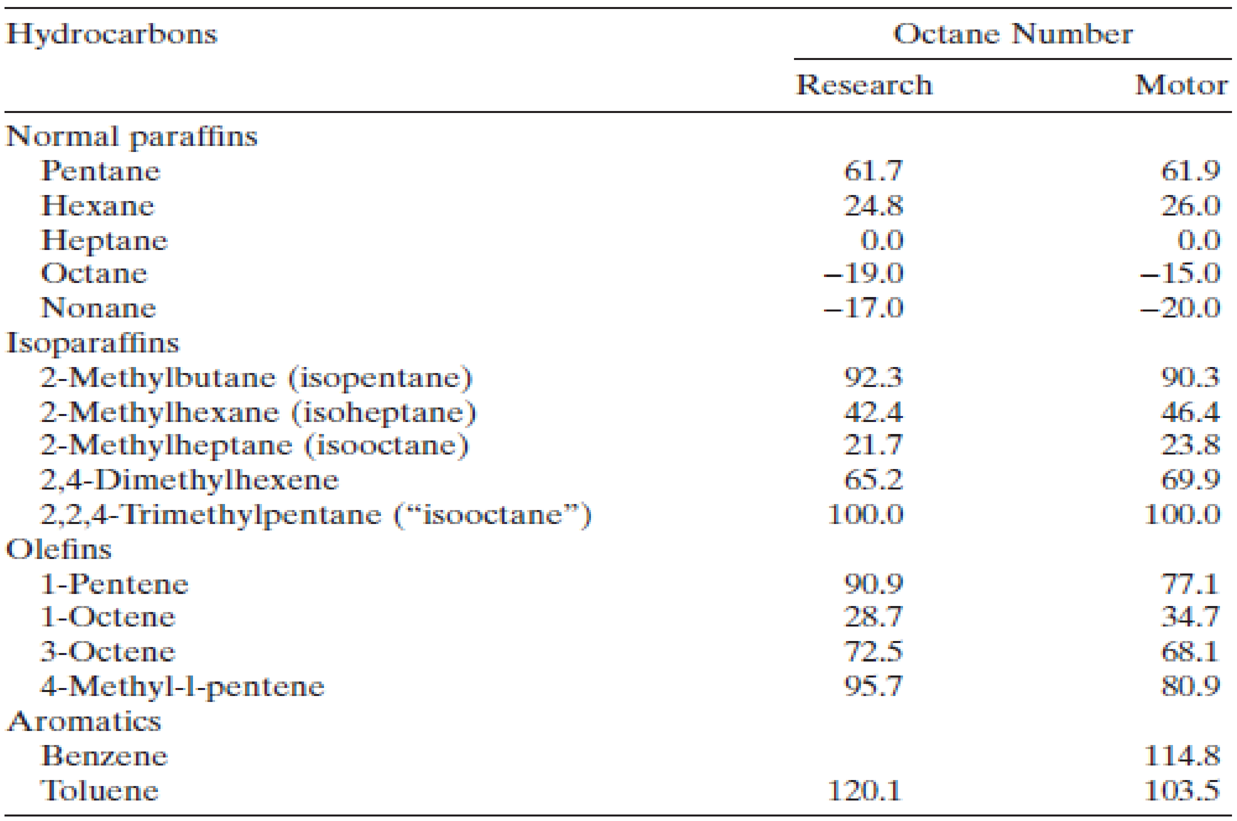
The lead compounds, if used alone, would cause an excessive accumulation of lead compounds in the combustion chambers of the engine and on sparking plugs and valves. Therefore "scavengers" such as dibromoethane, alone or in admixture with dichloroethane, are added to the lead alkyl and combine with the lead during the combustion process to form volatile compounds that pass harmlessly from the engine.

The total lead in gasoline may be determined gravimetrically (ASTM D-52, IP 96), polarographically (ASTM D-1269), by atomic absorption spectrometry (ASTM D-3237, IP 428), by the iodine chloride method (ASTMD-3341, IP 270), by inductively coupled plasma atomic emission spectrometry(ASTM D-5185), and by X-ray fluorescence (ASTM D-5059).When it is desired to estimate tetraethyl lead a method is available (IP 116), whereas for the separate determination of tetramethyl lead and tetraethyl lead Re course can be made to separate methods (ASTM D-l949, IP 188).

Test methods have been developed to measure ethers and alcohols in gasoline-range hydrocarbons, because oxygenated components such as methyl-tert-butylether and ethanol are common blending components in gasoline (ASTM D-4814, ASTM D-4815, ASTM D-5441, ASTM D-5599,ASTM D-5986 ASTM D-5622, ASTM D-5845, ASTM D-6293).[1]

1.4.2. Combustion Characteristics:

Combustion in the spark ignition engine depends chiefly on engine design and gasoline quality. Under ideal conditions, the flame initiated at the sparking plug spreads evenly across the combustion space until all the gasoline has been burned .The increase in temperature caused by the spreading of the flame results in an increase in pressure in the end gas zone, which is that part of the gasoline-air mixture that the flame has not yet reached. The increase in temperature and pressure in the end gas zone causes the gasoline to undergo pre flame reactions. Among the main pre flame products are the highly temperature-sensitive peroxides, and if these exceed a certain critical threshold concentration, the end gas will spontaneously ignite before the arrival of the flame front emanating from the sparking plug; this causes detonation or knocking. On the other hand, if the flame front reaches the end gas zone before the buildup of the critical threshold peroxide Concentration, the combustion of the gasoline-air mixture will be without *knock*. Normal heptane and normal pentane, both paraffins, have antiknock ratings (octane numbers) of 0 and61.9, respectively (Table 1.2) .Very generally, aromatic hydrocarbons (e.g., benzene and toluene), highly branched *iso*-paraffins (e.g., *iso*-octane), And Olefins (e.g., di isobutylene) have high antiknock values. In inter mediate position are *iso*-paraffins with little branching and naphthenic hydrocarbons (e.g., cyclohexane), whereas the normal paraffins (e.g., normal heptane) are of low antiknock value. The knock rating of a gasoline is expressed as *octane number* and is the percentage by volume of *iso*-octane (octane number 100, by definition) in admixture with normal heptane (octane number 0, by definition) that has the same knock characteristics as the gasoline being assessed.



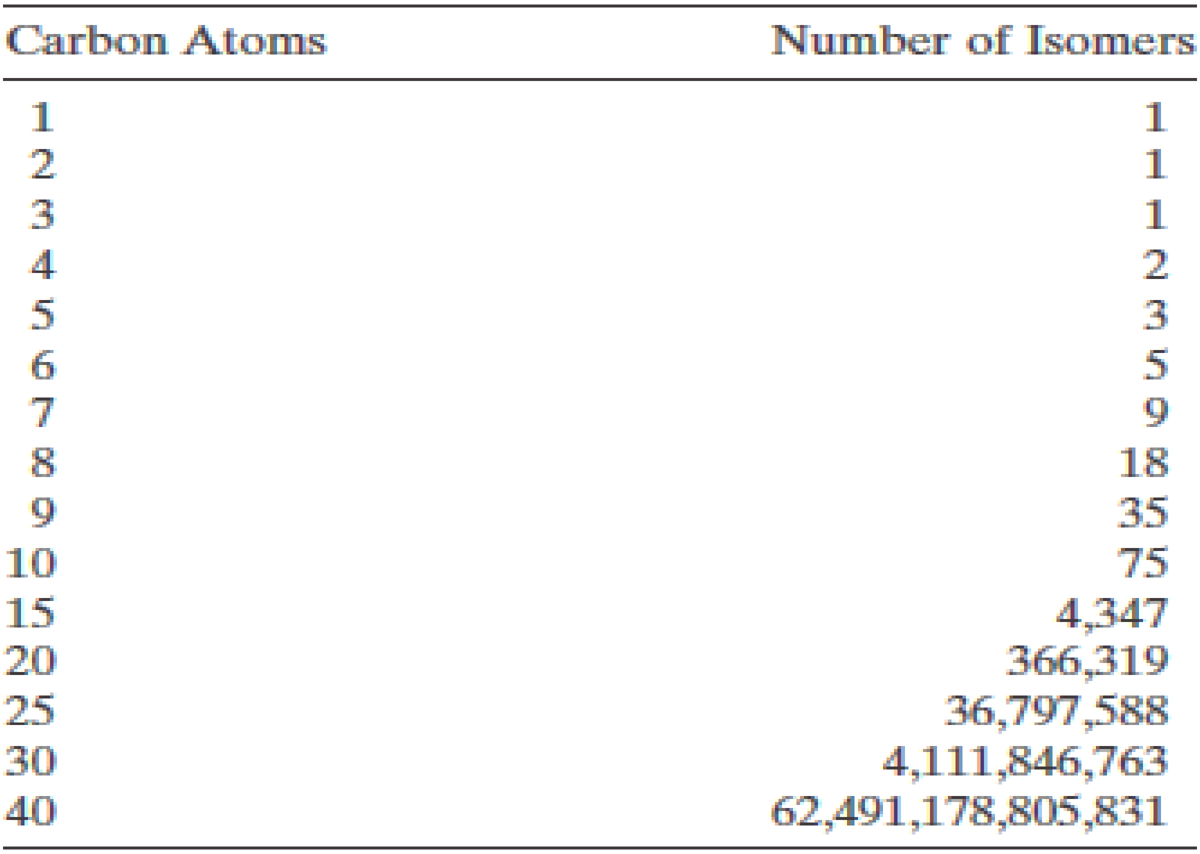
Hydrocarbons	Octane Number	
	Research	Motor
Normal paraffins		
Pentane	61.7	61.9
Hexane	24.8	26.0
Heptane	0.0	0.0
Octane	−19.0	−15.0
Nonane	−17.0	−20.0
Isoparaffins		
2-Methylbutane (isopentane)	92.3	90.3
2-Methylhexane (isoheptane)	42.4	46.4
2-Methylheptane (isooctane)	21.7	23.8
2,4-Dimethylhexene	65.2	69.9
2,2,4-Trimethylpentane (“isooctane”)	100.0	100.0
Olefins		
1-Pentene	90.9	77.1
1-Octene	28.7	34.7
3-Octene	72.5	68.1
4-Methyl-l-pentene	95.7	80.9
Aromatics		
Benzene		114.8
Toluene	120.1	103.5

Gasoline is normally rated by using two sets of conditions of differing severity. One, known as the research method (ASTM D-2699, IP 237), gives a rating applicable to mild operating conditions, that is, low inlet mixture temperature and relatively low engine loading such as would be experienced generally in passenger cars and light-duty commercial vehicles. The other is the motor method (ASTM D-2700, ASTM D-2885, IP 236), which represents more severe operating conditions, that is, relatively high inlet mixture temperature and high engine loading such as would be experienced during full-throttle operation at high speed. Research octane numbers are generally higher than those obtained by the motor method, and the difference between the two ratings is known as the *sensitivity* of the gasoline. The sensitivity of low-octane-number gasoline is usually small, but with high-octane gasoline it varies greatly according to gasoline composition and for most commercial blends it is between7 and 12 in the 90–00 research octane number range. The heat of combustion (ASTM D-240, ASTM D-2382, IP 12) is a direct measure of gasoline energy content and is determined as the quantity of heat liberated by the combustion of a unit quantity of gasoline with oxygen in a standard bomb calorimeter. This gasoline property affects the economics of engine performance, and the specified minimum value is a compromise between the conflicting requirements of maximum gasoline availability and consumption characteristics. [1]

1.4.3. Composition:

As with naphtha, the number of potential hydrocarbon isomers in the gasoline boiling range (Table 1.3) renders complete speciation of individual hydrocarbons impossible for the gasoline distillation range, and methods are used that identify the hydrocarbon types as chemical groups rather than as individual constituents.

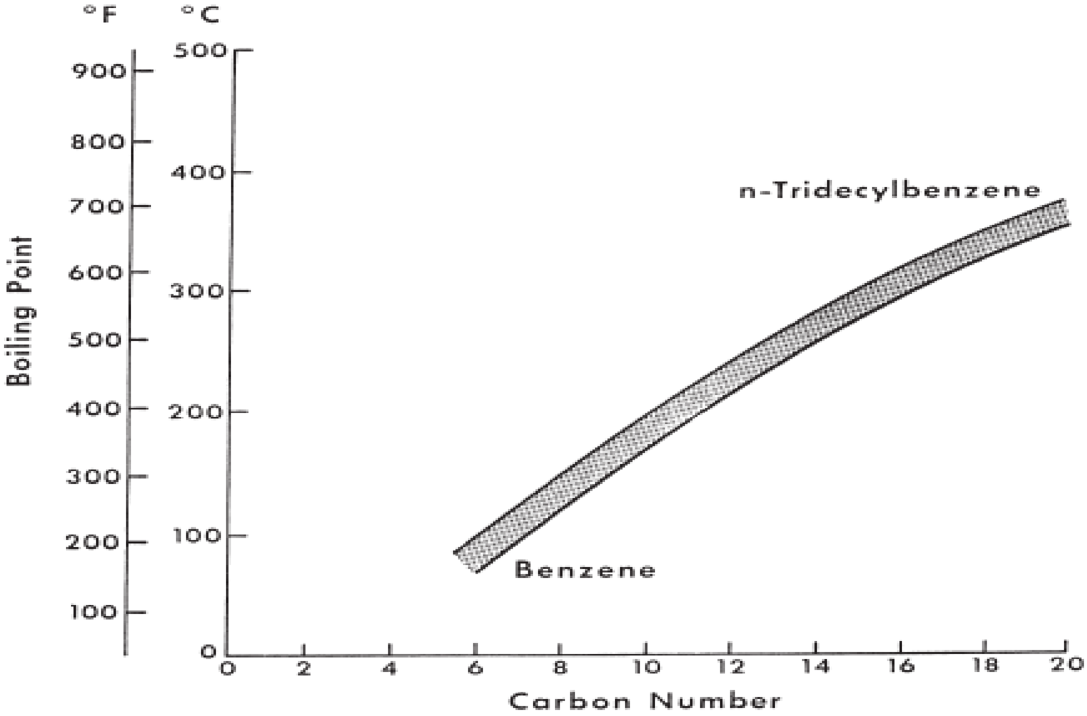
Table (1.3) increases in the number of isomers with carbon number



Carbon Atoms	Number of Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

In terms of hydrocarbon components, several procedures have been devised for the determination of hydrocarbon type, and the method based on fluorescent indicator adsorption (ASTM D-l319, IP 156) is the most widely employed. Furthermore, aromatic content is a key property of low boiling distillates such as gasoline because the aromatic constituents influence a variety of properties including boiling range (ASTM D-86, IP 123),viscosity (ASTM D-88, ASTM D-445, ASTM D-2161, IP 71), and stability(ASTM D-525, IP 40). Existing methods use physical measurements and need suitable standards. Tests such as aniline point (ASTM D-611) and kauri-butanol number (ASTM D-1133) are of a somewhat empirical nature and can serve a useful function as control tests. However, gasoline composition is monitored mainly by gas chromatography (ASTM D-2427, ASTMD-6296)A multidimensional gas chromatographic method (ASTM D-5443) provides for the determination of paraffins, naphthenes, and aromatics by carbon number in low olefinic hydrocarbon streams having final boiling points lower than 200°C (392°F). In this method, the sample is injected into a gas chromatographic system that contains a series of columns and switching values. First a polar column retains polar aromatic compounds, binaphthenes, and high-boiling paraffins and naphthenes. The eluant from this column goes through a platinum column that hydrogenates olefins and then to a molecular sieve column that performs a carbon number separation based on the molecular structure, that is, naphthenic and paraffins. The fraction remaining on the polar column is further divided into three separate fractions that are then separated on a nonpolar column by boiling point. A flame ionization detector detects eluting compounds.

In another method (ASTM D-4420) for the determination of the amount of aromatic constituents, a two-column chromatographic system connected to a dual-filament thermal conductivity detector (or two single filament detectors) is used. The sample is injected into the column containing a polar liquid phase. The nonaromatic are directed to the reference side of the detector and vented to the atmosphere as they elute. The column is back flushed immediately before the elution of benzene, and the aromatic portion is directed into the second column containing a nonpolar liquid phase. The aromatic components elute in the order of their boiling points and are detected on the analytical side of the detector. Quantitation is achieved by utilizing peak factors obtained from the analysis of a sample having a known aromatic content. However, the method may be susceptible to errors caused by alkyl-substituted aromatics (Fig.1.1)



Where the boiling point increases because of the alkyl side chain and this increase bear little relationship to the aromatic ring . Other methods for the determination of aromatics in gasoline include a method (ASTM D-5580) using a flame ionization detector and methods in which a combination of gas chromatography and Fourier transform infrared spectroscopy (GC-FTIR) (ASTM D-5986) and gas chromatography and mass spectrometry (GC-MS) (ASTM D-5769) are used. [1]

1.4.4. Corrosiveness:

Because a gasoline would be unsuitable for use if it corroded the metallic parts of the gasoline system or the engine, it must be substantially free from corrosive compounds both before and after combustion. Corrosiveness is usually due to the presence of free sulfur and sulfur compounds that burn to form sulfur dioxide (SO_2), which combines with water vapor formed by the combustion of the gasoline to produce sulfurous gasoline acid (H_2SO_3). Sulfurous acid can, in turn, oxidize to sulfuric acid (H_2SO_4), and both acids are corrosive toward iron and steel and would attack the cooler parts of the engine's exhaust system and its cylinders as they cool off after the engine is shut down.

Various methods are available for the determination of total sulfur content. The one most frequently quoted in specifications is the lamp method (ASTM D-1266, IP 107), in which the gasoline is burned in a small wick-fed lamp in an artificial atmosphere of carbon dioxide and oxygen; the oxides of sulfur are converted to sulfuric acid, which is then determined either volumetrically or gravimetrically. A more recent development is the Wick bold method (ASTM D-2785, IP243). This is basically similar to the lamp method except that the sample is burned in an oxy-hydrogen burner to give much more rapid combustion. An alternative technique, which has the advantage of being nondestructive, is X-ray spectrograph (ASTM D-2622). Total sulfur is determined by combustion in a bomb calorimeter (ASTMD-129, IP 61) and is often carried out with the determination of calorific value. The contents of the bomb are washed with distilled water into a beaker after which hydrochloric acid is added and the solution is raised to boiling point. Barium chloride is added drop by drop to the boiling solution to precipitate the sulfuric acid as granular barium sulfate. After cooling, and standing for 24 h, the precipitate is filtered off on an ash less paper, washed, ignited, and weighed as barium sulfate. % by weight sulfur = (wt. of barium sulfate \ 13.73)/wt. of sample As an addition to the test for mercaptan sulfur by potentiometric titration(ASTM D-3227, IP 342), a piece of mechanically cleaned copper is used to determine the amount of corrosive sulfur in a sample (ASTM test methods 119D-130, IP 112, IP 154, IP 411). The pure sheet copper (3.0≤ \ 0.5≤/75 \12mm) is placed in a test tube with 40 ml of the sample, so that the copper is completely immersed. The tube is closed with a vented cork and heated in a boiling-water bath for 3 h. The copper strip is then compared visa all with a new strip of copper for signs of tarnish. The results are recorded as:

No change: Result negative
Slight discoloration: Result negative
Brown shade: Some effect
Steel gray: Some effect
Black, not scaled: Result positive, corrosive sulfur present Black, scaled: Result positive, corrosive sulfur present thus visual observation of the copper strip can present an indication or a conclusion of the presence or absence of corrosive sulfur. There is also a copper strip corrosion method for liquefied petroleum gases (ASTM D-1838). [1]

1.4.5. Density (Specific Gravity):

Density (the mass of liquid per unit volume at 15°C) and the related terms specific gravity (the ratio of the mass of a given volume of liquid at 15°C to the mass of an equal volume of pure water at the same temperature.) and relative density (same as specific gravity) are important properties of petroleum and petroleum products . Usually a hydrometer, pycnometer, or digital density meter is used for the determination in all these standards.

The determination of density (specific gravity) (ASTM D-287, ASTM D-891, ASTM D-941, ASTM D-1217, ASTM D-1298, ASTM D-1555, ASTMD-1657, ASTM D-2935, ASTM D-4052, ASTM D-5002, IP 160, IP 235, IP 365) provides a check on the uniformity of the gasoline, and it permits calculation of the weight per gallon. The temperature at which the determination is carried out and for which the calculations are to be made should also be known (ASTM D-1086). However, the methods are subject to vapor pressure constraints and are used with appropriate precautions to prevent vapor loss during sample handling and density measurement. In addition, some test methods should not be applied if the samples are so dark in color that the absence of air bubbles in the sample cell cannot be established with certainty. The presence of such bubbles can have serious consequences for the reliability of the test data. [1]

1.4.6. Flash Point and Fire Point:

The flash point is the lowest temperature at atmospheric pressure (760mmHg, 101.3 kPa) at which application of a test flame will cause the vapor of a sample to ignite under specified test conditions. The sample is deemed to have reached the flash point when a large flame appears and instantaneously propagates itself over the surface of the sample. Flashpoint data are used in shipping and safety regulations to define flammable and combustible materials. Flash point data can also indicate the possible presence of highly volatile and flammable constituents in a relatively nonvolatile or nonflammable material. The flash point of a petroleum product is also used to detect contamination. A substantially lower flash point than expected for a product is a reliable indicator that a product has become contaminated with a more volatile product, such as gasoline. The flash point is also an aid in establishing the identity of a particular petroleum product.

Of the available test methods, the most common method of determining the flash point confines the vapor (closed cup method) until the instant the flame is applied (ASTM D-56, ASTM D-93, ASTM D-3828, 6450, IP 34, IP94, IP 303). An alternate method that does not confine the vapor (open cup method) (ASTM D-92, ASTM D-1310, IP 36) gives slightly higher values of the flash point. The Pensky–Marten apparatus using a closed or open system (ASTMD-

93, IP 34, IP 35) is the standard instrument for flash points above50°C (122°F), and the Abel apparatus (IP 170) is used for more volatile oils, with flash points below 50°C (122°F). The Cleveland open-cup method (ASTM D-92, IP 36) is also used for the determination of the fire point (the temperature at which the sample will ignite and burn for at least 5 s).

The Pensky–Marten apparatus consists of a brass cup mounted in an air bath and heated by a gas flame. A propeller-type stirrer, operated by a flexible drive, extends from the center of the cover into the cup. The cover has four openings: one for a thermometer and the others fitted with sliding shutters for the introduction of a pilot flame and for ventilation. The test methods 121 aperture of the oil in the cup is raised at a rate of 5–6°C/min (9–11°F/min).

The stirrer is rotated at approximately 60rpm.When the temperature has raised to approximately 15°C (27°F) from the anticipated flash point; the pilot flame is dipped into the oil vapor for 2 s for every 1°C (1.8°F) rise in temperature up to 105°C (221°F). Above 105°C (221°F), the flame is in traduced for every 2°C (3.6°F) rise in temperature. The flash point is the temperature at which a distinct flash is observed when the pilot flame meets the vapor in the cup. Erroneously high flash points can be obtained when precautions are not taken to avoid the loss of volatile material. Samples should not be stored in plastic bottles, because the volatile material may diffuse through the walls of the container. The containers should not be opened unnecessarily. The samples should not be transferred between containers unless the sample temperature is at least 20°F (11°C) below the expected flash point.

The Abel closed-cup apparatus (IP 170) consists of a brass cup sealed in a small water bath that is immersed in a second water bath. The cover of the brass cup is fitted in a manner similar to that in the Pensky–Marten apparatus. For crude oils and products with flash point higher than 30°C (>86°F), the outer bath is filled with water at 55°C (131°F) and is not heated further. The oil under test is then placed inside the cup. When the

temperature reaches 19°C (66°F) the pilot flame is introduced every 0.5°C (1.0°F) until a flash is obtained. For oils with flash points in excess of 30°C (>86°F) and less than 50°C (<122°F), the inner water bath is filled with cold water to a depth of 35mm. The outer bath is filled with
cold water and heated at a rate of 1°C/min (1.8°F/min). The flash point is obtained as before. From the viewpoint of safety, information about the flash point is of most significance at or slightly above the maximum temperatures (30–60°C,86–140°F)) that may be encountered in storage, transportation, and use of liquid petroleum products, in either closed or open containers. In this temperature range the relative fire and explosion hazard can be estimated from the flash point. For products with flash point below 40°C (104°F) special precautions are necessary for safe handling. Flash points above 60°C (140°F) gradually lose their safety significance until they become indirect measures of some other quality. The fire point is the temperature to which the product must be heated under the prescribed conditions of the method to burn continuously when the mixture of vapor and air is ignited by a specified flame (ASTM D-92,IP 36).[1]

1.4.7. Oxygenates:

Blends of gasoline with oxygenates are common and, in fact, are required in certain areas. These blends consist primarily of gasoline with substantial amounts of oxygenates, which are oxygen-containing, ash less, organic compounds such as alcohols and ethers. The most common oxygenates are ethanol and methyl-*t*-butyl ether (MTBE) with lesser attention focused on ethyl-*t*-butyl ether (ETBE), *t*-amyl methyl ether (TAME), and di-*iso*-propyl
Ether (DIPE) . Some of the test methods originally developed for gasoline can be used for gasoline-oxygenate blends, whereas certain other test methods for gasoline are not suitable for blends. To avoid the necessity of determining in advance whether a gasoline contains oxygenates there are test methods that

can be used for both gasoline and gasoline-oxygenate blends (ASTM D-4814). In general, the test methods for determining distillation temperatures lead content, sulfur content, copper corrosion, existent gum, and oxidation stability can be used for both gasoline and gasoline-oxygenate blends. Some of the test methods for vapor pressure and vapor-liquid ratio are sensitive to the presence of oxygenates in the gasoline and must be acknowledged accordingly.

Whereas gasoline and water are almost entirely immiscible, and will readily separate into two phases, a gasoline-oxygenate blend is used to dissolve water without phase separation. Hence the use of the term water tolerance. Gasoline-oxygenate blends will dissolve some water but will also separate into two phases when contacted with water that is beyond the threshold concentration. Such a phenomenon is a major issue for alcohol-containing blends.

Phase separation can usually be avoided if the gasoline is sufficiently water free initially and care is taken during distribution to prevent contact with water. Gasoline-oxygenate blends can be tested for water tolerance (ASTM D-4814) by cooling gasoline under specified conditions to its expected use temperature. Formation of a haze (analogous to the cloud point; ASTM D-2500, ASTM D-5771, ASTM D-5772, ASTM D-5773, IP219) must be carefully distinguished from separation into two distinct Phases and is not a reason for rejection of the gasoline. [1]

1.4.8. Stability and Instability:

The study of the analysis of crude oil products is incomplete without some mention of instability and incompatibility. Both result in formation and appearance of degradation products or other undesirable changes in the original properties of petroleum products. Test methods 123 In terms of the instability and incompatibility of petroleum and petroleum products, the unsaturated hydrocarbon content and the heteroatom content appear to represent the greatest influence. In fact, the sulfur and

Nitrogen content of crude oil is an important parameter in respect of the processing methods that must be used to produce gasoline of specification sulfur concentrations. There could well be a relation between nitrogen and sulfur content and crude oil (or product) stability; higher-nitrogen and—sulfur crude oils often exhibit higher sludge-forming tendencies. Gasoline manufactured by cracking processes contains unsaturated components that may oxidize during storage and form undesirable oxidation products. Because gasoline is often stored before use, it is essential that any components should not undergo any deleterious change under storage conditions and should remain stable during their passage from the gasoline tank of a vehicle to the cylinder of its engine so that no harmful deposits are built up in the tank and gasoline lines, in the inlet system, and on the valves.

During storage, gasoline is exposed to the action of air at ambient

Temperature, and in its path from vehicle tank to engine it is mixed with air and also subjected to the effects of heat. An unstable gasoline will undergo oxidation and polymerization under such conditions, forming gum, a resinous material, which in the early stages of chain reaction is initiated by the formation of peroxides and catalyzed by the presence of metals, particularly copper, which may have been picked up during refining and handling operations. Instability occurs because of a low resistance of the product to environmental (in use) influences during storage or its susceptibility to oxidative and/or other degradative processes. In case of incompatibility, degradation products form or changes occur because of an interaction of some chemical groups present in the components of the final blend.

The term instability is often used in reference to the formation of color, sediment, or gum in the liquid over a period of time. This term may be used to contrast the formation of a precipitate in the near term (almost immediately).However, the terms are often used inter changeably. The measurement of color (ASTM D-l56, ASTM D-848, ASTM D-1209, ASTM D-1555, ASTM D-5386, IP 17) provides a rapid method of check in the degree of freedom from contamination. Observation of the test for residue on evaporation (ASTM D-381, ASTM D-1353, IP 131) provides a further guard against adventitious contamination.

Tests should also be carried out for sediment if the gasoline has been subjected to events (such as oxidation) that could lead to sediment formation and instability of the gasoline and the resulting products. Test methods are available for the determination of sediment by extraction (ASTM D-473, IP 285) or by membrane filtration (ASTM D-4807, IP 286) and the determination of sediment simultaneously with water by centrifugation (ASTM D-96, ASTM D-1796, ASTM D-2709, ASTM D-4007, IP 373, IP 374).

Stability is also defined as the ability of the liquid to withstand long periods at temperatures up to 100°C (212°F) without degradation. Determination of the reaction threshold temperature for various liquid and solid materials might be beneficial (ASTM D-2883). Thus potential gum is determined by the *accelerated gum test* (ASTM D-873, IP 138), which is used as a safeguard of storage stability and can be used to predict the potential for gum formation during prolonged storage. In this test, the gasoline is heated for 16 h with oxygen under pressure in a bomb at 100°C (212°F). After this time, both the gum content and the solids precipitated are measured. [1]

1.4.9. Volatility:

The volatility of a liquid is its tendency to change from the liquid to the vapor or gaseous state. Thus volatility is a primary and necessary characteristic of most liquid gasoline. The distillation profile is also a measure of the relative amounts of the gasoline constituents in petroleum. The volatility of gasoline affects the performance of the engine in a number of ways, the chief of which are ease of starting, rate of warm-up, vapor lock, carburetor icing, and crankcase dilution (the dilution of the engine lubricating oil with the higher-boiling constituents of the gasoline).

The gasoline must be sufficiently volatile to give easy starting, rapid warm-up, and adequate vaporization for proper distribution between the cylinders. Conversely, it must not be so volatile that vapor losses from the Gasoline tank are excessive or that vapor is formed in the gasoline line, causing vapor lock that may impede the flow of gasoline to the carburetor.

The determination of the boiling range distribution of gasoline by gas chromatography (ASTM D-3710) not only helps identify the constituents but also facilitates on-line controls at the refinery. This test method is designed to measure the entire boiling range of gasoline with either high or low Reid vapor pressure (ASTM D-323, IP 69). In this method, the sample is injected into a gas chromatographic column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run. Calibration is performed with a known mixture of hydrocarbons covering the expected boiling of the sample.

Another method is described as a method for determining the carbon number distribution (ASTM D-2887, IP 321), and the data derived by this test method are essentially equivalent to that obtained by true boiling point distillation (ASTM D-2892).

The sample is introduced into a gas chromatographic column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible rate, and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time axis from a calibration curve, obtained under the test methods same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution may be obtained. However, this test method is limited to samples with a boiling range greater than 55°C (100°F) and having a vapor pressure (ASTM D-323,

ASTM D-4953, ASTM D-5190, ASTM D-5191,ASTM D-5482, ASTM D-6377, ASTM D-6378, IP 69, IP 394) sufficiently low to permit sampling at ambient temperature. The volatility of petroleum and petroleum products is an important Aspect of safety and quality. It would be unsafe to attempt to store highly volatile materials in the open sunlight or in an enclosed space where temperature can rise to be in excess of 37.8°C (100°F).And yet, without any indications of when the material might vaporize and spontaneously ignite, there is no way of even considering the correct storage and handling conditions.

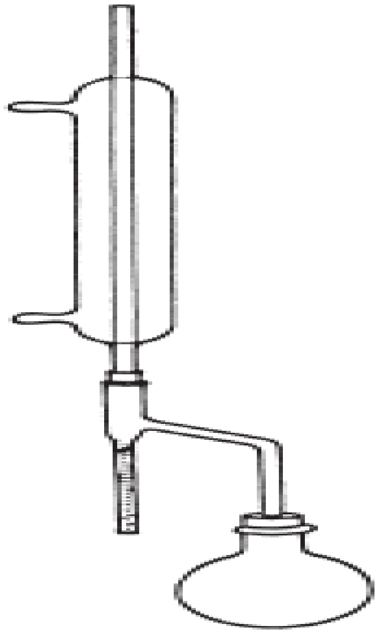
The vapor pressure of petroleum or a petroleum product is the force exerted on the walls of a closed container by the vaporized portion of a liquid. Conversely, it is the force that must be applied to the liquid to prevent it vaporizing further. The vapor pressure increases with increase in temperature and is variously expressed in terms of millimeters of mercury, pounds per square inch, or other equivalent units of pressure depending on common usage. Gasoline vapor pressure depends critically on its butane content, and in the refinery the final adjustment of vapor pressure of a gasoline to meet the specification is often made by butane injection. The Reid vapor pressure (ASTM D-323, IP 69, IP 402) is a measure of the vapor pressure of petroleum or a petroleum product an oil at 37.8°C (100°F) expressed as millimeters of mercury. The apparatus used to determine the Reid vapor pressure consists of a metal cylinder, or bomb, fitted with an accurate dial pressure gauge or a mercury manometer. The bomb consists of two parts, an upper expansion chamber and a lower liquid chamber. The sample is cooled and poured into the lower chamber until it is full. The temperature of the air in the upper chamber is taken, and the two chambers are connected together in a gas-tight manner. The bomb is immersed upright in a water bath at 37.8°C (100°F) and shaken repeatedly until a constant pressure reading is obtained. This is corrected, from tables, for initial air temperature and pressure. Another method (ASTM D-5191) is now most commonly referenced in gasoline regulations, and the method requires fewer samples and is much easier and faster to run. [1]

1.4.10. Water and Sediment:

However, before any volatility tests are carried out it, all water must be removed because the presence of more than 0.5% water in test samples of crude can cause several problems during distillation procedures .Water has a high heat of vaporization, necessitating the application of additional thermal energy to the distillation flask. Water is relatively easily superheated, and therefore excessive bumping can occur, leading to erroneous gasoline readings, and the potential for destruction of the glass equipment is real. Steam formed during distillation can act as a carrier gas, and high-boiling point components may end up in the distillate (steam distillation).Centrifugation can be used to remove water (and sediment) if the sample is not a tight emulsion.

Other methods that are used to remove water include:

1. Heating in a pressure vessel to control loss of light ends,
2. Addition of calcium chloride as recommended in ASTM D-1160,
3. Addition of an azeotroping agent such as *iso*-propanol or *n*-butanol.
4. Removal of water in a preliminary low-efficiency or flash distillation followed by re blending the hydrocarbon that co distills with the water into the sample (IP 74).
5. Separation of the water from the hydrocarbon distillate by freezing. Water is a contaminant in gasoline and should be measured with the Karl Fischer method (ASTM E-203, ASTM D-1364, ASTM D-1744, ASTM D-4377,ASTM D-4928,ASTM D-6304), by distillation using a Dean and Stark condenser (ASTM D-4006) (Fig. 5.3), or by centrifuging (ASTM D-96) and excluded by relevant drying methods.(fig.1.2) dean and stark adapter on the bottom of a condenser.



Tests should also be carried out for sediment if the gasoline has been subjected to events (such as oxidation) that could lead to sediment formation and instability of the gasoline and the resulting products. Test methods are available for the determination of sediment by extraction (ASTM D-473, IP 285) or by membrane filtration (ASTM D-4807, IP 286) and the determination of simultaneously sediment with water by centrifugation (ASTM D-96, ASTM D-1796, ASTM D-2709, ASTM D-4007, IP 373, IP374).[1]

1.5. Uses of Gasoline:

Gasoline is an important part of our day-to-day lives. We use it to fuel our cars and trucks, as well as our lawnmowers, weed trimmers, boats, a variety of off-road vehicles, portable electric generators and more. However, gasoline is highly flammable and can be extremely dangerous if not handled or stored safely. Following these safety tips will help protect you and your family. [3]

1.6. Hazards of Gasoline:

Gasoline is a colorless liquid with characteristic odor. It may be dyed yellow. Gasoline is an extremely flammable liquid and vapor. The liquid can accumulate static charge by flow or agitation. It can float on water and may spread to distant locations and/or spread fire .The vapor is heavier than air and may spread long distances making distant ignition and flash back possible. Gasoline is a possible cancer hazard. It may cause cancer (based on animal data). It is a central nervous system depressant and exposure to high vapor concentrations may cause headache, nausea, dizziness, drowsiness, unconsciousness and death. It is also an aspiration hazard. Swallowing or vomiting of the liquid may result in aspiration into the lungs. This chemical profile record refers to common, commercial unleaded gasoline used for automotive purposes, unless otherwise specified. [4]

1.6.1. Gasoline is a powerful fuel for engines and a Dangerous explosive:

Gasoline evaporates quickly when exposed to air. Most gasoline spilled in lakes, streams or soil evaporates. Some spilled gasoline can seep in to groundwater and remain unchanged for years. Private Wells located near a spill or a buried leaking tank may become contaminated. Scientists refer to gasoline components that mix with water as gasoline range organics (GRO). [5]

1.6.2-How are people exposed to gasoline?

1-Breathing: Exposure occurs when people breathe gasoline vapors while filling gas tanks. Exposure may also occur when using contaminated water to bathe or do laundry. Some people intentionally inhale gasoline vapors to get "high."

2-Drinking/Eating: Low level exposure can occur when contaminated water is used for drinking or preparing food.

3-Touching: Some ingredients in gasoline can pass through the skin when used as a cleaner or accidentally spilled on skin or clothing. People can also be exposed when handling contaminated soil or water. [5]

1.6.3. Will exposure to gasoline result in harmful health Effects?

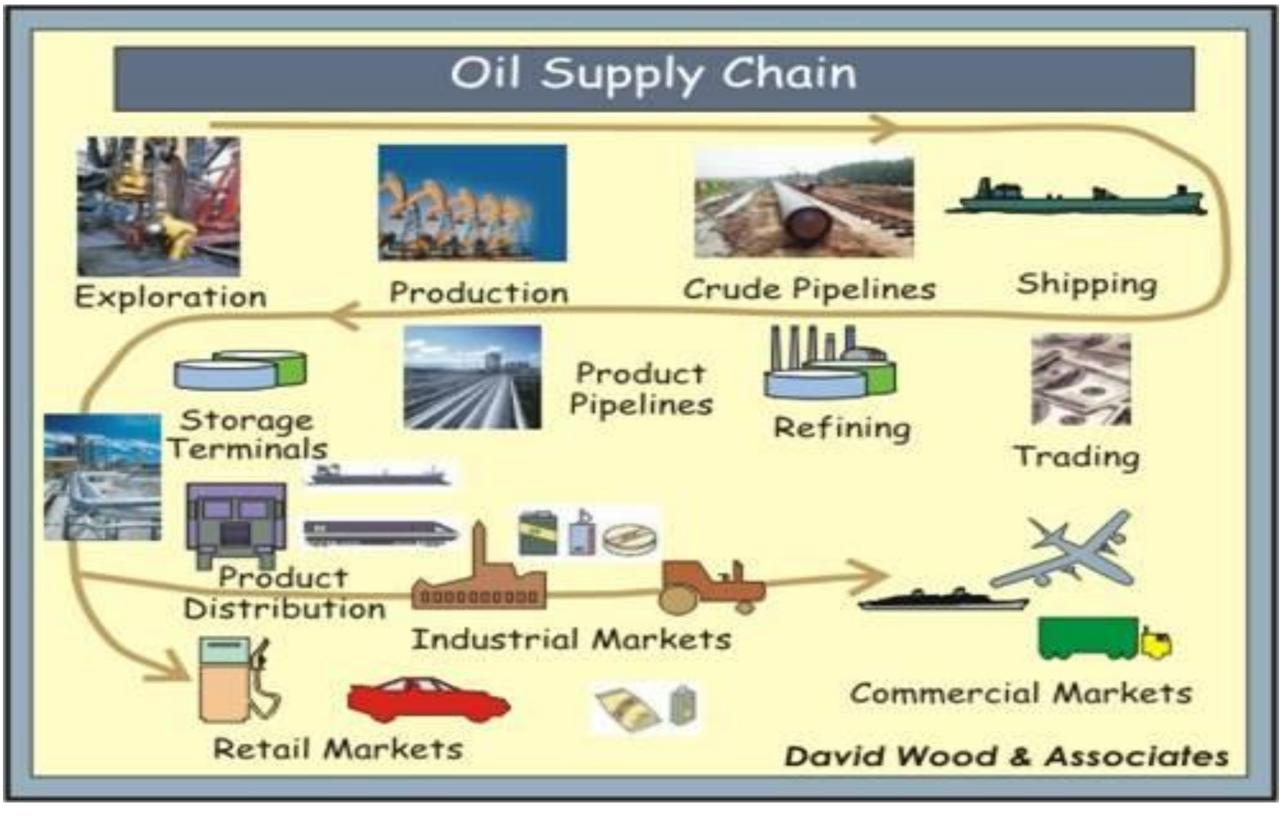
Immediately or shortly after breathing a high amount of gasoline, a person may experience nose or lung irritation, feel dizzy or have a headache. When swallowed, gasoline will causes to Mach irritation. Drinking gasoline or inhaling concentrated vapors can result in death. The following health effects can occur after several years of exposure to low levels of gasoline in air or in water:

1-Organ Systems: People can experience damaged nervous system or lungs.

2-Cancer: There is no evidence that exposure to gasoline causes cancer in humans. However, long-term exposure to high levels of benzene, a component of gasoline, may increase a person's risk of leukemia.

3-Reproductive Effects: There is not enough information available to determine if exposure to gasoline causes birth defects. In general, chemicals affect the same organ systems in all people who are exposed. However, the seriousness of the effects may vary from person to person. A person's reaction depends on several things, including individual health, heredity, previous exposure to chemicals including medicines, and personal habits such as smoking or drinking. It is also important to consider the length of exposure to the chemical; the amount of chemical exposure; and whether the chemical was inhaled, touched, or eaten. [5]

1.7. Manufacturing of Gasoline:



1.7.1. Raw material:

Gasoline is one of the products derived from distilling and refining petroleum. Compounds of organic lead were added to gasoline in the past to reduce knocking in engines, but due to environmental concerns this is no longer common. Other chemicals are also added to gasoline to further stabilize it and improve its color and smell in a process called "sweetening." [6]

1.7.2. Exploration:

1-The first step in the manufacture of gasoline is to find its parent ingredient, petroleum. Crude oil is trapped in areas of porous rock, or reservoir rock, after it has migrated there from the area of its origin. Possible areas of oil concentration may be pinpointed by looking for rock types that are commonly found in those areas. Explorers may examine the surface features of the land; analyze how sound waves bounce off.

2-After a possible oil reservoir is found, the area must be test drilled. Core samples are taken from test wells to confirm rock formations, and the samples are chemically analyzed in order to determine if more drilling is justified. Although the methods used today are more advanced than any of the past, there is still no certainty in oil exploration. [6]

1.7.3. Drilling:

Crude oil is recovered through wells that can reach over 1,000 feet (305 m) into the rock. The holes are made by rotary drillers, which use a bit to bore a hole in the ground as water is added. The water and soil create a thick mud that helps hold back the oil and prevent it from "gushing" due to the internal pressure contained in the reservoir rock. When the reservoir is reached, the mud continues to hold back the oil while the drill is removed and a pipe is inserted in this fig (1.3) show drilling. [6]

1.7.4. Recovery:

1-To recover the oil, a complicated system of pipes and valving is installed directly into the drilling well. The natural pressure of the reservoir rock brings the oil out of the well and into the pipes. These are connected to a recovery system, which consists of a series of larger pipes taking the crude oil to the refinery via an oil (liquid) and gas (non-liquid) separator. This method allows the oil to be recovered with a minimum of waste.

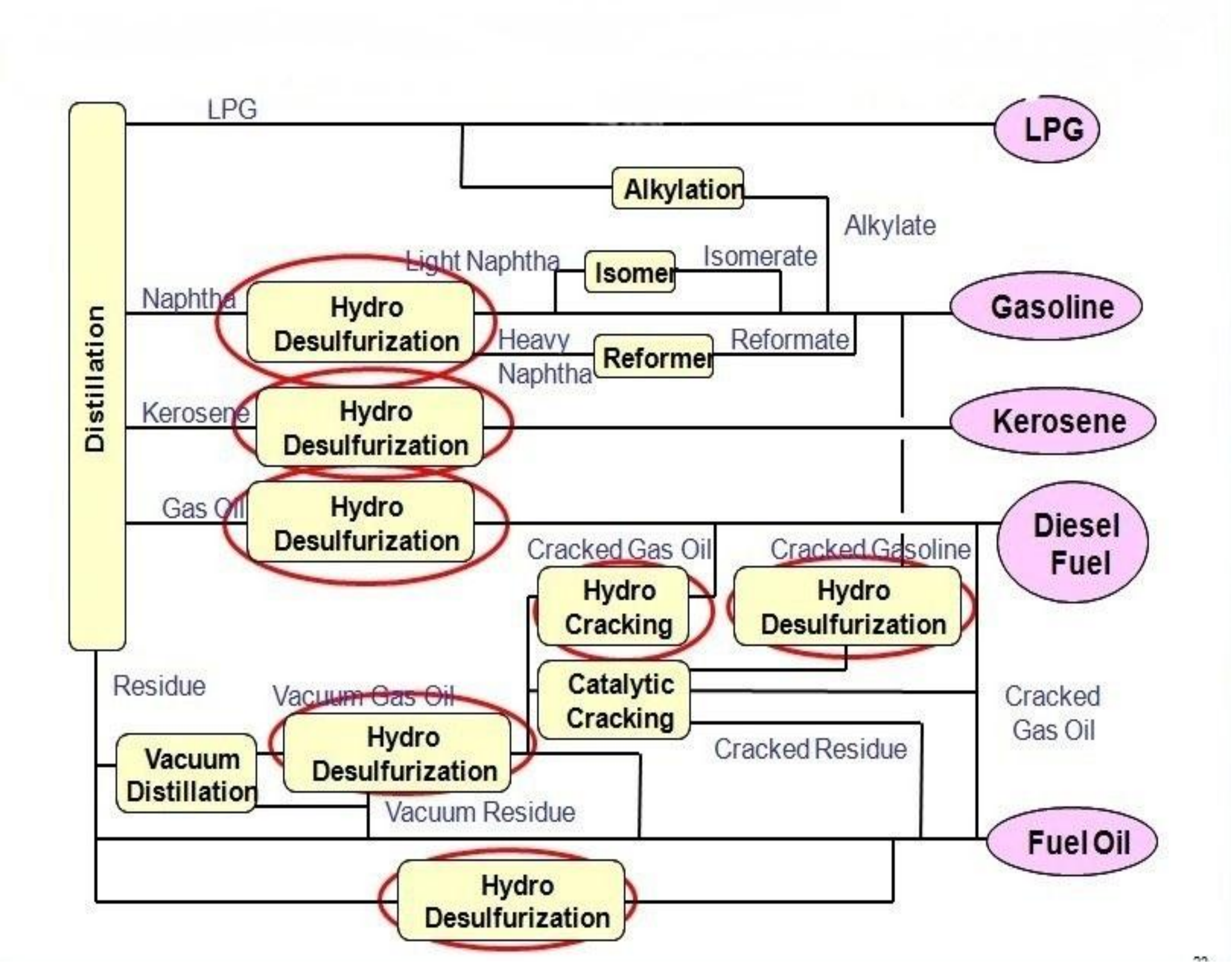
2-Eventually, the natural pressure of the well is expended, though great quantities of oil may still remain in the rock. Secondary recovery methods are now required to obtain a greater percentage of the oil. The pressure is restored by either injecting gas into the pocket above the oil or by flooding water into the well, which is far more common. In this process, four holes are drilled around the perimeter of the well and water is added. The petroleum will float on the water and come to the surface. [6]

1.7.5. Treatment of feedstock:

Desalting the crude oil is a major step of any oil processing. Failing to lower the salt and other contaminants from the crude oil can cause corrosion and fouling to the downstream equipment and also lower the economic value of the crude due to the high cost of production. Desalting is a major source of wastewater production in the refining process, and therefore a water treatment option should be considered alongside the process.

The theory behind the desalting process can be summarized as follows: the desalted removes contaminants from crude oil first by emulsifying the crude oil with chemicals and then washing the oil thoroughly with water, thereby ensuring thorough contact of the water and oil.

The salts containing some of the metals that can poison catalysts are dissolved in the water phase. After the oil has been washed and mixed, resulting in an emulsion of oil and water, demulsifying chemicals are added and electrostatic fields are used to break up the emulsion. Fig (1.4) show manufacturing gasoline [7]



1.7.6. The feedstock introduce to Fractionation crude oil in atmospheric distillation column:

Crude oil is not a good fuel, since it is not fluid and requires a very high temperature to burn. The long chains of molecules in crude oil must be separated from the smaller chains of refined fuels, including gasoline, in a petroleum refinery. This process is called fractional distillation. A fractional distillation tower is a huge unit that may hold up to 200,000 barrels of crude oil. The oil is first pumped into a furnace and heated to over 600°F (316°C), causing all but the largest molecules to evaporate. The vapors rise into the fractionating column, which may be as tall as 150 feet (46 m). The vapors cool as they rise through the column. Since the boiling points of all the compounds differ, the larger, heavier molecules will condense first lower in the tower and the shorter, lighter molecules will condense higher in the tower. Natural gases, gasoline, and kerosene are released near the top. Heavier compounds used in the manufacture of plastics and lubricants are removed lower in the tower. Fractional distillation itself does not produce gasoline from crude oil; it just removes the gasoline from other compounds in crude oil. Further refining processes are now used to improve the quality of the fuel. [8]

1.7.7. The product of naphtha from distillation column Change to gasoline by:

1.7.7.1. Catalytic Reforming:

Catalytic reforming of heavy naphtha is a key process in the production of gasoline. The major components of petroleum naphthas are paraffins, naphthenes, and aromatic hydrocarbons. The relative amounts of these hydrocarbons depend on the origin of the crude oil. The aromatic content of the reforming feed is usually below 20% of the total hydrocarbons whereas the paraffins and naphthenes vary between 10 and 70% depending on the origin of the crude oil. The aim of catalytic reforming is to transform, as much as possible, hydrocarbons with low octane to hydrocarbons with high octane. The chemical reactions that lead to these changes are guided by a catalyst under well-defined operating conditions. From the octane view point, the best hydrocarbon fuels for an internal combustion engine are isoparaffinic and aromatic hydrocarbons. For example, the aromatic hydrocarbons from C7 to C lo have research octane numbers (RON) of 118 to 171, whereas the corresponding cyclohexanes have octane numbers of 43 to 104. A similar comparison can be made between isoparaffins and normal paraffins. The chemical reactions of catalytic reforming are grouped according to the respective hydrocarbon type. [9]

Platinum-based reforming catalysts are used in the late of 1940. By time, in 1960, their performance was improved by the addition of some metals such as Ge, Sn, Re, and Ir. These additions have given the catalyst a better selectivity, a better stability of performance over time, and the possibility of operating at lower pressure. Most of the reforming catalysts are based on well-dispersed platinum on an alumina promoted by halogen, usually chlorine. Since 1970, many attempts were made to find a better performing system of catalyst. Nowadays the reforming process is generally carried out over bi-functional catalysts which consist of one or more metals, most commonly platinum or platinum combined with rhenium or tin or iridium, dispersed on an acidic support. [10]

1.7.7.2. Isomerization:

The light naphtha introduce to isomer unit by this unit it change to gasoline , Upgrading light hydrocarbon (C4–C6) streams in refineries and gas processing plants has increased in importance as new regulations affecting gasoline composition are enacted in many regions of the world. These regulations include lead phasedown, benzene minimization, and oxygen content requirements. Light-naphtha isomerization plays a key role in meeting octane demands in the gasoline pool that result from both lead phasedown and increasing market share for premium gasoline grades. By isomerization we mean the skeletal isomerization of paraffin to amore branched paraffin with the same carbon number; however, because of its nature, isomerization may also affect some of the naphthene components and will also hydrogenate aromatics. In fact, isomerization is the most-economic means available for reducing the benzene content in gasoline. An aluminum chloride catalyst for alkane isomerization was first developed in the 1930 s. The original application was for the conversion of *n*-butane to isobutane, which was, and still is, reacted with C3, C4, and C5 olefins to produce motor fuel alkylate. The catalyst such as Chloride alumina, the highest-activity paraffin isomerization catalyst available, increases the octane of a typical light-naphtha stream from about 70 to as high as 85 RONC in a once-through paraffin isomerization unit.[11]

1.7.8. Improving gasoline by increasing some Additives:

Once gasoline is refined, chemicals are added. Some are anti-knock compounds, which react with the chemicals in gasoline that burn too quickly, to prevent "engine knock." In leaded gasoline, tetraethyl lead is the anti-knock additive. (Unleaded gasoline is refined further so the need for anti-knock additives is minimal.) Other additives (antioxidants) are added to prevent the formation of gum in the engine. Gum is a resin formed in gasoline that can coat the internal parts of the engine and increase wear. [6]

1.7.9. The future:

Gasoline, though widely used in many applications today, is destined to become a fuel of the past because petroleum is a nonrenewable resource. Current technology centers on making the most of the remaining petroleum reservoirs and exploring alternative energy sources. New methods to accurately determine the extent of oil reservoirs, automated systems to control oil recovery, and ways of enabling workers to recover more oil from known reservoirs are all being investigated to fully utilize the oil stores available today. The newest methods in oil field exploration measure the physical size of the reservoir and its volume of oil. Frequently, the pressure inside the well is measured over a period of time as the oil is recovered. Using this data, scientists can determine the size of the reservoir and its permeability. An echo meter, which bounces sound waves off the sides of the reservoir, can also be used to discover the well's characteristics. Modern oil recovery methods are most often controlled, at least in part, by computerized systems. SCADA (Systems for Supervisory Control of Data Acquisitions) use specialized software to monitor operations through one or more master terminals and several remote terminals. These systems increase efficiency, help prevent mishaps that could harm the environment, and reduce the number of laborers with increased safety. Enhanced oil recovery methods increase the percentage of oil that can be obtained from a reservoir. In the past, workers were able to extract less than half of the oil contained in a reservoir. New methods involve injecting gases or foams into the well to force out the oil, drilling horizontally into the well, and using more geophysical information to accurately predict the characteristics of the reservoir. Because gasoline is produced from a limited supply of petroleum, scientists are looking for clean, renewable sources of energy to power machines of the future. Steam power, used in the steamboats of the past, is an energy source that is receiving renewed attention. Electric vehicles have been developed and solar and wind energies are also powering cars and homes. [6]

Chapter two

Atmospheric distillation column

Chapter two
Atmospheric distillation column

2.1. Introduction:

The first and the most fundamental step in the refining process (after the crude oil has been cleaned and any remnants of brine removed) is distillation, which is often referred to as the primary refining process. Distillation involves the separation of the different hydrocarbon compounds that occur naturally in a crude oil into a number of different fractions (a fraction is often referred to as a cut). In the atmospheric distillation process, heated crude oil is separated in a distillation column (distillation tower, fractionating tower, atmospheric pipe still) into streams that are then purified, transformed, adapted, and treated in a number of subsequent refining processes, into products for the refinery's market. The lighter, more volatile, products separate out higher up the column, whereas the heavier, less volatile, products settle out toward the bottom of the distillation column. The fractions produced in this manner are known as straight run fractions ranging from (atmospheric tower) gas, gasoline, and naphtha, to kerosene, gas oils, and light diesel, and to (vacuum tower) lubricating oil and residuum. The feed to a distillation tower is heated by flow through pipes arranged within a large furnace. The heating unit is known as a pipe still heater or pipe still furnace, and the heating unit and the fractional distillation tower make up the essential parts of a distillation unit or pipe still. The pipe still furnace heats the feed to a predetermined temperature, usually a temperature at which a predetermined portion of the feed will change into vapor. The vapor is held under pressure in the pipe in the furnace until it discharges as a foaming stream into the fractional distillation tower. Here the unvaporized or liquid portion of the feed descends to the bottom of the tower to be pumped away as a bottom nonvolatile product, whereas the vapors pass up the tower to be fractionated into gas oils, kerosene, and naphtha.the followng fig(2.1) show distillation column[12]

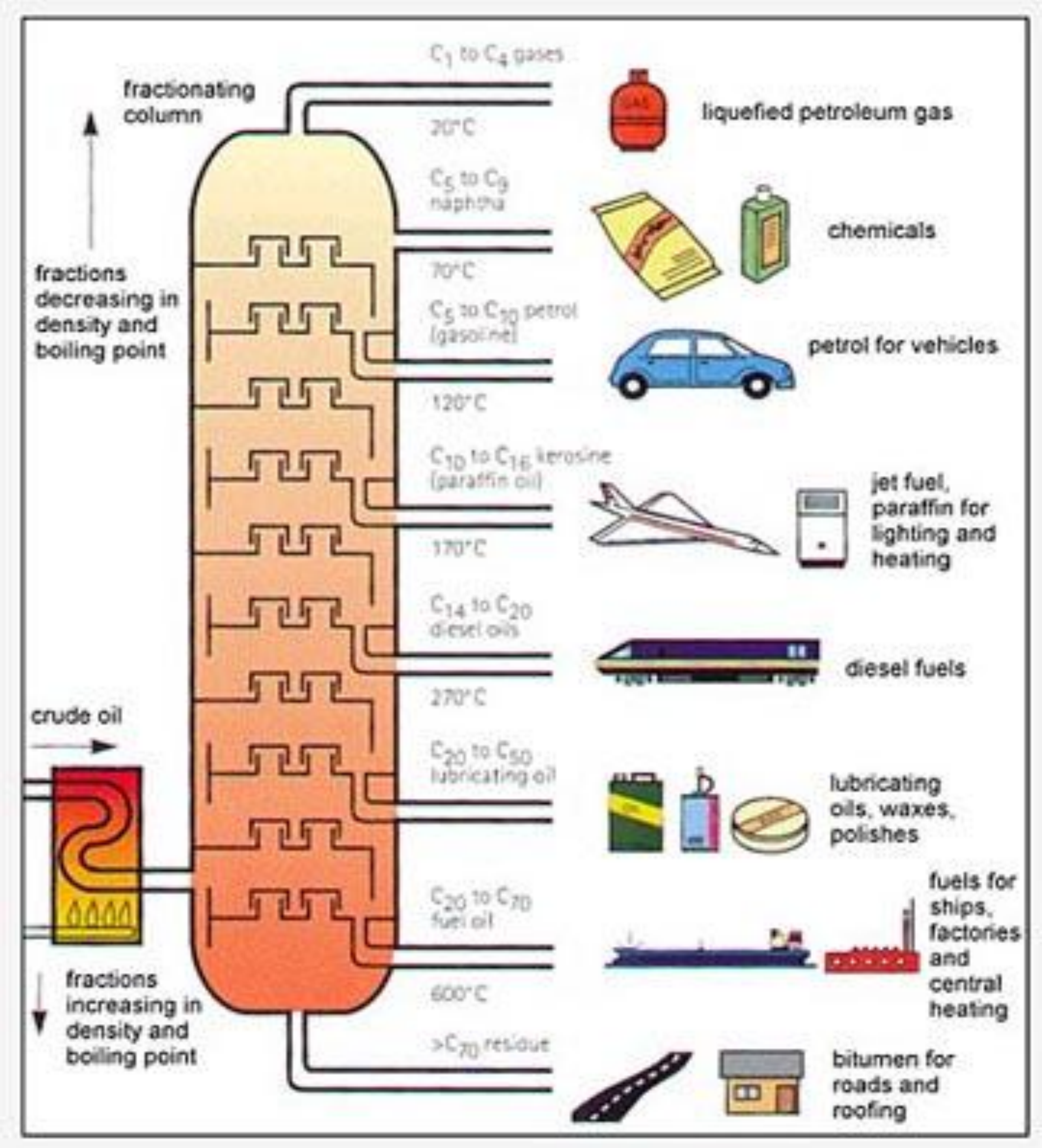


Fig (2.1) Distillation column

2.2. Overview:

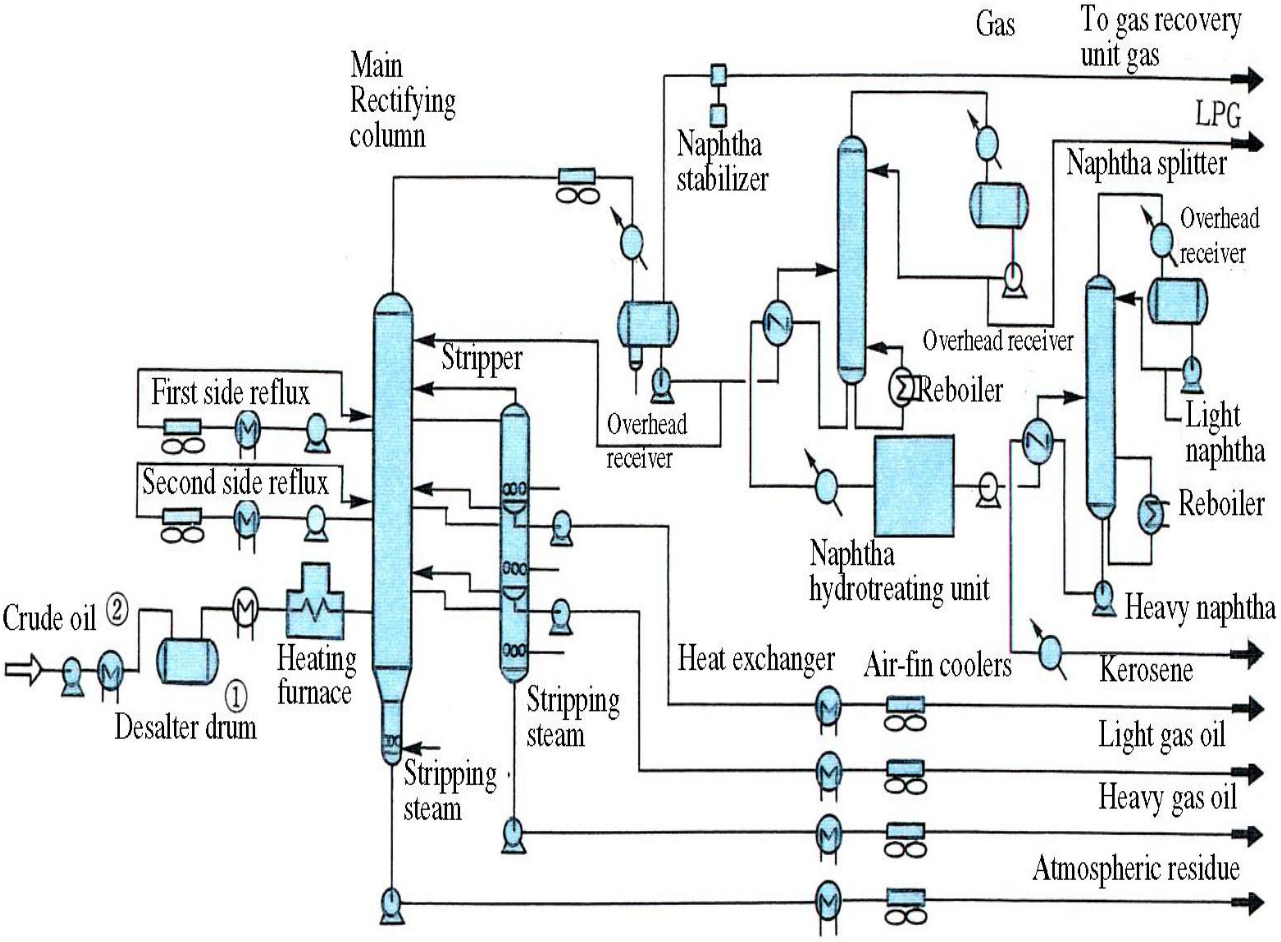
2.2.1. Process Objective:

To distill and separate valuable distillates (naphtha, kerosene, diesel) and atmospheric gas oil (AGO) from the crude feedstock . [13]

2.2.2. Primary Process Technique and flow diagram:

–Complex distillation.

In the bottom fig . (2.2) show diagram catalytic reforming [13]



2.2.3. Process description steps:

1-Crude oil is pumped from storage and is heated using hot overhead and product side streams using a heat exchanger network (HEN). The HEN enables the crude to achieve a temperature of about 200 - 250 of.

2-Eventually, the pre-heated crude oil is injected to remove salt in a desalted drum which does not remove any organic chlorides and removes dissolved salt.

3-Dissolved salt in the crude is removed using electrostatic precipitation as salt water. The salt water is sent to sour water stripper, cleaned and sent to oily waste sewage disposal.

4-Eventually crude enters a surge drum and some light ends entrained with water are flashed off the drum. The removed light ends are directly fed to the flash zone of the main column of the CDU.

5-A second HEN would energize the crude oil to higher temperatures after which the crude oil enters a furnace and is heated to a temperature that will vaporize distillate products in the crude tower.

6-Crude oil is often heated to vaporize about 5 % more than required for the distillate streams. This is called over flash and this ensures good reflux streams in the tower.

7-The heated crude then enters the fractionation tower in a lower section called flash zone. The un vaporized portion of the crude oil leaves the bottom of the tower via a stream stripper section. The distillate vapors move up.

8-Distillate products from the main column are removed from selected trays. These are called Draw off trays. The streams are called draw off streams. These streams are steam stripped and sent to storage.

9-From the tower top of the main column, full range naphtha (both light and heavy) will leave as a vapor. Eventually, the vapor will be condensed and separated in a phase separator. The separated naphtha product will be partially sent for reflux and the balance sent as reflux stream from the overhead drum.

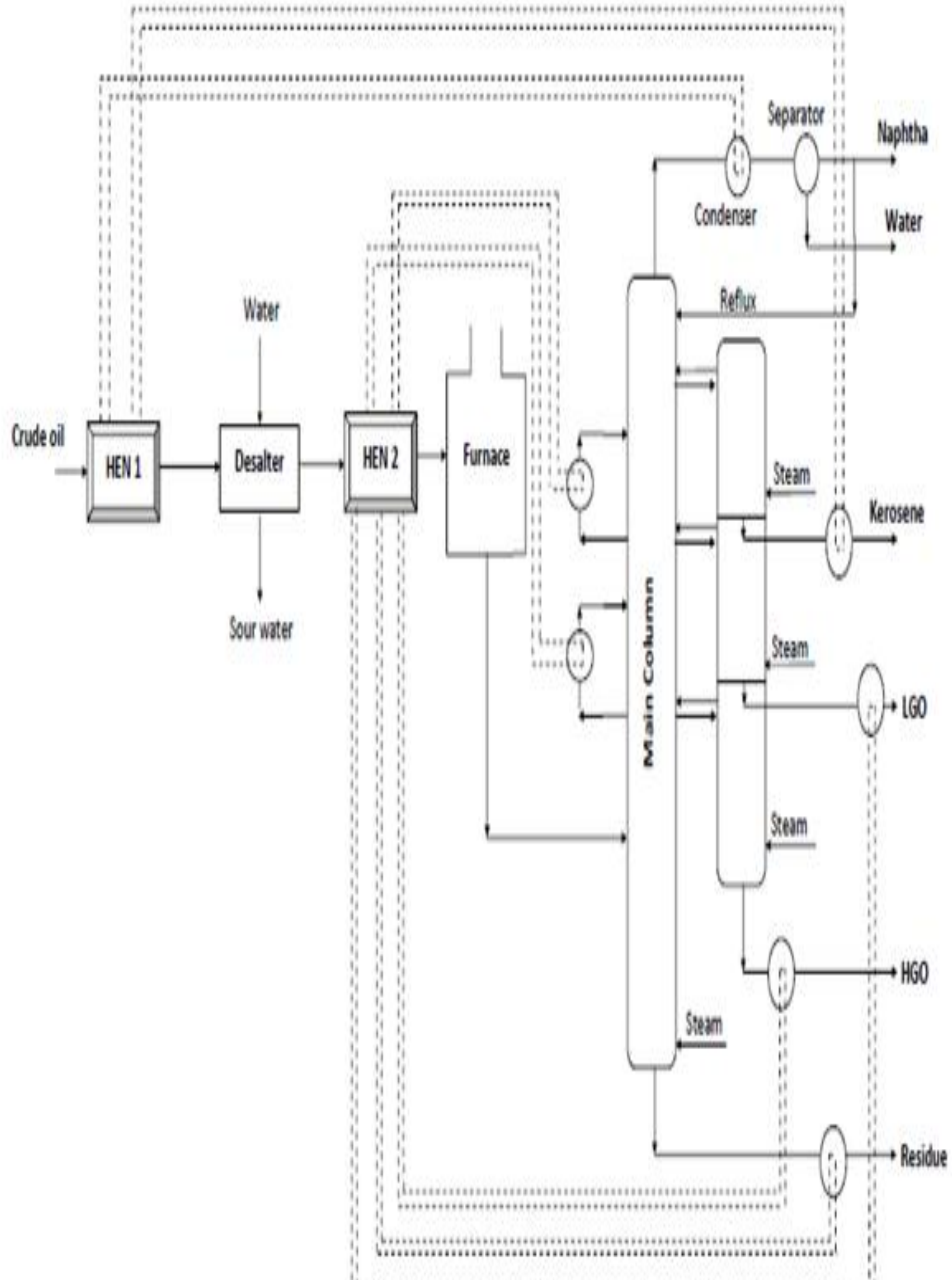
10-In addition, pump around units are included at the LGO draw off and HGO draw off. A pump around involves removing a hot side stream cool it and return it back to the column at a section above the draw off tray. The pump around is an internal condenser that takes out heat of that section and ensures reflux below that section.

11- Side stream distillate products are kerosene (Jet fuel), light gas oil (diesel) and heavy gas oil. These are stripped free of entrained light ends in separate stripping towers (called secondary columns). About 4 – 6 trays are required in these secondary columns. The purpose of secondary columns is to strip the side stream distillate products from entrained light ends. In these columns, steam is injected below the bottom tray which moves up the tower and leaves at the secondary column top along with light ends stripped out. The stripped steam (with light ends) is allowed to enter the main column just above the side stream draw off tray. Often, side stream stripper units (secondary columns) are stacked above one another in a single column (with distributed liquid and vapor traffic) so as to ensure free flow of side stream product from the draw off tray to the secondary column.

12-In certain circumstances such as kerosene stream sent to jet fuel blending, stripping is effected using a re-boiler.

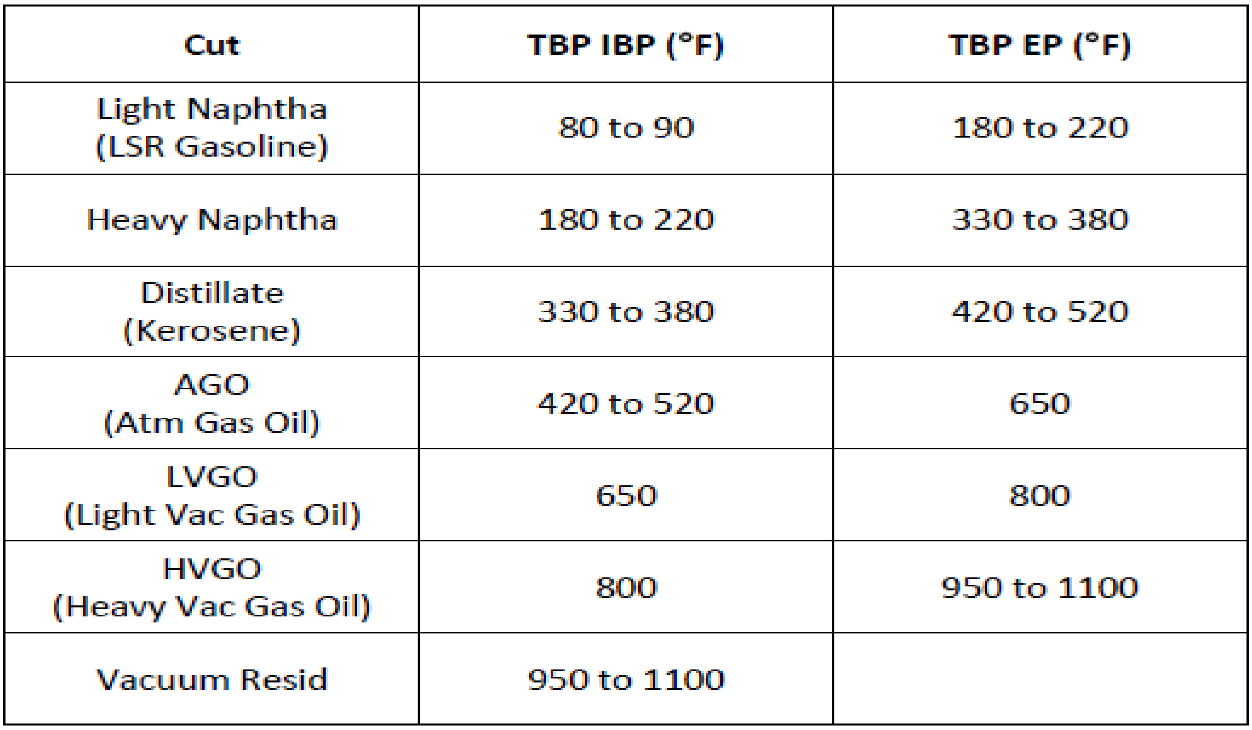
13- The residue product leaves the flash zone at the bottom of the main column. It is stripped free of light ends using steam injected at the bottom of the main column.

12-Live steam is pretty useful in the CDU operation. While steam enabled the reduction of installed costs of reboiler from cost perspective, it enables the flashing of the streams at a reduced partial pressure and therefore contributes significantly for the removal of light ends throughout the main and secondary column. A conceptual diagram of the CDU is presented in Figure (2.3). [14]



Separator
Naphtha
Condenser
Water
Reflux
Water
Crude oil
HEN 1
Desalter
HEN 2
Furnace
Sour water
Steam
Kerosene
Steam
LGO
Main Column
Steam
HGO
Steam
Residue

2.2.4.Typical yield :



Cut	TBP IBP (°F)	TBP EP (°F)
Light Naphtha (LSR Gasoline)	80 to 90	180 to 220
Heavy Naphtha	180 to 220	330 to 380
Distillate (Kerosene)	330 to 380	420 to 520
AGO (Atm Gas Oil)	420 to 520	650
LVGO (Light Vac Gas Oil)	650	800
HVGO (Heavy Vac Gas Oil)	800	950 to 1100
Vacuum Resid	950 to 1100	

Table (2.1.) [15]

2.3. Processing sequence and equipment type:

Processing sequence:

1-Fractionation systems have different objectives. The major processing objectives set the system type and the equipment configuration needed. The common objectives include removing a light component from a heavy product, removing a heavy component from a light product, making two products, or making more than two products. We will call these major categories are called stripping, rectification, fractionation, and complex fractionation.

2-Stripping systems remove light material from a heavy product.

3-Rectification systems remove heavy material from a light product.

4-Fractionation systems remove a light material from a heavy product and a heavy material from a light product at the same time.

5-Complex fractionation makes multiple products from either a single tower or a complex of towers combined with recycle streams between them. A good example of a multiple product tower is a refinery crude distillation tower making rough cuts of naphtha (gasoline), kerosene (jet fuel), and diesel from the same tower. A good example of a complex tower with internal recycle streams is a Petlyck (baffle) tower making three on-specifications products from the same tower.[12]

Equipment type:

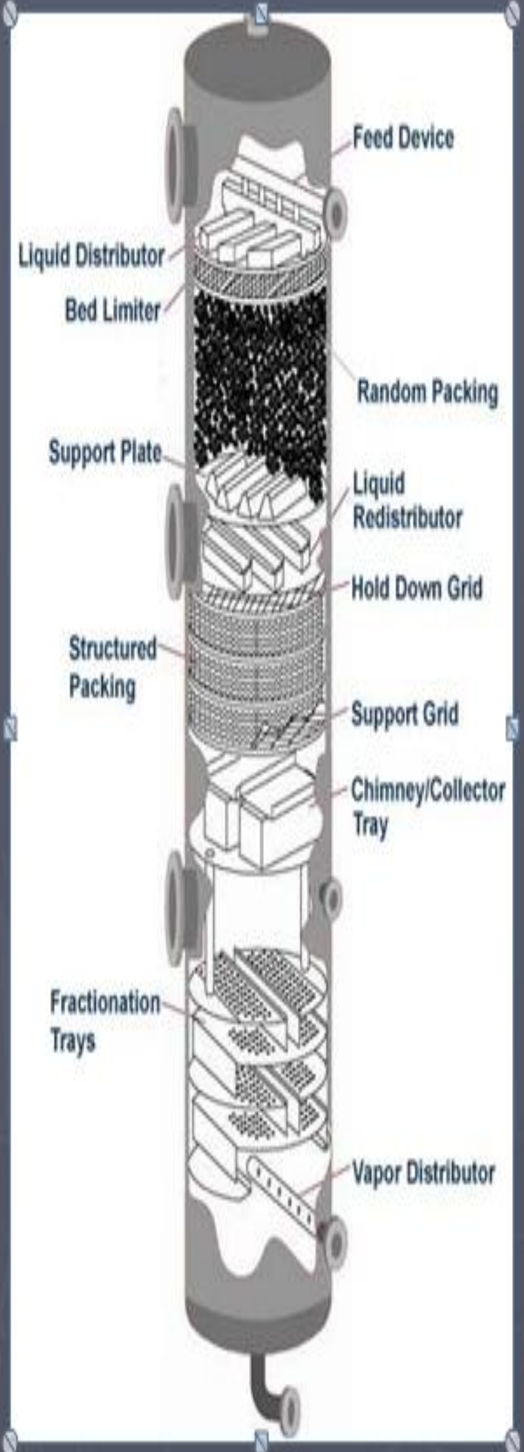
1-Distillation equipment includes two major categories, trays and packing.

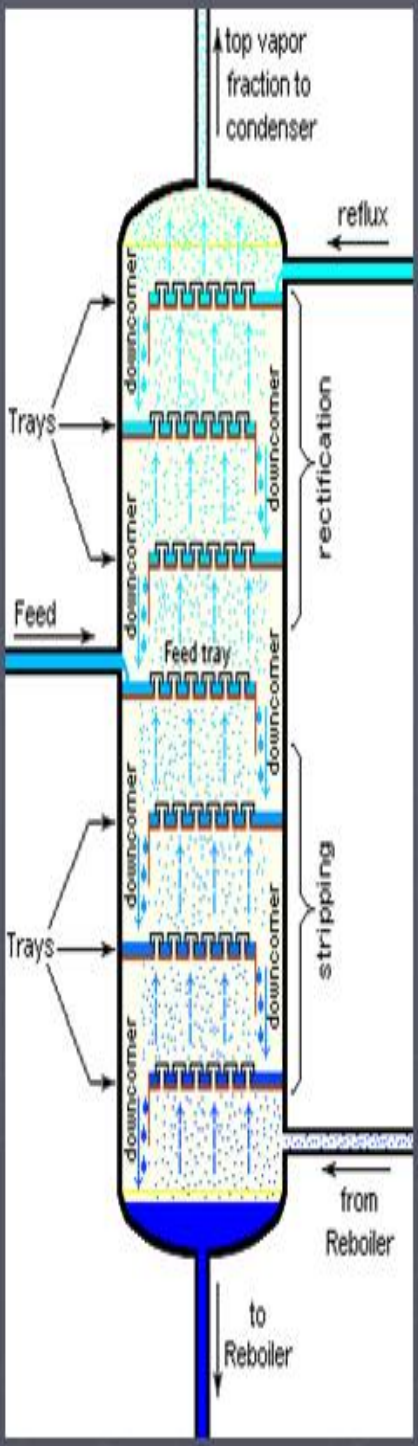
2-Trays force a rising vapor to bubble through a pool of descending liquid.

3-Packing creates a surface for liquid to spread on. The thin liquid film has a high surface area for mass-transfer between the liquid and vapor.show the bottom fig.(2.4) [12]

2.4. Reaction of distillation column:

Reactive distillation uses a reaction in the distillation equipment to help the separation. The reaction may or may not use a catalyst. DMT manufacture uses reactive distillation without a catalyst. One process to make methy-tert-butyl-ether uses a catalyst inside the distillation tower. The reaction changes the composition, allowing the distillation to work better[12]


Feed Device
Liquid Distributor
Bed Limiter
Random Packing
Support Plate
Liquid Redistributor
Hold Down Grid
Structured Packing
Support Grid
Chimney/Collector Tray
Fractionation Trays
Vapor Distributor


top vapor fraction to condenser
reflux
Trays
downcomer
rectification
Feed
Feed tray
stripping
from Reboiler
to Reboiler

Chapter three

Reformer and isomerization

Chapter three
Reforming and isomerization

Reforming

3.1. Introduction:

Reforming is essentially a treatment process designed to improve a gasoline octane number and may be accomplished in part by an increase in the volatility -reduction in molecular size- or chiefly by the conversion of n-paraffins to iso-paraffins, olefins, and aromatics and the conversion of naphthenes to aromatics. The process is carried out either thermally or catalytically. The nature of the final product is of course influenced by the source (and composition) of the feedstock. In thermal reforming, the reactions resemble the reactions that occur during gas oil cracking, that is, molecular size is reduced, and olefins and some aromatics are produced. [10]

3.1.2. There are two type of reforming:

3.1.2.1. Thermal reforming:

Thermal reforming was naturally developed from thermal cracking, as reforming is also a thermal decomposition reaction. Cracking converts heavier oils into gasoline; reforming converts (reforms) gasoline in to higher-octane gasoline. The equipment for thermal reforming is essentially the same as for thermal cracking, but higher temperatures are used (Nelson, 1958).In carrying out thermal reforming, a feedstock, such as a 205 °C (400 °F)end-point naphtha or a straight-run gasoline, is heated to 510 to 595 °C
(950 to 1100 °F) in a furnace much the same as a cracking furnace, with pressures from 400 to 1000 psi . As the heated naphtha leaves the furnace, it is cooled or quenched by the addition of cold naphtha. The quenched, reformed material then enters a fractional distillation tower where any heavy

product is separated. The remainder of the reformed material leaves the top of the tower to be separated into gases and reformate. The higher octane number of the product (reformate) is due primarily to the cracking of longer chain paraffins into higher-octane olefins. Thermal reforming is in general less effective than catalytic processes and has been largely supplanted. As it was practiced, a single-pass operation was employed at temperatures in the range of 540 to 760 °C (1000 to 1140 °F) and pressures in the range 500 to 1000 psi. Octane number improvement depended on the extent of conversion but was not directly proportional to the extent of cracking-per-pass.

The amount and quality of reformate is dependent on the temperature. A general rule is the higher the reforming temperature, the higher the octane number of the product but the yield of reformate is relatively low. For example, a gasoline with an octane number of 35 when reformed at 515°C (960 °F) yields 92.4% of 56 octane reformate; when reformed at 555°C (1030 °F) the yield is 68.7% of 83 octane reformate. However, high conversion is not always effective as coke production and gas production usually increase.

Modifications of the thermal reforming process caused by the inclusion of hydrocarbon gases with the feedstock are known as gas reversion and polyforming. Thus, olefinic gases produced by cracking and reforming can be converted into liquids boiling in the gasoline range by heating them under high pressure. As the resulting liquids (polymers) have high octane numbers, they increase the overall quantity and quality of gasoline produced in a refinery.

The gases most susceptible to conversion to liquid products are olefins with three and four carbon atoms. These are propylene ($CH_3.CH=CH_2$), which is associated with propane in the C_3 fraction, butylene($CH_3.CH_2.CH=CH_2$ or $CH_3.CH=CH.CH_3$) and iso-butylene[$(CH_3)_2C=CH_2$], which are associated with butane ($CH_3.CH_2.CH_2.CH_3$),and iso-butane [$(CH_3)_2CH.CH_3$] in the C_4 fraction. When the C_3 and C_4fractions are subjected to the temperature and pressure conditions used in thermal reforming, they undergo chemical reactions that result in a small yield of gasoline. When the C3 and C4 fractions are passed through a thermal reformer in admixture with naphtha, the process is called naphtha-gas reversion or naphtha polyforming. These processes are essentially the same but differ in the manner in which the gases and naphtha are passed through the heating furnace. In gas reversion, the naphtha and gases flow through separate lines in the furnace and are heated independently of one another. Before leaving the furnace, both lines join to form a common soaking section where there forming, polymerization, and other reactions take place. In naphtha reforming, the C3 and C4 gases are premixed with the naphtha and passed together through the furnace. Except for the gaseous components in the feedstock, both processes operate in much the same manner as thermal reforming and produce similar products. [10]

3.1.2.2. Catalytic reforming:

Like thermal reforming, catalytic reforming converts low-octane gasoline into high-octane gasoline (reformate). Although thermal reforming can produce reformate with a research octane number in the range of 65 to 808 depending on the yield, catalytic reforming produces reformate with octane numbers of the order of 90 to 95. Catalytic reforming is conducted in the presence of hydrogen over hydrogenation-dehydrogenation catalysts, which may be supported on alumina or silica–alumina. Depending on the catalyst, a definite sequence of reactions takes place, involving structural changes in the charge stock. The catalytic reforming process was commercially nonexistent in the United States before 1940.The process is really a process of the 1950s and showed phenomenal growth in the 1953–1959 period. As a result, thermal reforming is now somewhat obsolete. Catalytic reformer feeds are saturated (i.e., not olefinic) materials; in the majority of cases the feed may be a straight-run naphtha, but other by product low-octane naphtha (e.g., coker naphtha) can be processed after treatment to remove olefins and other contaminants. Hydrocarbon naphtha that contains substantial quantities of naphthenes is also a suitable feed. The process uses a precious metal catalyst (platinum supported by an alumina base) in conjunction with very high temperatures to reform the paraffin and naphthene constituents into high octane components.

Sulfur is a poison to the reforming catalyst, which requires that virtually all the sulfur must be removed from the heavy naphtha through hydrotreating before reforming. Several different types of chemical react ions occur in the reforming reactors:

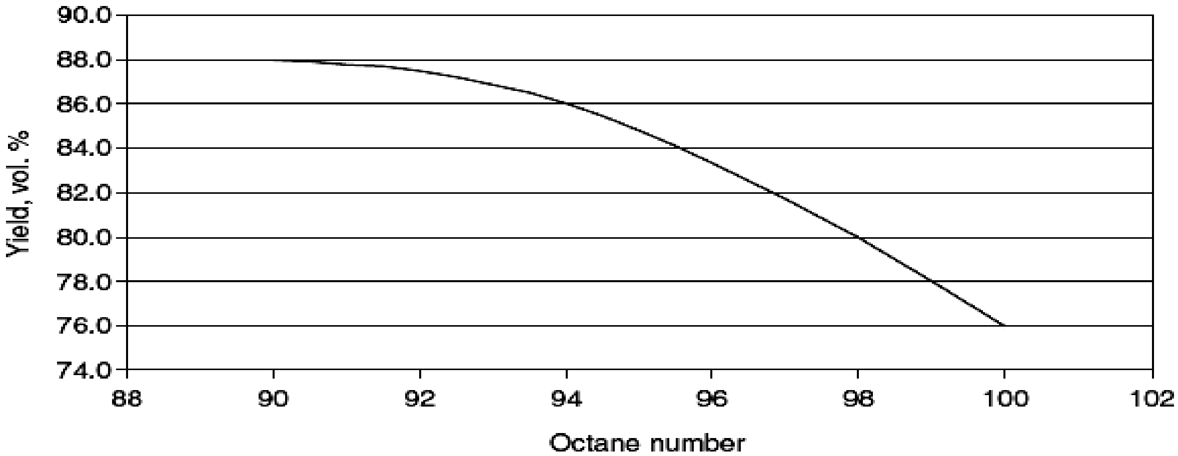
1. Paraffins are isomerized to branched chains and to a lesser extent to naphthenes, and
2. naphthenes are converted to aromatics.

Overall, the reforming reactions are endothermic. The resulting product stream (reformate) from catalytic reforming has a RON from 96 to 102depending on the reactor severity and feedstock quality. The dehydrogenation reactions that convert the saturated naphthenes into unsaturated aromatics produce hydrogen, which is available for distribution to other refinery hydro-processes.

The catalytic reforming process consists of a series of several reactors, which operate at temperatures of approximately 480 °C (900 °F). The hydrocarbons are reheated by direct-fired furnaces between the subsequent reforming reactors. As a result of the very high temperatures, the catalyst becomes deactivated by the formation of coke (i.e., essentially pure carbon) on the catalyst, which reduces the surface area available to contact with the hydrocarbons.9Catalytic reforming is usually carried out by feeding a naphtha (after pretreating with hydrogen if necessary) and hydrogen mixture to a furnace where the mixture is heated to the desired temperatures 450 °C to 520 °C (840 °F to 965 °F), and then passed through fixed-bed catalytic reactors at hydrogen pressures of 100 to 1000 psi. Normally, two (or more than one) reactors are used in series, and reheaters are located between adjoining reactors to compensate for the endothermic reactions taking place. Sometimes as many as four or five are kept on-stream in series while one or more is being regenerated. The on-stream cycle of anyone reactor may vary from several hours to many days, depending on the feedstock and reaction conditions. The product issuing from the last catalytic reactor is cooled and sent to a high-pressure separator where the hydrogen- rich gas is split into two streams:

1. One stream goes to recycle where it is mixed with the feed, and
2. The remaining portion represents excess hydrogen available for other uses.

The excess hydrogen is vented from the unit and used in hydrotreating, as a fuel, or for manufacture of chemicals (e.g., ammonia). The liquid product (reformate) is stabilized (by removal of light ends) and used directly in gasoline or extracted for aromatic blending stocks for aviation gasoline. Figure (3.1) shows the relation between reformate yield and its octane number.



The commercial processes available for use can be broadly classified as the moving-bed, fluid-bed, and fixed-bed types. The fluid-bed and moving-bed processes use mixed non-precious metal oxide catalysts in units equipped with separate regeneration facilities. Fixed-bed processes use predominantly platinum-containing catalysts in units equipped for cycle, occasional, or no regeneration. There are several types of catalytic reforming process configurations that differ in the manner that they accommodate the regeneration of the reforming catalyst. Catalyst regeneration involves burning off the coke with oxygen. The semi-regenerative process is the simplest configuration but does require that the unit be shut down for catalyst regeneration in which all reactors (typically four) are regenerated. The cyclic configuration uses an additional swing reactor that enables one reactor at a time to be taken off-line for regeneration while the other four remain in service. The continuous catalyst regeneration (CCR) configuration is the most complex configuration and enables the catalyst to be continuously removed for regeneration and replaced after regeneration. The benefits of more complex configurations are that operating severity may be increased as a result of higher catalyst activity but this does come at an increased capital cost for the process. Although subsequent olefin reactions occur in thermal reforming, the product contains appreciable amounts of unstable unsaturated compounds. In the presence of catalysts and hydrogen (available from dehydrogenation reactions), hydrocracking of paraffins to yield two lower paraffins occur. Olefins that do not undergo dehydrocyclization are also produced. The olefins are hydrogenated with or without isomerization, so that the end product contains only traces of olefins. The addition of a hydrogenation–dehydrogenation catalyst to the system yields a dual function catalyst complex. Hydrogen reactions hydrogenation, dehydrogenation, dehydrocyclization, and hydrocracking take place on the one catalyst, and cracking, isomerization, and olefin polymerization take place on the acid catalyst sites.

Under the high-hydrogen partial pressure conditions used in catalytic reforming, sulfur compounds are readily converted into hydrogen sulfide, which, unless removed, builds up to a high concentration in the recycle gas. Hydrogen sulfide is a reversible poison for platinum and causes a decrease in the catalyst dehydrogenation and dehydrocyclization activities. In the first catalytic reformers the hydrogen sulfide was removed from the gas cycle stream by absorption in, for example, diethanolamine. Sulfur is generally removed from the feedstock by use of11a conventional desulfurization over a cobalt–molybdenum catalyst. An additional benefit of desulfurization of the feed to a level of <5 ppm sulfur is the elimination of hydrogen sulfide (H2S) corrosion problems in the heaters and reactors. Organic nitrogen compounds are converted into ammonia under reforming conditions, and this neutralizes acid sites on the catalyst and thus represses the activity for isomerization, hydrocracking, and ehydrocyclization reactions. Straight-run materials do not usually present serious problems with regard to nitrogen, but feeds such as coker naphtha may contain around 50 ppm nitrogen and removal of this quantity may require high-pressure hydrogenation (800 to 1000 psi) overnickel–cobalt–molybdenum on an alumina catalyst.

The yield of gasoline of a given octane number and at given operating conditions depends on the hydrocarbon types in the feed. For example, high-naphthene stocks, which readily give aromatic gasoline, are the easiest to reform and give the highest gasoline yields. Paraffinic stocks, however, which depend on the more difficult isomerization, dehydrocyclization, and hydrocracking reactions, require more severe conditions and give lower gasoline yields than the naphthenic stocks. The end point of the feed is usually limited to about 190 °C (375 °F), partially because of increased coke deposition on the catalyst as the end point during processing at about 158 °C (278 °F).Limiting the feed end point avoids redistillation of the product to meet the gasoline end-point specification of 205 °C (400 °F), maximum.

Dehydrogenation is a main chemical reaction in catalytic reforming, and hydrogen gas is consequently produced in large quantities. The hydrogen is recycled through the reactors where the reforming takes place to provide the atmosphere necessary for the chemical reactions and also prevents the carbon from being deposited on the catalyst, thus extending its operating life. An excess of hydrogen above whatever is consumed in the process is produced, and as a result, catalytic reforming processes are unique in that they are the only petroleum refinery processes to produce hydrogen as a by-product. [10]

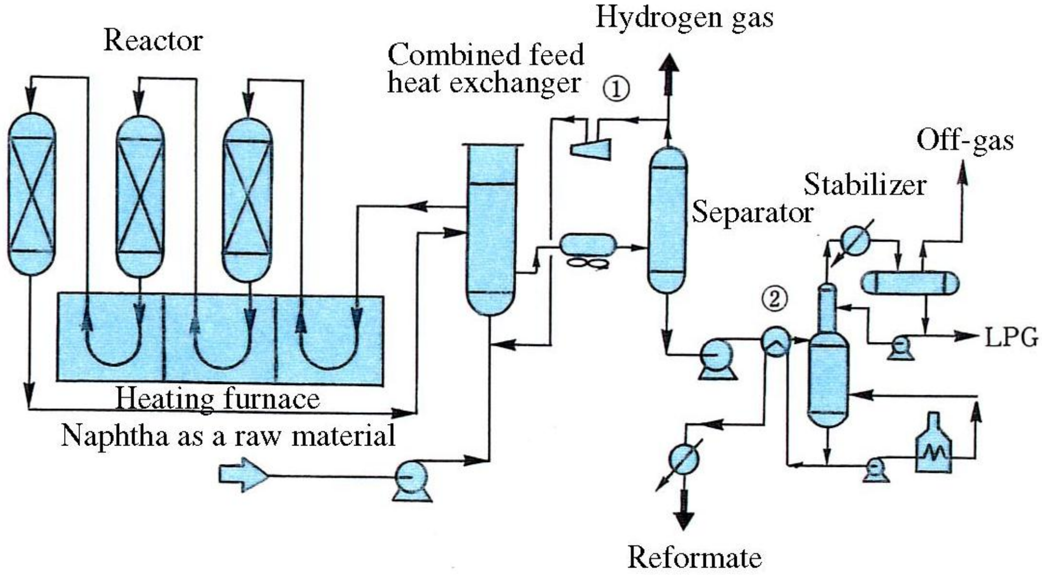
3.2. Overview:

3.2.1. Process objective catalytic reforming:

To convert low-octane naphtha into a high-octane reformate for gasoline blending and/or to provide aromatics (benzene, toluene, and xylene) for petrochemical plants. Reforming also produces high purity hydrogen for hydrotreating processes. [13]

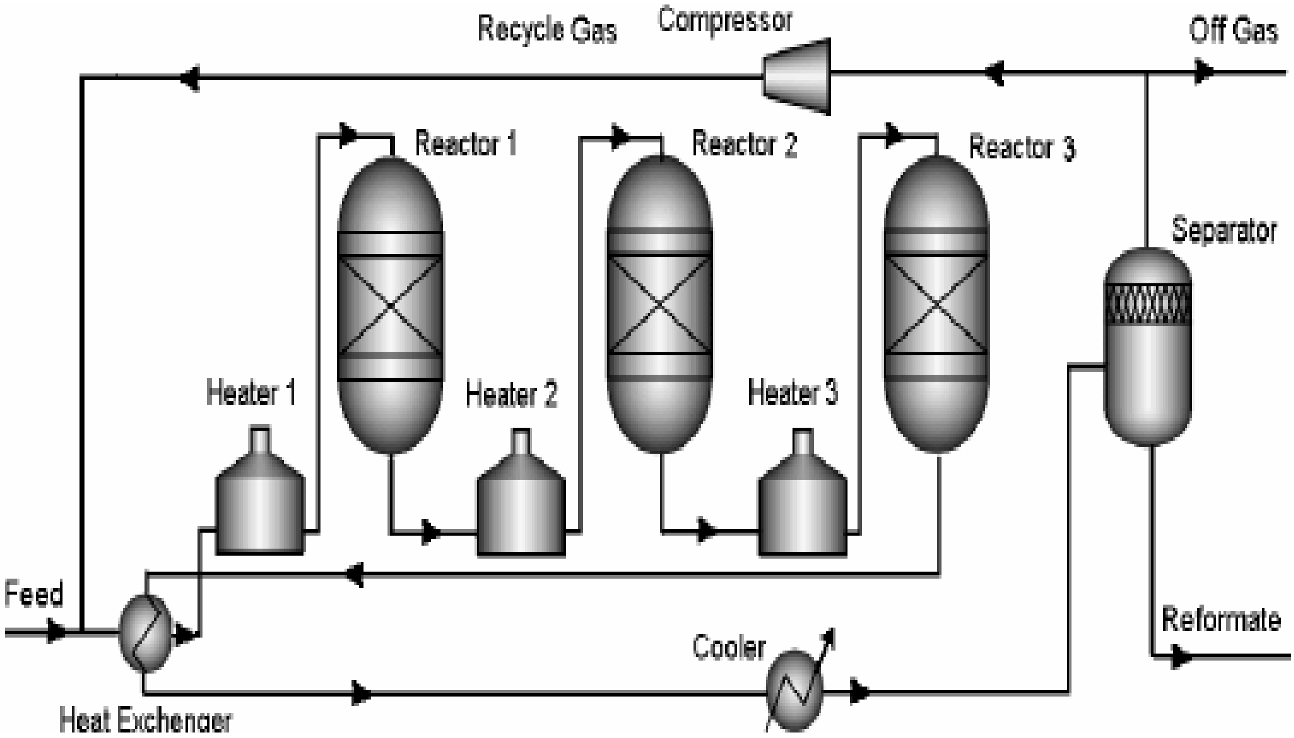
3.2.2. Primary Process Technique of catalytic reforming and flow diagram:

Reforming reactions occur in chloride promoted fixed catalyst beds; or continuous catalyst regeneration (CCR) beds where the catalyst is transferred from one stage to another, through a catalyst regenerator and back again. Desired reactions include: dehydrogenation of naphthenes to form aromatics; isomerization of naphthenes; dehydrocyclization of paraffins to form aromatics; and isomerization of paraffins. Hydrocracking of paraffinsis undesirable due to increased light-ends make .show this diagram fig.(3.2) [13]



3.2.3. Process description steps of catalytic reforming:

Catalytic naphtha reforming contains three reactors in series, as shown in Fig.(3.3) It is generally carried out in three/four fixed or moving bed reformers. The catalyst used in reformer is commonly a bifunctional bimetallic catalyst such as Pt-Re/Al_2O_3, providing the metal function and the acid function. The product stream from the first reactor after preheating enters the second reactor and similarly the product stream from the second reactor after preheating enters the third one. Thus, the reactor feeds are raised to the proper temperature by heaters located before the reactors, since the reactions are endothermic. The product stream from the final reactor enters a separator wherein hydrogen rich gas stream is separated from the products which is then recycled back and mixed with the first reactor fresh feed. Reactors are of different sizes, with the smallest one located in the first stage and the largest one in the last. [16]



3.2.4. Typical yield:

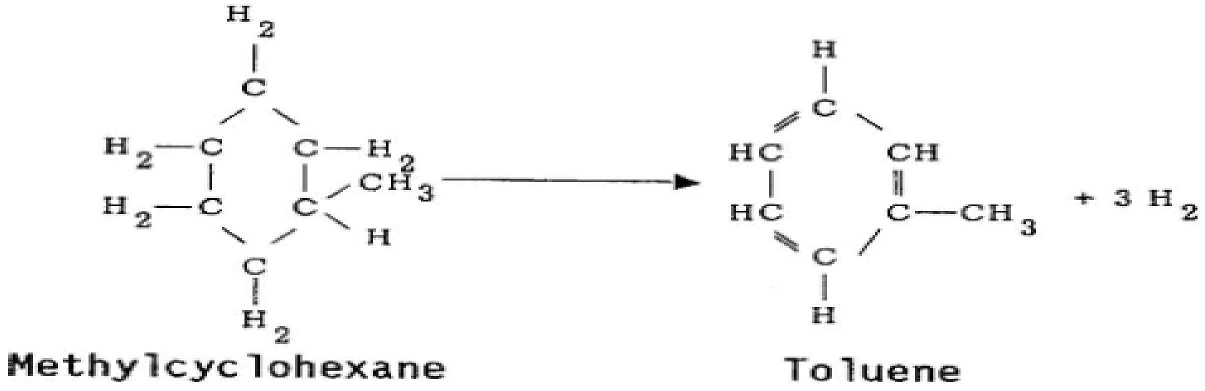
As mentioned before, catalytic reforming produces C5 + gasoline, hydrogen, but also a little amount of methane, ethane propane and butanes. In the last few decades the importance of the production of hydrogen, beside C5 +, has risen gradually with pressures going down to 10 bar and less as a result of improving catalysts. Table (3.1) typical yields on a middle eastern feed RON=98 P=15 bar. Gives an average product distribution from a paraffinic feed on a bimetallic at 15 bar and RON = 98. The desired products account for 85% weight and the ones with lower added value represent less than 5% weight (methane and ethane). [10]

Products	% wt/feed
H_2	2.5
CH_4	1.7
C_2H_6	3.1
C_3H_8	4.2
$(i + n)\ C_4H_{10}$	6.0
C_5^+	82.5

3.2.5. Catalytic Reforming reactions:

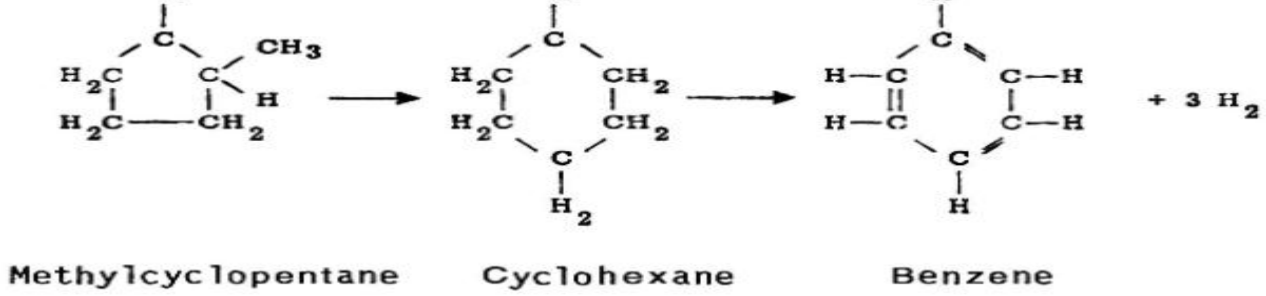
1-dehydrogenation of naphthenic to aromatics:

The dehydrogenation reactions are highly endothermic and cause a decrease in temperature as the reaction progresses. In addition, the dehydrogenation reactions have the highest reaction rates of the reforming reactions which necessitates the use of the inter heaters between catalyst beds to keep the mixture at sufficiently high temperatures for the reactions to proceed at practical rates. [17]



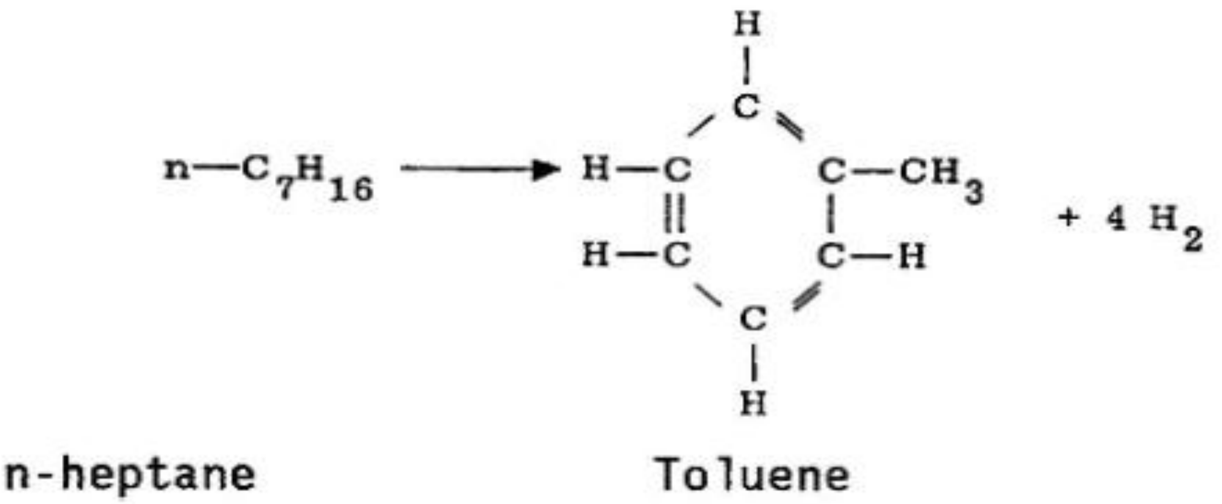
2-Isomerisation:

Isomerisation of paraffins is also a fast reaction. The reaction is almost thermo neutral, AH 2 kCal/mole. This reaction has a negligible effect on the final octane number. [17]



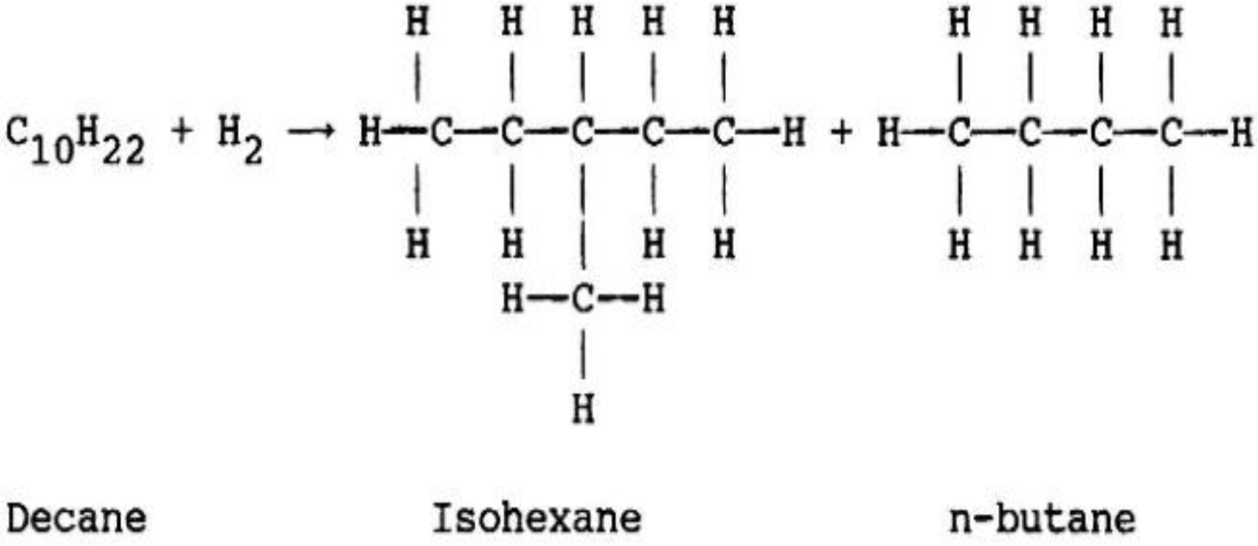
3-dehydrocyclization of paraffins to aromatics:

The dehydrocyclization of paraffins is the key reaction for producing high-octane gasoline. It is highly endothermic, AH 60kCal/mole. The yield of this reaction is limited by naphthenetics . The reaction rate is much slower than the naphthene dehydrogenation. Its contribution to increasing the octane number is extremely important ant because the change of a paraffin mixture to corresponding aromatics lead to increase in octane from 60 to 80. A lower rate of this reaction leads to more severe operating conditions and increase in coke formation. [17]



4-Hydrocracki~Hydrocracking:

are important in the reforming reactors. Unlike other reforming reactions, hydrocracking is exothermic with a heat release of 10kCal/mole. Compared to hydrodecyclization, the reaction rate is small at low temperature and conversion rates. However, the rate increases with higher temperatures and increases in aromatic content when it becomes an important competitor of hydrodecyclization reactions. The reaction products appear in the reformate and in the gases. The presence of light components Ca and C5 gives important volatility properties to reformate. Also, hydrocracking decreases the liquid yield and increases the aromatic content due to a concentration effect. [17]



3.2.6. Reforming catalyst:

Platinum-based reforming catalysts are used in the late of 1940. By time, in 1960, their performance was improved by the addition of some metals such as Ge, Sn, Re, and Ir. These additions have given the catalyst a better selectivity, a better stability of performance over time, and the possibility of operating at lower pressure. Most of the reforming catalysts are based on well-dispersed platinum on an alumina promoted by halogen, usually chlorine. Since 1970, many attempts were made to find a better performing system of catalyst. Nowadays the reforming process is generally carried out over bi-functional catalysts which consist of one or more metals, most commonly platinum or platinum combined with rhenium or tin or iridium, dispersed on an acidic support.[6]

The platinum must be dispersed over the alumina surface such that the maximum number of active sites for dehydrogenation is available. Platinum cluster size dimensions are on the order of angstroms, or 10−10 meters. The interaction of the platinum with the alumina surface is such that the platinum clusters are relatively immobile and do not agglomerate during reforming. Sulfidation of the platinum is sometimes used to partially poison the platinum, or reduce its activity; this has the beneficial effect of reducing a major portion of the hydrogenolysis, or metal-catalyzed cracking reactions. Liquid product yields are improved and the light gas production, particularly methane, is reduced. [6]

The alumina support is usually in the eta (η) or gamma (γ) phase, but most often gamma is used in reforming. Chloride is added to promote acidity. A simplified schematic diagram of the alumina functionality Catalysts that are used in reactors where the catalyst bed is not easily removed after deactivation must have long catalyst life cycles. A typical fixed bed catalyst life cycle may be a year or longer. Modifiers are added to reduce the effect of coke buildup and to lengthen the catalyst cycle length, either by hydrogenating the coke to a less graphitic species or by cracking the coke precursors. Elements that are commonly added to the catalysts are rhenium and, to a lesser extent, iridium.

In moving bed units .the catalyst flows through the reactors and is regenerated continually in a separate regeneration vessel that is part of the reactor–regenerator loop. Process conditions are much more severe, thus shortening catalyst life and requiring regeneration cycles of only a few days. In moving bed catalysts elements are added, such as tin and germanium, to increase liquid, aromatic, and hydrogen yields by reducing the activity of the platinum for hydrogenolysis or metal-catalyzed cracking reactions. These components also provide some stabilization of the catalyst relative to Pt alone. [10]

ISOMERIZATION:

3.2.1. Introduction:

The skeletal isomerization of alkanes is one of many important industrial applications of acid-function-promoted catalysis. Other examples of the wide commercial application of acid-catalyzed industrial hydrocarbon reactions are the alkylation of paraffins and aromatics with olefins, transalkylation and disproportionation of aromatics, metathesis of olefins, oligomerization of olefins, etherification and hydration *UOP LLC of olefins, and hydrocracking. Although these various applications have some similarities, they are all promoted by an acidic catalyst and often by a metal function. The specific catalytic requirements for achieving a highly economic result have led to the proliferation of specialized catalytic materials. This paper focuses on light paraffin isomerization. The primary commercial use of the branched isomers of C4, C5, and C6 paraffins is in the production of clean-burning, high-performance transportation fuels. The elimination of tetraethyl lead over the last 30 years as a means of improving the antiknock properties of gasoline and more recent regulations restricting motor fuel composition have led refiners to select alternative means of producing high-quality gasoline. As a result of benzene concentration restrictions, end-point and olefin content limitations, and potential limitations on total aromatics concentration, the choices of high-quality gasoline blending components available in the typical refinery are limited. Isomerate, the gasoline blending component from light paraffin isomerization, is an ideal choice. Another equally valuable blending component is alkylating resulting primarily from the acid-catalyzed reaction of isobutene with an aliphatic olefin. Both isomerization and alkylation yield highly branched, high-octane paraffinic blending components that by themselves can satisfy the strictest environmental requirements. Often, *n*-

butane isomerization is one of the sources for the isobutane requirements in alkylation.

Because of the heightened demand for isomerate, refiners continue to look for increasingly effective and economic means of producing this valuable blending component. Over the years, UOP has developed and continues to develop new catalyst systems in order to improve process economics and operability. This paper discusses two examples, the LPI-100 and I-80 catalysts in terms of their fundamental improvement over existing catalysts in various processing options and, most important, the increased value available to refiners who use these new high-performance isomerization catalysts.[11]

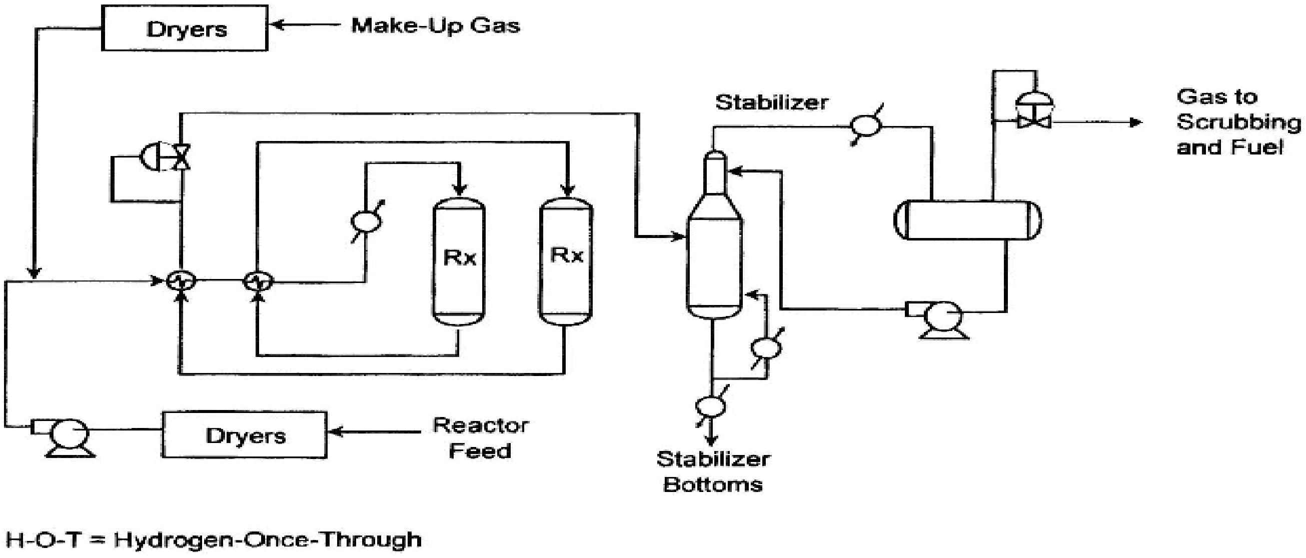
3.2.2. Overview:

3.2.2.1. Process Objective:

To convert low octane n-paraffinsto high-octane iso-paraffins. [13]

3.2.2.2. Primary Process Technique and diagram:

Isomerization occurs in a chloride promoted fixed bed reactor where n-paraffins are converted to iso-paraffins. The catalyst is sensitive to incoming contaminants (sulfur and water). Show this fig.(3.4) [13]

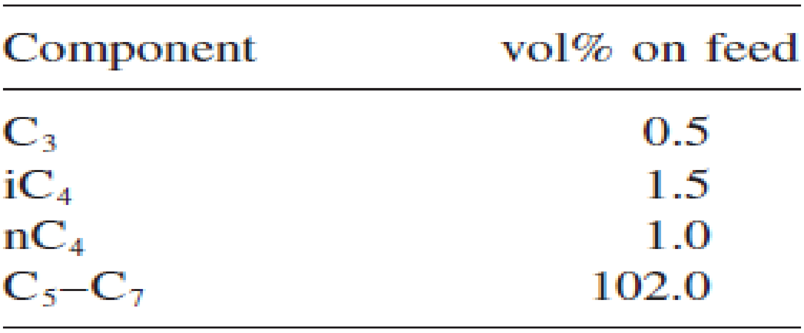


3.2.2.3. Process description steps:

–Desulfurizedfeed and hydrogen are dried in fixed beds of solid dessicantprior to mixing together
–The mixed feed is heated and passes through a hydrogenation reactor to saturate olefins to paraffins and saturate benzene
–The hydrogenation effluent is cooled and passes through a isomerization reactor
–The final effluent is cooled and separated as hydrogen and LPGs which typically go to fuel gas, and isomerate product for gasoline blending. [13]

3.2.2.4. Typical yield:

Yields vary with feedstock properties and operating severity. A typical product yield is given in Table (3.2) for a 13 number improvement in both RON and MON clear for a 12 psi RVP C5_ isomerate product. **[17]**



Component	vol% on feed
C_3	0.5
iC_4	1.5
nC_4	1.0
C_5–C_7	102.0

3.2.3. Reaction of isomerization:

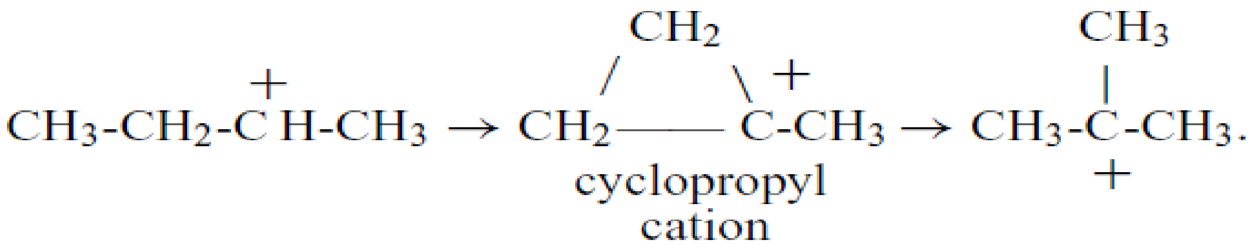
Paraffin isomerization is most effectively catalyzed by a dual-function catalyst containing a noble metal and an acid function. The reaction is believed to proceed through an olefin intermediate, which is formed by paraffin dehydrogenation on the metal site (reaction (1)):

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \overset{Pt}{\leftrightarrow} CH_3\text{-}CH_2\text{-}CH = CH_2 + H_2.$$

Although the equilibrium conversion of the paraffin in reaction (1) is low at paraffin isomerization conditions, sufficient olefins are present to be converted to a carbonium ion by the strong acid site (reaction (2)):

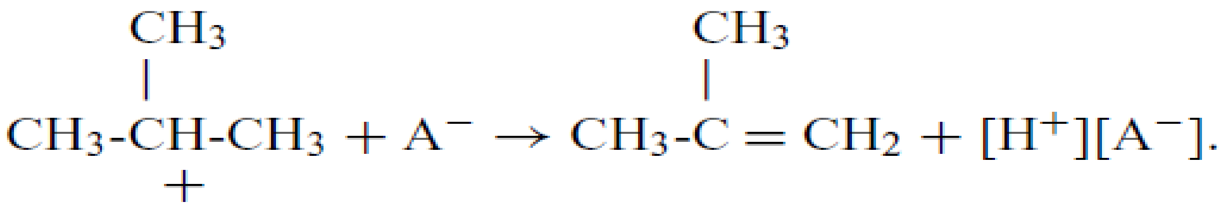
$$CH_3\text{-}CH_2\text{-}CH = CH_2 + [H^+]\,[A^-] \rightarrow CH_3\text{-}CH_2\text{-}\overset{+}{C}H\text{-}CH_3 + A^-.$$

The formation of the carbonium ion removes product olefins from reaction (1) and allows the equilibrium in reaction (1) to proceed. The carbonium ion in reaction (2) undergoes a skeletal isomerization, probably through a cycloalkyl intermediate as shown in reaction (3):



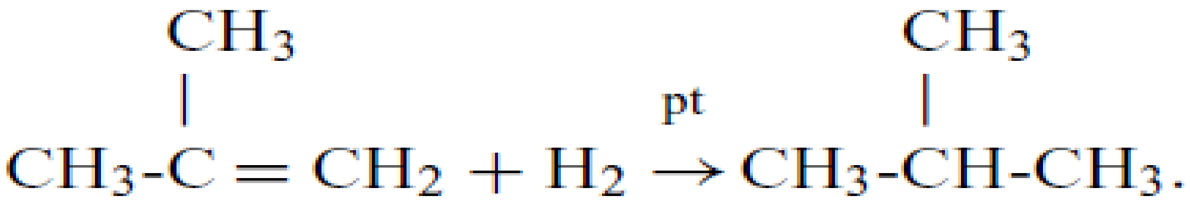
$$CH_3\text{-}CH_2\text{-}\overset{+}{C}H\text{-}CH_3 \rightarrow \underset{\text{cyclopropyl cation}}{\overset{CH_2}{CH_2 \text{——} \overset{+}{C}}}\text{-}CH_3 \rightarrow CH_3\text{-}\underset{+}{\overset{CH_3}{\overset{|}{C}}}\text{-}CH_3.$$

Reaction (3) proceeds with difficulty because it requires the formation of a primary carbonium ion at some point in the reaction. Nevertheless, the strong acidity of isomerization catalysts provides enough driving force for the reaction to proceed at high rates. The isoparaffinic carbonium ion is then converted to an olefin through loss of a proton to the catalyst site (reaction (4)):



$$CH_3\text{-}\underset{+}{\overset{CH_3}{\overset{|}{CH}}}\text{-}CH_3 + A^- \rightarrow CH_3\text{-}\overset{CH_3}{\overset{|}{C}} = CH_2 + [H^+][A^-].$$

In the last step, the isoolefin intermediate is hydrogenated rapidly back to the analogous isoparaffin (reaction (5)):



$$CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2+H_2\xrightarrow{pt}CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{-}CH_3.$$

In addition to these primary reaction pathways, some evidence indicates the existence of a bimolecular reaction mechanism, in which olefinic intermediates dimerize, internal carbon atoms are protonated, skeletal isomerization occurs, and the dimer undergoes beta scission that results in the product isoparaffin. In addition to the C13 labeling experiments that support this mechanism, a relatively small amount of hydrocarbons containing carbon numbers higher than the feed are always found in the reaction products. The bimolecular mechanism has a minor impact on commercial isomerization processing. [11]

3.2.4. The catalytic of isomerization:

An aluminum chloride catalyst for alkane isomerization was first developed in the 1930 s . The original application was for the conversion of *n*-butane to isobutane, which was, and still is, reacted with C3, C4, and C5 olefins to produce motor fuel alkylate. The first application of this high-octane product was in the production of high-octane aviation gasoline. Subsequent developments of this predominantly Lewisacid catalyst resulted in the current alumina-supported, bifunctional catalyst. UOP’s I-8 catalyst is one commercial example of this catalyst system, which has seen wide commercial application since 1981.

Chloride alumina, the highest-activity paraffin isomerization catalyst available, increases the octane of a typical light-naphtha stream from about 70 to as high as 85 RONC in a once-through paraffin isomerization unit.

Higher product octanes, up to 93 RONC, can be obtained by recycling low-octane hydrocarbons. The C+ 5 yield from chloride alumina catalysts is the highest from any commercial catalyst because of high catalyst selectivity and low operating temperature. Because chloride alumina systems are not economically regenerable, eventual reloading of the isomerization catalyst must be considered. Nevertheless, the chloride alumina system is often the most-economic choice because of its inherent high activity. In addition, only chloride alumina catalysts have enough activity to economically isomerize butanes. As a result of ongoing intensive research and development in paraffin isomerization technology, UOP's I-80 catalyst is one of the highest-activity chloride alumina catalysts currently available. The I-80 catalyst, is significantly more active than the I-8 catalyst, and is based on a unique formulation and manufacturing technique. By simply reloading the I-80 catalyst in existing reactors, a gain of 0.5–1.0 RON can be realized compared with the product RON when I-8 catalyst is used. Zeolite isomerization catalysts, such as UOP's HS-10™ or I-7™ catalysts, operate at higher temperatures than chloride alumina catalysts. The maximum product octane that can be achieved is limited by the unfavorable equilibrium at these conditions. Yields are also lower as a result of the higher operating temperature and the less elective characteristics of zeolite catalysts. A typical octane upgrade for a once through zeolite isomerization unit is from 70 to about 79 RONC. Higher product octanes (86–88) can be obtained in a recycle operation, such as a TIP™ unit.[11]

Chapter four

Design catalytic reformer

Chapter four

Design catalytic reforming

4.1. Material balance:

Crude flow rate = 1.2 * 10^6 ton/yr

Sweet naphtha flow rate = 18 % of crude flow rate

☐ Naphtha flow rate =

$$\frac{1.2\times10^{6}\times0.18\times10^{3}\times2.2046}{330\times24}=60125\ lb/hr$$

Molar flow rate of naphtha = 60125 / 107.6 = 558.78 lbmol /hr
By using catalytic reforming yield correlations at (K =11.7, R.O.N.C.=98):-

From refinery book
1) [C5+ vol% =82%]
2) [C4 vol% = 6.4%]
3) (6-5): [(C1 + C2) wt% = 2.25%,C3 wt% = 3%]
4) [H2 wt% = 2.8%]

From Kern by tmean = 40 * 1.8 + 32 = 104 f°

∴ ρNaphtha = 0.71 * 62.4 = 44.3 lb/ ft^3

∴ Volume flow rate of Naphtha = 60125 / 44.3 = 1357.22 ft3/hr

∴ Volume flow rate of C5+ = 0.82 * 1357.22 = 1112.92 ft3/hr

At tmean = 104 f° ,and 45° API:

∴ ρC5+ = 0.787 * 62.4 = 49.11 lb/ft3

∴ Mass flow rate of C5+ = 49.11 * 1112.92 = 54655.5 lb/hr

∴ Mass flow rate of (C1 + C2) = 0.0225 * 60125 = 1352.81 lb/hr

∴ Mass flow rate of C3 = 0.03 * 60125 = 1803.75 lb/hr

∴ Mass flow rate of H2 = 0.028 * 60125 = 1683.5 lb/hr

∴ Mass flow rate of C4 = 60125 – (54655.5+1352.81+1803.75+1683.5)

=629.44 lb/hr

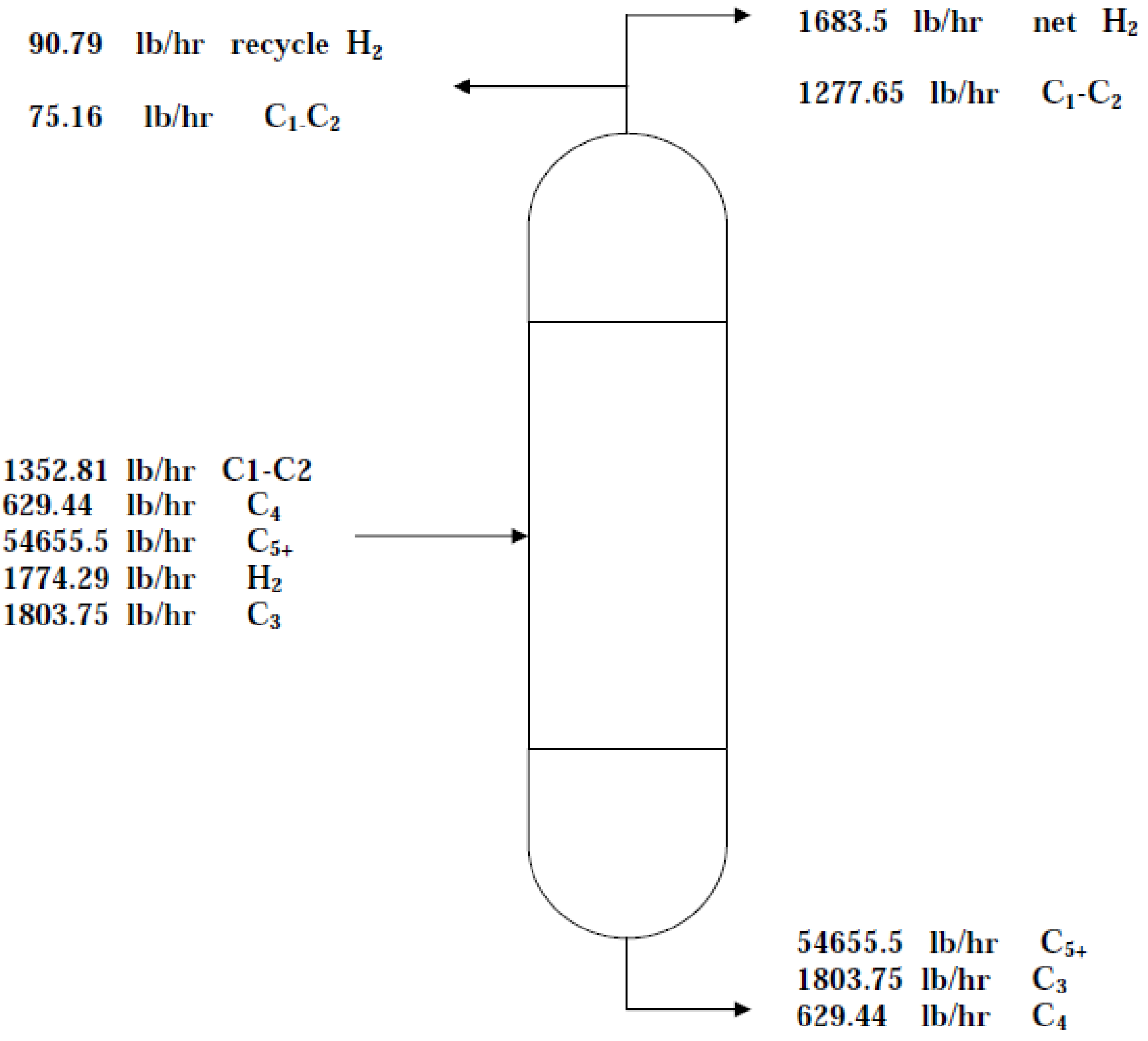
Assume recycle ratio of H2 = 8000 Scf /bbl

= 0.00151 lb H2/lb Naphtha

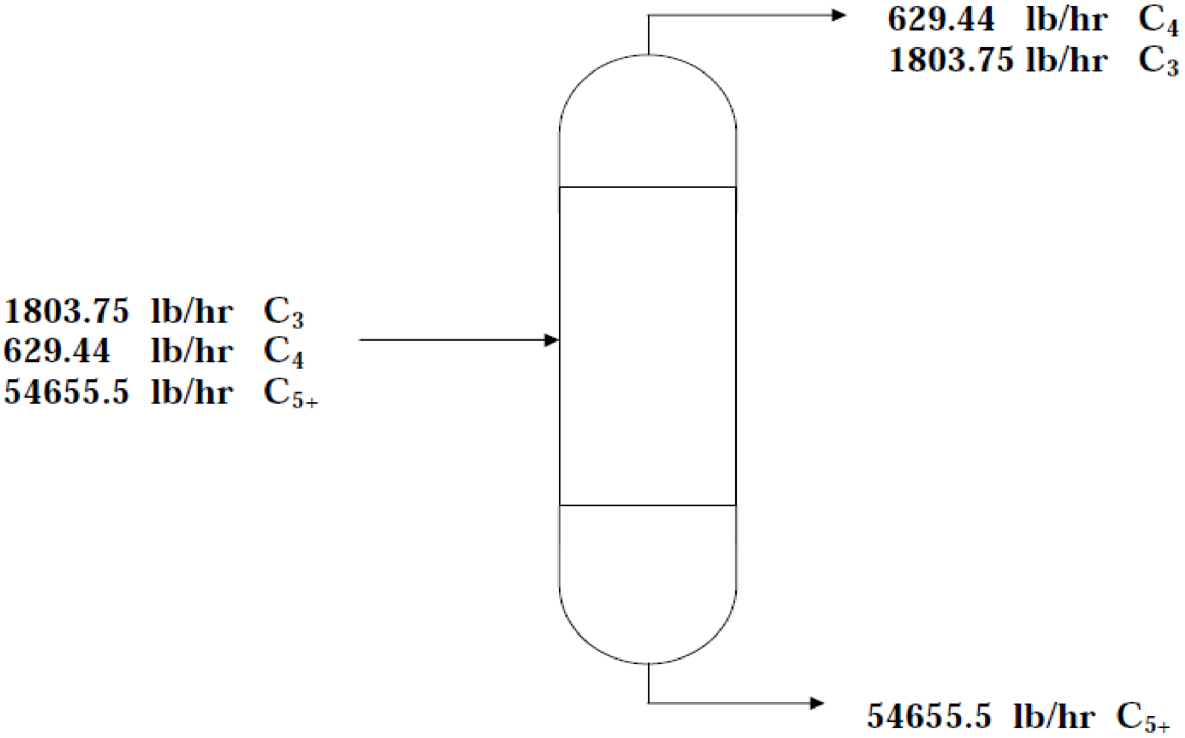
∴ Mass flow rate of recycled H2 = 60125 * 0.00151 = 90.79 lb/hr

∴ Mass flow rate of total H2 = 1683.5 + 90.79 = 1774.29 lb/hr

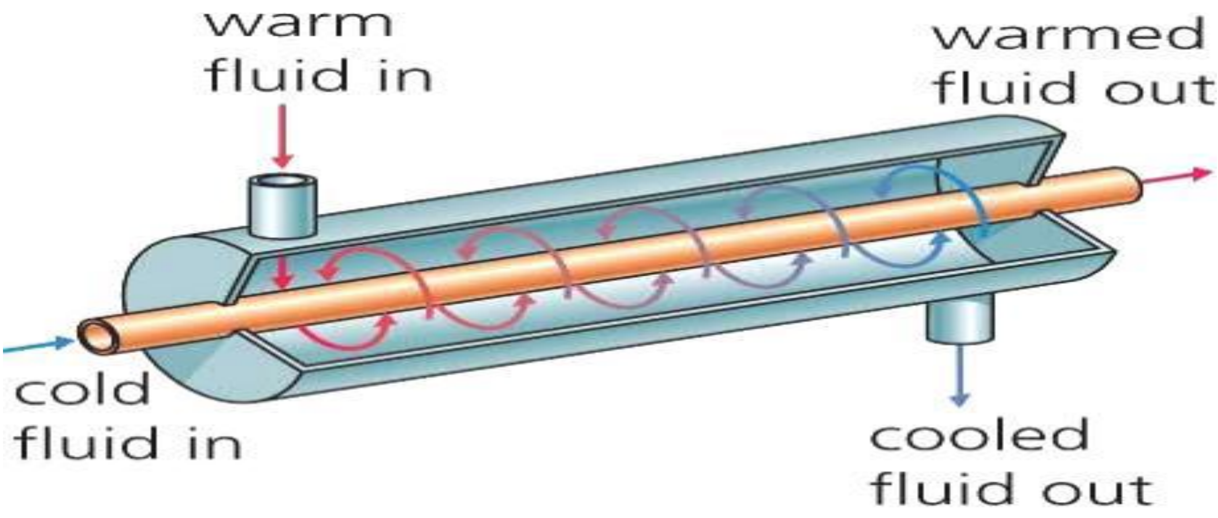
4.2. Material balance on flash drum:



4.3. Material balance on stabilizer:



4.4. Design of heat exchanger:



Data given:

Hot fluid: Vapor from 3rd reactor

m_{vapor}= 60290 lb/hr

T_1=550 ˚f

T_2=250 ˚f

Cold fluid: Naphtha feed

$m_{naphtha}$ = 60125 lb/hr

t_1=100˚f

Design Steps:

Step (1): Heat duty of heat exchanger.

For hot vapors:

1. T_{mean}= (550+250)/2 = 400 ˚f & API= 61.8˚

2. from kern book find physical properties of hot fluid:

From heat transfer book

- a- C_P= 0.545 Btu/lb.˚ f
- b- K= 0.082 Btu/hr.ft.˚f
- c- µ= 0.14*2.42=0.3388 lb/hr.ft
- d- Sp.gr= 0.57

3. Assume 85% of hot vapor amount used to heat naphtha and 15% used to heat recycle H_2 in separated heat exchanger

So M_1= 0.85*60290 = 51246.5 lb/hr

4. Heat duty Q Btu/hr:

$Q = M_1 C_P (T_1 - T_2)$

= 51246.5*0.545*(550-250)

= 8378802.75 Btu/hr

Step (2): Outlet temperature of naphtha feed t_2=? ˚f

for cold fluid :

m_{cold}= 60125 lb/hr

t_1=100˚f t_2= ? ˚f

$Q_{\text{constant}} = m_{cold}\, Cp_c\, (t_2-100)$

$8378802.75=60125\ Cp_c\ (t_2-100)$
$139.356= Cp_c\ (t_2-100)$

Assume t_2 °f	T_{mean} °f	Cp_c Btu\lb.° f	Y=139.356
300	200	0.586	116.6
350	225	0.602	150.5
330	215	0.593	136.39
335	217.5	0.595	139.4 ≈ y

So $t_{2correct}$=335°f and t_{mean}= 217.5 °f , API=61.8°

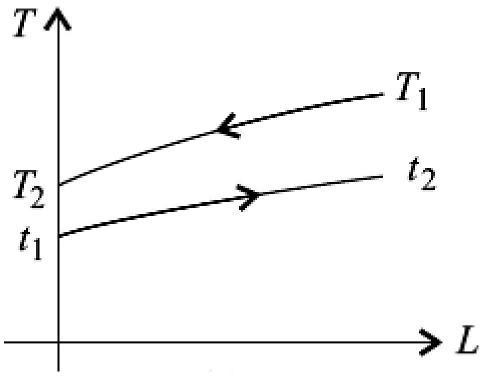
From Kern Book:

- Cpc=0.595 Btu\lb.° f
- Kc= 0.087 Btu\hr.ft.°f
- μc=0.31*2.42=0.7502 lb\ft.hr
- Sp.gr= 0.653

Step (3): L.M.T.D:

Use counter-flow heat exchanger which fluids flow in opposite direction. So rate of heat transfer between two fluids will be

$$\mathrm{LMTD} = \frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1/\Delta T_2)}$$



Hot: T1=550°f T2=250°f
Cold: t1=100 °f t2=335°f
ΔT1=215°f ΔT2=150 °f
LMTD =(215-150)/ln (215/150)
=180.55°f

Correction factor for ΔTlm:

A- Capacity rate ratio:

$$P = \frac{t_2 - t_1}{T_1 - t_1}$$

P = (335-100)/(550-100)
= 0.52

B- The cold-side effectiveness:

$$R = \frac{T_1 - T_2}{t_2 - t_1}$$

R = (550-250)/(355-100)
= 1.1765

[1shell pass and 2 or more tube passes] We found **f=0.9**

$LMTD_{corrected}$ = 0.9*180.55=162.5 ˚f

Step (4): Assuming overall heat transfer coefficient U Btu/ft^2.˚f.hr

From heat transfer book
U Range= (40-75) Btu/ft^2.˚f.hr
Assume **U=57** Btu/ft^2.˚f.hr

Step (5): Area calculation

$A = Q / U * \Delta T_{lm}$
A_{cal} = 8378802.75 / (57*162.5) = 904.6 ft^2

Step (6): Heat exchanger layout

Using floating head heat exchanger for expansion and **[1"O.D , 1.25" P , ΔBWG14, L=16 ft]**

1. Number of tubes required N_{tubes}:

$N_{tubes} = A / (L-0.5) * a_i$
a_i: area of tubes per ft of length ft^2/ft
N_{tubes} = 904.594/ (16-0.5)*0.2618 = 222.92 ≈ 223 tubes

2. Actual no of tubes N_t:

From table heat transfer book

Choosing 4 passes, N_{tubes} = 242 tube, ID_S=24 in

,$N_{tubes/pass}$=242/4 = 60.5 ≈ 61 tubes

Step (7): Velocity inside tubes

Choosing naphtha feed (cold fluid) inside tubes

V= W (lb/hr) /3600*Sp.gr*62.4*$N_{tubes/pass}$*0.003

= 60125/3600*0.653*62.4*61*0.00379

= 1.79 ft/sec < 3 ft/sec

(1) Increase no of passes to 6 passes From table N_{tubes}=232 tubes ,$N_{tubes/pass}$ =232/6=38.6=39 tubes

V=2.81 ft/sec < 3 ft/sec

(2) Increase no of passes to 8 passes

From table at N_{tubes}=228 tubes, $N_{tubes/pass}$= 228/8=28.5=29 tubes

V= 3.79 ft/sec ≈ 3.8 ft/sec

Check: V in range (3-6) ft/sec ok

Choose : N_{tubes}=228 tubes $N_{tubes/pass}$ = 29 tubes,

No of passes =8 ID_s=24 in

Step (8): Tubes side film coefficient (h_{io}):

1- a_t = $N_{tubes/pass}$ * cross section area of tubes(ft^2)

= 29*0.00379

= 0.1099≈ 0.11 ft^2

2- G_t = 60125/0.1099

= 547038.486 lb/ft2.hr

3- Re =G_t*D_i/μ_c

=547038.486*0.0965/0.7502

=50692.23

4- L/D_i=16/0.069=230

5- from heat transfer book by Re, L/D_i

J_H=160

6- h_i = J_H*(K/D_i)*$(\mu * C_p/K)^{1/3}$

= 160*(0.087/0.0695)*$(0.7502*0.595/0.087)^{1/3}$

= 345.4 Btu/ft^2.˚f.hr

7- h_{io} = 345.4*(0.834/1)

=288.076 Btu/ft^2.˚f.hr

Step (9): Shell side film coefficient (ho):

1- assume baffle spacing B= 24 in its range(24"-2")

2- a_s = ID*C*B/144*P , C=0.25 in, P=1.25 in

= 24*0.25*24/144*1.25

= 0.8 ft^2

3- Gs =51246.5/0.8

= 64058.125 lb/ft2.hr

4- Re = G_s*D_e/μ_h

= 64058.125*0.06/0.3388

= 11337.72

5- From heat transfer book by Re, baffle cut Δ,25% **J_H = 57**

6- h_o = J_H*(K/D_e)*$(\mu_h*C_p/K)^{1/3}$

= 57*(0.082/0.06)*$(0.3388*0.545/0.082)^{1/3}$

= 102.1 Btu/ft^2.˚f.hr

Step (10): Fouling resistance R_o,R_i

R_i =reformer charge = 0.0015 from heat transfer book

R_o =reformer effluent = 0.0015

Step (11): Calculation of overall heat transfer coefficient U Btu\ft^2.˚f.hr

(1/u) = (1/hio)+(1/ho)+Ri+Ro

=(1/288.076)+(1/102.1)+0.0015+0.0015

U = 61.48 Btu/ft^2.˚f.hr > U assume =57 Btu/ft^2.˚f.hr so ok

Step (12): Area required and Area available

A-Area required:

A_{req}=Q/U*ΔT_{lm}

=8378802.75/ (61.48*162.5)

$= 838.7\ ft^2$

B- Area available:

$A_{av}=N_t*(L-0.5)*0.2618$

$= 228*15.5*0.618$

$= 925.2\ ft^2$

C- Check: Excess Area % = [(Aav- Areq)/ Areq]*100

= [(925.2-838.7)/838.7]*100

= 10.3% ok in range (10-25%)

Step (13): Pressure drop

A-Pressure drop in Shell side:

$$\Delta P_s = \frac{f(G)^2(D_s)(N_c+1)}{5.22\,(10)^{10}(D_e)(s)(\phi_s)}$$

1- φ_s is neglect

2- Ns+1=L/B =16*12/24=8

3- from heat transfer book at Δ ,25% and Re=11337.72

f=0.00251

4- D_s=ID=24 in ,De=0.06 ft

$$5\text{-}\Delta P_s= \frac{0.00251*(64058.125)^2*24*8}{5.22*10^{10}*0.06*12*0.57}$$

= 0.09231≈0.1 psi < 5 psi ok

B-Pressure drop in tubes side:

$\Delta P_{tubes}=\Delta P_t+\Delta P_r$

$$[1]\quad \Delta P_t = \frac{f*Gt^2*L*N_{passes}}{5.22*10^{10}*D_i*S}$$

a- N_{passes}=8 pass ,L=16 ft

D_i=0.0695 ft, S=0.653

b- from heat transfer book at Re=50692.23

f=0.00017

$$\Delta P_t = \frac{0.00017*(547038.486)^2*16*8}{5.22*10^{10}*0.0695*0.653}$$

= 2.7486 ≈ 2.75 psi

[2] End Return Losses(ΔP_r):

a- from fig.(10-139) by V=3.8 ft/sec , Sp.gr=0.653

Δp_r (fig) = 0.6 psi

b- $\Delta P_r = \Delta p_r$ (fig)* no of passes

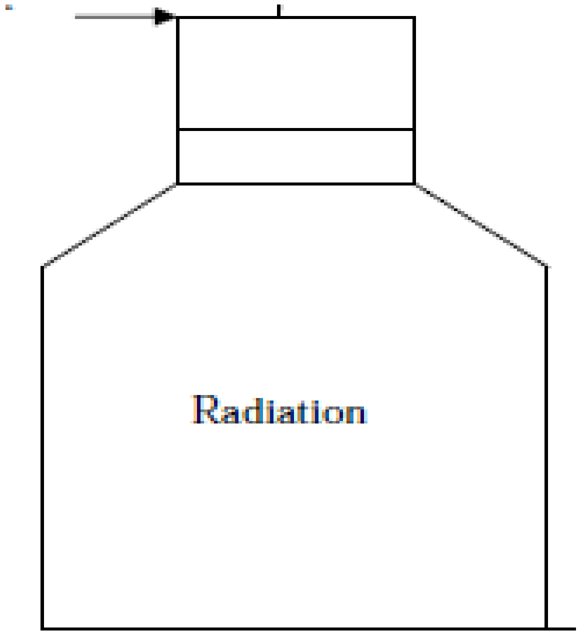
= 0.6*8

= 4.8 psi

$\Delta P_{tubes} = \Delta P_t + \Delta P_r$

= 2.75+4.8 = 7.55 psi < 10 psi check is o.k. [18]

4.5. Design of furnace:



Data given:-

Fluid:-

Heavy sweet naphtha, 61.8° API, Flow rate ($G_{naphtha}$) = 60125 lb/hr,
Boiling range (171-400 F°)
Recycle H_2, Flow rate (G_{H2}) = 90.79 lb/hr
Recycle (C_1 –C_2), Flow rate (G $_{(C1-C2)}$) =75.16 lb/hr
[Total flow rate= 60290.95 lb/hr]
Inlet temperature (t_1) = 871 F°
Outlet temperature (t_2) =1010 F°
Fuel gas, LHV=19700 Btu/lb

Design basis:-

Vertical –cylindrical heater with horizontal –tube convection section.
Excess air, 15%
Average radiant rate, 10000 Btu/hr ft^2

Design steps:-

Step 1:- Efficiency

1- FGT= 871 + 150 =1021 F° [>400 F°] O.K.
2- From fig. (3) Berman:
By excess air =15 %, and FGT = 1021 F°
Ha, FGT = 14733.33 Btu/lb

3- % heat extracted = (14733.33 / 19700) * 100 =74.788%

4- Calculated efficiency = 74.788 - 2
ξ =72.788%

5- At (t_m= (871 + 1010) / 2 = 940.5 F°) of fluid and 61.8 API from Kern obtain its physical properties:-
$Cp_{naphtha}$= 0.765 Btu/lb F° , Cp_{H2}= 3.5 ,$Cp_{(C1-C2)}$ = 0.85

6- Q duty = [60125 * 0.765 + 90.79 * 3.5 + 75.16 * 0.85] *[1010 - 871]
= 6446441.364 Btu/hr
7- Heat fired = 6446441.364 / 0.72788 = 8856461.73 Btu/hr

8- Fuel consumed = 8856461.73 / 19700 = 449.567 lb/hr

9- from fig. (2) Berman:
By excess air =15%, L.H.V=1000 Btu/ft^3

Flue gas / fuel ratio =19.0625 lb-flue/lb-fuel

10-flue- gas flow = 449.567 * 19.0625= 8569.863 lb/hr

Step 2:- Radiant /convection duty split

1-select tube coil having 3 passes of 4 in IPS Sched. 40 [4.5 in O.D. * 0.237 in avg. wall]
2- Fluid mass velocity=
(60125 + 90.79 + 75.16) / (3600 * 3 * 0.0884) = 63.15 lb/s ft^2
O.k. in the range [45-70 lb/s/ft^2]

3-fluid temperature at radiant inlet (t_c)=

$$\frac{t_c - 871}{1010 - t_c} = \frac{5}{12}$$

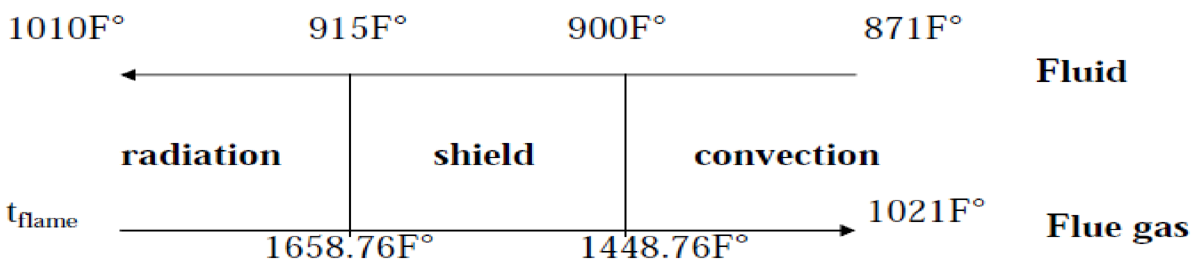
t_c = 911.88 F°

Assume fluid temperature at radiant inlet = 915 F°
4-radiant section average fluid temperature:

$$t_B = \frac{1010 + 915}{2} = 962.5 F^{\circ}$$

5- Radiant section average tube metal temperature:
t_m= 962.5 + 75 = 1037.5 F°

6- Bridge wall temperature (Bwt)
From fig. (6a) Berman by
t_m= 1037.5 F° and aveg. Radiant rate (q_r) =10000 Btu/ft^2 hr
Bwt =1658.76 F



7- from fig. (3) Berman:
By excess air=15% and Bwt=1658.76 F°

H_a,Bwt = 10790 Btu/lb
Q_R =(10790 / 14733.33) * 6446441.364 = 4721071.361 Btu/hr
Q_c= 6446441.364 - 4721071.361 = 1725370 Btu/hr

Step 3:- Furnace layout

1- A_R = (4721071.361 / 10000) = 472.11 ft$_2$

2- Assume 24 radiant tubes on 8 in center

3- Tube circle diameter (TCD) =(24* 8) / (12*π) = 5.093 ft

4- $ETL_{\text{shield bank}}$ = 5.093 – 1 = 4.093 ft ≃ 4.1 ft

5- With 6 tubes per row on 8 in center

6- Shield bank free area = 6* 4.1* ((8 - 4.5) / 12) = 7.175 ft$_2$

7- $g_{\text{flue gas}}$= 8569.863 / (3600 * 7.175) = 0.332 lb/s/ft$_2$

8-surface area of one shield row = 6 * 4.1 * π * (4.5 / 12) = 28.981 ft$_2$

9- Vertical tube radiant surface area= 472.11-28.981 = 443.129 ft$_2$

10-vertical tube radiant length= (443.129 * 12) /(24* π* 4.5) =15.672ft

11-check for L/D ratio = 15.672 / 5.093 = 3.08
O.k. in the range [2-4]

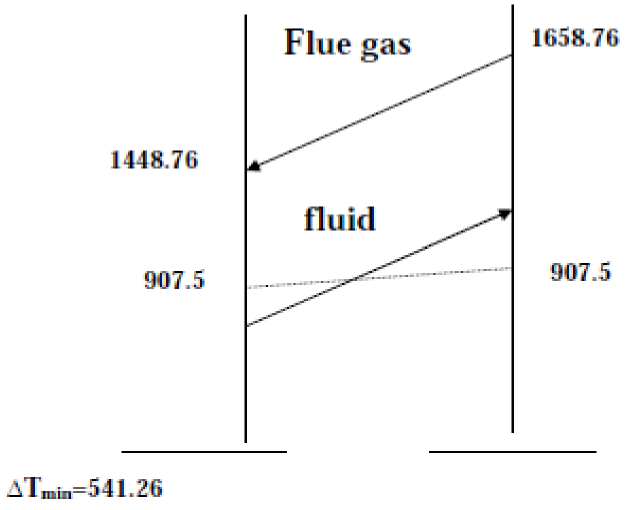
Step 4:- Shield bank

1- Average fluid temperature in shield bank=(915 + 900) / 2 =907.5 F

2- $$\Delta T_{lm} = \frac{751.26 - 541.26}{Ln(\frac{751.26}{541.26})} = 640.53 F^{\circ}$$

3-T_{ga} = ((1658.76 + 1448.76) / 2) + 460 = 2013.76 R°

ΔT_{max}=751.26



4-

$$h_c = \frac{2.14 * (0.332)^{0.6} * (2013.76)^{0.28}}{(4.5)^{0.4}} = 5.0925 \frac{Btu}{ft^2 F^\circ hr}$$

5-h_{rg} = 0.0025* (2013.76 - 460) - 0.5 = 3.3844 Btu/ft^2F°hr

6- h_0 =1.1 * (5.0925 + 3.3844) = 9.3246 Btu/ft^2F°hr

7-determine physical properties of fluid at $t_{avg.}$= 907.5 F°

Cp_{mix}= 0.754 Btu/lb F°

K_{mix}= 0.07 Btu/ft^2F°hr

M_{mix}= 2.42 * 0.03 = 0.0726 lb/ft hr

8- Re = (63.15 * 4.5 * 3600) / (0.0726 * 12) = 1174276.86

P_r= (0.754 * 0.0726) / 0.07 = 0.782

$$h_i = 0.027 * (1174276.86)^{0.8} * (0.782)^{0.333} * \frac{12 * 0.07}{4.5}$$

$$h_i = 333.185 \frac{Btu}{ft^2 F^\circ hr}$$

9- h_w= 324 / 0.237 = 1367 Btu/ft^2F° hr

10- R_i= (4.5 / 4.026) * (1 / 333.185) = 0.00335

R_0= 1 / 9.3246= 0.1072

R_w= (4.5 / 4.026) * (1 / 1367) = 0.000818

R_t= 0.00335 + 0.1072 + 0.000818 = 0.1114

U_{shield}= 1 / 0.1114 = 8.975 Btu/ft^2F° hr

11- A_{sh}= 3 * 28.981 = 86.943 ft^2

12- Q_{shield} = 8.975 * 86.943 * 640.53 = 499814.158 Btu/hr

13- Check of flue gas temperature above shield bank
$H_{a,shield}$= [(4721071.361 + 499814.158) / 4721071.361] * 10790
= 11932.324 Btu/lb
By $H_{a,shield}$=11932.324 Btu/lb and excess air=15%
From fig.(3) Berman T_{sh}=1475 F° O.k. ≃ (BWT - 210) = 1448.76 F°

Step 5:- convection section

1-$Q'_{c\ pure}$=1725370 - 499814.158 = 1225555.842 Btu/hr

2- $$\Delta T_{lm} = \frac{548.76 - 150}{\ln \frac{548.76}{150}} = 307.44\ F^{\circ}$$

3-try 3 fins/in with each 3/4in high *0.05in thick (A_t=7.33 ft^2/ft)

4-fin bank free area

$$= 6 * 4.1 * \left[\frac{8 - 4.5}{12} - \frac{2 * 0.05 * 0.75 * 3}{12}\right] = 6.7138\ ft^2$$

5-$G_{flue\ gas}$= 8569.863 / 6.7138=1276.464 lb/ft^2hr

6- Determine physical properties of flue gas at
$T_{avg.}$=(1448.76 + 1021) / 2= 1234.88 F°
M= 0.1 lb/ft hr, Cp= 0.268 Btu/lb F° , K= 0.037 Btu/ftF° hr
7-Re= (1276.464 * 4.5) / (12 * 0.1) = 4786.74

8- From fig. (7) by Re= 4786.74
J= 0.013

9- $$h_0 = \frac{0.013 * 0.268 * 1276.464}{\left(\frac{0.1 * 0.268}{0.037}\right)^{\frac{2}{3}}} = 5.578\ \frac{Btu}{ft^2\ F^{\circ}\ hr}$$

10-From fig. (8) by KT= 1.35 ,H= 0.75 in and h_0= 5.578 Btu/ft^2F° hr

ξ_{fin} = 84%

11- $h_{o(eff.)}$ =

$$\frac{5.578}{7.33} \times (0.84 \times (7.33 - \frac{\Pi \times 4.5}{12}) + \frac{\Pi \times 4.5}{12})$$

$$\therefore h_{o(eff.)} = 4.829\ \frac{Btu}{ft^2 F^{\circ} hr}$$

12- R_o= (1 / 4.829) = 0.2071
R_i = (7.33 / 1.054) * (1 / 333.185) = 0.02087
R_w = (7.33 / 1.054) * (1 / 1367) = 0.005087

∴ R_t = 0.2071 + 0.02087 + 0.005087 = 0.23305

∴ $U_{conv.}$ = (1 / 0.23305) = 4.291 *ft F hr*

13- $A_{conv.} = \frac{1225555.842}{4.291 \times 307.44} = 929.0056\ ft^2$

14- Surface area per convection row = 6 * 4.1 * 7.33 = 180.318 ft^2

15- Number of finned rows = (929.0056 / 180.318) = 5.15

∴ Number of finned rows = 6 rows

Step 6 :- Stack design:

Size stack for mass velocity of 0.8 $\frac{Lb}{sft^2}$ at 125% of design gas flow

Cross-sectional area $= \frac{1.25 \times 8569.863}{3600 \times 0.8} = 3.72\ ft^2$

□ Stack diameter (D) $= \sqrt{\frac{4 * 3.72}{\Pi}} = 2.176\ ft$

Assume average gas temperature in stack = 1021 – 75 = 946 f$^\circ$
Assume stack-exit gas temperature = 871 f$^\circ$
Draft under arch = 0.05 in

At $t_{avg.}$ = 1553.76 f$^\circ$ in shield-bank of flue gas,

∴ ρ_{flue} =0.007 lb/ft^3
Shield-bank loss = 3 * 0.2 * 0.003 * $(1.2 * 0.332)^2$ * (0.33 /0.007)

∴ Shield-bank loss = 0.0147 in
At $t_{avg.}$ =1234.88 f$^\circ$ in convection of flue gas,

∴ ρ_{flue} = 0.0088 lb/ft^3
Fin-bank loss = 6 * 1* 0.003 * $(1.25 * (1276.464/3600))^2$ * (1276.464/(3600*0.0088)) = 0.14247 in

At $t_{avg.}$ = 946 f° in stack of flue gas,

∴ $\rho_{flue} = 0.025$ lb/ft^3

Stack-entrance loss = 0.5 * 0.003 * $(0.8)^2$ * (0.8/0.025) = 0.03072 in

Damper loss = 1.5 * 0.003 * $(0.8)^2$ * (0.8/0.025) = 0.09216 in

At $t_{avg.}$ = 871 f° in stack exit of flue gas,

$\rho_{flue} = 0.03$ lb/ft^3

Stack-exit loss = 1 * 0.003 * $(0.8)^2$ * (0.8/0.03) = 0.0512 in

Subtotal = 0.0147 + 0.14247 + 0.03072 + 0.09216 + 0.0512 + 0.05

Subtotal = 0.38125 in

Convection-section draft gain=

$$0.52 \times 4.3 \times 14.69 \times \left[\frac{1}{540} - \frac{1}{1694.9}\right] = 0.04145\ in$$

The required stack draft = 0.38125 – 0.04145 = 0.3398 in

Stack draft gain/ft

$$= 0.52 * 1 * * 14.69\left[\frac{1}{540} - \frac{1}{1406}\right] = 0.00871\ in$$

$$\text{Stack fractional loss} = \frac{(0.8)^2 \times 1406}{211000 \times 2.176} = 0.00196\ in$$

Net stack effect/ft = 0.00871 – 0.00196 = 0.00675 in

Stack height required = (0.3398 / 0.00675) = 50.34 ft

Step 7:- Fluid pressure drop:-

1- For (Convection + Shield) :-

$N_{passes,shield}$ = 6 / 3 = 2 passes

N_{row} = 3 + 6 = 9 rows

L_e = 2 * 9 * (4.1 + 1.5) + (2 * 9 – 1) * 50 * (4.026 / 12) = 385.975 ft

2- For (Radiation) :-

$N_{passes,rad.}$ = 24 / 3 = 8 passes

L_e = (8 – 1) * 50 * (4.026 / 12) + 8 *15.672 = 242.8 ft

3- For (Crossover) :-

L_e = 2 * 4.1 + 3* 30 * (4.026 / 12) = 38.395 ft

4- $L_{e,total}$ = 385.975 + 242.8 + 38.395 = 667.17 ft

5- By t_{avg} = (871 + 1010) / 2 = 940.5 f° of fluid ,
sp.gr = 0.03, and μ= 0.0726 lb/ft hr

6- $Re = \frac{4.026 \times 63.15 \times 3600}{12 \times 0.0726} = 1050586364$

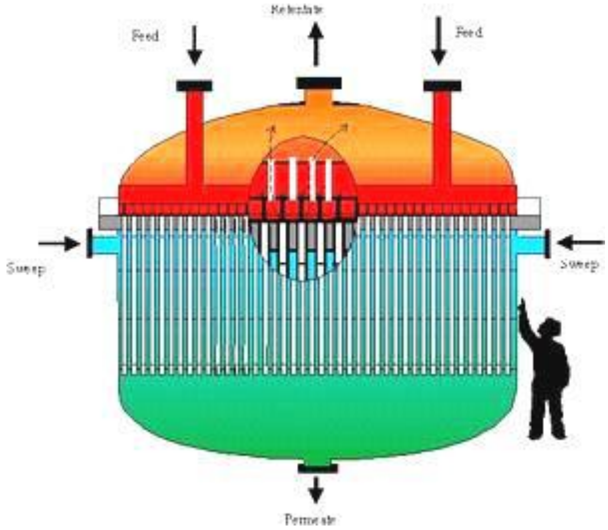
7- f = $(0.117 / (1050586.364)^{0.25}) = 0.00365$

8- $\Delta P = \frac{0.00517 \times 0.00365 \times (63.15)^{2} \times 667.17}{62.4 \times 0.03 \times 4.026}$

ΔP = 6.662 psi

9- $\Delta P_{act.}$ = 1.25 * 6.662 = 8.33 psi

4.6. Design of reactor:



Data Given and Calculated

Naphtha Feed Mw. = 112 (C_8H_{16})
Naphtha Density = 755 (56 °API)
Hydrogen recycle = 8000 scf H_2/bbl naphtha
= 0.186 mol H_2/kg naphtha
Naphtha Feed = 60,000 lb/hr = 18288.2 kg/hr
= 217717 mol/hr

Design Procedure

Recycle H_2 = 0.186 x 18288.2 = 3402 mol H_2/hr

F_{Ao} = 3402 + 217717 = 221119 mol/hr …………………….(1)

For basis of 1 hr, and isothermal reactor
$n_{XA=0} = 221119$ mol

$n_{XA=1} = 3402 + 4 \times 217717 = 874271$ mol

$$\varepsilon_A = \frac{n_{XA=1} - n_{XA=0}}{n_{XA=0}} = \frac{874271 - 221119}{221119}$$

$$\varepsilon_A = 2.95 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

* Volume at $X_A=0$ (T=798 °K and P=30 atm)

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{221119 \times 1 \times 22.4}{1000 \times 273} = \frac{V_2 \times 30}{798}$$

Hence, V = 482.61 m^3

Hence, **C_{Ao} = (221119/482.61) = 458 mol/m^3 ……………(3)**

From **(1), (2), (3), I n (*)**

V = 0.105 (1 + 2.95) (221119/458) = 200 m^3

Using the assumption of L = 3D for the reactor
200 m^3 = $(3\pi/4)\, D^3$
D = 4.3 m
L = 12.9 m

Notes

The reactor volume seems to be very large for :

- The massive flow rate of naphtha.
- The small assumed M.wt of 112 of naphtha feed that led to the high no. of moles in the gaseous phase which led to the high volume of feed.

If the presence of hydrogen in the feed is neglected, the volume of the reactor would be 150 m^3 and (D = 4 m , L = 12 m) **[18]**

4.7. Design of stabilizer:

Component	Flow rate lb_{mole}/hr	X_f	X_d	X_b
H_2	0.0462	0.0000743	0.0004125	0.000
C_1	16.910	0.02719	0.15098	0.000
C_2	36.108	0.05807	0.32293	0.000
C_3	40.904	0.06578	0.36521	0.000
$i\text{-}C_4$	4.164	0.0067	0.037179	0.000
$n\text{-}C_4$	6.650	0.01070	0.051817	0.000867
$i\text{-}C_5$	16.470	0.02648	0.04234	0.02269
$n\text{-}C_5$	11.060	0.01770	0.02966	0.01518
C_6^+	489.50	0.7872	0.000	0.96126
summation	621.81	1.000	1.000	1.000

Flow rate of naphtha = 621.81 Kg_{mol} / hr

- Feed API = 50 ~ 53°
- Yield = 83% by vol.
- Feed temperature =164 $_{o}$C.
- Top temperature = 86 $_{o}$C .
- Bottom temperature = 243 $_{o}$C.

- Top pressure = 1 atm
- Bottom pressure = 2 atm .

Design steps :

Step (1)

F= 621.81 Kg_{mol} / hr.

Total Material Balance :-

F = D+B

Individual Material Balance on the component :-

$FX_f = DX_d + Bx_B$.

621.81 (0.0000743) = D (0.0004125) + 0

D= 112.00117 Kg_{mol} /hr

B=509.8088 Kg_{mol} / hr.

Step(2):

Light key is (n-C_4).

Heavy key is (i-C_5).

Feed enters at boiling point ;-

q = 1

Feed properties

Composition	Boiling Pt. (°F)	P_i° (psia)	Heat of vaporization KJ / Kg.	α_i
C_3	-43.474	1000	425.5	2.564
i-C_4	11.048	800	365.56	2.0513
n-C_4	31.352	650	385.79	1.667
i-C_5	82.4	390	342.1	1
n-C_5	97.16	290	357.1	0.744
C_6^+	244.04	50	292.6	0.1282

By using underwood's shortcut method to calculate the minimum reflux ($R_{min.}$)

$$1 - q = \sum_{i=1}^{n} \frac{\alpha_i \, x_{if}}{\alpha_i - \theta}$$

$$R_{min} + 1 = \sum_{i=1}^{n} \frac{\alpha_i \, x_{id}}{\alpha_i - \theta}$$

Solution :-

$\theta = 1.268$

$R_{min} = 1.1$

Calculation of the minimum number (N_{min}) of theoretical plates by the Fenske equation :-

$$N_{min} = \frac{\log \left[\dfrac{X_{dLk}}{X_{dhk}} \quad \dfrac{X_{bHk}}{X_{bLk}} \right]}{\log \left[\dfrac{\alpha_{Lk}}{\alpha_{Hk}} \right]}$$

$N_{min} = 17.6$

$R_{op} = 1.2\, R_{min}$, $R_{op} = 1.32$

To calculate theoretical number of plates :

By using Gilliland correlation relating number of stages to reflux ratio :

$Y = 0.608295 - 1.1893X + 0.332227X^{2} + 0.532489X^{3} - 0.347484X^{4}$

Where:

$X = (R_{opt} - R_{min}) / R_{opt} = 0.16667$

$Y = (N_t - N_{min}) / (N_t - 1) = 0.4935$

If take plate efficiency $\eta = 50\%$

$N_{theor} = 18.2$ plate .

$N_{act} = N_{thoer} / \eta = 18.2 / 0.5 = 36$ trays

By Gilliland–Eduljee method **:**

$Y = 0.75 - 0.75X^{0.5663}$

$= 0.4783$

$N_{theor} = 19.365$ plate .

If take plate efficiency $\eta = 50\%$

$N_{act} = N_{thoer} / \eta = 19.365 / 0.5 = 39.27 = 40$ trays**Step (3) :**

To calculate the tower diameter and tower height :

(1)Tower height (Z):

Z = no. of trays * H / 12 + 2*5

H = 24 in

Z = 40 * 24/12 + 2 * 5 = 90 ft.

2) Tower diameter (D) :

P =latm , T_D=86$_o$C.
V_D = 359 * (460+86)/(460+32)* 1/1
V_D = 398.4 ft3 /lb$_{mol}$
V_D = 398.4 * 259.84=103520 ft$_3$ / hr.
L =RD
V = D (R + 1) = 259.84 ft$_3$ /hr.
ρ_L =48.1 Ib / ft$_3$
ρ_v = 0.8 Ib / ft$_3$
$V_{c.s}$ =K ((ρ_1 - ρ_v) /ρ_v)$_{1/2}$
K = 0.16 from (Fig 2)

$V_{C.S}$ = 1.23 ft./sec.
$V_{C.S\ Design}$ = $V_{C.S\ Max.}$ / 1.15 = 1.07 ft./sec.
A = V/v = 26.879 ft.$_2$
D = (4A / π)$_{½}$ = 5.85 ft.
standard D= 6 ft

Sieve Tray design :

Given data :

D = 6 ft. , H = 24 in. , L = 1650 Gpm
From (Fig 3)
Type of flow is double pass.

Advantages of sieve tray :

(1)lower pressure drop than bubble cap tray
(2)performance and design is more simple
(3) stability condition is achieved on each tray

[1] Down flow area :

A_{df} / A_T = 20%
A_{dc} / A_T = 10%
A_{dc1} / A_T = 0.05
A_T = π/4 D$_2$
A_T = 28.274 ft$_2$
A_{dc1} = 0.05 * 28.274 = 1.4137 ft$_2$
L_{w1} / D = 0.59
d_{wl}/D = 0.097
L_{wl} = 42.48 in , d_{wl}= 6.984 in
A_{dc2} /A_T =0.45

A_{dc2} = 28.274 (0.45) =12.7233 ft_2
L_{W2} / D = 0.997 ,d_W /D = 0.461
L_{w2}=0.997*6*12=71.784 in
d_W =0.461 (6) *12=33.192 in
d_{w2} = D - 2d_w
d_{w2} = 4* 12 – 2 (33.192) = 5.616 in

[2] Effective area :

assume :
α =2 in, x = 5in , y = 3in
D_n' = D - 2 α
=12*6-2(2)
D_n' = 68 in
A_n' = $\pi/4(D_n)^2$ =3631.68 in^2
d_{wl}' = d_{wl} + y-a
d_{wl} '= 6.984 +5-2
d_{wl} ' = 9.984 in
d_{wl} '/D_n ' = 9.984/68 = 0.1469
From Ludwig Fig (5-4)
A_{dcl}' /A_n' = 11.5%
A_{dcl}' = 0.115(3631.68) =417.64 in_2 =2.9 ft_2
A_{dcs}' /A_n' = 0.45
d_w' / D_m' = 0.461
d_w' = 0.461 (68) =31.348 in
d_{w2}' = D_n' – 2 (d_w')
= 68 - 2(31.348) = 5.304 in
L_{w2}' = 0.997 (68) = 67.796 in
d_{w3}' = d_w' + 1/2 d_{w2}'
= 31.348 + 1/2 (5.304)
d_{w3} '= 34 in
d_{w3}'/A_n' = 0.5 from Ludwig - fig (8-48)
A_{dc3}' /A_n'= 0.5
A_4 = A_n' * 2 (A_{dc3}' / A_n' - A_{dc2}' / A_n')
A_4 = 0.1 (3631.68) =363.168 in_2
A_{eff} =A_n '-2A_{dcl}' - A_4' -2 (L_{w2}' * x)
A_{eff} = ((3631.68)-2 (417.64)-363.168 -2 (67.796*2))
A_{eff} = 2162.408 in_2=15.0142 ft_2

[3] Liquid distribution area :

A_{dis} = 2(L_{W1} *5/12)+2(LW_2*5/12)

=2(3.54 * 5)+2(67.796 * 5)
A_{dis} = 890.36 in$_2$ = 6.183 ft$_2$
Distribution area percent: 21.867%

[4] end westage area :

$A_{west} = A_T – A_{dc} – A_{liq} – A_{eff}$
= 28.274 – 0.2 *28.274 -6.183 -15.01422
A_{west} = 2.822 ft$_2$

[5] Check on residence time (T_R):

$T_R = (A_{d.c} * H * 37.4)/L$
T_R = (5.655 * 24 * 37.4) / (1650/2)
T_R = 6.152 sec > 5 sec

[6] Hole size (do) and spacing (c):

d_o = 3/16 in$_2$
c =2.5 d_o

[7] Tray thickness (t) :

t = 1/4 in$_2$

[8] % of hole area (□) :

assume β =12.8 % (very small diameter)From ludwig fig (5-5)

[9] Height of weir(hw) :

Assume h_w = 1 in
$h_{ow} = 0.092((L/2)/l_{w2})_{2/3}$
h_{ow} = 0.4867 > 1/4 in liq so, it's good liquid distribution
assume h_{Ls} = 1.75 in

[10] Minimum hole velocity (Fsmin) "weeping" :

1) d_o/t = 0.75
from (Fig. 5-6)
c_o = 0.837 in.
2) calculate dry pressure drop (h_{dt}) :

$$h_{dt} = 0.003\, \bar{f}_s^{\,2} * (\rho_w / \rho_l)\ \bar{(}(1-\beta^2) / c_o^{\,2})$$
$$= 5.476 * 10^{-3}\, f_{smin}^{\,2}$$

3) effective head (h_e) :
assume h_e = 1.7
4) total wet pressure drop on tray (h_t) :
$h_t = h_{dt} + h_e$

Then by using - Fig(5-7) $F_{s\ min} = 16$

[11] Max ... Hole velocity (Fs max) " Flooding ":

1- assume $F_{s\ max} > 16$

where $F_{s\ max}$ at $H_d = 1/2\ (H+h_w)$.

2- $H_d = H_t + h_{1s} + h_{du}$

$h_{hu} = 0.56\ ((L/2) / 449\ (Ad))_2$

$h_{du} = 0.031$ in

$H_d = h_t + 1.8$

3- assume $h_e = 1.5$ in

4-$h_{dt} = 5.476 * 10_{-3}\ F_{2s\ max}$

$F_{s\ max} = 47$ at $H_d = 1/2\ (24+1) = 12.5$

[12] Design hole velocity - (Fs design):-

$F_{s\ design} = (\ F_{s\ min} + F_{s\ max}\ ) /2$

$F_{s\ design} = 31.5 = 32$

$V_{o\ design} = F_s / \rho_{v1/2} = 32/0.8_{1/2}$

$= 35.78$ ft/sec

[13] Number of holes available on the tray :-

$V = N*(\pi/4)*(d_{o2}/144)*v_0$

N= 2360 holes

From fig available no of holes =2860 holes

Excess no of holes =2860-2360=500 hole

Excess area =500/4.62 =108.225 in_2

[14] Total wet pressure drop (hi) :-

$F_{sdesign} = 32$, $h_e = 1.2$

$h_{dt} = 5.476 * 10_{-3}\ f_{s2}$

$h_t = h_{dt} + 1.5$

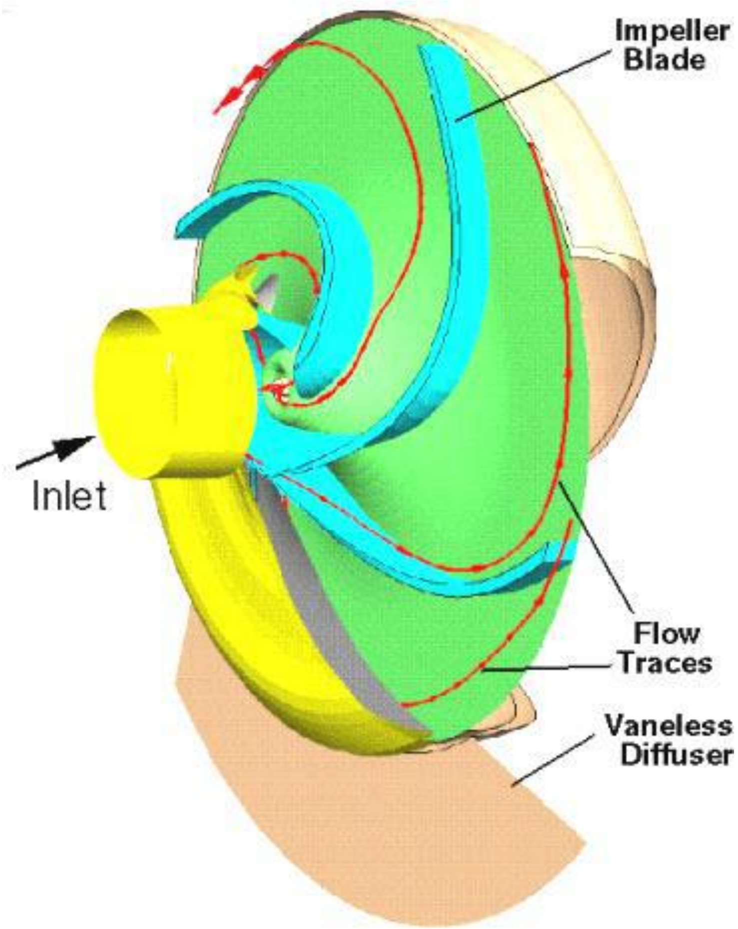
$= 6.81$ in. liq

[15] Pressure drop for tray (Δ p) :

$\Delta p = (\ h_t * \rho_L\ ) / (12*144)$

$= 0.189$ psi < 0.2 psi **[18]**

4.8. Design pump:



Data: -

m_f = 60125 Lb/hr
API = 61.5
T = 40 C° = 104 °f
Total dynamic head = 49 m = 161 ft

Design steps:-

from kern charts by T = 104 °F , API = 61.5 find specific gravity =0.71

density = 0.71 * 62.4 = 44.3 Lb / ft^3
Q= mass flow rate / density
= 60125 / 44.3 = 1357 ft^3/hr
= 1357 * 7.48 / 60 = 169.2 G.P.M

Step(1) :calculation of specific speed(N_s)

- it should to be in the range (500-3000)
- assume N= 2900 r.p.m in the range of (1450-2950).
- N_s= N *$(Q)^{0.5}$ / $(H)^{0.75}$
= 2900* $(169.2)^{0.5}$/ $(161)^{0.75}$
= 834 r.p.m (in the range so it is ok)

Step(2): calculation of manometric efficiency (η_{man})

from chart(1.1) by using NS = 834 r.p.m , Q = 169.2 G.P.M
find $\eta_{overall}$ = 64.5%
-assume η_{mech} from range (70% - 90%) take it = 75 %
- η_{man}= $\eta_{overall}$ $\eta_{overall}$ / η_{mech}*100
= 64.5 / 75 * 100
= 86 %

Step(3): Calculation of inlet and outlet diameter of plate (D_1,D_2)

-assume (n) from range (0.1-0.4) take it = 0.1
- n= B_1/D_1 so B_1=0.1 D_1
- assume (D_2/D_1) from range (1.5 – 3) take it = 2.7
- so D_2= 2.7 D_1
-assume (Ψ) from range (0.1-0.3) take it =0.15
- $V_{F2} = \Psi * (2 * g * H)^{0.5}$
$=0.15 * (2 * 32.2 * 161)^{0.5}$
= 15.28 ft / sec
$V_F = V_{F1} = V_{F2}$ = 15.28 ft / sec
- Q = π* B_1 *D_1 * V_{F1}
1357/3600 = π* (0.1 D_1) * D_1 * 15.28
D_1 = 0.28 ft
= 3.36 in
D_2 =2.7 * 0.28
=0.756 ft
=9.027 in

Step(4) : Calculation of inlet and outlet width of impeller (B_1,B_2)

- Q = π* B_2 * D_2 * V_{F2}
B_2 = 1357 / (π* 0.756 * 15.28 * 3600)

$= 0.01$ ft

$= 0.125$ in

- $B1 = 0.1 * 0.28$

$=0.028$ ft

$=0.336$ in

Step (5) : Calculation of inlet and outlet tangential velocity (U_1,U_2)

- $U_1 = (\pi * D_1 * N) / 60$

$= (\pi * 0.28 * 2900) / 60$

$= 42.52$ ft / sec

- $U_2 = (\pi * D2 * N) / 60$

$= (\pi * 0.756 * 2900) / 60$

$= 114.8$ ft / sec

Step (6) : calculation of inlet and outlet wirl velocity (V_{W1}, V_{W2})

- V_{W1} = zero
- $V_{W2} = (H * g) / (U2 * \eta_{man})$

$= (161 * 32.2) / (114.8 * 0.86)$

$=52.5$ ft /sec

Step (7): calculation of pump's angles

a) absolute outlet angle calculation (β) :-

- $\beta = \tan^{-1} (V_{F2} / V_{W2})$

$= \tan^{-1} (15.28 / 52.5)$

$=16.23^{o} (< 20^{o})$ so it is ok .

b) plate angle at outlet calculation (α) : -

$\alpha = \mathrm{Tan}^{-1} (V_{F2} / (U_2 – V_{W2}))$

$= \mathrm{Tan}^{-1}(15.28 / (114.8 – 52.5))$

$= 13.8^{o} (< 90^{o})$ so it is ok .

c) plate angle at inlet calculation (θ) : -

$\theta = \mathrm{Tan}^{-1} V_{F1} / U_1$

$= \mathrm{Tan}^{-1} (15.28 / 42.52)$

$= 19.8^{o}$ in range (20^{o} - 45^{o}) nearly satisfy.

Step (8): check on design

a)speed ratio(ϕ) must be in range (0.95 – 1.25) : -

- $\phi = U_2 / (2 g H)^{1/2}$

$=114.8 / (2 * 32.2 * 161)$

$=1.127$ in range (0.95 - 1.25) so it is ok .

b) $N_{MIN} < N_{ASSUMED}$: -

$$N_{min} = \frac{120 * \eta_{man} * V_{W2} * D_2}{3.1416*(D_2^2-D_1^2)}$$

$= 2645$ r.p.m (< 2900) so it is ok .

Step(9): calculation of horse power required(HP)

$HP = \gamma Q H / 75\ \eta_{overall} *3600$

$= 5$ HP (standardized) **[18]**

4.9. Design of compressor:

Data given: -

- suction pressure $(P_1) = 14.7$ psia
- final pressure $(P2) = 205$ psia
- suction temperature $(T_1) = 85$ ˚F
- air flow rate $m_{air} = 5100$ lb / hr
- pressure drop of inter cooler $(\Delta P) = 5$ psia
- cooling water temperature $(T_w) = 90$˚F

Design steps:-

Step (1): Calculation of compression ratio (R_{Ct})

$R_{Ct} = P_2/P_1$

$= 205/14.7$

$= 13.9 >> 5$

- So we must divide the compressor to multi stage.

Step (2): calculation of number of stage (n)

$R_{ci} = (R_{ct})^{(1/n)}$

$= (13.9)^{0.5} = 3.72$ (in range (3 - 5) so it is ok)

- So there are two stages.

Step (3): Calculation of discharge pressure

a)Discharge pressure for the first stage(P_{12}) : -

$\mathbf{P_{12}} = (R_{ci} * P_1) + (\Delta P / 2)$

$= (3.72 * 14.7) + (5 /2)$

$=57.2$ psia

b) Inlet pressure for the second stage (P_{22}): -

$\mathbf{P_{22}} = P_{12} - \Delta p/2$

$= 57.2 - 5$

$= 52.2$ psia

$R_{CI} = P_{12} / P_1$
$= 57.2 / 14.7$
$=3.91$

$R_{c2} = P_2 / P_{22}$
$= 205 / 52.2$
$=3.92$
CHECK: is ok

Step (4): Calculation of outlet final temperature

- from table (12.1) find k for air $k_{air} = 1.4$

$T_F = T_1 * R_C^{(K-1)/K}$
$= (85+460) * 3.9^{(1.4-1)/1.4}$
$= 804\ ^\circ R = 344^\circ F$ (<350 ˚F) SO IT IS OK

Step (5): Calculation of capacity at actual condition (Q_{a1}, Q_{a2})

$Q_s = 5100 / 0.0766$
$= 66580$ SCF/hr
$= 1.6$ MMSCFD

a) for first stage :-

Q_{a1} (at 14.4 Psia, T1=85˚F) $= 1.96314 * 10^{-3} * Q_S * (T_i+460)$
$= 1.96314 * 10^{-3} * 1.6\ (85+460)$
$= 1.71$MMSCFD

b) for second stage :-

Q_{a2} (at 14.4 Psia, T =100˚F) $= 1.96314 * 10^{-3} * 1.6 * (100+460)$
$=1.76$ MMSCFD

Step (6): calculation of Brake horse power

- from figure (7 -2) by known (Rc =3.9, K= 1.4) find BHP/MMCFD=88

a) For first stage:-

$(BHP)_1 = Q_{a1}$ * BHP/MMCFD (@14.4 Psia, T=85˚f)
$= 1.71 * 88$
$=150.5$ HP

b) For second stage:-

$(BHP)_2 = Q_{a2}$ * BHP /MMCFD (@14.4 Psia, t = 100˚f)
$=1.76 *88$
$= 154.9$ HP

- total Brake horse power $= (BHP)_1 + (BHP)_2$
$= 305.5$ BHP

- standardized $(BHP)_{total} = 350$ HP

$BHP)_{1st} = BHP)_1 * BHP)_{st} / BHP)_t$
$= 150.5 * 350 / 305.5$

= 173

BHP)$_{2st}$ = BHP)$_{2}$ * BHP)$_{st}$ /BHP)$_{t}$

= 154.9 * 350 /305.5

= 177

Step (7): Cylinder selection of size for each stage

PDEV = HP * 10^4 / (BHP/MMCFD)(P_i – 0.5)

a) for first stage:-

PDEV)$_{1}$= 173 *10^4 / 88(14.7 - 0.5)

= 1385 CFM

- from table (7 – 1) single stage horizontal type try to use cylinder of PD = 1410 CFM

EV % = 100 – R_c – V_{pc} ($R_c^{1/k}$ – 1)

= 100 – 3.9 – 24 ($3.9^{1/1.4}$ – 1)

= 56.65 %

PDEV)$_{1st}$ = 1410 * 0.5665

= 800 CFM

b) for second stage : -

PDEV)$_{2}$= 177 *10^4 / 88(52.5 - 0.5)

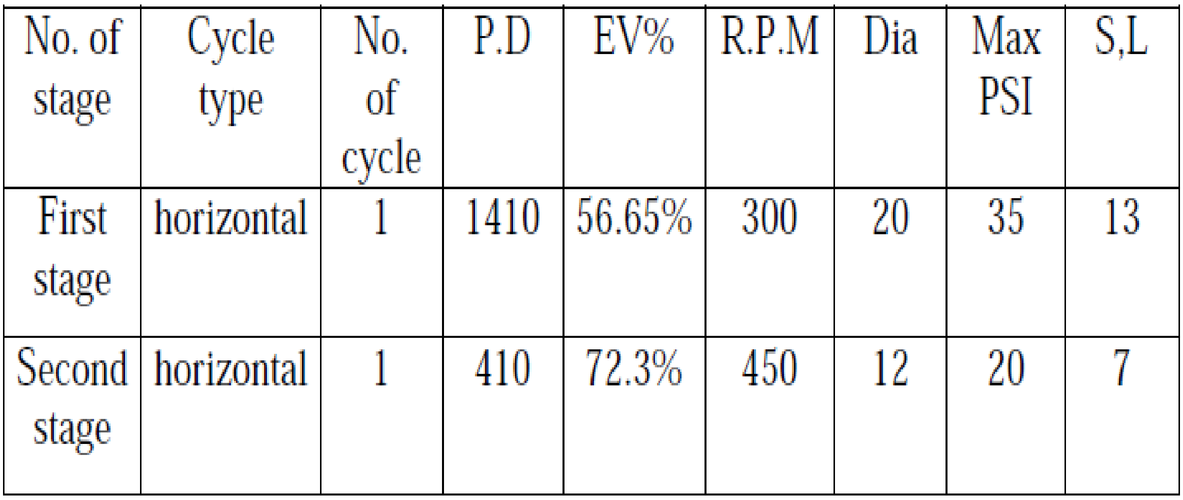
- from table(7 – 1) single stage horizontal type try to use cylinder of PD= 410 CFM

EV% = 100 – 3.9 – 14.5 ($3.9^{1/1.4}$ – 1)

= 72.3 %

PDEV)$_{2st}$ = 410 * 0.723

= 297 CFM **[18]**



No. of stage	Cycle type	No. of cycle	P.D	EV%	R.P.M	Dia	Max PSI	S,L
First stage	horizontal	1	1410	56.65%	300	20	35	13
Second stage	horizontal	1	410	72.3%	450	12	20	7

4.10. Tank design:

Data given: -

- m_p = 56000 lb / hr
- API = 44.94
- T = 104 ˚F

Design steps: -

- from kern chart by known (API = 44.56, T = 104 ˚F). find specific gravity of reformate = 0.783
- density = 0.783 * 62.4 = 84.86 lb / ft^3

so Q = mass flow rate / density

= 5600 / 84.86

= 1146.13 ft^3 / hr

assume production capacity = 30 day

- V = 1146.13 * 24 * 30

= 825,228.4 ft^3

= 825,228.4 / $(3.281)^3$

= 23,364 m^3 >> 1000 m^3

(so we wil design large tank)

Step(1) : calculation of suitable dimensions of tank (D, H)

1)- calculate $D/H)_{OPT}$:-

$D/H)_{OPT} = 4 C_1 / (C_2+C_3 + C_4 + C_5)$

$C_4 = C_5 =$ zero

$C_1 = C_3 = 2C_2$

$D/H)_{OPT} = 8 / 3$

2)- calculate the hieght of tank(H):-

$V=(\pi * D_2 * H) / 4$

$H= (825{,}228.4 * 4) / (\pi * (8/3)^2)^{(1/3)}$

$=52.87$ ft

standrized (H) by find the aproximately number which can divide into (6,8).

$H_{st} = 54$ ft (which can divide into 6 and give 9)

so the number of courses = 9

3)- calculate the diameter of tank(D) :-

$D= ((4 * V) / (\pi * H))^{0.5}$

$=((4 * 825{,}228.4) / (\pi * 54))^{0.5}$

$= 139.5$ ft

$D_{st}= 140$ ft

4)- calculation of actual volume(V_{act}) : -

$V_{act} = (\pi * D_{st2} * H_{st}) / 4$

$= (\pi * 140_2 * 54) / 4$

$= 831{,}265.42\ ft_3$

5)- check $((V_{act} – V_{given})/ V_{act}) < 10\%$:-

$= ((831{,}265.42 -825{,}228.4) /831{,}265.42) *100$

$= 0.73\ \% <<< 10\%$ (SO IT'S OK)

Step(2) : - design of shell courses (t_n) :-

$t_n = 0.0001456 * D_{st} * (H – n)$ (n from 1 to 9)

n	1	2	3	4	5	6	7	8	9
H (ft)	6	12	18	24	30	36	42	48	54
T_{st}(in)	0.25	0.25	0.35	0.47	0.60	0.72	0.84	0.96	1.03

$\Sigma\ t_n = 0.25+ 0.25 + 0.35 + 0.47 + 0.6 + 0.72 + 0.84 + 0.96 +1.03$

$= 5.\ 47$ in

Step(3): volume of steel(V_{steel})calculation

$V_{steel} = \pi * D_{st} * 6 * (\Sigma\ t_n /12)$

$= \pi * 140 * 6 * (5.47 / 12)$

$= 1202\ .9\ ft_3$

Step (4): Volume of Bottom & Roof (V_{bot}, V_{roof}) Calculation

$V_{bottom} = \pi * D_{st}^2 /(4 * 4 * 12)$

$= \pi * 140^2 / (4 * 4 * 12)$

$= 320.7\ ft^3$

$V_{roof} = 2 * V_{bottom}$ ………….. (rough estimation)

$= 2 * 320.7$

$= 641.4\ ft^3$ **[18]**

Conclusion:

We could distillated a crude oil from Distillation Column and then we can get Naphtha, but we can’t using Naphtha directly because it has low Octane number, Therefore we improved this Naphtha by Reforming Process However we have many ways to improved Naphtha but in our project we focused on catalytic reforming, because this way it is common way in the world, and economic method and it has high octane number.

Discussion:

In this project produce gasoline because gasoline best important fuel in the world, we design atmospheric distillation column to produce heavy naphtha and Catalytic reforming used to improved heavy naphtha because the heavy naphtha have few octane number by catalytic reforming increase octane number of naphtha .there are many process to improve naphtha but catalytic reforming .

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