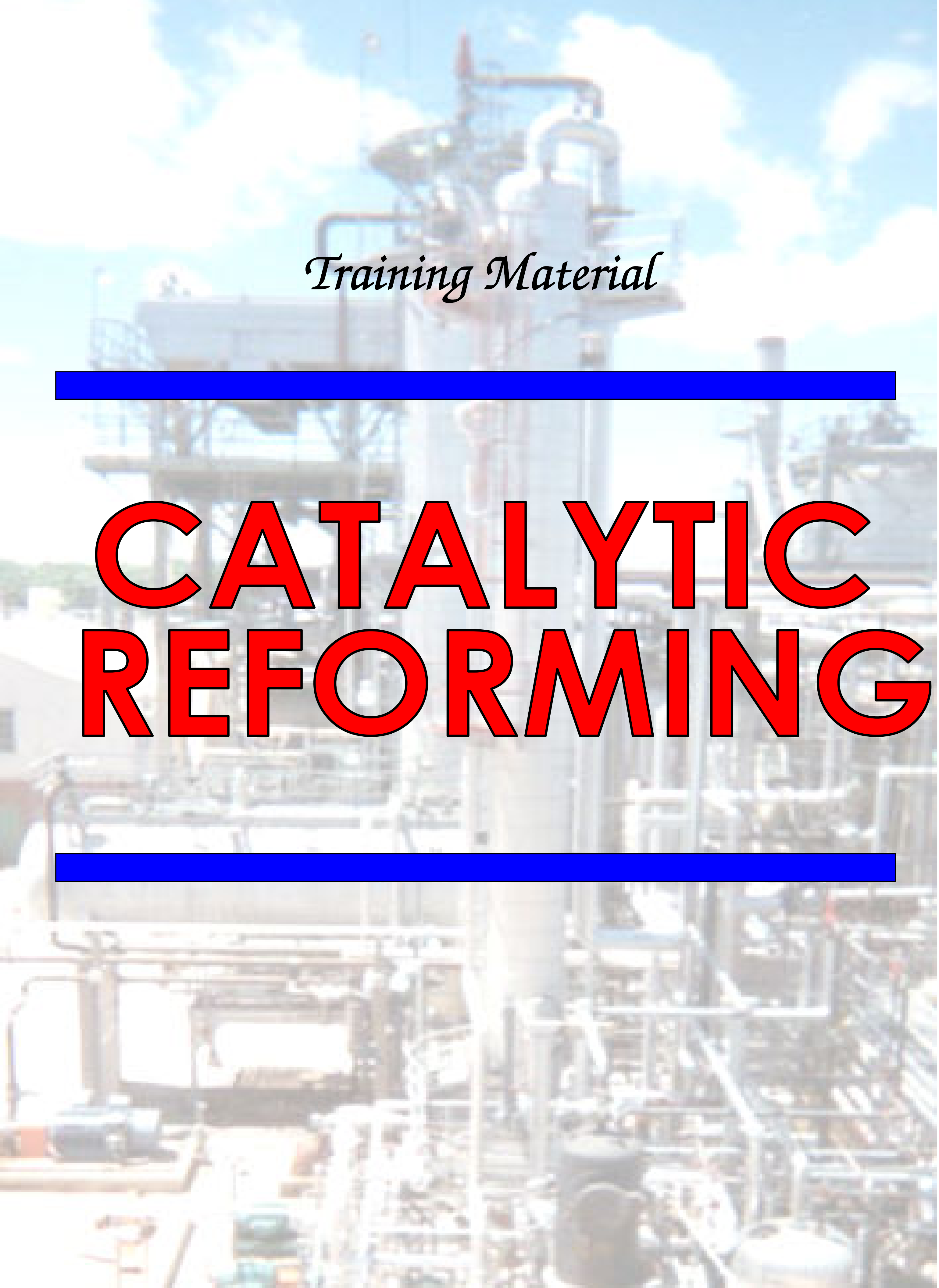

Training Material

CATALYTIC REFORMING

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CH.1

Basic Principles

1.1 INTRODUCTION

The problem of low octane ratings of naphtha is solved by increasing the contents of isomers and aromatics in its composition. Catalytic Reforming involves some reactions such as Isomerization, Dehydrogenation, and Dehydrocyclization which convert the low octane number components in naphtha into very high octane number components, consequently enhancing the antiknock quality of gasoline. Two types of reactors are used in the catalytic reforming process: the fixed-bed reactor and the moving-bed reactor. The used catalyst for catalytic reforming processes is the platinum supported on a silica or silica-aluminum base for fixed bed processes and non-precious metal oxide catalysts for fluid and moving bed processes. Most of the catalytic reforming reactions favor high temperatures, low pressures, and low space velocities.

1.2 THE PROBLEM OF ANTIKNOCK QUALITY

A very important property of an automobile gasoline is its resistance to knock, detonate or ping during service. Knocking occurs in the combustion chamber in the cylinder of motor engines, this knocking is a result of the sudden combustion of the gasoline-air mixture in the cylinder. The more the fuel-air mixture is compressed, the more power the engine can produce.

With the increase of loads and duties on engines over years and the subsequent development of automobile engines, compression ratios of engines are increased to deliver more power. But this increase in performance goes together with an increase in knocking and detonation. The gasoline which occurs in the crude oil is too poor in the antiknock quality to be used alone as a fuel in the modern automobile engines that are designed on using high compression ratios. Hence when straight-run gasoline (Naphtha) is used directly in engines, it will knock causing a lose in power and a loud noise.

1.3 OCTANE NUMBER

The antiknock property of a gasoline is generally expressed as its octane number. This number is the percentage of iso-octane in a blend with n-heptane that produces the same amount of knocking produced by the tested gasoline. ASTM has standardized octane number test methods into Research Octane Number (RON), and Motor Octane Number (MON) tests. (RON) is produced using normal road conditions, while (MON) is produced using sever or high-speed conditions on the testing equipment. The arithmetic average [(RON+MON)/2] is increasingly used nowadays. Worth mentioning here is that when octane number is reported or assigned to gasoline without definition, then research octane number is the meant measurement, unless stated otherwise.

1.4 COMPOSITION EFFECT ON OCTANE NUMBER

Extensive studies of octane numbers of individual compounds have brought to light some general rules. Table (1.1) shows the octane numbers of several hydrocarbons. Normal paraffins have the least desirable knocking characteristics and they become progressively worse as the molecular weight increase, while iso-paraffins and naphthenes have higher octane numbers than the corresponding normal paraffins. The octane number of the iso-paraffins increases with the increase of branching of the chain. Olefins have markedly higher octane numbers than the corresponding paraffins and aromatics usually have very high octane numbers.

Comparing the different hydrocarbon series, aromatics – except for Benzene – are the hydrocarbons with the highest octane numbers. Hence, to increase the octane number of gasoline, the paraffinic and naphthenic contents in gasoline should be transformed into aromatics and iso-paraffins. Such a transformation process is called the Reforming Process.

Pure Hydrocarbons	**RON**
Paraffins	
n-Butane	113
i-Butane	122
n-Hexane	19
2-Methylpentane	83
2,2-Dimethylbutane	89
2,3-Dimethylbutane	96
n-Heptane	0
2-Methylhexane	41
n-Octane	-19
Olefins	
1-Pentene	91
1-Octene	29
3-Octene	73
Naphthenes	
Methylcyclopentane	107
Ethylcyclopentane	75
1,1-Dimethylcyclopentane	96
Aromatics	
Benzene	99
Toluene	124
o-Xylene	120
m-Xylene	145
p-Xylene	146
Oxygenates	
Methanol	106
Ethanol	99
2-Propanol	90
(MTBE)	117

Table (1.1), RON for some pure hydrocarbons.

Another solution for the low antiknock problem of gasoline was used in 1922 which was the use of TEL (Tetra Ethyl Lead). TEL increases the octane number greatly when added to gasoline in small quantities.

However, over years, in many countries the amount of added lead has been decreased gradually by strict regulations in order to pave the way for completely preventing its use for its harmful effect on man's health and environment. Nowadays lead-free gasoline is used in most countries around the world and as a substitute additive for TEL to the gasoline, oxygenates such as alcohols, MTBE, and TAME are now used to increase the octane number of gasoline. Table (1.2) shows the Maximum allowable contents of some oxygenates.

The ethers may be produced at the refinery by reacting suitable alcohols such as methanol and ethanol with branched olefins from the fluid catalytic cracker, such as iso-butene and iso-pentene, under the influence of acid catalysts. In the mid-1990s, methyl-t-butyl ether (MTBE) -made by etherification of iso-butene with methanol- became the predominant oxygenate used to meet reformulation requirements for adding oxygen to mitigate emissions from gasoline-powered vehicles.

Environmental issues involving MTBE have made it more desirable to dimerize isobutene from the catalytic cracking unit rather than etherify it. Fortunately, iso-butene dimerization may be achieved with minimal modifications to existing MTBE plants and process conditions, using the same acidic catalysts. Where olefin levels are not restricted, the extra blending octane boost of the di-iso-butylene can be retained. Where olefin levels are restricted, the di-iso-butylene can be hydrotreated to produce a relatively pure iso-octane stream that can supplement alkylate for reducing olefins and aromatics in reformulated gasoline.

Oxygenates	**Maximum, Volume %**
Methanol	3
Ethanol	5
Iso-propyl Alcohol	10
Iso-butyl Alcohol	10
Tert- butyl Alcohol	7
Ether (5 or more C atoms)	15
Other oxygenates	10

Table(1.2), Oxygenates allowed on Gasoline.

1.5 REFORMING

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.

1.5.1 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 into 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_4 fractions 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 C_3 and C_4 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 the reforming, polymerization, and other reactions take place. In naphtha reforming, the C_3 and C_4 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.

1.5.2 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 80 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:

- Paraffins are isomerized to branched chains and to a lesser extent to naphthenes, and
- 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 102 depending 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.

Catalytic 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 any one 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:

- One stream goes to recycle where it is mixed with the feed, and
- 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 (1.1) shows the relation between reformate yield and its octane number.

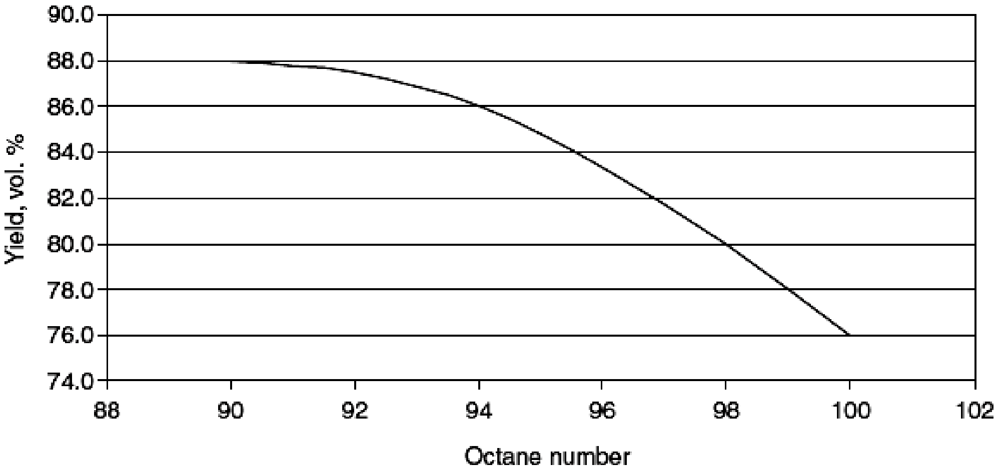


Figure (1.1), Reformate Yield and its Octane Number.

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 occurs. 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 dualfunction 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 of a 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 (H_2S) 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 dehydrocyclization 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) over nickel–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.

1.6 FEED TREATMENT BY HYDROGEN

Nondestructive or simple hydrogenation is generally used for the purpose of improving product quality without appreciable alteration of the boiling range. Mild processing conditions are employed so that only the more unstable materials are attacked. Nitrogen, sulfur, and oxygen compounds undergo reaction with the hydrogen to remove ammonia, hydrogen sulfide, and water, respectively. Unstable compounds which might lead to the formation of gums, or insoluble materials, are converted to more stable compounds.

Hydrotreating, Figure (1.2), is carried out by charging the feed to the reactor, together with hydrogen in the presence of catalysts such as tungsten–nickel sulfide, cobalt–molybdenum–alumina, nickel oxide–silica–alumina, and platinum–alumina. Most processes employ cobalt–molybdena catalysts which generally contain about 10% of molybdenum oxide and less than 1% of cobalt oxide supported on alumina. The temperatures employed are in the range of 260 to 345 °C (500 to 655 °F), while the hydrogen pressures are about 500 to 1000 psi.

The reaction generally takes place in the vapor phase but, depending on the application, may be a mixed-phase reaction.

1.6.1 Hydrofining

Hydrofining is a process that first went on-stream in the 1950s and is one example of the many hydroprocesses available. It can be applied to lubricating oils, naphtha, and gas oils. The feedstock is heated in a furnace and passed with hydrogen through a reactor containing a suitable metal oxide catalyst, such as cobalt and molybdenum oxides on alumina. Reactor operating conditions range from 205 to 425 °C (400 to 800 °F) and from 50 to 800 psi, and depend on the kind of feedstock and the degree of treating required. Higher-boiling feedstocks, high sulfur content, and maximum sulfur removal require higher temperatures and pressures.

After passing through the reactor, the treated oil is cooled and separated from the excess hydrogen which is recycled through the reactor. The treated oil is pumped to a stripper tower where hydrogen sulfide, formed by the hydrogenation reaction, is removed by steam, vacuum, or flue gas, and the finished product leaves the bottom of the stripper tower. The catalyst is not usually regenerated; it is replaced after about one year's use.

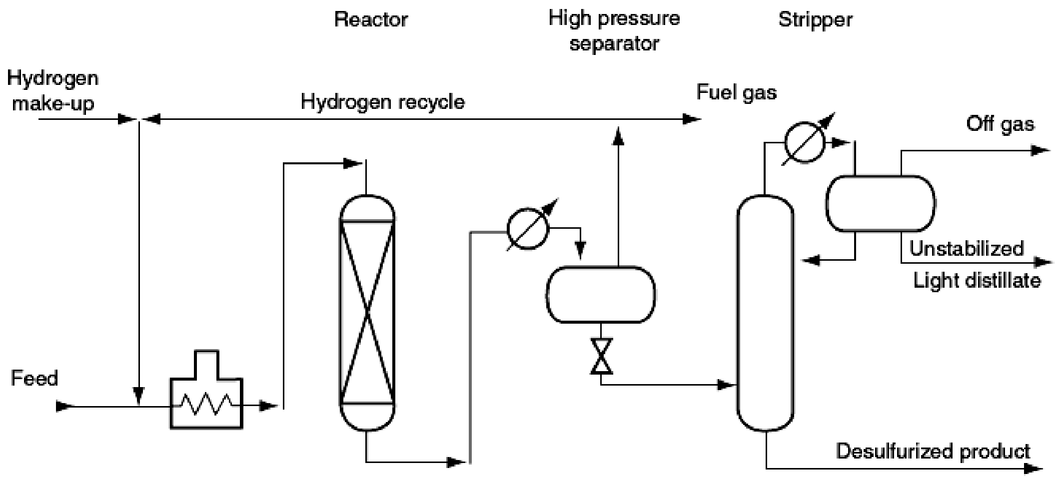
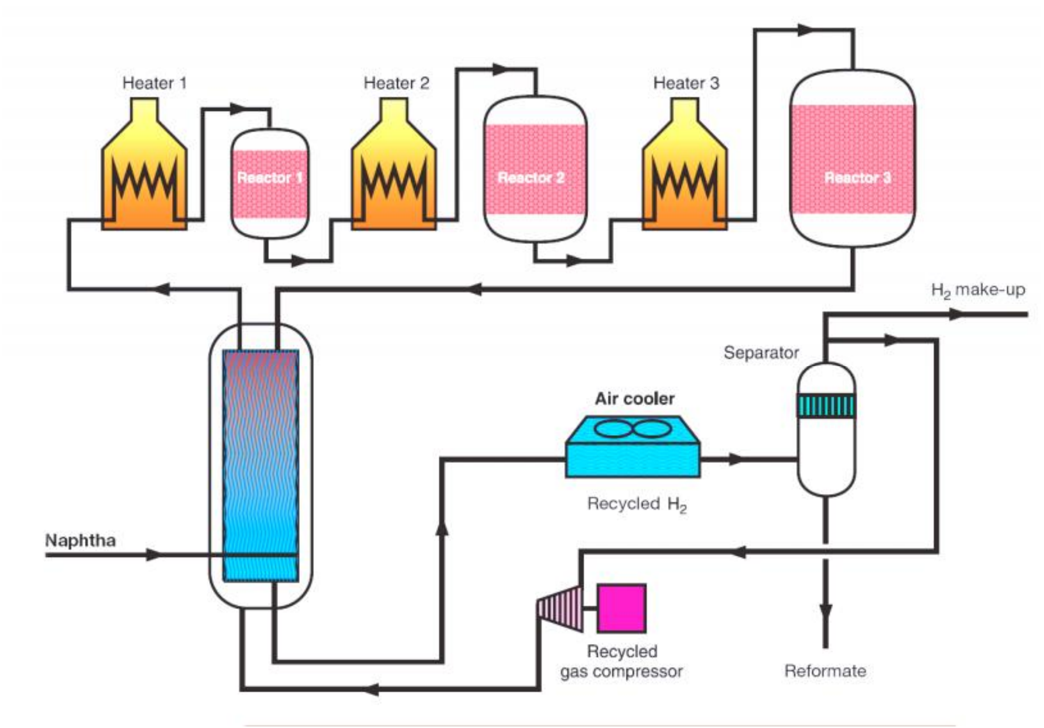


Figure (1.2), A distillate hydrotreater for hydrodesulfurization. (From OSHA Technical Manual, Section IV, Chapter 2, Petroleum Refining Processes.)

CH.2

The Catalytic Reforming Process



2.1 INTRODUCTION

The catalytic reforming process is designed to transform the low octane number constituents in the gasoline composition into very high octane rating aromatics in the range of 6 to 10 carbon atoms. This process aims to enhance the properties of gasoline to satisfy some basic specifications such as:

- Maximum Octane Number by increasing aromatic and isomer contents.
- Minimum capacity to form gums - when storing and shipping - caused by unstable olefinic compounds.
- Minimum vapor pressure to avoid vapor lock problems.
- Minimum tendency to produce smoke or smog and low carbon deposition into cylinder caused by high boiling fractions in the gasoline composition.

A large number of catalytic reforming processes were operational during the II World War. They used catalysts with alumina as a support and chromium or molybdenum oxides as active elements and were implemented in fixed or moving bed reactors. But a great turning point happened in the beginning of 50s when UOP developed the "Platforming" process based the use of a platinum catalyst on chlorinated alumina. This catalyst allowed the operation to be carried out at pressures of approximately 70 bar. It was a semi-regenerative process, the catalyst was being regenerated after a few months of operation. Cyclic regeneration was introduced by EXXON using the same type of catalyst (Pt/chlorinated Al_2O_3 or Pt on silica alumina).

During 50s and 60s, catalysts were improved allowing lower operating pressures of about 30 bar. The hydrogenation reaction favors lower operating pressures to enhance the production of aromatics from naphthenes. That was before the use of bimetallic catalysts - in the late 60s - which allowed lower operating pressures.

In the early 70s, the third major modification occurred when the continuous regeneration was introduced in the catalytic reforming units. This allowed pressures of approximately 10 bar. In the late 80s, even lower pressures were achieved: 3 bar.

These continuous modifications of catalysts caused the operating conditions be more sever, higher RON and space velocity and an effort to get better yield. These modification didn't stop in the past and will continue in the future with more and more sever operating conditions and producing gasoline with higher specifications.

2.2 FEED TO CATALYTIC REFORMING

The typical feed to the catalytic reforming process is the heavy straight-run gasolines (HSR) or naphthas (90 °C to 160 °C). The reason for the use of heavy naphthas as feeds for Catalytic Reforming is that the ease of cyclization and isomerization reactions in the process increases with the increase of carbon atoms. Light naphtha (C_5^+ - 90 °C) tends to crack forming butane and light gases causing a lose in yield, hence it is not economical. Heavier feeds than the heavy naphtha causes formation of carbon deposits on the catalyst and partially deactivate it.

Table (2.1) gives the composition of two typical feeds. The RON is low: 50 for the paraffinic feed and 66 for the naphthenic feed. The average molecular weigh is about 115, centered around C_8. Sulfur is present in the feed in the range of 500 and 350 ppm, which are representative of straight run gasolines (SR) coming from atmospheric distillation of crude. But values lower than 100 ppm are found in a few particular crudes (Hassi Messauod, for example). These SR feeds contain limited amounts (a few ppm) of nitrogen in the form of amines, or oxygenated compounds in the form of phenol or carboxylic acid. In some cases, traces (<1 ppm) of metals or metalloids can be found in the feed, depending on the origin of the crudes. For instance, mercury and, more seldom, arsenic are found in some crudes.

If the "Octane Barrel" requirements can't be met by reforming heavy naphtha (90 - 160 °C), then it may be necessary to increase the amount of feed processed in reforming, by using cuts distilling in the same range of SR naphtha which is produced from conversion units and have low octane number. For instance, visbreaking or coking gasolines can be sent to reforming which are characterized by – in comparison with SR feeds – a high olefin and acid sulfur content and larger amounts of nitrogen compounds. Hydrocracking gasoline is another feed, it is clean since it is free of sulfur and nitrogen compounds because the use of hydrogen in the hydrocracking process works as a hydrotreating process, but such a feed is mainly made up of cyclopentane-structure naphthenes and isoparaffins. FCC gasoline is another possible feed . Its is characterized by significant olefins and aromatics concentrations as well as by the presence of molecules containing heteroatoms such as S or N.

	Paraffinic (Arabian Light)	**Naphthenic (Nigeria)**
RON	50	66
Av. Mw.	114	119
S (weight ppm)	500	350
Paraffins	66.8	29.3
Naphthenes	21.8	61.85
Aromatics	11.4	8.85

Table (2.1), The composition of two typical feeds.

2.3 PRODUCT FROM CATALYTIC REFORMING

As stated before, the main objective of any reforming process is to increase the octane number by increasing the aromatic content in the gasoline. As a result of the reactions taking place during the process, reformates consist – mainly – of branched paraffins and especially aromatics, most of which have fewer than 10 carbon atoms. Figure (2.1) shows the total changes taking place in the reformer to produce the desired aromatics and isoparaffins. Olefins are saturated to form paraffins by hydrogenation. Paraffins from the feed and from olefins saturation are essentially isomerized to iso-paraffins and, to some extent, cyclized to the corresponding naphthenes. Naphthenes are then dehydrogenated to aromatics. Aromatics of the feed are essentially left without change. In addition to the reformate, the reactions produce considerable amounts of gases such as Hydrogen, Methane, Ethane, Propane and (*i* + *n*) Butanes.

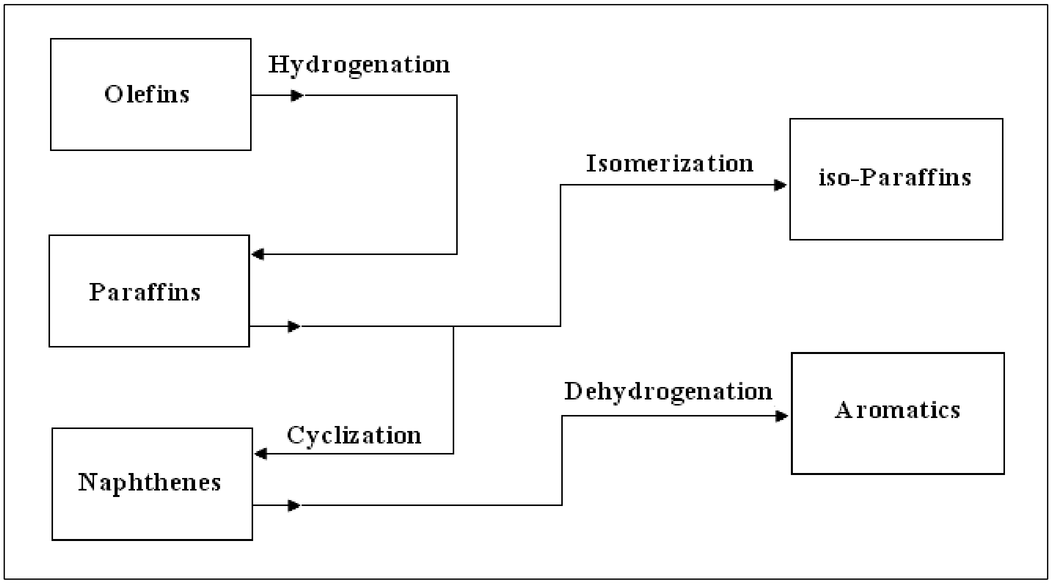


Figure (2.1), Total changes to produce iso-Paraffins and Aromatics.

2.3.1 The Typical Yield

As mentioned before, catalytic reforming produces C_5^+ 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 C_5^+, has risen gradually with pressures going down to 10 bar and less as a result of improving catalysts.

Table (2.2) 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).

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

Table (2.2), Typical yields on a Middle Eastern feed.
RON = 98 P = 15 bar.

2.3.2 Reformate Composition

Olefins and naphthenes concentrations are lower than 1% wt except for low pressure reformates which approach 1% wt. Table (2.3) shows a typical analysis for a low pressure reformate. It should be noted that to achieve RON = 98, the aromatic content should be close to 70% wt. The octane rating in a reformate is generally provided by C_7 to C_{10} aromatics and by light iso-paraffins, especially C_5. This is because the C_6, C_7 and C_8 isoparaffins are not very branched and so they have a low RON.

The reformate is basically made up of C_6 to C_{10} aromatics, but increasingly it is limited to C_7, C_8 and C_9. The aromatics concentration is directly related to the desired research octane number. It is important also to note that reformates don't contain any sulfur ($S \leq 0.1$ ppm).

Number of carbon atoms	nP	iP	P	O	N	A	Total
4	0.57		0.57				
5	1.51	2.37	3.88	0.1	0		3.98
6	1.69	1.97	5.66	0.16	0.19	2.34	8.35
7	2.5	8.42	10.92	0.35	0.4	14.16	25.83
8	1.16	4.91	6.07	0.44	0.34	26.28	33.13
9	0.26	1.04	1.3	0.08	0	21.08	22.46
10	0.07	0.28	0.35	0	0	4.76	5.11
11	0	0.02	0.02	0	0	0.55	0.57
Total	**7.76**	**21.01**	**28.77**	**1.13**	**0.93**	**69.17**	**100**

nP: normal paraffins. **iP**: branched paraffins. **P**: total paraffins.
O: olefins. **N**: naphthenes. **A**: aromatics

Table (2.3), Analysis for a low pressure reformate (% wt).
RON = 98 sp.gr = 0.85 $S \leq 0.1$ ppm.

The RON is related to the aromatics concentration as indicated in figure (2.2). High pressure reformates contain few olefins. However, in modern units running at low hydrogen partial pressure, there are more and more olefins, as indicated in figure (2.3), since the RON is the fixed parameter for the run. These olefins lower the MON of gasolines and often make hydrogen purification more complicated.

2.3.3 Reformate Specifications

Table (2.4) lists the main administrative specifications in effect for Eurosuper in the first of January 2000. Developments are expected with respect to the maximum allowable sulfur (≤ 50 ppm), the mandatory presence of oxygenated compounds (oxygen content ≥ 2% wt), and a more stringent limit on total aromatics (≤30% wt). Also expected is a reduction in the end point in order to lower the heavier aromatics concentration along with a limit on high volatility C_4-C_6 olefin concentrations, whose effect on ozone production has been demonstrated.

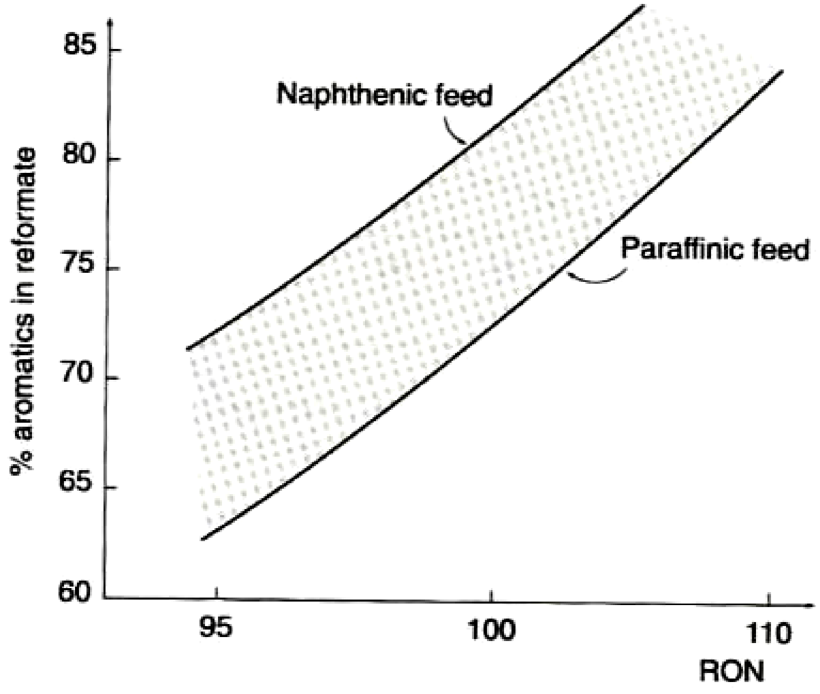


Figure (2.2), Relationship between the RON and % aromatics in the reformate.

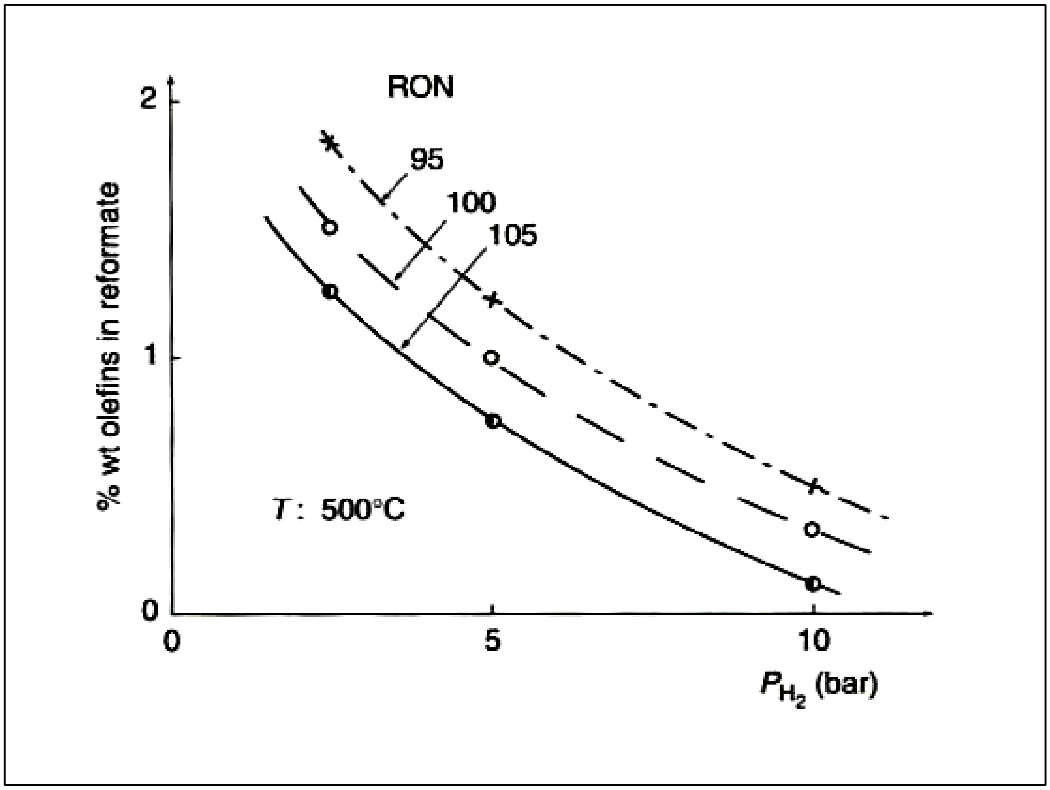


Figure (2.3), Olefin content in the reformate.

Properties	Values
RVP (kpa) max	60
Distillation (% vol min)	
at 100 °C	46
at 150 °C	75
Benzene (% vol max)	1
Aromatics (% vol max)	42
Olefins (% vol max)	18
Oxygen content (% wt max)	2.8
Sulfur max (ppm)	150
Lead (g/l max)	0.005

Table (2.4), Main Specifications for Eurosuper (January 2000).

Table (2.5) shows the ASTM distillation analysis for the same low pressure reformate discussed above. The end point is limited, usually to around 205 °C, to comply with the corresponding gasoline specification, but mainly to prevent large-scale formation of naphthalene derivatives which color the reformate and cause rapid catalyst deactivation.

% distilled	°C
IBP	56
5	83
10	92
20	103
30	113
40	121
50	128
60	135
70	142
80	150
90	160
95	168
EP	194
% distilled	98.4
% residue	1.5
% losses	0.1

Table (2.5), Distillation characteristics of a low pressure reformate.
RON = 98 sp.gr = 0.85 S ≤ 0.1 ppm.

2.4 CATALYTIC REFORMING TECHNIQUES

The first commercial units of catalytic reforming were built practically simultaneously in the United States, in November 1940, under the name of Hydroforming, and in Germany, under the name of D.H.D. They used a catalyst of molybdenum or chromium oxide on alumina, discovered by Moldavschi and Kamusher in 1936. At the time, the process was used especially for producing toluene, which was necessary during World War II for the production of trinitrotoluene, by nitration. The catalysts of chromium and molybdenum oxide could not compete with platinum catalysts and were gradually abandoned, despite improvements achieved over the years, including the processes in moving bed or fluidized bed. The first catalytic reforming unit using platinum catalyst on Al2O3 support was built by Dutch Refining in 1949.

The continuously improved performances were the result of modified process conditions with the corresponding modifications in the unit design and the use of bi- and poly-metallic catalysts. As an example, the evolution of the UOP process ‘‘Platforming.’’. The high octane rating of the reformed gasoline, the efficiency of the process, and the broad availability of feedstock (naphtha) contributed to make Platforming in a relatively short period of time, the premier process for high octane gasoline. In addition, through continuous improvements, the process was capable of satisfying the increasing market requirements in the conditions of the gradual prohibition of the leaded gasoline.

In January 1990, the worldwide Platforming capacity was 373.9 million tons/year (excluding the former Eastern Block), placing it in second place in the production of gasoline, after catalytic cracking with 539.5 million tons/year. The evolution of reforming capacities from 1990–2010 is shown in Table (2.6).

At the same time, the position of catalytic reforming increased strongly for the production of aromatic hydrocarbons, feedstocks for the petrochemical industry. It provides almost all the world's need for xylenes.

Region	1990	1995	1998	2000	2010
North America	4,487	4,278	4,333	4,380	4,700
Western Europe	2,017	2,268	2,386	2,420	2,500
Pacific Rim and South Asia	1,090	1,700	2,050	2,360	3,450
Eastern Europe and C.I.S.	**na**[a]	1,654	1,746	1,850	2,400
Latin America	**na**[a]	329	429	480	600
Middle East	311	640	790	850	1,100
Africa	530	404	429	470	690
Total	8,766	11,273	12,163	12,810	15,440

[a] Not Available.

Table (2.6), Evolution of Reforming Capacity from 1990–2010 (thousands bpsd).

The different technologies basically involve three configurations:

1. Fixed-bed type.
2. Moving-bed type.
3. Fluid-bed type.

The fixed bed could be operated whether cyclic or semi-regenerative, according to the time required to regeneration. Moving bed is only operated continuously. These different types of configurations are going to be discussed in details in the following sections.

2.4.1 Fixed-Bed Technology

This is the oldest technology. The fixed bed configuration implies that the catalyst is fixed in its location in the reactor, while the feed is passed over it until the time of regeneration. The fixed bed configuration has two different types of runs:

- Non-regenerative, in which the spent catalyst is replaced without regeneration in the end of its life (months).
- Semi-regenerative, which involves the total regeneration of all the catalyst after finishing the running period (usually years), with the unit being shutdown during regeneration.
- Regenerative (Cyclic), which involves the regeneration of a part of the catalyst after its deactivation (occurs in days), during switching the operation to a substitute (swing) reactor, with no shutdown of the unit.

2.4.1.1 Type of reactors

In the beginning, the pressures used were greater than 50 bar and reactor pressure drop had little influence in comparison with total pressure drop. This is why axial reactors - which have simple internals and therefore less costly - were chosen to implement the process at these times.

Figure (2.4) shows the two types of reactors. Radial reactors made their appearance some time in the seventies at the same time of the appearance of the bimetallic catalysts that allow operation at pressures lower than 25 bar. Here, pressure drop in the reactors became significant in relation to the total pressure drop. In addition, the cost of recycle hydrogen compression became a non-negligible item.

The evolution toward continuous reforming and the implementation of continuous catalyst circulation imposed the radial type of low-pressure drop reactor once and for all. The trend toward a total pressure of 3 bar left no other choice.

Reactors are built of low-alloy carbon steel that can withstand hydrogen corrosion and oxidizing atmosphere during regeneration and oxychlorination operations.

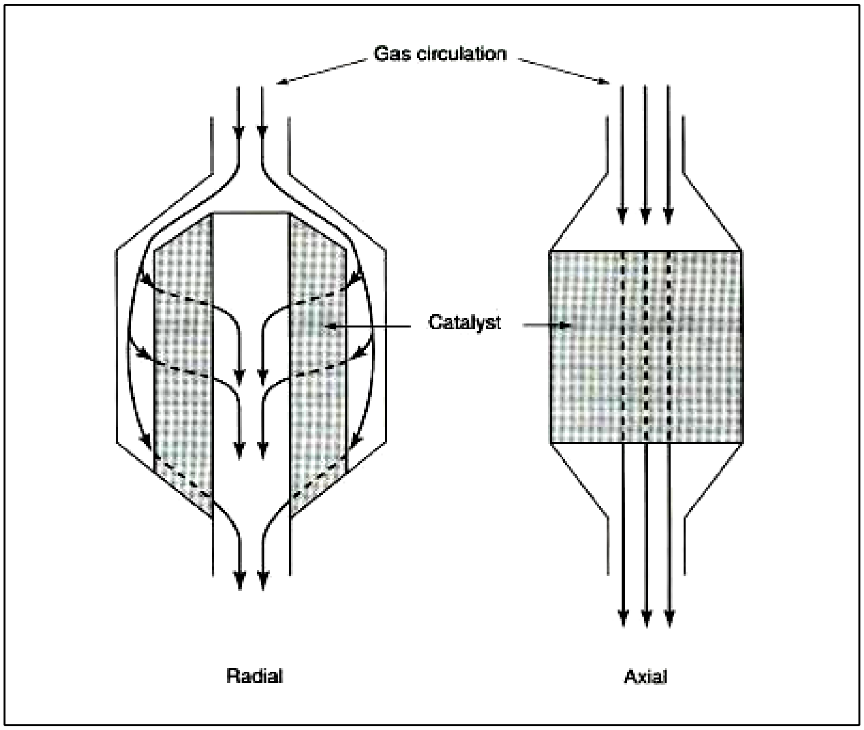


Figure (2.4), Reactor types.

2.4.1.2 Reactor Configuration

As mentioned earlier, catalytic reforming involves mostly endothermic and equilibrated reactions whose rates differ by a factor of 50. A set of isothermal reactors with a heat input could have been the solution, but it is expensive and lacking in flexibility. The choice of adiabatic reactors in conjunction with furnaces was eventually made. Differences in rate between cyclohexane dehydrogenation, cyclopentane hydro-isomerization-dehydrogenation and paraffin dehydrocyclization as a ratio is approximately 50/5/1. As a result, the final is a series of 3 or 4 (furnace + reactor) groups depending on the type of feed: 3 for paraffinic feeds and 4 for naphthenic feeds.

Figure (2.5) shows a simple reactors layout. Each (furnace + reactor) group takes reaction rates into account. F_1 is large and R_1 is small, while F_3 is small but R_3 is large. The figure also shows the variation in temperature in the reactors: significant drop in R_1, smaller drop in R_2 and finally less variation in R_3, where the endothermicity of dehydrocyclization is partially offset by the exothermicity of cracking, since the two reaction rates are comparable. The aromatics concentration rises gradually. Catalyst distribution among the three reactors is usually around 15% (R_1), 15 - 30% (R_2) and 55 - 60% (R_3).

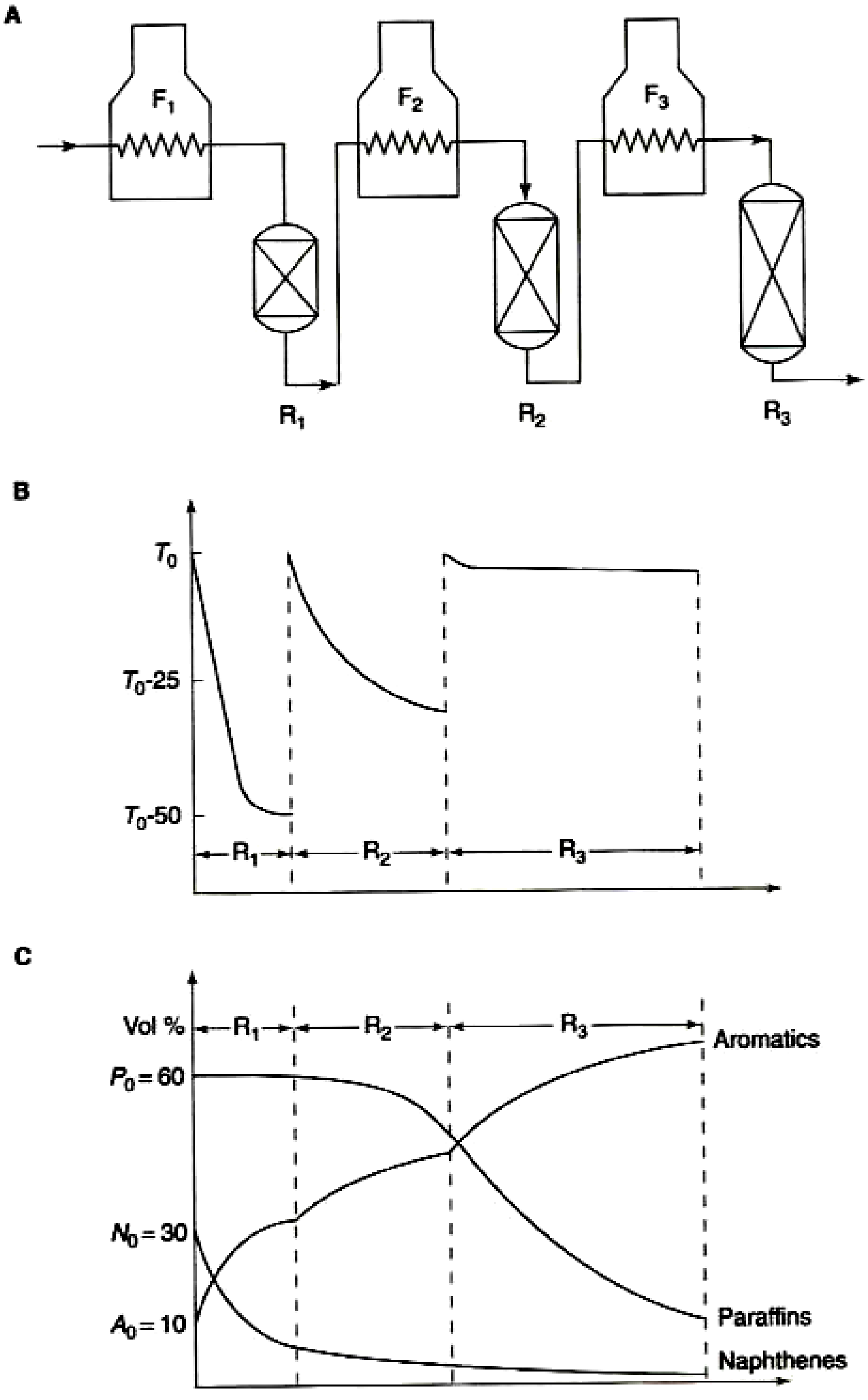


Figure (2.5): A. Furnace (F_1, F_2, F_3) and reactor (R_1, R_2, R_3) layout.
B. Variation in temperature in reactors R_1, R_2, R_3.
C. Variation in effluent composition (paraffins-naphthenes-aromatics) in the reactors.

2.4.1.3 Non-Regenerative Process

The non-regenerating system was used in the first type of catalytic reforming unit, the ‘‘Platforming’’ of UOP. Operation at high pressure (above 35 bars) ensured a catalyst life of over 10 months when using as feed a naphtha with final boiling point between 192–205 °C. For this reason, the units are not provided with the means for regenerating the catalysts. The coked catalyst is replaced and sent off-site for regeneration. The advantages of operating at a higher severity, i.e., at lower pressure led to switching the non-regenerative units to semi-regenerative ones.

2.4.1.4 Semi-Regenerative (SR) Fixed Bed Process

This type of process is given its name because catalyst regeneration causes the unit to be shut down at the end of the run. The semi-regenerative system provides a total duration of catalyst utilization of about 7–10 years and even longer. The necessary equipments are added for the regeneration of catalyst without its removal from the system. On contrary of, non-regenerative process which send the spent catalyst off-site to be regenerated outside the system. Figure (2.6) shows a semi-regenerative process flow scheme. The reactor configuration is the same as described earlier in the previous section.

Ancillary units are designed to allow optimum use of catalysts and to offset some of their drawbacks:

- The catalyst is sensitive to impurities: nitrogen-, oxygen- and sulfur-containing compounds and metals. Consequently, a feed purification section must be provided. The feed is purified by hydrotreating, which blocks the metals and produces ammonia, hydrogen sulfide and water, eliminated in the purification section. The feed can be further treated on molecular sieves to knock out the few ppm of residual water and also on a sulfide compound trapping agent.
- The catalyst becomes rapidly deactivated in the absence of hydrogen. Deactivation is considerably reduced by hydrogen, so high hydrogen partial pressure is created (H_2/HC > 8 for monometallic catalysts) by compressing and recycling part of the hydrogen produced during the reaction. It may contain some impurities : water, hydrochloric acid and sometimes H_2S, and needs to be dried, dehydrochlorinated and desulfurized on specific

adsorbers. Such installations are mainly used during start up but not only.

- Finally, the catalyst produces light C_1 to C_4 hydrocarbons in addition to hydrogen, and they are separated from the reformate in a stabilization section. Depending on the operating pressure, separation systems of varying degrees of complexity will be implemented to get relatively pure hydrogen and high gasoline recovery: a simple separating drum, re-contacting purification systems, ultra-cooling, etc.

2.4.1.5 Regenerative (Cyclic) Process

An initial solution, to avoid shutting down units, was carried out by using an extra reactor. With a complex valve system, three reactor can be running while the fourth is being regenerated. Here, the four reactors are of the same size and are located in position R_1, R_2, R_3 alternatively. This line up requires installation of a regeneration system and doesn't always allow the regenerated catalyst to be restarted in optimum conditions.

The operation of the unit can be cyclic, a mode of operation in which one of the reactors is constantly under regeneration, or in a swinging mode where the spare reactor (swing reactor), is coupled, occasionally when regeneration becomes necessary.

The regeneration of the catalyst without stopping the operation of the unit allows for a higher severity than that in the semi-regenerative system. In general, this means a lower pressure in the reaction system, which leads to a higher octane rating at equal yield, or to a higher yield of reformate for a given octane rating. That also allowed the use of higher reactor inlet temperatures that may reach 550 °C. Such operation can lead to octane ratings higher by approximately 5 units than the semi-regenerative system.

The regeneration of the catalyst is carried out at short time intervals, on average 5-15 days. The reactor of the last step is regenerated more often. In many designs, the additional reactor occupies a central position on the platform of the industrial plant in order to shorten the length of the connecting lines.

The first plant of this type was patented in 1953 and built in 1954 under the name of ‘‘Ultraforming’’ by Standard Oil of Indiana (Amoco). In

1956, the process ‘‘Powerforming’’ was patented and built by EXXON. Figure (2.7) shows a schematic flow of EXXON Powerformer.

In January 1984, the regenerative system represented 22% of the total capacity of catalytic reforming units operated in the United States. Compared with the semi-regenerative units, their investment is about 10–15% higher.

Worldwide at the end of 1982, there were 39 ‘‘Ultraforming’’ units in use, with a total processing capacity of 84,000 m^3/day, while the ‘‘Powerforming’’ units had a total processing capacity of 220,000 m^3/day.

2.4.1.6 Commercial Processes

2.4.1.6.1 Hydroforming

The hydroforming process made use of molybdena–alumina (MoO_2–Al_2O_3) catalyst pellets arranged in fixed beds; hence the process is known as fixed-bed hydroforming. The hydroformer had four reaction vessels or catalyst cases, two of which were regenerated; the other two were on the process cycle. Naphtha feed was preheated to 400 °C to 540 °C (900 °F to 1000 °F) and passed in series through the two catalyst cases under a pressure of 150 to 300 psi. Gas containing 70% hydrogen produced by the process was passed through the catalyst cases with the naphtha. The material leaving the final catalyst case entered a four-tower system where fractional distillation separated hydrogen-rich gas, a product (reformate) suitable for motor gasoline and an aromatic polymer boiling above 205 °C (400 °F).

After 4 to 16 h on process cycle, the catalyst was regenerated. This was done by burning carbon deposits from the catalyst at a temperature of 565 °C (1050 °F) by blowing air diluted with flue gas through the catalyst. The air also re-oxidized the reduced catalyst (9% molybdenum oxide on activated alumina pellets) and removed sulfur from the catalyst.

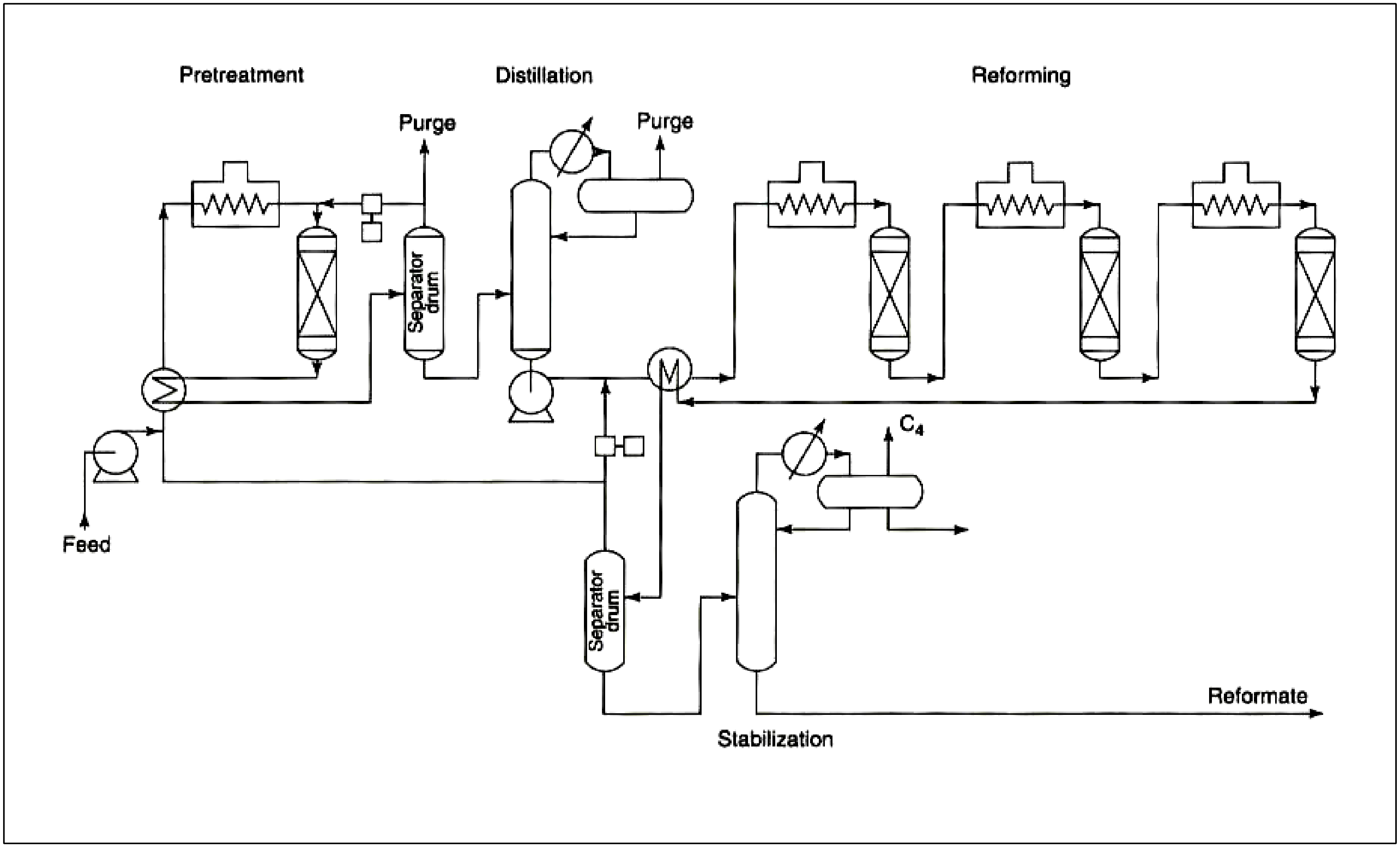


Figure (2.6), Semi-regenerative process flow scheme.

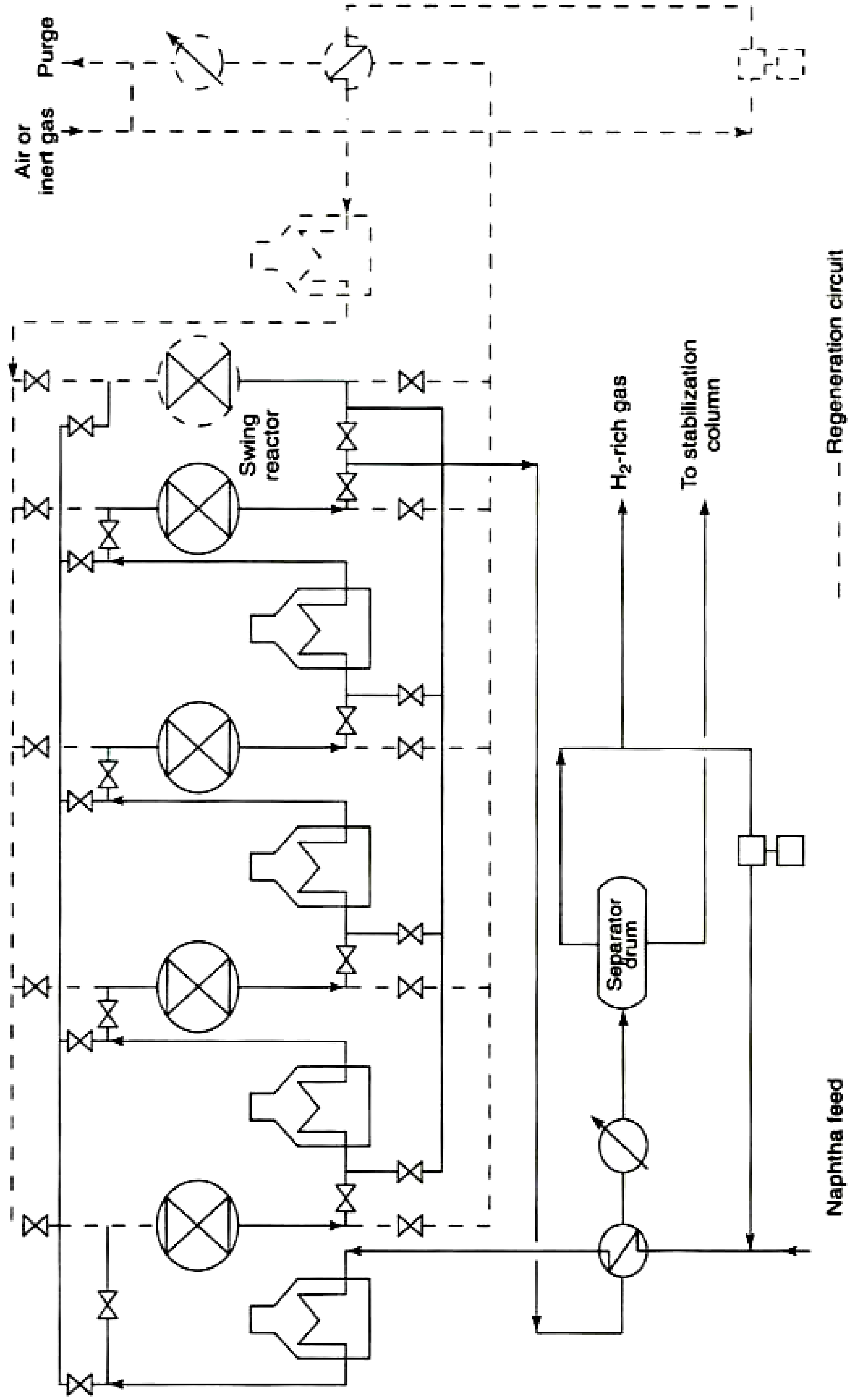


Figure (2.7), Powerformer flow scheme

2.4.1.6.2 Houdriforming

The introduction of an additional reactor followed by a stripping column, before the classical reaction system, for the protection of the catalyst against compounds of S, N, and O, was patented by Houdry in 1951. The first unit of this type was built in 1953. The guard reactor used the same catalyst as the main reaction system.

The subsequent practice of hydrotreatment of the feed to catalytic reforming eliminated the need for such a solution. The purification of the feedstock within the unit before the reactors, is current practice. The distinction is that the purification is made by adsorption. Such a system was developed by Chevron in the ‘‘Reniforming’’ process. The heavy naphtha passes through an adsorber before being mixed with recycle hydrogen. As suggested by the name of the process, it uses a Pt-Re catalyst that allows operating at low pressures.

2.4.1.6.3 Platforming

The first step in the platforming process, Figure (2.8), is the preparation of the naphtha feed. For motor gasoline manufacture, the naphtha feed is distilled to separate a fraction boiling in the 120 °C to 205 °C (250 °F to 400 °F) range. As sulfur adversely affects the platinum catalyst, the naphtha fraction may be treated to remove sulfur compounds. Otherwise, the hydrogen-rich gas produced by the process , which is cycled through the catalyst cases, must be scrubbed free of its hydrogen sulfide content.

The prepared naphtha feed is heated to 455 °C to 540 °C (850 °F to 1000 °F) and passed into a series of three catalyst cases under a pressure of 200 to 1000 psi. Further heat is added to the naphtha between each of the catalyst cases in the series. The material from the final catalyst case is fractionated into a hydrogen-rich gas stream and a reformate stream. The catalyst is composed of 1/8 in. pellets of alumina containing chlorine and about 0.5% platinum.

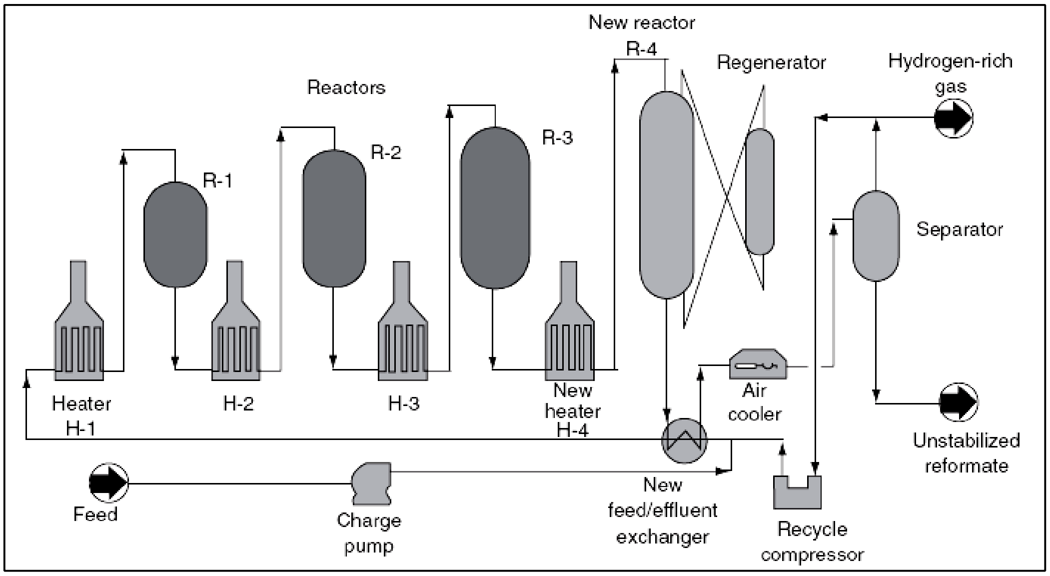


Figure (2.8), Platforming Process.

Each pound of catalyst reforms up to 100 bbl of naphtha before losing its activity. It is possible to regenerate the catalyst, but it is usual to replace the spent catalyst with a new catalyst.

Other fixed-bed processes include Catforming, in which the catalyst is platinum (Pt), alumina (Al_2O_3), and silica–alumina (SiO_2–Al_2O_3) composition, which permits relatively high space velocities and results in very high hydrogen purity. Regeneration to prolong catalyst life is practiced on a block-out basis with a dilute air in-stream mixture. In addition, Houdriforming is a process in which the catalyst may be regenerated, if necessary, on a blockout basis. A guard bed catalytic hydrogenation pretreating stage using the same Houdry catalyst as the Houdriformer reactors is available for high-sulfur feedstocks. Lead and copper salts are also removed under the mild conditions of the guard bed operation.

2.4.1.6.4 Powerforming

The cyclic Powerforming process, figure (2.7), is based on frequent regeneration (carbon burn-off) and permits continuous operation. Reforming takes place in several (usually four or five) reactors and regeneration is carried out in the last (swing) reactor. Thus, the plant need not be shutdown to regenerate the catalyst. The cyclic process assures a continuous supply of hydrogen gas for hydrotreatment operations and tends to produce a greater yield of higher octane reformate . Choice between the semi-regenerative process and the cyclic process depends on the size of plant required, type of feedstocks available, and the octane number needed in the product.

2.4.1.6.5 Rexoforming

Rexoforming is a combination process using platforming and aromatic extraction processes in which low-octane raffinate is recycled to the platformer. Operating temperatures may be as much as 278 °C (508 °F) lower than conventional platforming, and higher space velocities are used. A balance is struck between hydrocyclization and hydrocracking, excessive coke and gas formation thus being avoided. The glycol solvent in the aromatic extraction section is designed to extract low-boiling high-octane iso-paraffins as well as aromatics.

2.4.1.6.6 Magnaforming

The ‘‘Magnaforming’’ system, built by Engelhard Corp., is characterized by a small hydrogen/feed molar ratio in the first two reaction steps. This is followed by the injection of additional hydrogen-rich recycle gases, so that the ratio reaches normal values in the latter reaction steps.

The advantage of the system is that it favors the aromatization and the dehydrocyclization in the first two reaction stages as a result of the reduced (H_2/hydrocarbon) ratio that displaces the thermodynamic equilibrium in the desired direction. Since in the latter and especially the last reaction steps the danger of coke formation is higher, the (H_2/hydrocarbon) ratio is increased to prevent this occurrence.

2.4.2 Moving-Bed Technology

2.4.2.1 Reactor Configuration

Although the moving bed was used on MoO_3/Al_2O_3 type catalyst before 1940, its use on platinum-alumina catalysts came into being only in the early seventies. UOP put a continuous regeneration system on the market, figure (2.9), where three or four reactors are located one on top of the other. The effluent coming out of each reactor goes through a furnace before entering the next one. The catalyst moves downward by gravity from R1, to R2 then R3, loaded with coke, by a lift to the top of the regenerator. It goes through the regenerator by gravity then sent back to the top of R1. The rest of the unit flow scheme is very close to the fixed bed process.

The technology developed by IFP uses the conventional SR reformer layout of "side by side" reactors. The catalyst at the bottom of each reactor is raised by lifts to the top of the following reactor. From the last reactor it goes to the regenerator, figure (2.10), and then back to the top of the first reactor.

UOP regeneration is continuous, while IFP's can be either continuous or batch.

2.4.2.2 Advantages of the Moving Bed

The introduction of moving bed technology has had the following effects:

- Reformates are produced with a very high octane number even from difficult feeds and without any run duration problems.
- Units are operational all year round, regularly producing the hydrogen that modern refineries constantly need.
- Catalysts are less stable over time but more selective, making it possible to improve yields.
- Recycle rates are lower, thereby improving yields and reducing operating costs.
- Operating pressures are significantly lower and this is highly favorable for the reformates and the hydrogen yields.

Generally, as shown in figure (2.11), pressure has gone from P = 35 bar and $H_2/HC = 7$ to P = 3 bar and $H_2/HC = 2$ with yield gains of nearly 10 points for C_5^+ and over 1% for hydrogen.

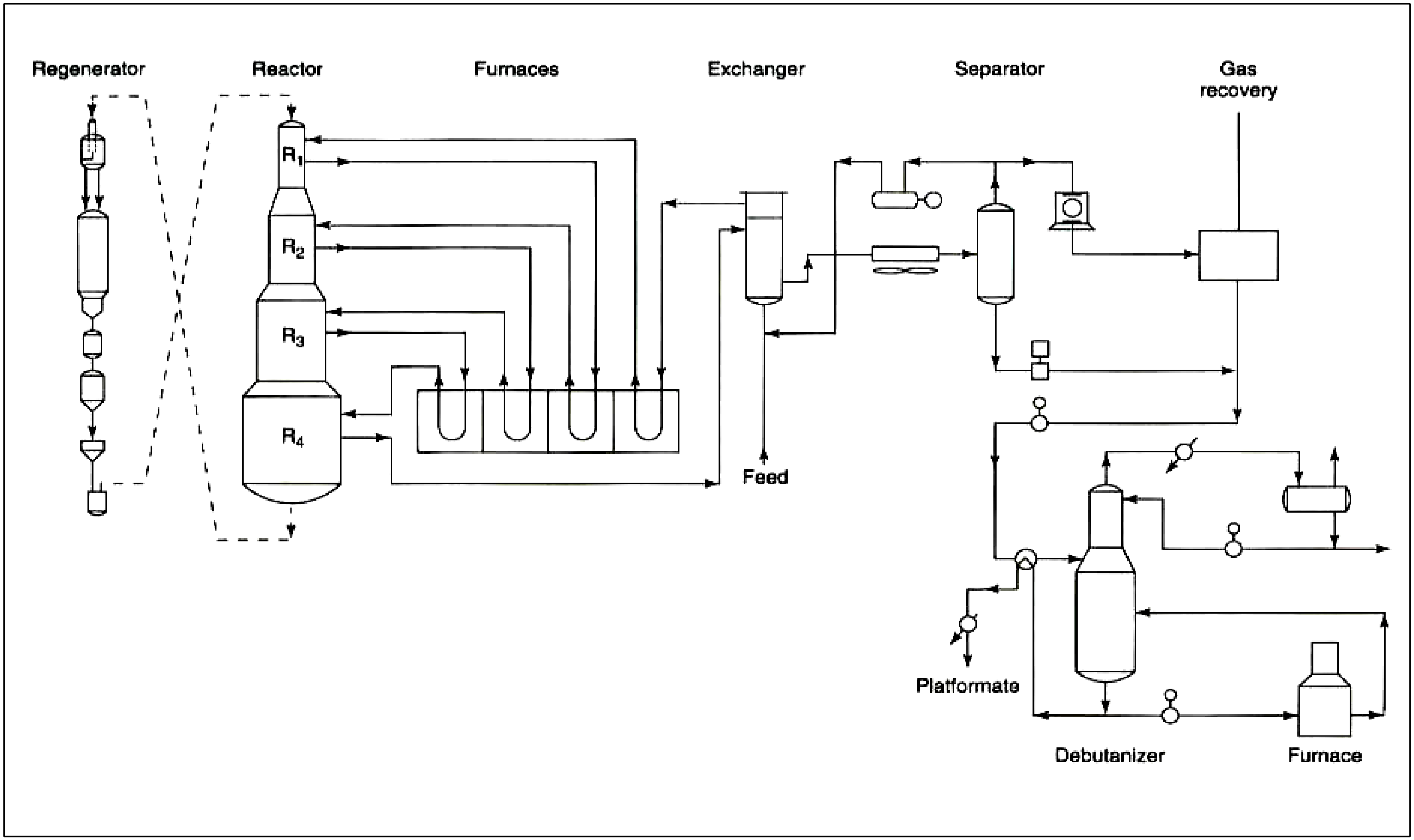


Figure (2.9), Continuous regeneration reformer (UOP: "CCR" Platforming).

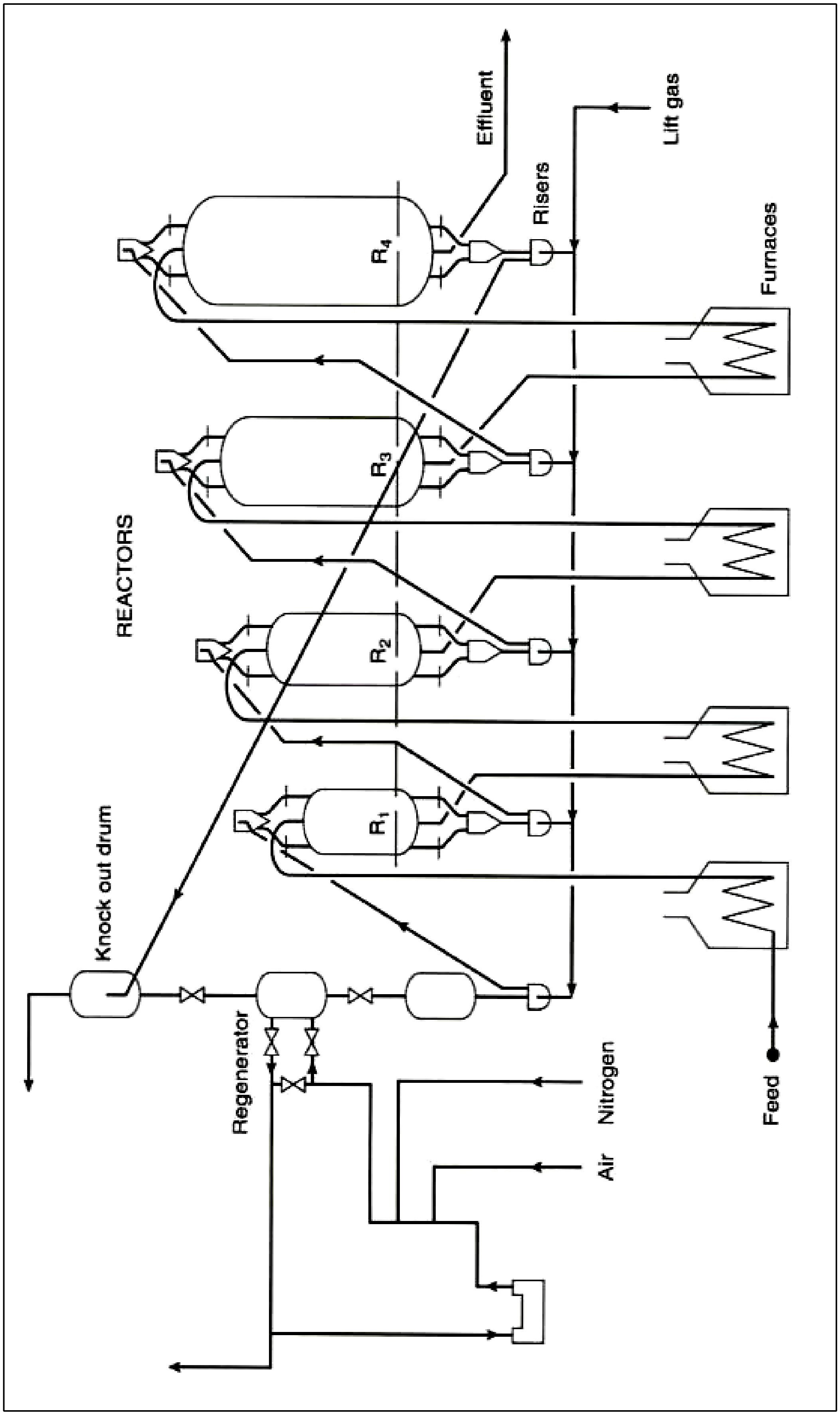


Figure (2.10), Continuous regeneration reformer (IFP: Octanizing). Catalyst circulation regenerator.

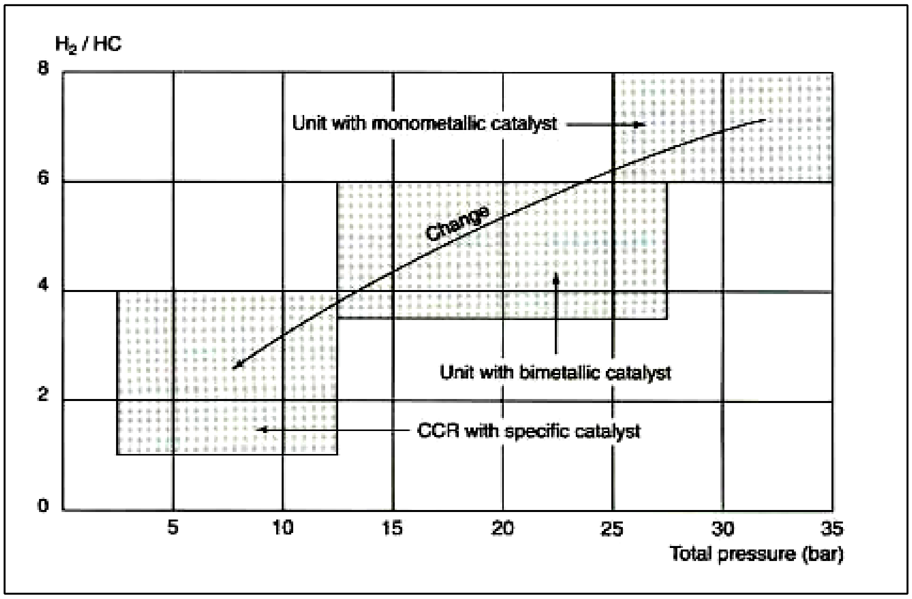


Figure (2.11), Various types of reforming units.

2.4.2.3 Commercial Processes

2.4.2.3.1 IFP "Octanizing" Process

The French Institute of Petroleum developed a process with integral circulation of the catalyst named "Octanizing", as shown in Figure (2.10). IFP also developed two solutions for the problem of revamping the existing old semi-regenerative processes. The first solution is called "Dualforming" and the second is called "Dualforming Plus". Both solutions involve the addition of extra moving-bed equipments to narrow the gap between the fixed- and the moving-bed techniques. Procatalyse offers the bimetallic catalyst CR201 in the form of spheres with high resistance to attrition. This is useful for systems with circulating catalyst such as Dualforming, Dualforming Plus, and Octanizing. For the production of aromatic hydrocarbons, Procatalyse offers the catalysts AR401 and AR405.

The catalyst discharged at the bottom of a reactor is conveyed by a stream of gas, through lift lines and is introduced at the top of the next reactor and so on, until the catalyst exits the last reactor where it is lifted to the top of the regenerator. The agent of transport is hydrogen between reactors and nitrogen between the reactor and the regenerator. The catalyst regeneration system consists of four interdependent zones: primary combustion, final combustion, oxychlorination, and calcination.

2.4.2.3.2 UOP "CCR" Platforming Process

The Platforming® process is a UOP®-developed and -engineered catalytic reforming process in widespread use today throughout the petroleum and petrochemical industries. The first UOP Platforming unit went on-stream in 1949. The Platforming process has since become a standard feature in refineries worldwide. For this reason, it will be discussed in some details.

Historical Background In the years following the invention of Platforming, the need for high-octane gasoline blend components and the demand for aromatics for petrochemicals steadily increased. This increasing market demand required refiners to operate their Platforming units at ever higher severity. Eventually, improvements in the catalyst and process could not keep up, and the need to regenerate catalyst at shorter and shorter intervals became a serious limitation of the SR Platforming units. UOP developed the CCR Platforming process, figure (2.9), to overcome this limitation. In the CCR Platforming unit, partially coked catalyst in the reactors is continuously replaced with catalyst that has been freshly regenerated in an external regenerator (CCR section) to maintain a low average coke for the reactor catalyst. Thus, continuous high-selectivity and high-activity characteristics associated with new catalyst can be achieved at significantly higher severities than with the SR Platforming process. For example, a SR Platforming unit operates at a severity that steadily builds coke up on the catalyst surface over the length of a cycle (6 to 18 months), at which point the unit is shut down and the catalyst regenerated. Throughout the cycle, yields decline. In contrast, with a modern CCR Platforming unit, the catalyst is regenerated approximately every 3 days, and yield remains constant at fresh catalyst levels.

Reactor Configuration In a conventional SR Platforming unit, the reactors are configured side-by-side. The CCR Platforming unit uses a UOP-patented reactor stack. The reactors are stacked one on top of another to achieve a compact unit that minimizes plot area requirements. The catalyst flows gently by gravity downward from reactor to reactor, and this flow simplifies catalyst transfer and minimizes attrition. This configuration eliminates the need to lift the catalyst between reactors, used in the IFP "Octanizing" unit, which leads to a great simplification of the process. In the CCR process, catalyst is lifted only twice during each cycle: from the bottom of the reactor stack to the top of the regenerator and then from the bottom of the regenerator back to the top of the reactor stack. The catalyst transfer requires no operator intervention. Catalyst transfer rates have been designed from as low as 91 kg/h (200 lb/h) to as high as 2721 kg/h (6000 lb/h), depending on the capacity and the operating severity of the Platforming unit.

CCR System The ability to continuously regenerate a controlled quantity of catalyst is the most significant innovation of the CCR Platforming unit. The catalyst flows by gravity from the last reactor into an integral (to the reactor) catalyst collector vessel. The catalyst is then lifted by either nitrogen or hydrogen lifting gas to a catalyst hopper above the regeneration tower. Catalyst flows to the regeneration tower, where the catalyst is reconditioned. Regenerated catalyst is then returned to the top of the reactor stack by a transfer system similar to that used in the reactor-regenerator transfer. Thus, the reactors are continuously supplied with freshly regenerated catalyst, and product yields are maintained at fresh catalyst levels.

The regeneration and reactor sections of the unit are easily isolated to permit a shutdown of the regeneration system for normal inspection or maintenance without interrupting the Platforming operation. Improvements are continuously being made in the CCR regeneration section design. In addition to its atmospheric and pressurized regenerators, UOP introduced the CycleMax® regenerator in 1995 which combines new innovations with the best aspects of previous CCR designs at lower cost.

UOP Commercial Experience UOP has designed more than 730 Platforming (both SR and CCR) units around the world with a total feedstock capacity of more than 9.1 million barrels per standard-day (BPSD). The feedstocks range from benzene-toluene (BT) cuts to full-range, lean Middle East naphthas and rich U.S. and African naphthas and hydrocracked stocks with capacities ranging from 150 to 60,000 BPSD. Research octane numbers run from 93 to 108 over a wide range of catalysts.

The UOP CCR Platforming process is the most successful reforming process offered by any licenser. As of mid-2002, UOP unparalleled commercial experience included:

- 171 UOP CCR Platforming units operating around the world.
- 52 units operating at state-of-the-art reactor pressure of 75 lb/in^2 gage.
- 82 units operating at or below 100 lb/in2 gage reactor pressure.
- 4,000,000 BPSD CCR Platforming unit operating capacity.
- 99.5% of all CCR Platforming units ever started up still operating.
- 31 more UOP CCR Platforming units in design and construction.

2.4.2.3.3 UOP "RZ" Platforming

RZ Platforming is the latest development in UOP long tradition of reforming process improvements. The process is built around a new type of catalyst called RZ-100. RZ-100 is a zeolitic catalyst, activated with platinum, that gives the highest obtainable yields of benzene (B) and toluene (T) from naphtha feedstocks. The RZ process is ideally suited for use in aromatics production facilities especially when large amounts of benzene are required. The ability of the RZ Platforming process to convert light paraffinic feeds and its flexibility in processing straight-run naphtha fractions provide many options for improving aromatics production and supplying highly desired hydrogen. Figure (2.12) shows the RZ Platforming Process.

2.4.3 Fluid-Bed Technology

In catalytic reforming processes using a fluidized solids catalyst bed, continuous regeneration with a separate or integrated reactor is practiced to maintain catalyst activity by coke and sulfur removal. Cracked or virgin naphtha is charged with hydrogen-rich recycle gas to the reactor. A molybdena (Mo_2O_3, 10.0%) on alumina catalyst, not materially affected by normal amounts of arsenic, iron, nitrogen, or sulfur, is used. Operating conditions in the reactor are about 200 to 300 psi and 480°C to 950°C (900°F to 950°F).

Fluidized-bed operation with its attendant excellent temperature control prevents over- and under-reforming operations, resulting in more selectivity in the conditions needed for optimum yield of the desired product.

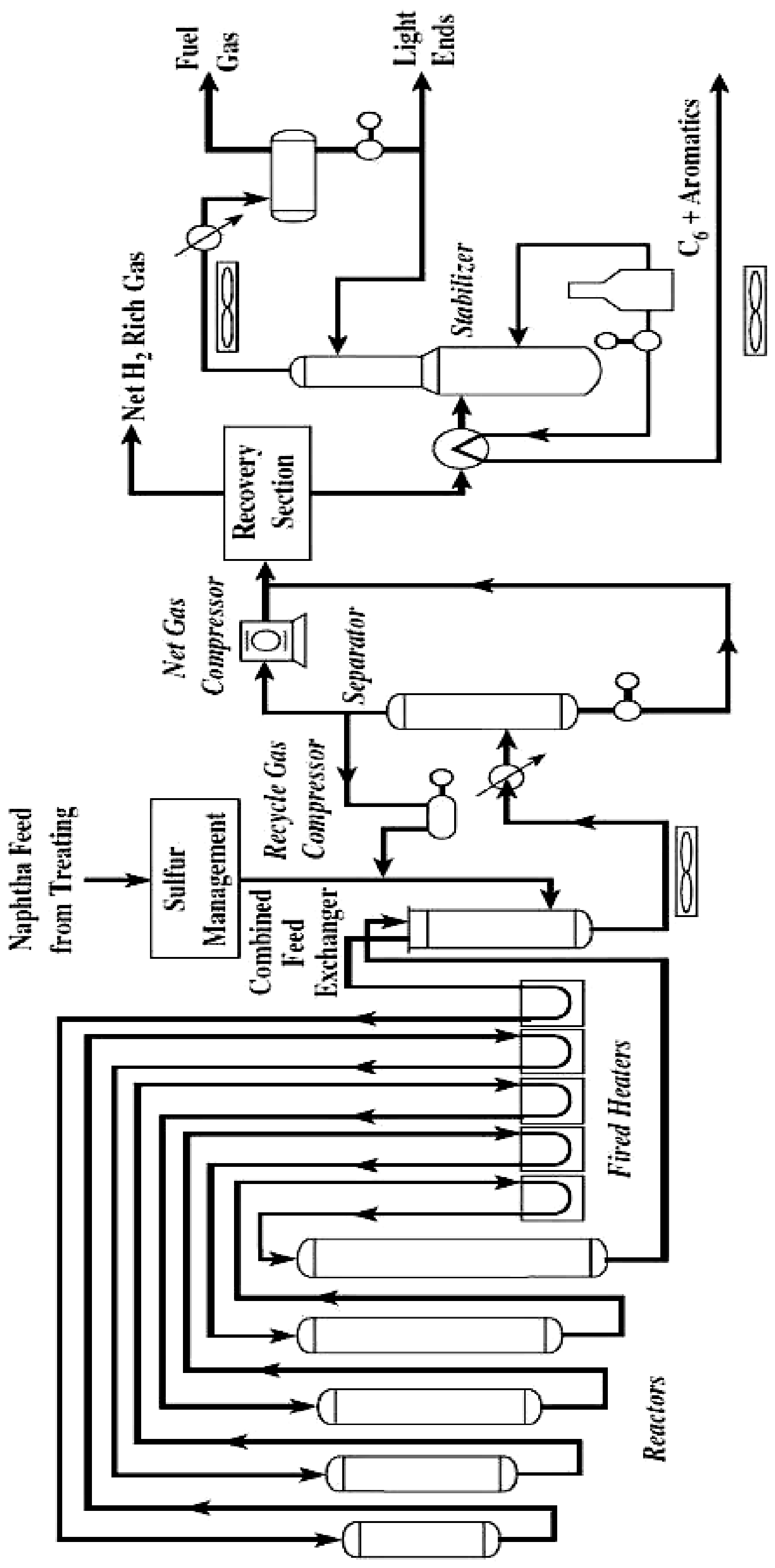
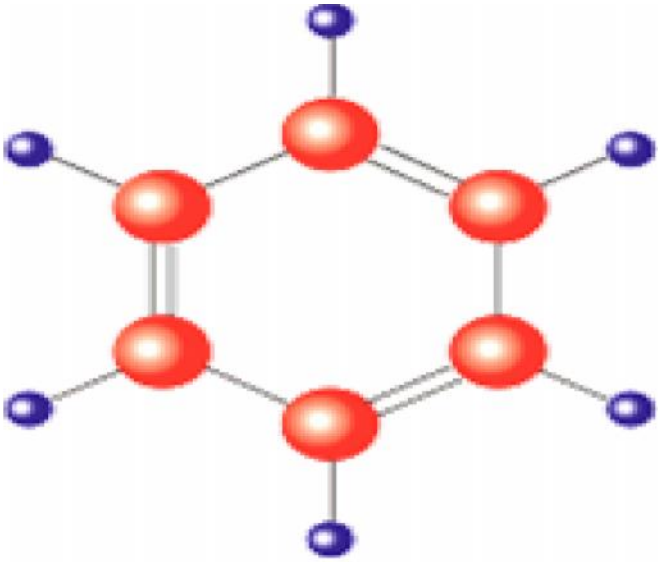


Figure (2.12), The UOP "RZ" Platforming Process.

CH.3

Process Chemical Reactions & Thermodynamics



3.1 INTRODUCTION

Platforming reactions can generally be grouped into four categories: dehydrogenation, isomerization, dehydrocyclization, and cracking. The reactions are promoted by two kinds of active sites on the catalyst, acidic and metallic. The extent to which each of the reactions occurs for a given Platforming operation depends on the feedstock quality, operating conditions, and catalyst type.

Because the Platforming feed is made up of many paraffin and naphthene isomers, multiple reforming reactions take place simultaneously in the Platforming reactor. The rates of reaction vary considerably with the carbon number of the reactant. Therefore, these multiple reactions occur in series and in parallel to one another. The generalized reaction network is illustrated in Figure (3.1), and examples of the individual reactions are shown in Figure (3.2).

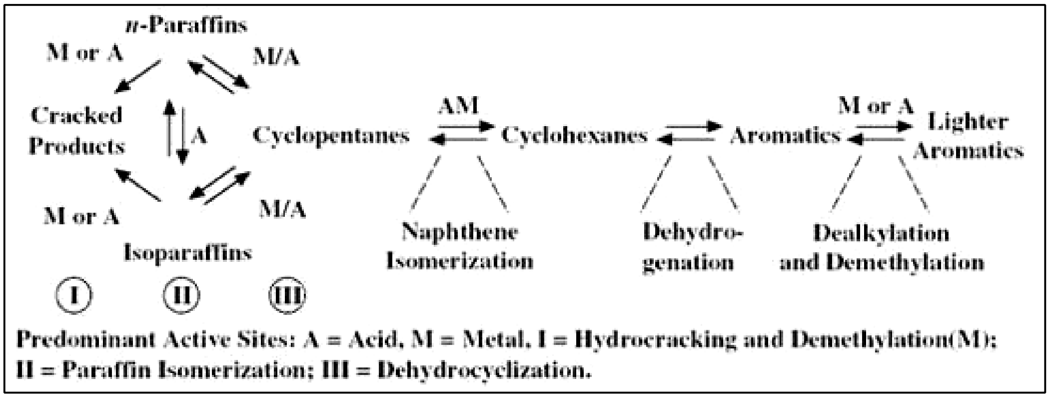


Figure (3.1), Generalized Platforming reaction network.

3.2 PROCESS REACTIONS

3.2.1 Dehydrogenation of Naphthenes

The principal Platforming reaction in producing an aromatic from a naphthene is the dehydrogenation of an alkylcyclohexane. This reaction takes place rapidly and proceeds essentially to completion. The reaction is highly endothermic, is favored by high reaction temperature and low pressure, and is promoted by the metal function of the catalyst. Because this reaction proceeds rapidly and produces hydrogen as well as aromatics, naphthenes are the most desirable component in the Platforming feedstock.

3.2.2 Isomerization of Paraffins and Naphthenes

The isomerization of an alkylcyclopentane to an alkylcyclohexane must take place before an alkylcyclopentane can be converted to an aromatic. The reaction involves ring rearrangement, and thus ring opening to form a paraffin is possible. The paraffin isomerization reaction occurs rapidly at commercial operating temperatures. Thermodynamic equilibrium, however, slightly favors the isomers that are more highly branched. Because branched-chain isomers have a higher octane than straight-chain paraffins, this reaction improves product octane. Isomerization reactions are promoted by the acid function of the catalyst.

3.2.3 Dehydrocyclization of Paraffins

The most-difficult Platforming reaction to promote is the dehydrocyclization of paraffins. This reaction consists of molecular rearrangement of a paraffin to a naphthene. Paraffin cyclization becomes easier with increasing molecular weight of the paraffin because the probability of ring formation increases. Partially offsetting this effect is the greater likelihood of the heavy paraffins to hydrocrack. Dehydrocyclization is favored by low pressure and high temperature and requires both the metal and acid functions of the catalyst.

3.2.4 Hydrocracking and Dealkylation

In addition to naphthene isomerization and paraffin cyclization reactions, the acid function catalyzes paraffin hydrocracking. Paraffin hydrocracking is favored by high temperature and high pressure. As paraffins crack and disappear from the gasoline boiling range, the remaining aromatics become concentrated in the product, thereby increasing product octane. However, hydrogen is consumed, and the net liquid product is reduced, making this reaction undesirable.

Dealkylation of aromatics includes both making the alkyl group (a side chain on the aromatic ring) smaller and removing the alkyl group completely. Examples are converting ethylbenzene to toluene and converting toluene to benzene, respectively. If the alkyl side chain is large enough, the reaction is similar to paraffin cracking. Dealkylation is favored by high temperature and high pressure.

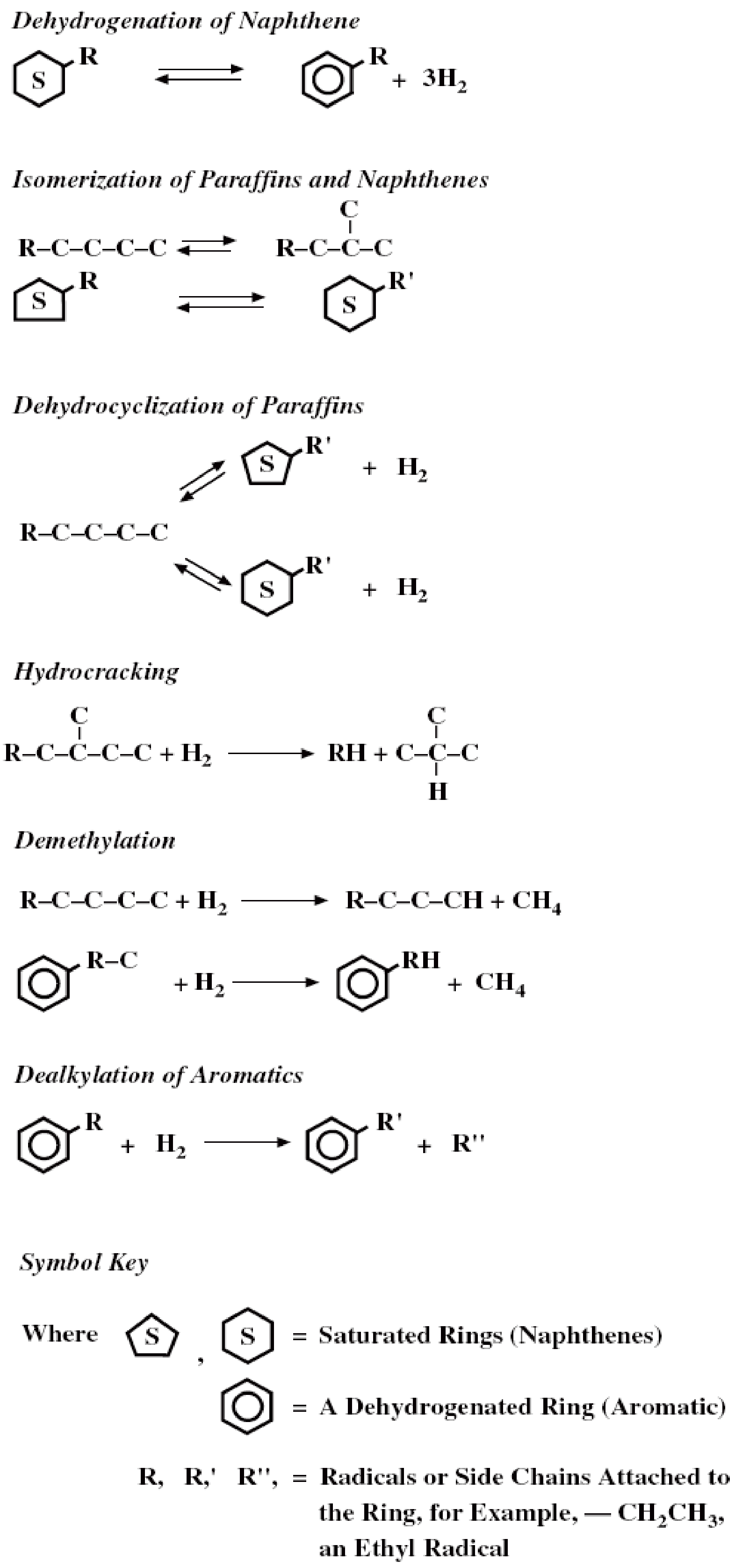


Figure (3.2), Generalized Platforming Individual Reactions.

3.3 RELATIVE REACTION RATE

The primary reactions for the C_6 and C_7 paraffins proceed at vastly different rates. Because the hydrocracking rate for hexane is at least 3 times greater than the dehydrocyclization rate for hexane, only a small fraction of normal hexane is converted to aromatics. The rate of heptane dehydrocyclization is approximately 4 times that of hexane. Therefore, a substantially greater conversion of normal heptane to aromatics occurs than for hexane.

Reactions of naphthenes in the feedstock show significant differences between the alkylcyclopentanes and the alkylcyclohexanes. The alkylcyclopentanes react slowly and follow two competing paths. The desired reaction is isomerization to an alkylcyclohexane followed by dehydrogenation to aromatics. The competing reaction is decyclization to form paraffins. In contrast, the alkylcyclohexanes dehydrogenate rapidly and nearly completely to aromatics.

The relative ease of isomerization to an alkylcyclohexane increases with increasing carbon number. For example, the ratio of alkylcyclopentane isomerization rate to total alkylcyclopentane reaction rate is 0.67 for methylcyclopentane at low pressure. This ratio increases to 0.81 for dimethylcyclopentane, one carbon atom higher.

The conversion of hydrocarbon types as a function of position in the catalyst bed for a moderate-severity Platforming operation is shown in Figures (3.3 to 3.6). The feedstock is a rich BTX naphtha with a paraffin, naphthenes, and aromatics (PNA) content of 42, 34, and 24 wt %, respectively. As the naphtha feed passes through the catalyst bed, total aromatics concentration increases and the concentration of naphthenes and paraffins decreases as they undergo conversion Figure (3.3). The high rate of conversion of cyclohexanes is shown by the rapidly decreasing concentration of naphthenes in the first 30 percent of the catalyst volume. The remaining naphthene conversion occurs at a slower rate and is indicative of cyclopentane conversion and dehydrocyclization of paraffins through a naphthene intermediate. By the reactor outlet, the naphthene concentration approaches a low steady-state value, which represents the naphthene intermediary present in the paraffin dehydrocyclization reactions. In contrast, paraffin conversion is nearly linear across the reactor bed.

Figure (3.4) illustrates the conversion of the three reactive species in the Platforming feedstock. The relative rates of conversion are markedly different. In the first 20 percent of the catalyst, 90 percent of the cyclohexanes are converted, but conversion is only 15 percent for cyclopentanes and 10 percent for paraffins. Cyclopentanes are much less reactive than cyclohexanes.

Figure (3.5) shows the relative reaction rate of cyclopentanes by carbon number. Heavier components, which have a greater probability of isomerizing from a five- to six-carbon ring, convert more readily than do the lighter components. The most-difficult reaction, the conversion of paraffins, is characterized by carbon number in Figure (3.6). As with the cyclopentanes, the heavier paraffins convert more readily than do the lighter paraffins. The relative ease of conversion associated with increasing carbon number for alkylcyclopentanes and paraffins explains why higher-boiling-range feedstocks are easier to process.

In summary, paraffins have the lowest reactivity and selectivity to aromatics and are the most difficult components to process in a Platforming unit. Although alkylcyclopentanes are more reactive and selective than paraffins, they still produce a significant amount of nonaromatic products. Alkylcyclohexanes are converted rapidly and quantitatively to aromatics and make the best reforming feedstock. As a general rule, heavier components convert more easily and selectively to aromatics than do the lighter components.

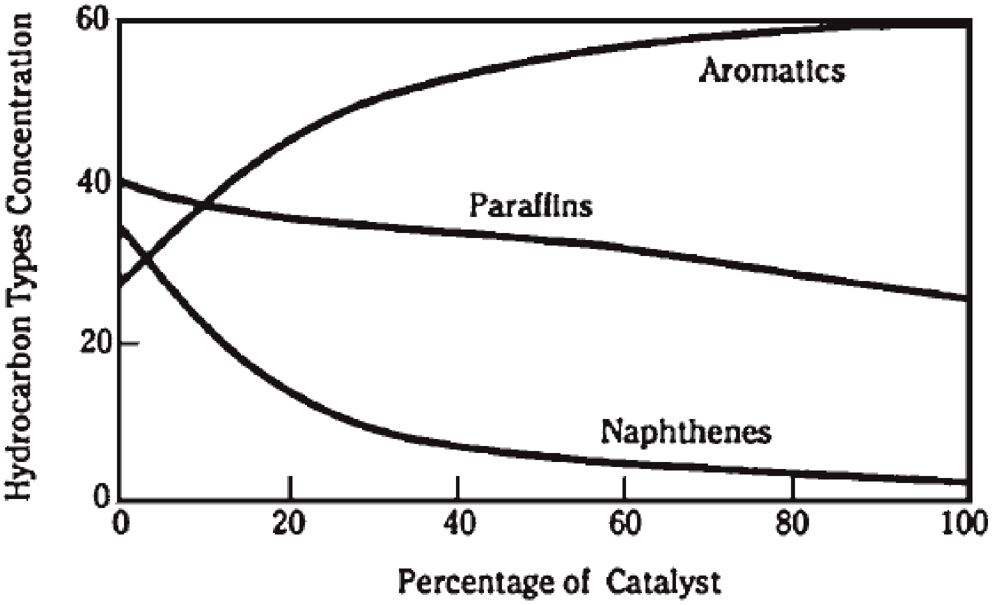


Figure (3.3), Hydrocarbon Type Profiles.

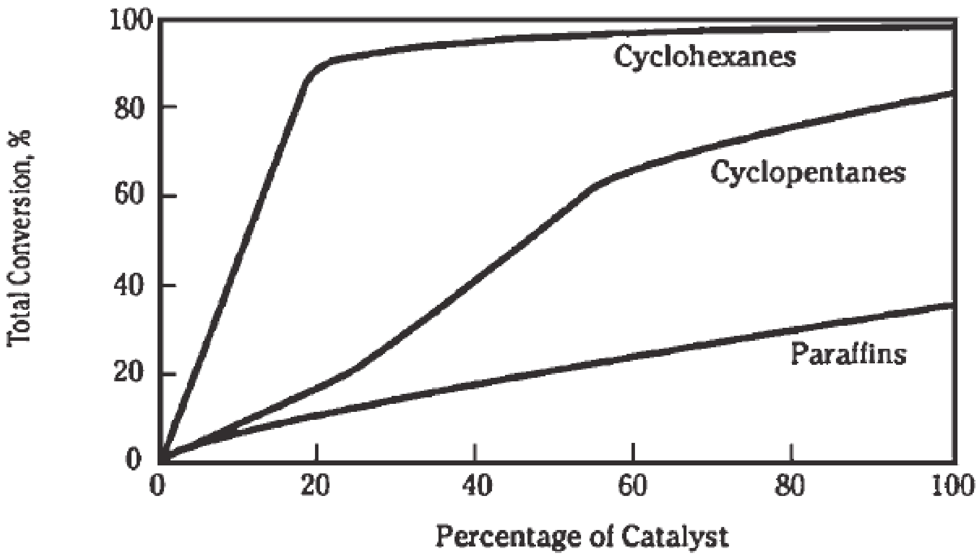


Figure (3.4), Reactant-Type Conversion Profiles.

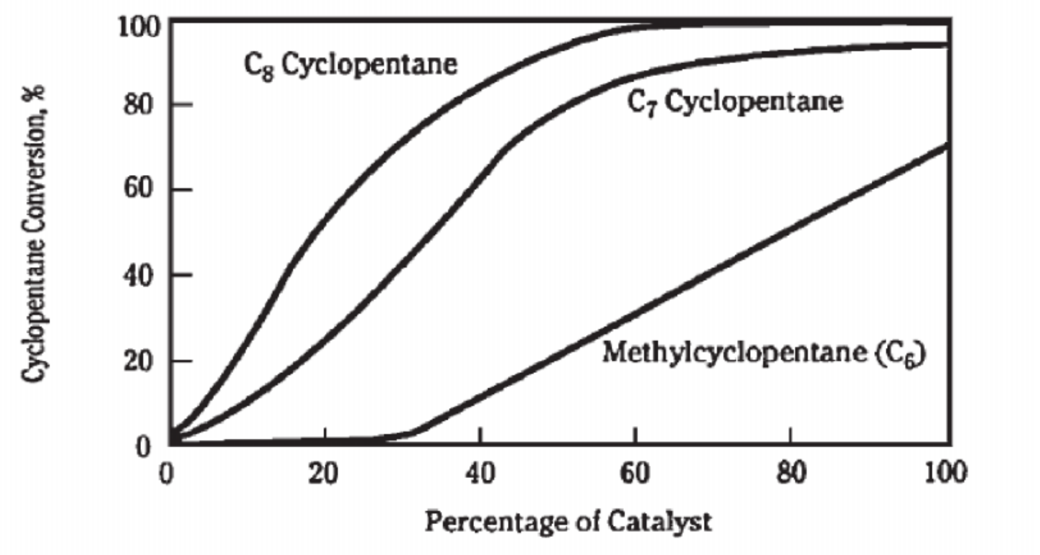


Figure (3.5), Cyclopentane conversion by carbon number.

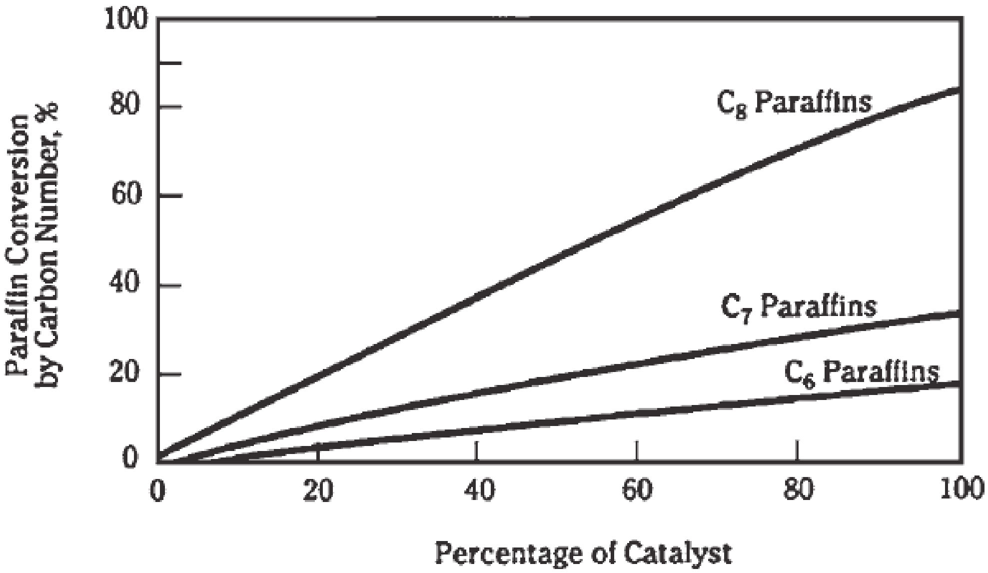


Figure (3.6), Paraffin Conversion by Carbon Number.

3.4 HEATS OF REACTION

Typical heats of reaction for the three broad classes of Platforming reactions are presented in table (3.1). The dehydrocyclization of paraffins and dehydrogenation of naphthenes are endothermic. In commercial Platforming units, the majority of these reactions take place across the first two reactors, as indicated by the large negative-temperature differentials observed. In the final reactor, where a combination of paraffin dehydrocyclization and hydrocracking takes place, the net heat effect in the reactor may be slightly endothermic or exothermic, depending on processing conditions, feed characteristics, and catalyst.

Reaction	ΔH, kJ/mol H_2
Paraffin to naphthene	+44 (endothermic)
Naphthene to aromatic	+71 (endothermic)
Hydrocracking	−56 (exothermic)

Table (3.1), Heats Of Reactions.

CH.4

Catalytic Reforming Catalyst

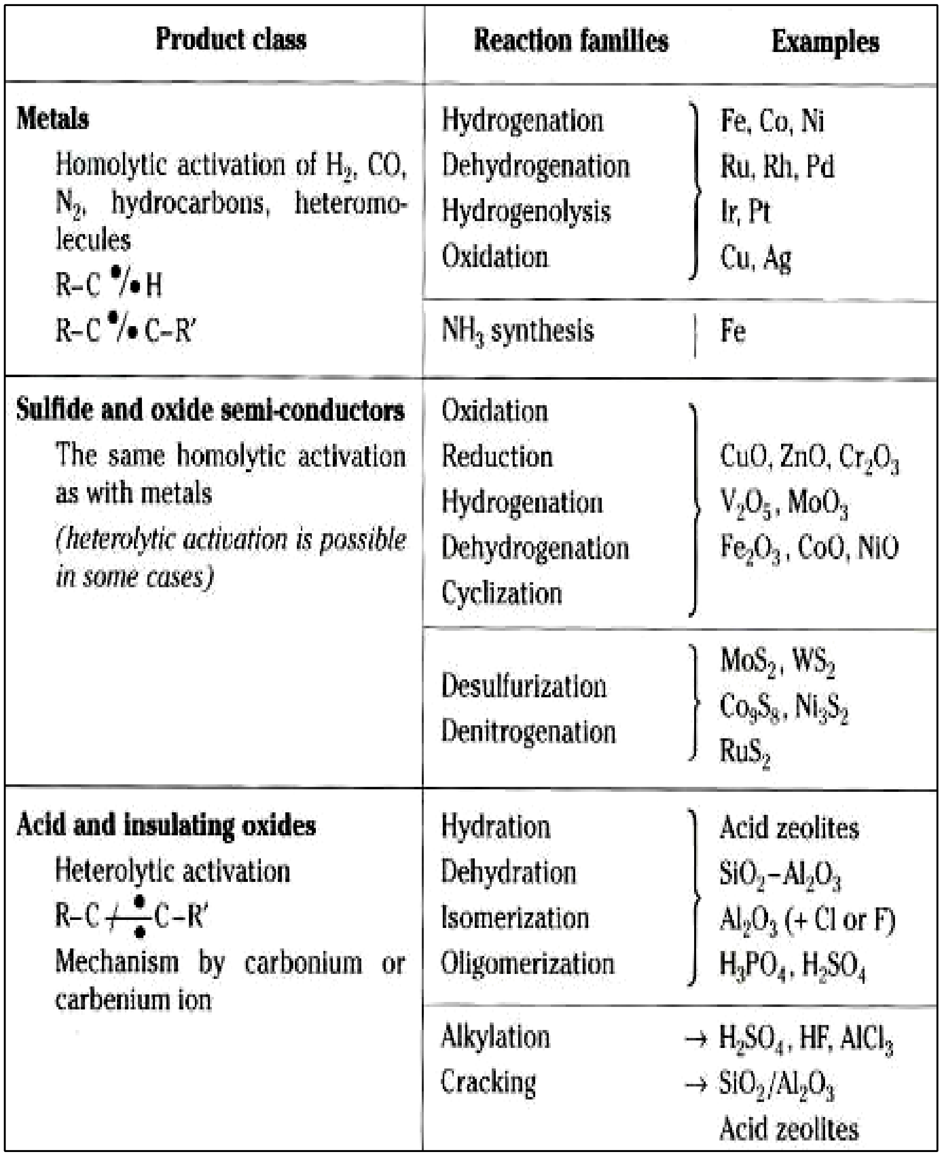
4.1 INTRODUCTION

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.

4.1.1 Classification of Catalyst

4.1.1.1 Empirical Classification

It distinguishes, on the one hand, the active element causing homolytic or radical activation. On the other hand there are the active elements responsible for heterolytic or ionic activation of hydrocarbons (insulating oxides). An example of the empirical classification is given in Table (4.1).



Product class	Reaction families	Examples
Metals Homolytic activation of H_2, CO, N_2, hydrocarbons, heteromolecules $R{-}C\,{}^{\bullet}/_{\bullet}\,H$ $R{-}C\,{}^{\bullet}/_{\bullet}\,C{-}R'$	Hydrogenation Dehydrogenation Hydrogenolysis Oxidation	Fe, Co, Ni Ru, Rh, Pd Ir, Pt Cu, Ag
	NH_3 synthesis	Fe
Sulfide and oxide semi-conductors The same homolytic activation as with metals *(heterolytic activation is possible in some cases)*	Oxidation Reduction Hydrogenation Dehydrogenation Cyclization	CuO, ZnO, Cr_2O_3 V_2O_5, MoO_3 Fe_2O_3, CoO, NiO
	Desulfurization Denitrogenation	MoS_2, WS_2 Co_9S_8, Ni_3S_2 RuS_2
Acid and insulating oxides Heterolytic activation $R{-}C\overset{\bullet}{\underset{\bullet}{\not{+}}}C{-}R'$ Mechanism by carbonium or carbenium ion	Hydration Dehydration Isomerization Oligomerization	Acid zeolites $SiO_2{-}Al_2O_3$ Al_2O_3 (+ Cl or F) H_3PO_4, H_2SO_4
	Alkylation Cracking	→ H_2SO_4, HF, $AlCl_3$ → SiO_2/Al_2O_3 Acid zeolites

Table (4.1), The Empirical Classification of Catalyst.

4.1.1.2 Explicative Correlations

They relate catalytic properties of active elements alone or associated with the intrinsic properties of the active solid or with the interaction properties that the solid exhibits with the reaction medium, especially with the properties characterizing, absorption and adsorption.

Active phase catalyst properties can be radically modified by adding promoters, sometimes only as traces.

4.1.2 Main Types of active phases of Catalyst

There are four types of active phases of catalysts:

1. **Bulk catalysts :** Are exclusively made up of active phase. For Example: Claus catalysts, and heterogeneous oligomerzation catalysts.
2. **Supported catalysts :** The active phases of refining catalysts are usually consists of an active phase dispersed on an oxide support under control on a previously shaped oxide support. For Example: catalytic reforming catalyst made up of approximately 0.5% platinum and a promoter dispersed on a chlorinated γ alumina support. In contrast to bulk catalysts the use of a pre-shaped oxide allows control of its genesis and especially the optimization of its textural, structure, mechanical and morphological properties.
3. **Catalysts resulting from unit operation :** Combining shaping and the addition of an active phase or precursor salts. For Example: Catalytic cracking catalysts.
4. **homogeneous catalysts :** Are produced from organo-metallic complexes interacting with an appropriate solvent medium. They are added in trace amounts in the reaction medium. They are used especially in light olefin oligomerization for motor fuel production, in gasoline and kerosene sweetening.

4.1.3 General Catalyst Characteristics and Properties

4.1.3.1 Basic Characteristics

Three basic features characterize the catalyst's action:

4.1.3.1.1 Catalyst Activity

Expresses reactant transformation rate under given operating conditions in several different ways.good activity means a high reaction rate with two possible advantages:either a small amount of catalyst can be used or operating conditions can be less severe, especially the operating temperature which can be relatively low.

4.1.3.1.2 Catalyst Selectivity

Characterizes the aptitude to activate reactant transformation towards the required product among all those that could be formed. High selectivity allows a good yield of the required product to be achieved and reduces side reactions to a minimum.

4.1.3.1.3 Catalyst Stability

Defined as the period during which its activity and selectivity remain unchanged.

4.1.3.2 Intrinsic Characteristics

4.1.3.2.1 Structural Properties

The quality of sites dispersed on the active surface, which governs catalysis as such, is determined by the characteristics of the accessible active phase (structure, local chemical composition, defects). These characteristics in turn determine the intrinsic characteristics of the accessible sites (nature, strength, density, stability, etc.).

4.1.3.2.2 Textural Properties

These properties govern the possibility of reactant access (by diffusion) to the above-mentioned sites as well as the possibility of evacuating the reaction products outside by diffusion. Catalyst texture is determined by the total specific surface area, the active specific surface area (expressed in per cent of accessibility for dispersed metals), the accessible pore volume, and the interconnectivity of the pore network.

4.1.3.3 Non-Catalytic Characteristics

4.1.3.3.1 Mechanical Properties

during its lifetime the catalyst is exposed to a number of different mechanical constraints (production, transportation, storage, loading into the reactor, unit start up and shut down which cause settling, utilization in the unite, unloading, off site regeneration, reloading, etc.) with the resulting breakage, abrasion and attrition. Actual use in the unit is sometimes a critical period, especially when the catalyst circulates.

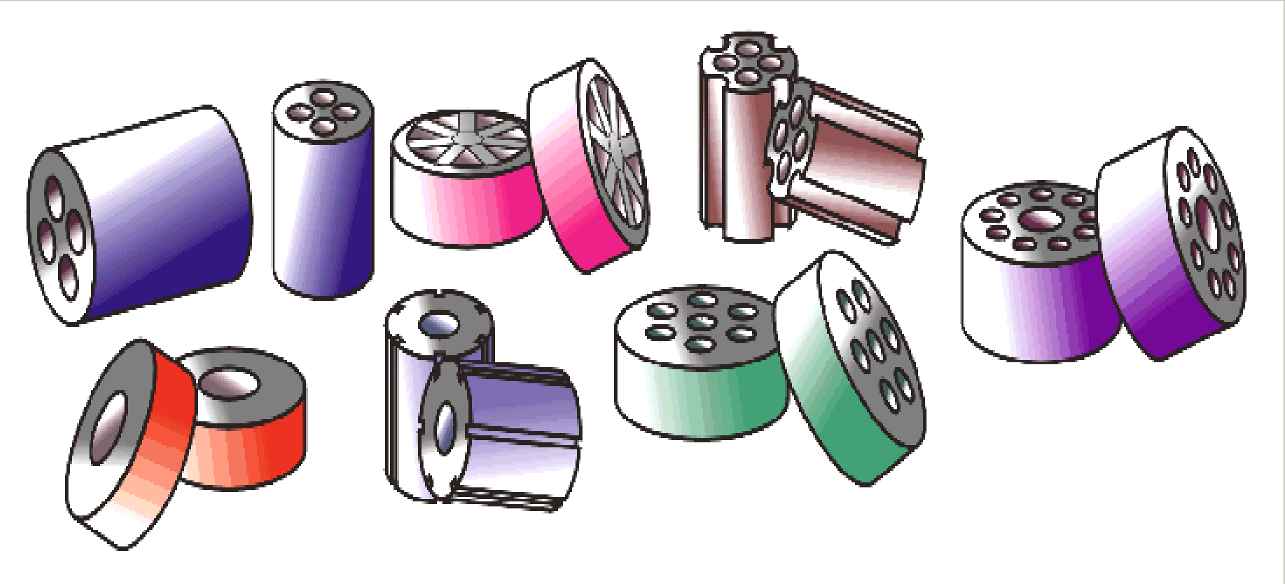
Resistance to mechanical degradation is therefore an important property and should be monitored.

4.1.3.3.2 Thermal Properties

When reactions are highly endothermic or exothermic, good thermal conductivity allows temperature gradients to be limited in the catalyst grain and bed, thereby promoting the heat transfer. If the catalyst is to function as a heat carrier (in catalytic cracking for example) it should have maximum heat capacity: the heat energy stored during coke combustion will be returned during the reaction, thereby offsetting its endothermicity.

4.1.3.3.3 Morphology of Catalyst (shape and granulometry)

Depends on where it is used. Ex:-a spherical shape is recommended for entrained or bulleting fluid beds and rings are used when minimum pressure drop is required.

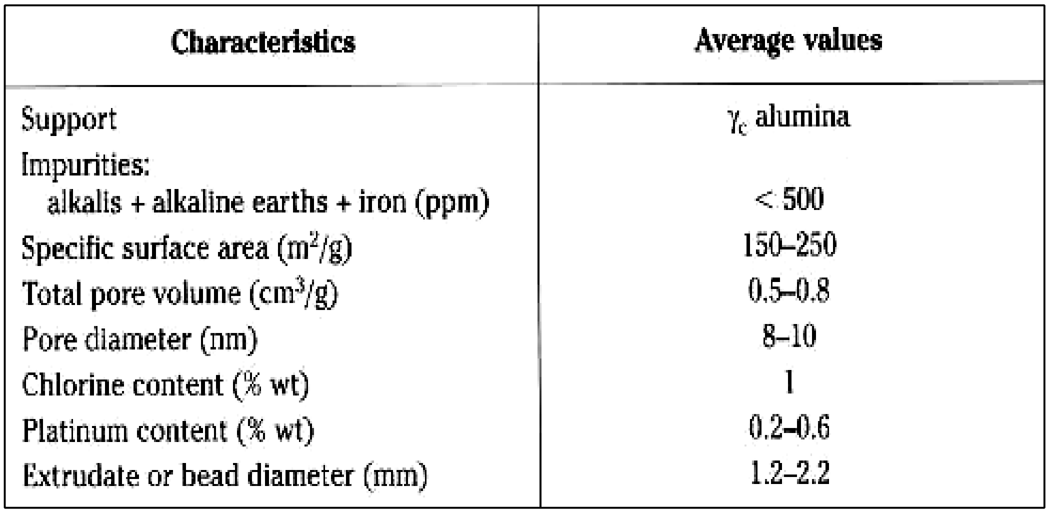


4.2 TYPES OF CATALYTIC REFORMING CATALYST

All current catalysts are derived from platinum on chlorinated alumina as introduced by UOP in 1949.

4.2.1 Platinum on Chlorinated Alumina

A few hundred tons of this type of catalyst are still being used in the world. Table (4.2) gives its main characteristics.



Characteristics	Average values
Support	γ_c alumina
Impurities:	
alkalis + alkaline earths + iron (ppm)	< 500
Specific surface area (m^2/g)	150–250
Total pore volume (cm^3/g)	0.5–0.8
Pore diameter (nm)	8–10
Chlorine content (% wt)	1
Platinum content (% wt)	0.2–0.6
Extrudate or bead diameter (mm)	1.2–2.2

Table (4.2), Main Characteristics of Pt/Al_2O_3.

The base is γ_c alumina; chlorinated at approximately 1% wt. the specific area ranges from 150 to 250 m^2/g, and the pore volume from 0.5 to 0.8 cm^3/g. The average pore diameter is approximately 10nm. The alumina used are very pure and the alkaline metals, alkaline earths, iron etc., always account for less than 500 ppm on new catalysts and usually less than 100 ppm. The amount of platinum is on a downward trend, usually ranging between 0.2 and 0.6% wt. the catalyst is implemented in the form of beads (fixed and moving beds) or extradites (fixed bed), approximately 1.2 to 2.2 mm in diameter.

In addition to the properties of the support and the amount of platinum, it is crucial to make the most of the small amount of platinum (cost of platinum = $15/g) on the catalyst. As such, each platinum atom should be accessible to the reactants and therefore should be in unit amounts of the smallest size possible. A gram of platinum well dispersed on the surface of an alumina will represent an area of approximately 260 m^2 and will have maximum hydrogenating or dehydrogenating activity. If on the contrary non-optimum operations are carried out during catalyst implementation, values lower than 100 m^2/g of platinum will be obtained and the catalyst will be approximately three times less active.

Dispersion D is define by the ratio between the real area and the theoretically possible area per gram of platinum. The theoretical area can be achieved on industrial catalysts.

4.2.2 Bimetallic

They consist of platinum associated with another metal (iridium, rhenium, tin or germanium). The use of Pt/Re is now most common in semi-regenerative processes and Pt/Sn in moving beds. Catalyst properties can be adapted to the unit's operating conditions. An interaction between two metals, whose properties and chemistry are widely different, must be achieved on the scale of the nanometer and this is the manufacturers' secret.

The effects of different metals on performance have not been publicly quantified, since there is no non-proprietary literature available. However, it can be stated that the different elements do have a positive effect, although the effects differ. The following properties are involved: stability of dispersion over time, modification of coking resistance, change in selectivity and especially for high concentrations of iridium, and a significant effect on activity.

Figure (4.1) illustrates the influence of elements such as tin, indium, rhenium and iridium on the evolution in the platinum surface over time as compared with platinum alone. In all cases, the effect is highly positive. This is why these elements have been selected for numerous industrial catalysts.

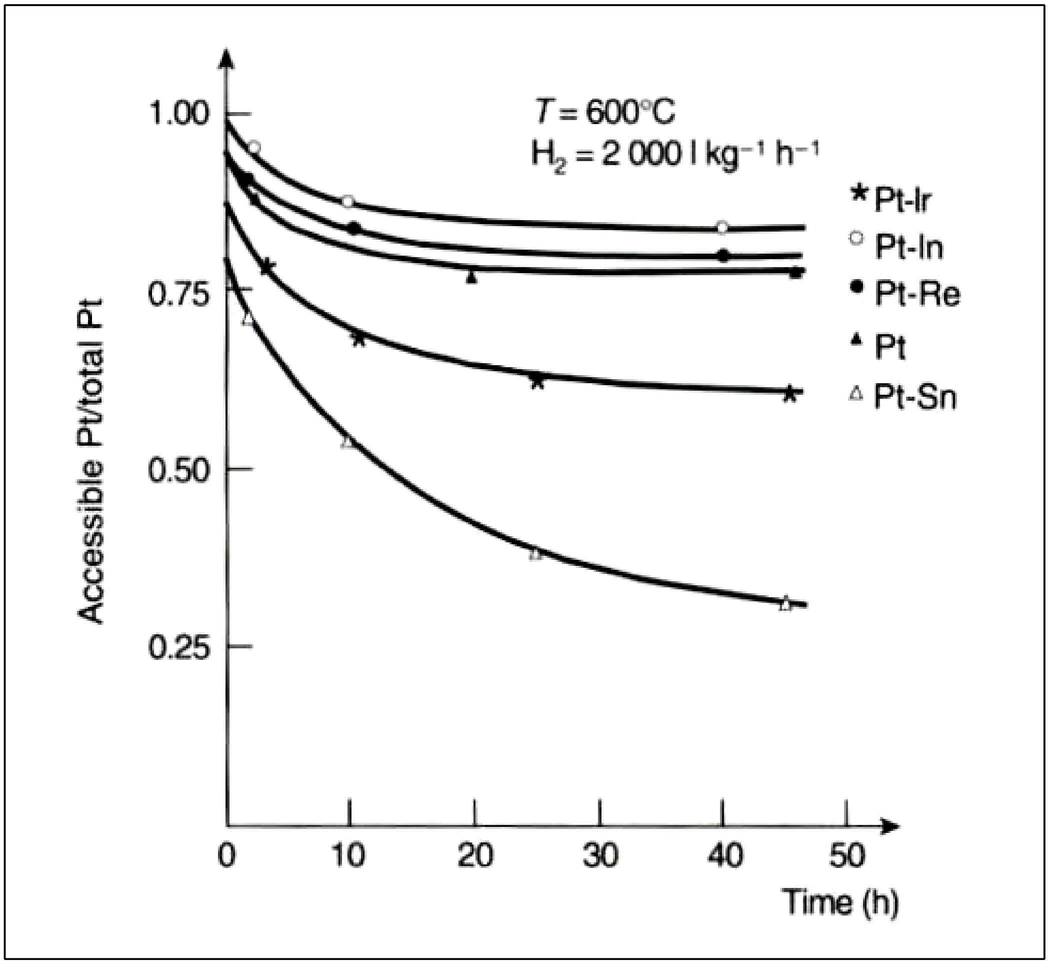


Figure (4.1), Effect of Different Metals on Platinum Sintering Under Hydrogen Pressure.

Figure (4.2) shows the variation in octane number in a constant temperature test versus time. In these operating conditions-feed end point very high and test duration short-deactivation is related only to coke formation and/or coke toxicity with respect to activity. The bimetallic catalyst, here platinum-rhenium, proves incomparably more stable than the monometallic one. The other "second metals", Sn and Ir, give the same type of effects.

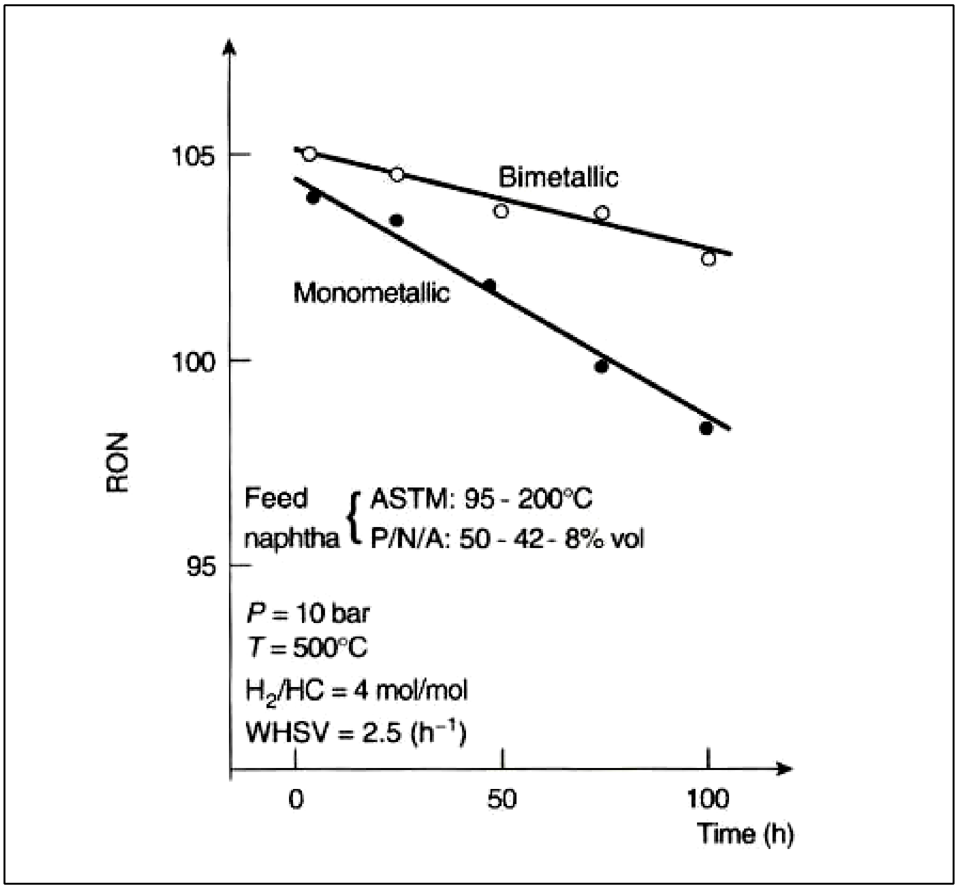


Figure (4.2), Compared Stability of mono- and bi-metallic Catalysts.

4.3 EFFECT OF PLATINUM CONTENT OF CATALYST

Platinum content of the catalyst is in the range (0.3 – 0.8 % wt).

- At higher levels there is some tendency to effect dimethylation and naphthene ring opening, which is undesirable, while at lower levels the catalyst tends to be less resistance to poisons.

- Platinum is extremely expensive. As the platinum content of catalyst is reduced, it's resistance to deactivation is also reduced.

- The high platinum catalysts (0.6 – 0.8 % wt pt) are used for sever operations such as the production of 100 octane number gasoline from feeds with only moderate naphthene contents.

-The latest development is the use of bimetallic catalyst which incorporated other metals (Rhenium and Tin) in addition to platinum this catalyst can operate at lower hydrogen partial pressure than can the normal platinum catalyst without deactivation.

4.4 CATALYST PREPARATION

There are two methods for catalyst preparation:

4.4.1 Optimizing the formulation

Step 1
The choice of active phases is based on experience (empirical or scientific correlation).

Step 2
Aims to identify which initial reactants include or prefigure the desired active phase.
Step 3
Design an operating mode.
Finally to implement it.

Step 4
Determining basic catalyst properties in addition to the test reaction in order to validate the result.

Step 5
Once an initial result has been obtained and the active phase has been characterized, the required catalyst qualities are ranked: catalyst, physicochemical and mechanical properties. The most critical are singled out and the key preparation unit operations are listed. To the extent possible, the textural and structure properties that can be correlated to performance are identified.

At the same time, on the basis of published data and initial kinetic experiments, a simplified approach to the reaction mechanism is used to identify the limiting steps and the possible inhibiting effects. In particular, it is used to define the level of diffusional limitations.
At this stage, the activity and selectivity of an initial catalytic formula have been established and performance stability has proved satisfactory. Then the evolution of the active phase (and/or the support) should be assessed in the reaction medium and if possible its stationary state should be characterized.

The catalyst formula under study can now be considered valid and a number of correlations can be established linking its catalytic properties, the intrinsic characteristics of the active phase (and/or the support) , the preparation conditions, then the pretreatment conditions in the reactor and the stabilization conditions in the reaction medium.

As soon as laboratory formulation has been optimized and the catalysis results have been validated in a continuous pilot on a real feed, it will be possible to scale up the operating mode to produce a pilot test batch of catalyst (10 to 50 liters) and then to begin optimizing the operating conditions of the future production process. This will result in a representative pre-industrial sample which will be tested in a large pilot unit.

4.4.2 Unit Operations

The aim is to produce a catalyst at the lowest possible cost, consisting of the required active agents, with the desired surface area and porosity, external morphology and necessary mechanical properties for the process technology under consideration.The choice being made between different possible manufacturing methods. The resulting manufacturing technique will be based on a sequence of unit operations. The number and sequencing order of these operations must be optimized to minimize the manufacturing cost and obtain the most high-performance and reproducible product possible. Figure (4.3) describes the sequence of main unit operation.

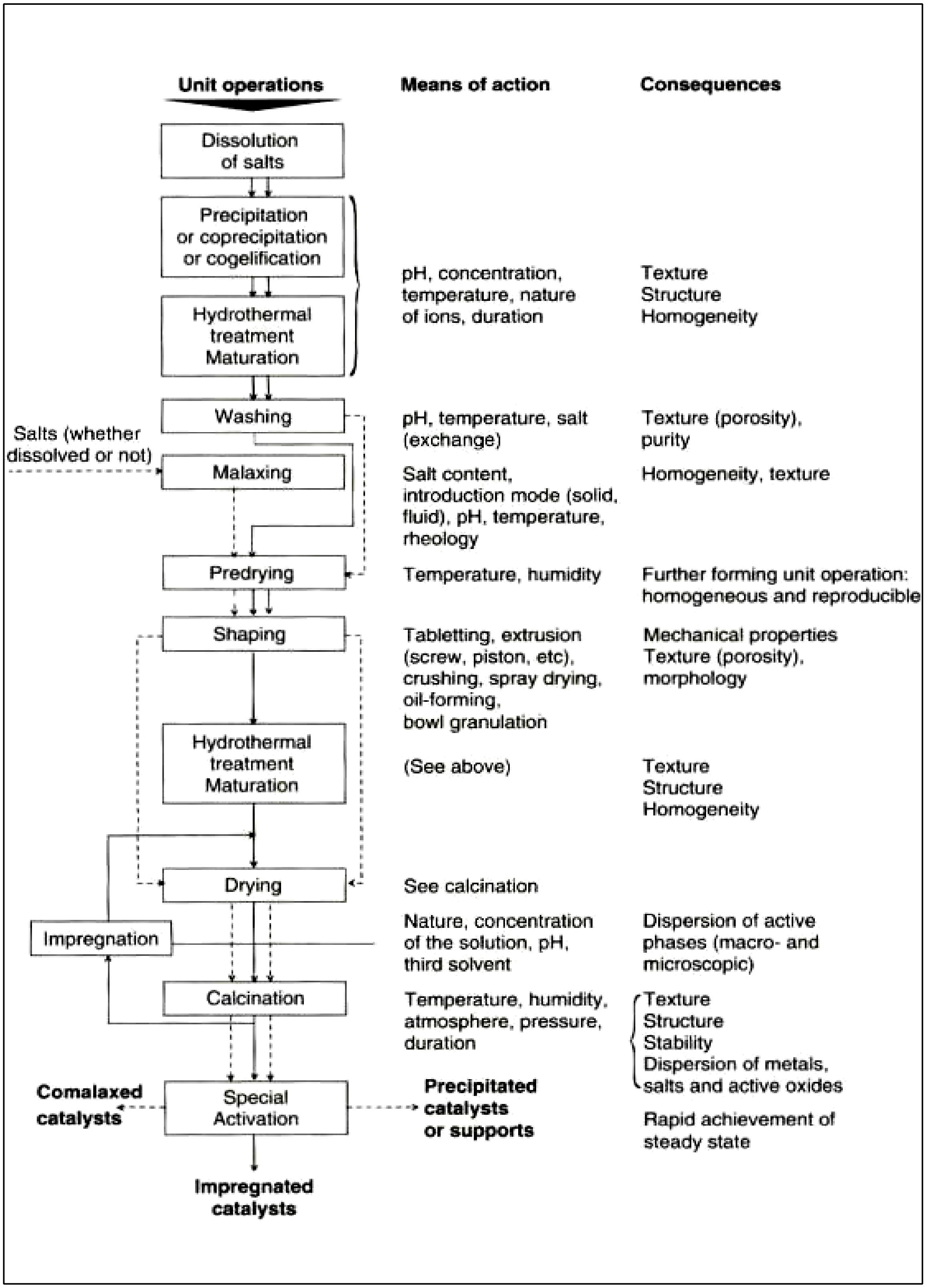


Figure (4.3), The Sequence of Unit Operations.

The following will be examined by way of examples:

- Shaping supports and catalysts.
- Preparing catalyst.
- Preparing supports, their properties.
- Catalysts impregnated on supports.

4.4.2.1 Shaping supports and catalysts

The choice of the catalyst shaping process is generally the result of a compromise after asset of constraints has been studied, particularly with respect to:

- The characteristics of the catalytic process (Catalyst slurry, fixed, circulating or fluid bed).
- The intrinsic characteristics of the solid that is to be shaped (crystallinity, chemical reactivity, plasticity).
- Economic imperative (cost of the shaping process).

4.4.2.2 Preparing catalyst

Catalyst can be prepared by precipitating an:
a) Alumina hydro gel by reaction of ammonium hydroxide with Al chloride and washing the gel until the chloride content is less then 0.1 wt
b) The gel is filtered
c) The correct quantity of halogen (as HCL or HF) solution is added
d) The Platinum is then added in the form of Chloroplatinic acid solution treated with H_2S
e) After mixing, the gel is dried, pelleted and calcined at about 500 C$^{\circ}$.
Zeolite containing Tellurium is very selective for the dehydrocyclization of n-hexane to benzene but is rapidly deactivated. Especially K-1,
K-Ba-1 are highly selective for the dehydrocyclization of n-hexane and n-heptane, but are sensitive to poisoning by sulfur compounds.
Activity and selectivity performances similar to these of platinum on zeolite were obtained by replacing the latter zeolite with a support based on mixed aluminum and Mg oxide obtained by the decomposition of hydro-talcite.

4.4.2.3 Preparing supports: Properities

Refining catalyst supports consist of alumina, silica, silica-alumina or titanium oxide. They can also contain some zeolite (mordenite, Y zeolite, ZSM5, etc.)
They are characterized by:

1. High chemical purity.
2. Morphology, grain size distribution and texture suited to the process chemistry:
    - Surface acid-base properties.
    - Ion exchange properties.
    - Mechanical properties suited to the process technology.

- Economic feasibility that allows significant production.

Aluminas represent a large group including alumina hydrates, transition alumina, and a- Al_2O_3

4.4.2.3.1 The methods for preparing the hydrates

a) Acidification of sodium aluminates
b) Neutralization of an aluminum salt
c) Hydrolysis of an aluminum alcholate

The two main alumina supports used in catalytic reforming are two transition alumina N & Y Al_2O_3 :-

1- N-Al_2O_3 :- is obtained by calcinations above 250-300 ^{o} C of alumina tri-hydrate bayerite in air or in vacuum of gibbsite.

2- Y-Al_2O_3 :- is obtained by calcinations of bohmite in air

4.4.2.3.2 Influence of alumina acidity

The increased acidity caused by the fixation of halogen on the surface of an alumina. The acidity promoted in different ways according to the halogen used (F or Cl). The type of acidity seems to depend on fixed chloride content and the chloride precursor used.

The catalyst must have an acid activity, to activate for isomerization of both paraffins and naphthenes, but balance between these two activities, is most important in a reforming catalyst.

For example :

1- In the case of gasoline production from a naphthenic feed, the hydrocracking should be minimized to avoid loss of yield by lowering the acid activity.

2- In the case of gasoline production from a paraffinic feed, the acid activity can be obtained by means of halogens (F or Cl) or silica incorporated in the Alumina base.

4.4.2.4 Catalysts impregnated on a support

This can be done by two ways:

4.4.2.4.1 Impregnation Without Interaction

The support is simply wetted by the precursor solution (by spraying or immersion). The solution penetrates the pore network, gradually filling it (in a few minute to a few hours). The three characteristics of the method are:

- Its exothermicity (heat of adsorption).
- The high pressure developed in the pores, since part of the air initially present is trapped by the liquid and compressed. The Young-Laplace law:

  $$\Delta p = (2\gamma/r_p) \cos \theta$$

  (γ: surface tension, θ: junction angle of the meniscus, r_p:pore radius)

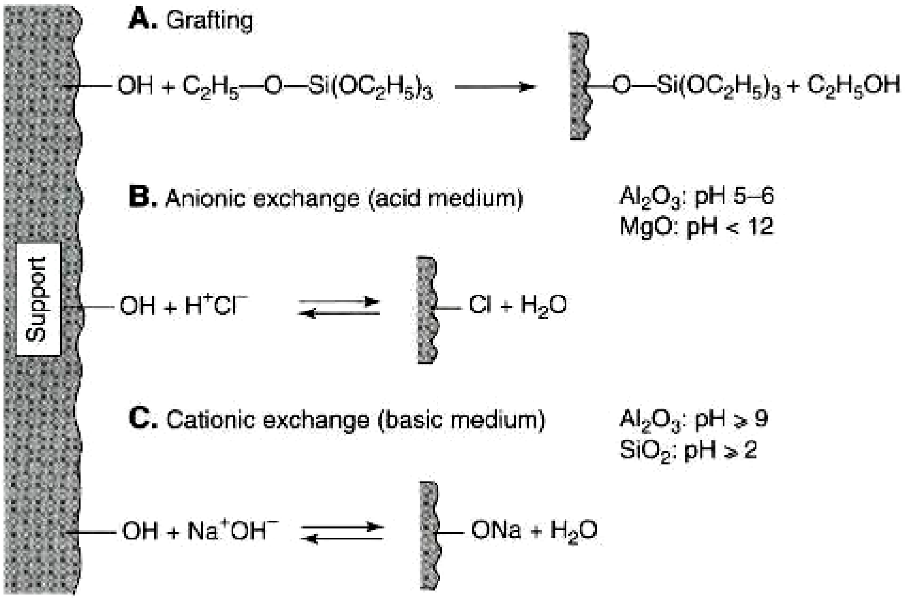
  Shows that pressure can reach several hundred bars in the mesopores with $r_p < 10$nm. Under such pressure the support particles can burst.

- The duration of impregnation. The solution penetrates very rapidly by means of capillary forces (a few minutes), but its diffusion is slowed down in the meso- and micro pore network by dissolution and diffusion of the trapped air. During the operation of solution equidistribution, then subsequent maturation and drying, the active phase precursor becomes deposited.

4.4.2.4.2 Impregnation with interaction

The support is immersed in an excess of solution containing the precursor salt. The salt interacts with the surface as shown in figure (4.4).

- Interaction can consist in formation of a chemical bond between the precursor and the support: the interaction is then a grafting. In this way it is possible to fix silicon or tin from tetrabutoxy tin in a hyper dispersed form. Later on, thermal activation releases the organic fragments and forms the surface oxide molecule.
- Precursor-support interaction can also be ionic in nature, of the acid –base type for example. This is the case for anionic and cationic exchanges. A competitor ion(Cl^- for $PtCl_6^{2-}$, NH_4^+ for $Pt(NH_3)_4^{2+}$)is generally added to the reaction medium in order to control exchange kinetics and get homogeneous distribution of active elements in the grain in a hyper dispersed form. The support-anchored hyper dispersed phases are obtained after drying and thermal activation.



Grafting or ion exchange on an oxide support.
The surface hydroxyls of an amphoteric support can react in a non-aqueous medium with an organometallic compound (A). Or they can be ionized differently depending on the pH in an aqueous medium. With an acid pH (B), the support is an anionic exchanger, fixing anions (Cl^- $PtCl_6^{2-}$ etc.). With a basic pH (C), the support is a cationic exchanger, fixing cations (Na^+ $Pt(NH_3)_4^{2+}$).
Each support is characterized by its isoelectric point (equilibrium pH in an aqueous medium) where exchange properties are at a minimum.

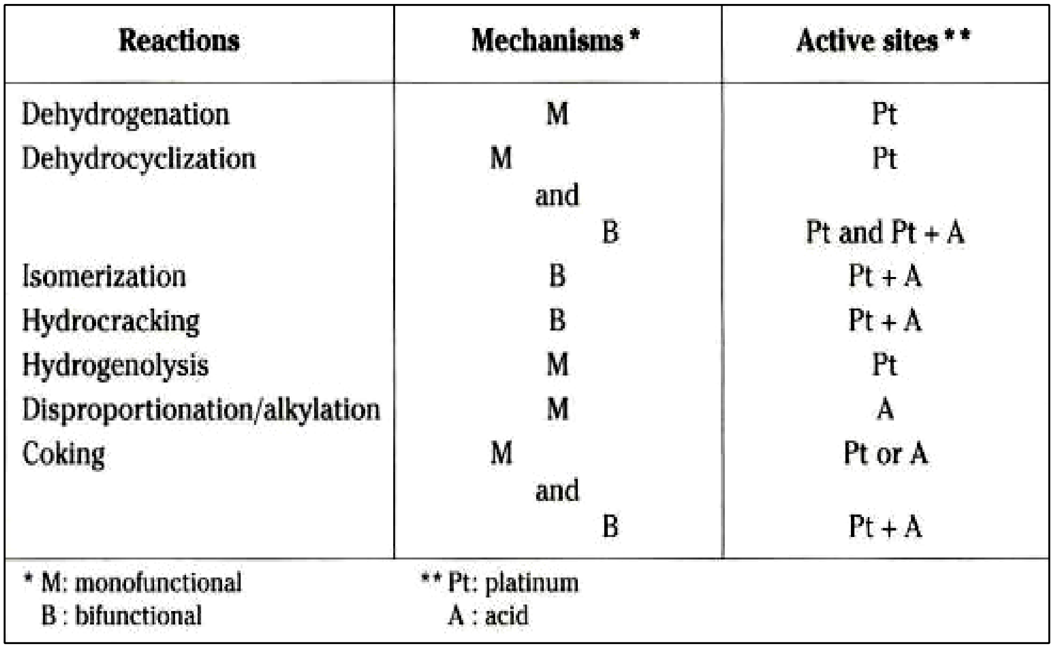
Figure (4.4), Impregnation with Interaction.

4.5 REACTION MECHANISMS

The platinum on chlorinated alumina catalyst has two functions, table (4.3):

- A hydrogenating-dehydrogenating function provided by the platinum, and
- An acid function provided by the alumina.

In catalytic reforming, an operation where gaseous hydrocarbons are in contact with the catalyst solid, the reaction occurs on the surface of the solid as long as temperatures remain lower than 550 °C. Above this, thermally activated homogeneous phase reactions can take place. On the catalyst surface there are a large number of adsorbed species that are dehydrogenated to a greater or lesser extent, either on the metal or on the acid part of the support. The adsorbed species change by isomerization, cyclization or cracking and are then desorbed. Note that there is naturally also adsorbed hydrogen.



Reactions	Mechanisms *	Active sites **
Dehydrogenation	M	Pt
Dehydrocyclization	M and B	Pt Pt and Pt + A
Isomerization	B	Pt + A
Hydrocracking	B	Pt + A
Hydrogenolysis	M	Pt
Disproportionation/alkylation	M	A
Coking	M and B	Pt or A Pt + A

* M: monofunctional
B : bifunctional

** Pt: platinum
A : acid

Table (4.3), Reactions Mechanisms.

4.5.1 Hydrogen Action

Hydrogen is not involved as a reactant in most reactions, except for hydrogenolysis and hydrocracking. It is involved in the reactant and product adsorption- desorption equilibrium and as a product of equilibrium reactions. It limits the conversion of certain hydrocarbons.

4.5.1.1 Product Yield and Quality

The impact of hydrogen on reformat quality is related mainly to the presence of more or fewer residual naphthenes. However, the principle effect is the presence of olefins, which can go up to more than 1% when the process is run at pressure lower than 5 bar.

4.5.1.2 Effects on Reaction Kinetics

The kinetics of heterogeneous reactions is generally very complex and this is particularly true for the dehydrocyclization reaction. As illustrated in figure (4.5), this with the variation in dehydrocyclization rate of n-heptane at 470°C versus the hydrogen pressure P_{H2} for different hydrocarbon partial pressures. Note that, depending on P_{H2}, there is a maximum whose ordinate and abscissa depend on the hydrocarbon pressure.

Hydrogen is involved in generating unsaturated species on the catalyst surface (it limits formation of overly unsaturated species that could develop solely into coke and would block part of the catalyst), but also by the fact that it is adsorbed on the catalyst, thereby blocking certain sites that are no longer available to activate reactions. As an example, figure (4.6) shows the variation in methyl-cyclopentane conversion, either to benzene which has a high RON, or to C_6 paraffin which have a lower RON, versus hydrogen pressure for three different catalysts: platinum, platinum-tin and platinum-rhenium. At a hydrogen pressure of 25 bar, benzene is formed twice as fast as hexanes, while at 7 bar, it is formed five to six times faster with platinum and platinum-rhenium and 12 times faster with platinum-tin.

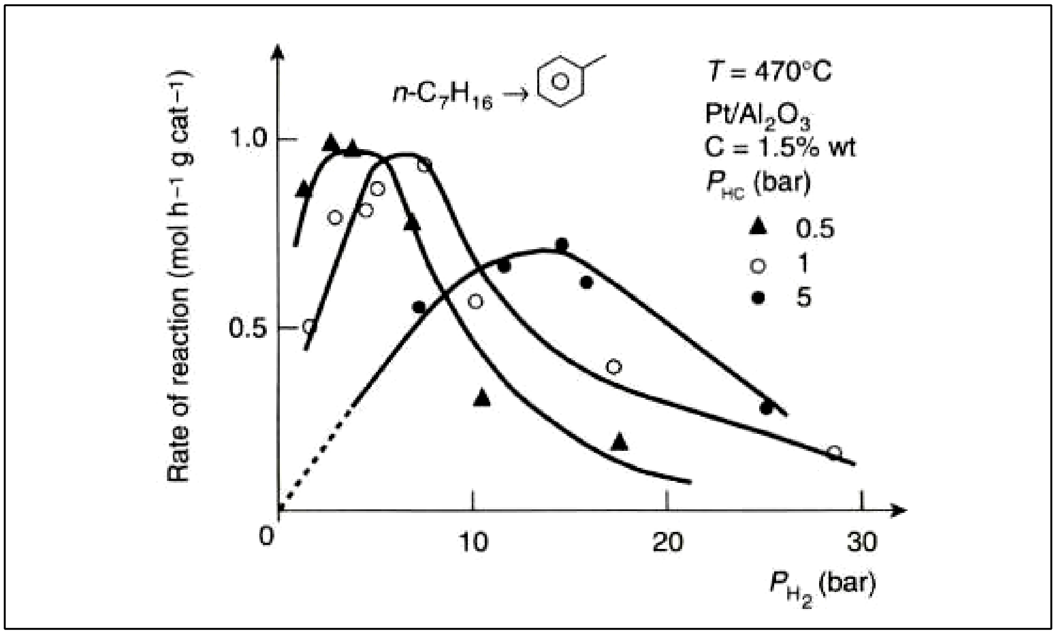


Figure (4.5), Dehydrocyclization Rate vs. Hydrogen Pressure.

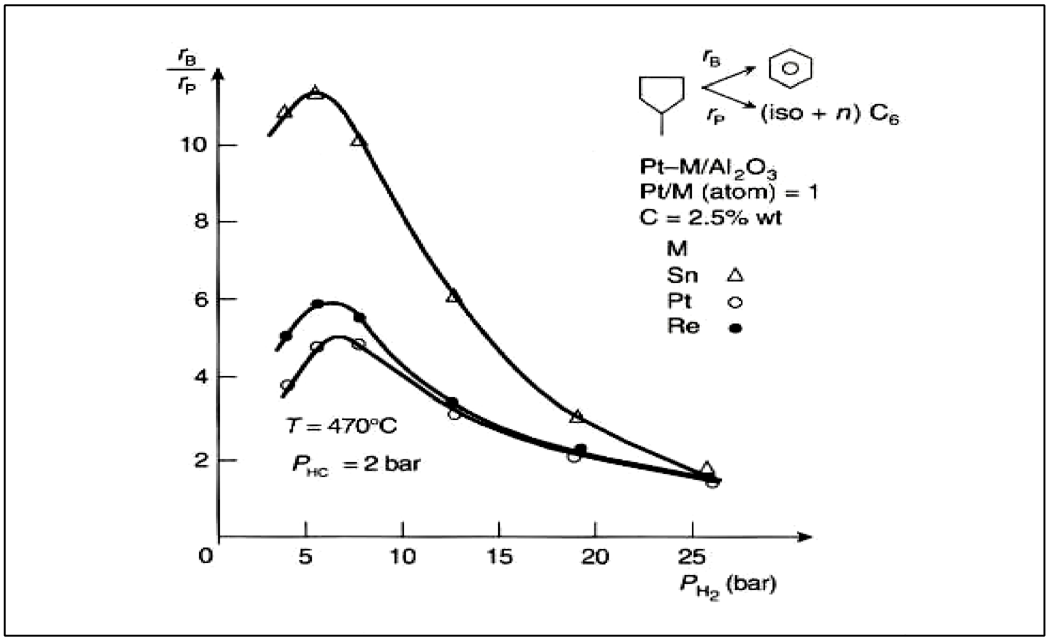


Figure (4.6), Influence of hydrogen pressure on the selectivity of Methylcyclopentane conversion.

4.5.1.3 Effect on Coking

Hydrogen influence polyunsaturated species concentrations on catalysts. It therefore limits the average concentration in intermediates likely to develop into coke. For instance, the time required to lay down an amount of coke on a catalyst is determined, 1.5% wt in figure (4.7). The time is seen to increase very quickly as the molar ratio H_2/heptane rises at constant total pressure.

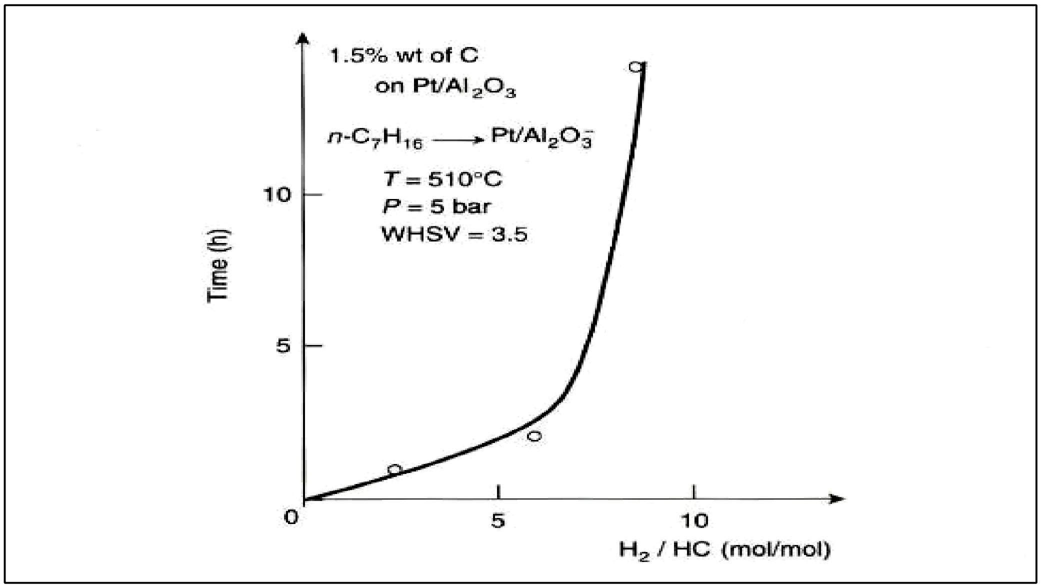


Figure (4.7), Effect of Hydrogen Pressure on Coke Formation Rate.

4.5.2 Sulfur Action

Sulfur influences the performance of mono and bimetallic reforming catalyst. In such cases:-

- ($Pt\text{-}Re/Al_2O_3$), it was found that sulfur on Rhenium restricts the formation of graphitic coke, thus improving the stability of the catalyst.

- ($Pt\text{-}Ir/Al_2O_3$), the high activity resulting from the addition of Iridium allows some degree of sulfur in the feed

- For the reforming of industrial naphtha it was found the sulfur has an effect on aromatic yield when its concentration in the feed stock exceeds 0.03 wt %.It was observed in these experiments , an increase in sulfur conc. has two principles effects:

1. Initial inhibition of aromatics formation.
2. Declined the accelerated catalyst activity.

Catalyst. age	Sulfur	C_5 and lighter
9.7-10.3	0.026	9
7.6-8.6	0.026	9.4
8.7-9.6	0.052	9.7

- These result show that the sulfur acts to enhance the acidity and inhibit the dehydrogenation activity of catalyst.

4.5.2.1 The different options

- The presence of sulfur reduces the pt life span of catalyst.
- If the catalyst is presulfided, the activity can be prolonged.
- Sulfur introduced with feed has a stabilizing effect on the overall activity.
- The sulfiding of Pt/Al_2O_3 catalyst increase the thermal stability but decrease the activity for dehydrogenation of cyclohexane.
- In studying the reforming of naphtha and pure hydrocarbons, indicated that the beneficial effect on catalyst stability, involving high severity processing conditions is related to the formation of Pt-S complex of lower reactivity than the original Platinum species to reactions such as coking. And this is due to an adsorption phenomenon in which only a fraction of the available platinum sites are deactivated by Pb adsorption and the identity of those deactivated sites changes constantly because of the dynamic nature of sulfur adsorption.

4.6 CATALYST DEACTIVATION

In the oil refinery, the deactivation of the catalyst by carbonaceous deposits is an important technological problem.

Deactivation in the reforming process is attributed to coke formation and deposition. In fact, for reforming reactions of naphtha's, the thermodynamics are such that it would be desirable to work at high temperature and low pressure. However, such operating conditions favor coke formation, and many reforming units operate under high pressure in order to increase the life time of the catalyst.

It is obvious that reducing the rate of coking formation would represent a desirable improvement, particularly at a time when production of lead-free gasoline is requiring more severe operating conditions (higher temperature and lower pressures).

4.6.1 Characterization of Coke

Coke deposit on bifunctional catalyst is characterized by:

4.6.1.1 Quantitative analysis and localization of coke

This can do by the combustion under oxygen of coked catalysts. It was found that the coke is not deposits in the form of a monolayer but, on the contrary, three-dimensional deposition appear from the onset of coking.
The coke localized on metallic particle and support, this show the heterogeneity of the coke distribution on the catalyst.

4.6.1.2 Composition and structure of coke

The composition of coke calculated by analysis of coke combustion products to determine the H/C ratio.

Measuring the amounts of oxygen consumed and carbon dioxide produced during temperature-programmed oxidation figure (4.8).

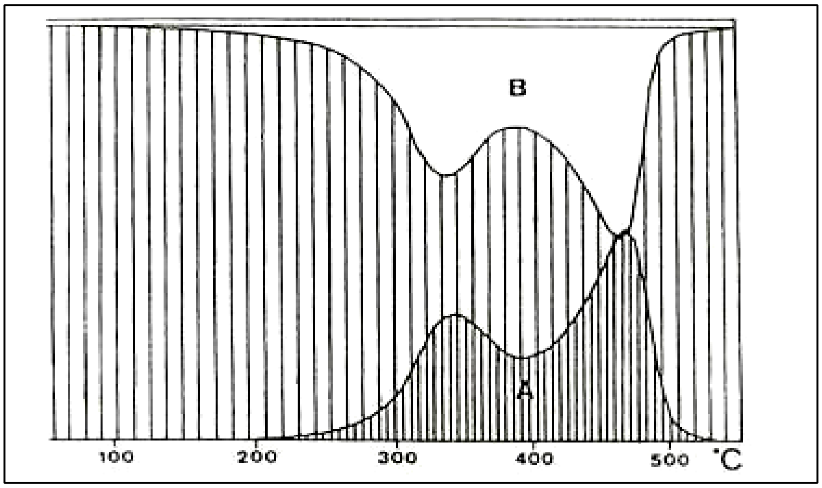


Figure (4.8), Temperature-Programmed combustion of a coked Pt/Al$_2$O$_3$ catalyst (A) CO2 production; (B) O2 consumption.

4.6.2 Effects of reaction conditions on coking Deactivation

4.6.2.1 Hydrogen and hydrocarbon pressure, space velocity

From thermodynamic view, it would be best to operate reforming units at the lowest possible hydrogen pressure; however, catalysts are unstable under such operating condition.

Figure (4.9) shows that although deactivation is relatively slow at 50 bar, it becomes very fast under 10 bar of hydrogen pressure.

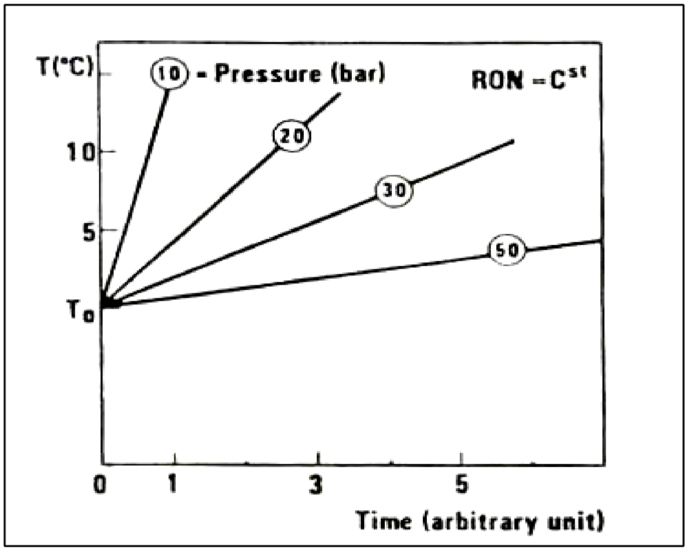


Figure (4.9), Typical influence of pressure on stability.

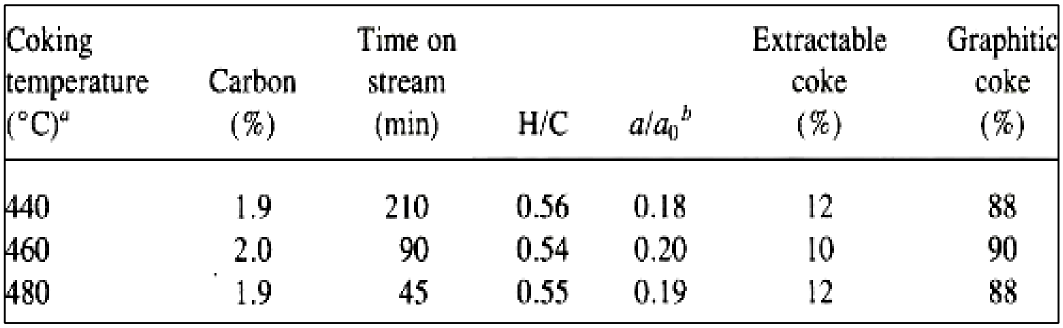
4.6.2.2 Temperature of the reaction

Temperature is the operating variable used for activity maintenance in an industrial unit and therefore it is important to know its influence on coke fouling.
On platinum single-crystal surface its shows that the morphology of the carbonaceous deposit appears to vary continuously from two-dimensional at low reaction temperature (<277°c) to three-dimensional for higher temperature than about 327°C. Thus is the range of reforming temperature s, coke deposits will be always three-dimension.

The amount of coke increase with increasing temperature and this evolution can be explained by the effect of high temperatures on the number of unsaturated products which are coke precursors.

The evaluations capable explain by the effect of high temperatures on the number of unsaturated products which are coke precursors.
Increasing temperature also accelerates the graphitization process of coke, its shows that the fraction of reversible coke (partially hydrogenated) decrease as the temperature and amount of coke increase.

The coke grows mainly on the support with increasing temperature and that is more dehydrogenated.
Increasing temperature not change the location of coke (on the metal or on the support) because the catalytic activity of the metal for constant coke conversion is comparable on the different samples, what ever the coking temperature. Table (4.4).



Coking temperature (°C)[a]	Carbon (%)	Time on stream (min)	H/C	a/a_0[b]	Extractable coke (%)	Graphitic coke (%)
440	1.9	210	0.56	0.18	12	88
460	2.0	90	0.54	0.20	10	90
480	1.9	45	0.55	0.19	12	88

Table (4.4), Effect of the coking temperature on the characteristics of coke.
[a] coking with cyclopentane at atmospheric pressure; H_2/H.C ration 2.33.
[b] Relative activity in benzene hydrogenation.

4.6.2.3 Nature of hydrocarbons in feed

Reforming feed stocks very widely in their boiling range and hydrocarbon type distribution (paraffin's, aromatics and naphthenes) depend on their origin, generally, heavier cuts produce more coke.

It was state that for cuts around 204°C end boiling point there is (1.6-2.3 %)in cycle length per °c increase in feed end, whereas at end boiling point are 216°c the decease in cycle length (2.1-2.8%) per °C, but the cut's with the lowest boiling range have a high content of cyclopentanic compounds are great coke producers.

Hydrocarbons such cyclopentane, n-dodecane turned out to be very good coke precursors. Adding low amounts of di-cyclic aromatics to n-paraffin (n-hexane, n-heptane) increase catalyst aging significantly.

Figure (4.10) is studied the coke fouling on Pt/Al_2O_3 catalyst for different hydrocarbon have 6 carbon atoms. Methyl cyclo pentane >3-methyl pentane > n-hexane >2-methyl pentane >benzene > cyclo hexane.

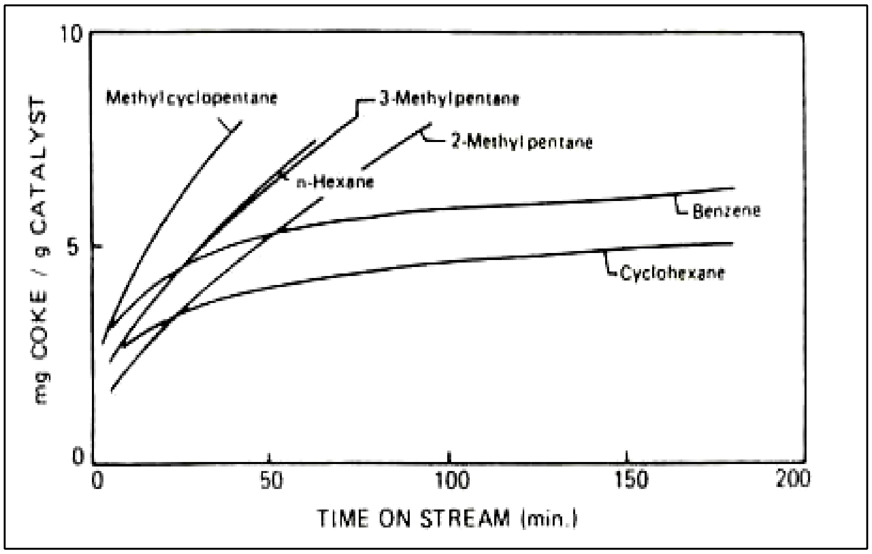


Figure (4.10), Coke deposition on Pt/Al_2O_3 for various H.C at 500 °C.

Effect of n-paraffin, on deactivation found that coke deposition and catalyst deactivation is minimum for n-heptane, but aromatics with paraffin chain tendency to produce coke increase.

For naphthenes if the ring has five carbon atoms, coke formation and catalyst deactivation higher than six carbon atoms rings.

The coke deposition increase in order cyclopentane < cyclopentene <cyclo pentadiene, which is the coke agent responsible for the deposition of coke.

In case of bi functional catalyst the coke deposition occurs mainly on the acidic sites of support.

4.6.2.4 Effect of sulfur on the coking reaction

Sulfur compounds are recognized as poisons for reforming catalysts and they can cause a complete loss of activity. In order to avoid deactivation, sulfur concentrations need to be less than 1 ppm in feed. But on the other hand sulfur is not totally unwanted because a low concentration of sulfur in feed or during start-up of units can reduce excessive hydrogenolysis at beginning of run and improve the catalyst stability.

The presence of sulfur implies a higher reaction temperature for the same performance, figure (4.11), and therefore a higher coke fouling rate.

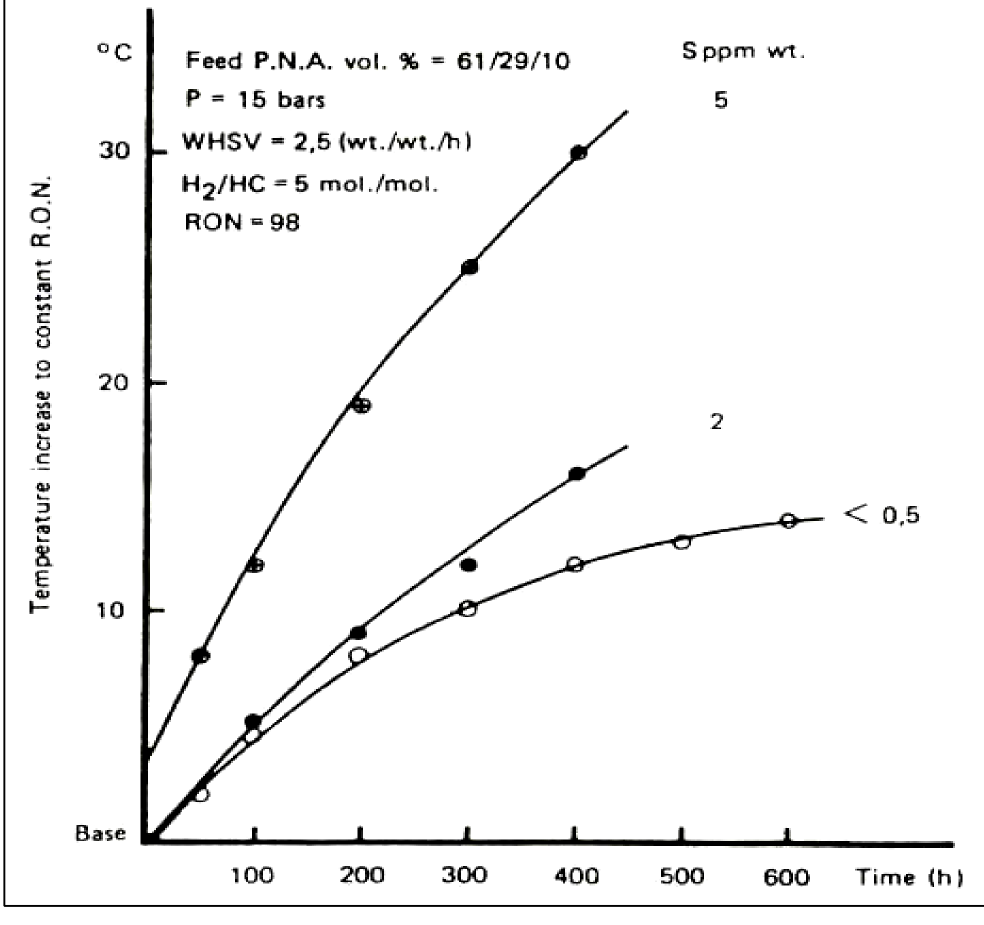


Figure (4.11), Rate of deactivation versus sulfur content of the feed. Monometallic Pt/Al_2O_3 at approximately 500 °C.

4.6.2.5 Effect of carbon deposits on reforming reactions

We can say coke deposits are poison that can alter the selectivity of bi-functional catalyst, as they show different toxicities according to the reaction taken into consideration. Table (4.5) shows that dealkylation of toluene most sensitive to coke.

Reagent	**Reaction**	**toxicity**
n-heptane	**Dehydrogenation** **Cracking** **Isomerization** **Coke formation**	**430** **300** **125** **360**
Methylyclohexane	**Dehydrogenation** **Coke formation**	**110** **720**
Toluene	**Dealkylation** **coke formation**	**700** **750**
3,3Dimethylbutene	**Isomerization**	**30**

Table (4.5), Initial toxicity of coke (in g. of deactivated catalyst per g. of deposited coke) at 430°C.

4.6.2.6 Effect of deactivation on the performance of reforming catalyst

The stability of activity and selectivity of catalyst over a period of time is dictated by the nature of deactivation, which may by sintering of the catalyst activity or poisoning/coking caused deposition of the feed stream impurities or the formation of some surface residue (coke) by other side reactions.

4.6.3 Mechanism of Coke Formation

Coking of bi-functional catalyst results from accumulation of coke on the metal and on support, and therefore two mechanisms of coke formation have to be proposed.

4.6.3.1 On Metal Sites

There are two typical models for coke production:

4.6.3.1.1 The first model

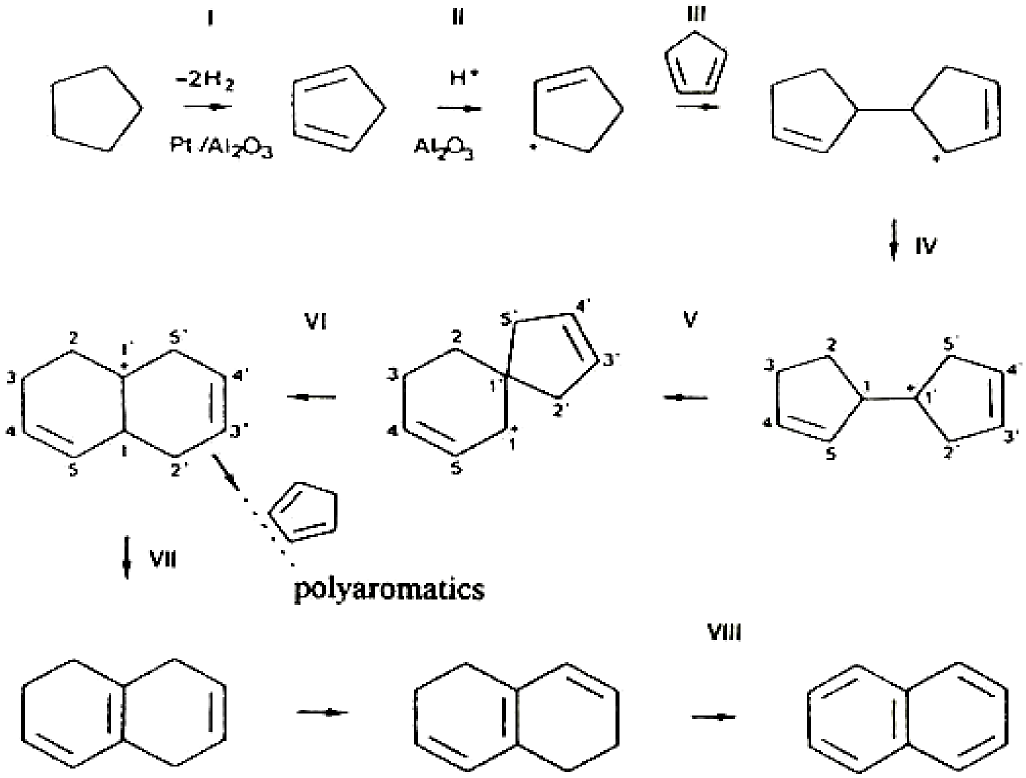
Involves a series of fragmentation reactions and successive dehydrogenation reaction which lead to the formation of carbon atoms, this atoms are partially hydrogenated intermediate may combine to form more graphitic and more toxic coke deposits.

4.6.3.1.2 The second mechanism

Suggests that the routs of coke deposition are based on polymerization reactions with the formation of different types of carbonaceous deposits on the metal surface. For large platinum crystallites increase the rate of coke deposition because of the ability to give higher stabilization for adsorbed cyclopentadiene precursor produced during the reaction.

4.6.3.2 On acid sites

It's assumed that coke arise from the polymerization of dehydrogenated intermediates generated by the metallic function. In case of coking reaction with cyclo pentane, this cyclo pentane can lead to naphthalene or heavier poly aromatics compounds through the following sequence of the reaction:



4.6.4 Poisoning of Naphtha Reforming Catalyst

Catalyst poisoning is on of the most severe problems associated with the operation of commercial catalysts. The most common type of catalyst poisoning is caused by any impurity that is either present in the gas stream or formed by some process during reactions.

The poison formed by some process during reactions. The poison becomes adsorbed on the active sites of the catalyst causing either a temporary or permanent decrease in the all over activity.

Poisoning of naphtha reforming catalysts occur typically as result of inadequate use of naphtha pretreatment conditions. In commercial practice, the life of naphtha reforming catalyst may be reduced to a few months or weeks into the presence of only small concentration of poison contaminants in the feed.

In most cases, because of the essentially irreversible adsorption of poison compounds on the metal surface, regenerations usually impossible or impractical. The importance of poison molecules in the inhibition of the reforming-type reaction is shown in table (4.6) This shows the initial toxicities of different compounds obtained for hydrogenation of benzene on a pt/Al_2O_3 catalyst.

It seems that the adsorption of a poison deactivates the surface on which it adsorbed, and the toxicity depends on the number of geometrically blocked metal atoms.

The quantity of poison absorbed on the metal sites cannot be readily measured. It is only possible to know the quantities of impurities injected or deposited on the whole catalyst.

Sulfur present as impurities in the naphtha feed stock in concentrations of organic sulfide of up to 1500 ppm.

Poisoning due to nitrogen compounds are known to inhibit principally the acid function of the catalyst. Metal impurities most commonly named as poisons of reforming catalysts are arsenic, sodium, copper, mercury, and lead.

It was found that they have a strong affinity for platinum that results in an irreversible poison effect as result of the formation of stable chemical compounds with platinum.

4.6.4.1 Poisoning by Sulfur Compounds

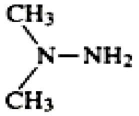
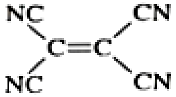
Sulfur is known to adsorb strongly at very low gas phase concentration and can remain as a very stable adsorbed species under different reaction condition.

In case of catalytic reforming, sulfur compound, in high concentrations in the hydrocarbon feed, have been found to have an adverse effect on the catalytic properties of the catalyst.

Catalyst poisoning typically results from strong chemisorption of sulfur compounds on the surface of the metal.

4.6.4.1.1 The sulfur limits in each catalyst

- Monometallic pt/Al_2O_3; sulfur concentration in the feed must be kept below 20 ppm.
- Bimetallic catalyst (Pt-Re/ Al_2O_3); the level should be maintained well below 1 ppm.
- Catalysts containing higher Re/Pt ratio; are more sensitive to sulfur compound, maximum sulfur of 0.5 ppm is allowed.

Poison	Toxicity, t^a	Relative activity at poison saturation[b]
$(CH_3)_2SO_4$	0	
SO_2	1.0	0
$(CH_3)_2SO_2$	0.02	0.55
$(CH_3)_2SO$	3.0	0
Thiophene	5.0	0
Dibenzothiophene	4.5	0
NH_3	0.10	0.67
Pyridine	0.12	0.042
	0.50	0.18
$C_6H_5NO_2$	0.24	0.10
$CH_3CH_2CH_2CH_2NH_2$	0.11	0.043
Piperidine	0.48	0.031
Quinoleine	0.50	0.033
Aniline	0.14	0.033
N,N-Dimethylaniline	0.90	0.50
Phenol	0.075	0.55
Resorcinol	0.27	0.035
Diphenyl oxide	0.50	0.55
EtOEt	0	
	0.065	0.13
$C_6H_5C_6H_5$	0.013	0.71
$C_6H_5CH_2C_6H_5$	0	
CO	1.18	0
H_2O	0.00018	0.5
BF_3	0.002	0
$Si(CH_3)_4$	0.002	0.73
$As(C_6H_5)_3$	1.9	0
$Pb(CH_3)_4$	3.4	0.05
Na^+	0	
K^+	0	
Ca^{2+}	0	
Ba^{2+}	0	
Cr^{3+}	0	
Mn^{2+}	1.4	0
Fe^{2+}	1.1	0
Co^{2+}	1.0	0
Ni^{2+}	1.0	0
Cu^{2+}	2.0	0
Zn^{2+}	2.5	0
Ag^+	0.7	0
Sn^{2+}	7.6	0
Hg^{2+}	15	0
Tl^+	14	0
Pb^{2+}	5.2	0

[a] Toxicity defined as number of platinum atoms poisoned by one molecule/atom of poison.
[b] Activity is metal-catalyzed benzene hydrogenation.

Table (4.6), Initial Toxicities of various compounds on Pt/Al_2O_3 catalyst.

In case of the bimetallic t-Re/ Al_2O_3 catalysts, it was found that sulfur on rhenium restricts the formation of graphitic coke; it's improving the stability of the catalyst. However, for Pt-Ir/ Al_2O_3,

The high activity resulting from the addition of iridium allows some degree of sulfur in the feed. Figure (4.12) shows the effect of sulfur on reforming of naphtha feed.

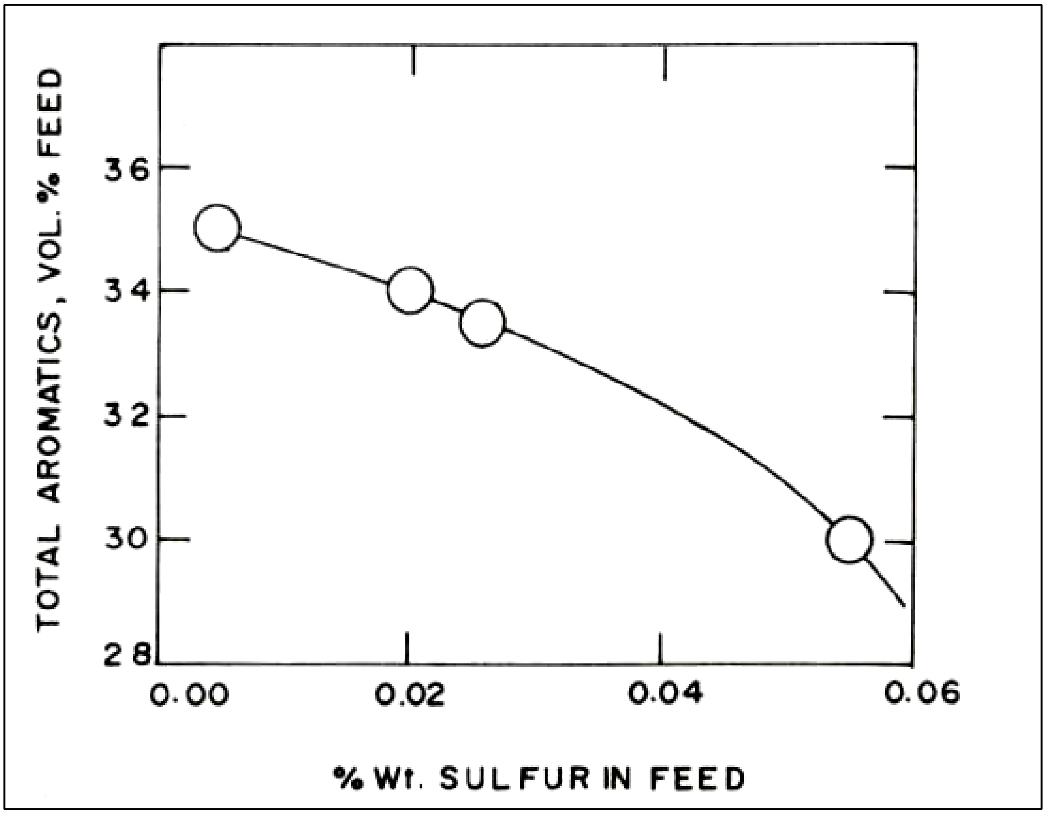


Figure (4.12), Effect of sulfur on Reforming of naphtha feed at constant catalyst life.

4.6.4.1.2 Increasing sulfur concentration has two principal effects

1. Initial inhabitation of aromatic formation and accelerated catalyst activity decline. The inhibition of the catalyst activity appeared to be a reversible reaction.
2. It was found that for n-heptane reforming with 0.8% sulfur, dehydrocyclization is reduced and hydrocracking is increased. These results show that sulfur acts to enhance the acidity and inhibit the dehydrogenation activity of the catalyst.

4.6.4.1.3 The effect of varying concentration of sulfur on the activity and selectivity of platinum reforming catalyst

They found that sulfiding of Pt/Al_2O_3 catalyst increases the thermal stability but decreases the activity for dehydrogenation of cyclo-hexane.

The concept of selective and nonselective poisoning on reforming reactions working with Pt/Al_2O_3,they found that certain poisons such as H_2s and SO_2 are nonselective; they have the same effect in the different reaction studies: hydrogenation of benzene (nondemanding reaction) and hydrogenolysis of cyclopentane, a (demanding reaction.).

On other hand, Atomic sulfur is a selective poison that reduces the rate of hydrogenolysis of cyclopentane more than that of hydrogenation of benzene.

The figure (4.11) shows clearly the importance of the effect of sulfur on catalyst deactivation rate expressed as inlet reactor temperature necessary to achieve a constant reformate quality as a function of operating time.

4.6.4.2 Poisoning by Nitrogen Compounds

Nitrogen compounds are generally present in the form organic compounds that decompose into ammonia at reforming conditions.

They inhibit principally the acid function of the catalyst, but to some extent they can alter the metallic properties of the platinum.

It is clear that nitrogen compounds have a little effect on the dehydrogenation reaction. On the other hand, hydrocracking, Isomerization, and dehydrocyclization are adversely affected, indicating that acid sites are more involved in these reactions. Figure (4.13) shows the effect of nitrogen content on catalyst aging

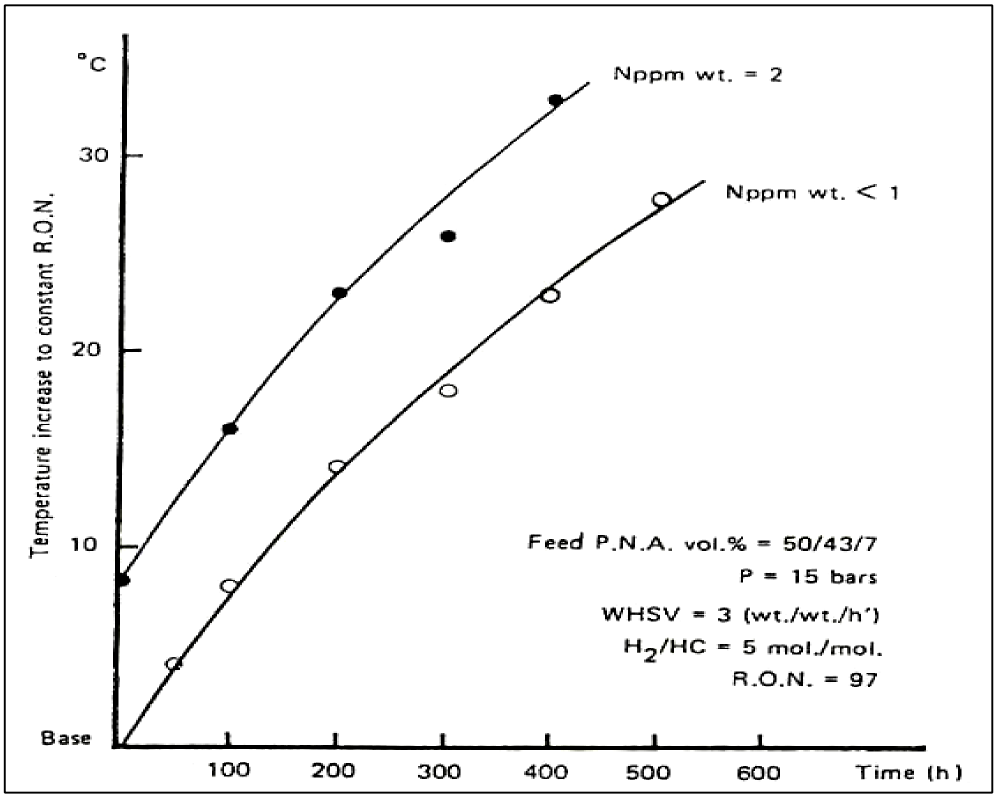


Figure (4.13), The effect of nitrogen content on catalyst aging.

4.6.4.3 Poisoning by Metals

Deactivation of naphtha reforming catalysts by metal contaminates has received little attention and only a few fundamental investigation has been reported it is known that the metallic poisons are rarely eliminated by regeneration, and as a consequence all necessary precaution need to be taken to prevent them from coming into contact with the catalyst.
It is known that platinum metal can be activated by metallic ions such a mercury, arsenic, lead, bismuth, copper and iron.

One of the most affected reactions is dehydrogenation. Studies carried out using lead showed this effect, figure (4.14).

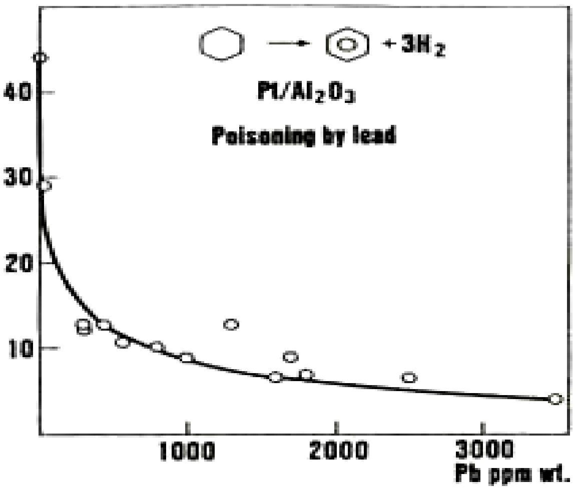


Figure (4.14), Poisoning of dehydrogenation by lead.

Similarly, small amounts of iron and copper can accelerate the deactivation in the dehydrocyclization reaction figure (4.15).

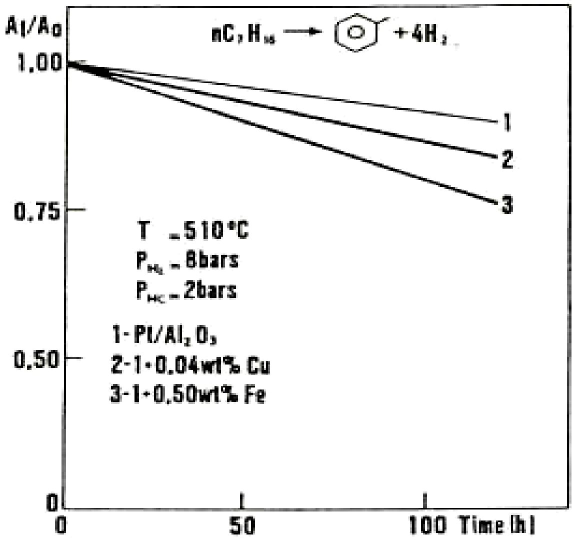


Figure (4.15), Poisoning by copper and iron.

From the results it is clear that metal contamination generally causes a decrease in the dehydrogenation and dehydrocyclization functions.

4.6.4.3.1 Effect of arsenic on Pt/AL$_2$O$_3$

They found 0.01-0.02 wt % on the catalyst have little effect on reforming reaction. An increase in arsenic concentration on catalyst to 0.5 wt% decreases dehydrogenation activity.

4.7 CATALYST REGENERATION

They found 0.01-0.02 wt % on the catalyst have little effect on reforming reaction. An increase in arsenic concentration on catalyst to 0.5 wt% decreases dehydrogenation activity.

4.7.1 Effect of the Type of Process on Cycle Length

a. **Semi-regenerative**: the operation may last several thousand to more than 10,000hours before it's interrupted for regeneration.
b. **Fully regeneration** :(swing- reactor type) or continuous (moving bed reactor type) cycle may last only a few hundred hours or even less.

4.7.2 Catalyst Regeneration Steps

1. Elimination of coke by controlled burning
2. Catalyst rejuvenation, which comprises:
    a. Restoration of the acid function and metallic dispersion by chlorination.
    b. Reduction with hydrogen.
    c. Passivation by sulfiding.

4.7.3 Factors affecting coked catalyst reactivity

1. Coke structure which is dependent on the nature of catalyst and reaction conditions.
2. The chemistry and the nature of carbon deposition and the
3. Characterization of coked catalyst.

4.7.4 Regeneration of Coked Catalyst

4.7.4.1 Regeneration with Hydrogen

Hydrogen is found to have a significant impact on hydrocarbon reaction over the naphtha reforming process. It's already known that high hydrogen pressures lower the concentration of coke precursors, thereby keeping the coke rates low. This because the strong dehydrogenation reactions involved in coking are restricted by the presence of hydrogen.

On the metal surface, coke levels controlled by hydrogen cleaning. The cleaning action of hydrogen occurs by catalytic hydrogenation, whereas the slow removal of coke occurs by catalytic hydrogasification.

The mechanism showed in figure (4.15) is for the hydrogen cleaning of platinum surfaces. This mechanism is based on the distribution of two types of coke on metal sites, one being easily removed by hydrogen (Reversible coke) and the other less readily removed (irreversible coke).

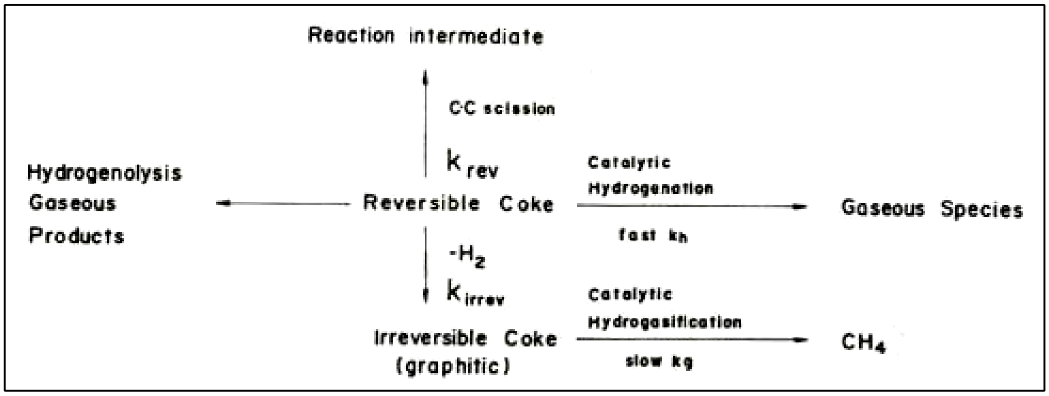


Figure (4.15), Model of carbon removal by hydrogen.

- For bi-functional catalysts, a small amount of the coke is deposited on the metal where the majority is accumulated on the alumina.
- Hence a large part of the coke which is destroyed by hydrogen treatment is deposited on the support.
- These phenomena can be explained by either the mobility of carbonaceous deposits on the catalyst surface or the hydrogen mobility.
- The presence of an optimum surface chloride concentration in the regeneration of Pt / Al_2O_3 catalysts by H_2 was found to be an important parameter.

A catalyst with about 0.5 wt% Cl shows a complete regeneration during static and dynamic H2 spillover from Pt alumina which restores the catalyst surface freeing it from H.C residues.

4.7.4.1.1 The effect of the nature of bi-functional catalysts on their regeneration by H_2:

The carbon remaining decrease and the activity of the catalyst for benzene hydrogenation increases with the temperature of hydrogen treatment.

4.7.4.1.2 The effect of time of H_2 treatment on the amount of coke remaining on the catalyst:

It was found that increasing the time of treatment result in decreasing coke content. But the carbonaceous deposits become more and more dehydrogenated showing that more hydrogenated compounds are eliminated first.

The metallic activity is totally regenerated but a large amount of coke still remains on the catalyst at 430°C at 20 hrs.

4.7.4.2 Regeneration with oxygen

Regeneration in presence of oxygen can be complicated by the fact that metal sintering can be promoted at high temperature.

The burning of coke start with the coke deposited on the platinum because of the catalytic action of platinum and because the deposit is richer in hydrogen.

The burning then spreads to the carbon on the support by the action of oxygen spillover, with burning at lower temperatures when more platinum is present.

The last part of the coke to be burned is the most distant from the metal and the coke poorest in hydrogen. Comparing the pt/Al2O3 catalysts with different metal-to-acid ratios, it is accepted that pt catalyzes the burning of the coke.

The higher the metal-to-acid ratio, the lower the burning temperature. Also Pt deceases the oxidation temperature of graphite.

Greater amounts of Pt are present; the coke is less polymerized because of the Pt-catalyzed hydrogenation of coke precursors occurring during the reaction. The less polymerized deposit would oxidize at a lower temperature.

The acceleration of coke burning in the presence of pt can be explained by:

1- Oxygen is adsorbed on Pt in an activated form.
2- Travels by spillover along the support (Al_2O_3) to the coked alumina particles.
3- The activated oxygen spills along the pores of the coked alumina, eliminating the coke by burning at lower temperature than that of the gaseous oxygen.

The effect concentration of Rhenium in pt Re/Al_2O_3catalyst on the regenerative behavior:

1- For the catalyst which have less than 50% Re :

The regeneration occurs at the same temperature as for pt/ Al2O3 (500C)

2- For Re is above 50% :

The coke would not burn off until much high temperature was reached. The presence of Re decrease of spillover cause it's not capable of promoting spillover.

Figure (4.16) shows that when Pt is present, the oxidation starts at lower temperatures and the temperature peak is also at lower temperature. Although the amount of carbon is the same.

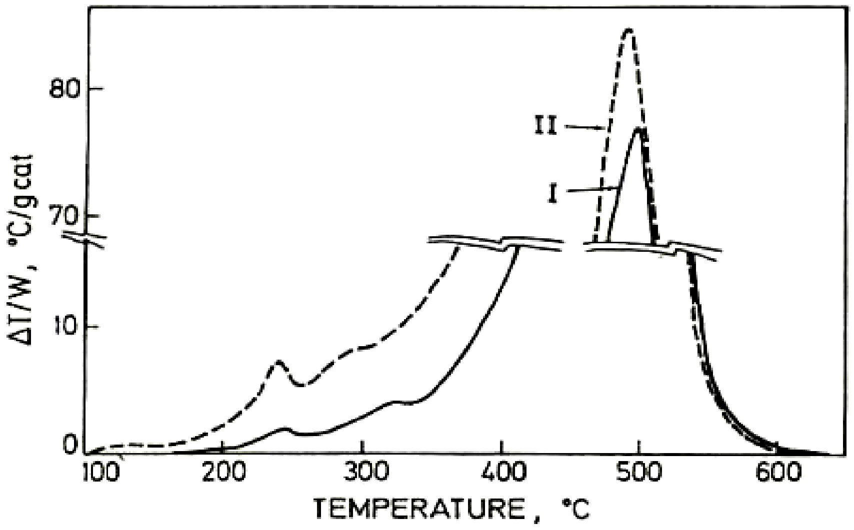


Figure (4.16), TPO of alumina samples mixed with platinum –alumina after coking with naphtha during 6 hr.

4.7.5 Regeneration of sulfur- contaminated catalysts

When naphtha reforming catalysts are contaminated with sulfur, a special procedure has to be employed during the regeneration to diminish the sulfation of the support . When the sulfur content of the catalyst exceeds 1000 ppm, a special regeneration procedure to remove the sulfur is followed before any attempt to burn the coke.

Oxidation and reduction studies of the formation and elimination of sulfated on $Pt/Al_2\ O_3$ catalysts indicate the oxidation eliminated the sulfur, deposited on the metal , however the oxidized sulfur compounds were strongly held on the support.

4.7.5.1 Effect of sulfur on catalyst performance

In industrial units, sulfur cause the formation of iron sulfide from the reactor materials .When carbon removal takes place, the iron sulfide is oxidized into metal oxide (fe_2O_3) and sulfur trioxide (SO_3) .The (SO_3) formed reacts with the alumina to form the thermally very stable alumina sulfate, diminishing the surface hydroxyl concentration.

Sulfur can be removed either after oxy-chlorination or before catalyst regeneration by this procedure:

1- It consists of reduction of the sulfur species under hydrogen at about (500°C) .
2- The formed hydrogen sulphide is eliminated from the gas by washing with an aqueous sodium carbonate solution.
3- It is recommended that the procedure be continues until the hydrogen sulphide concentration is lower than 2 ppm, for at least l hour.
4- When performed after oxy-chlorination: This is in order to increase the Al sulfate reduction and limit the loss of chloride from the catalyst, a chlorinated compound is injected during the operation. In the presence of sulfate ions, operating temperatures have to be increased of rapidly to maintain the octane number constant until the sulfate removal step is employed. Stated that during reduction at 500 ˚C, the sulfate is reduced to H_2S, escaping with the exist gases of the reformer .Where the reduction at 300 ˚C cannot convert sulfates to H_2S. The $Pt\text{-}Re/Al_2O_3$ regeneration was found to

be more complicated if sulfate and sulfite species were present on the alumina surface during calcinations, theses sulfite are converted to H2S during reduction.

4.8 PROCEDURE OF REGENERATION

4.8.1 Pre-shutdown

1-Prepare auxiliary regeneration equipment.
2-Ensure that all necessary chemicals and materials are available.

4.8.2 Shutdown

1. Reduce reactor inlet temperatures to 454˚C (850˚F) then stop charge to the unit.
2. Lower reactor inlet temperatures to 400˚C (750 ˚F).
3. Remove residual liquid hydrocarbons.
4. Nitrogen blankets the unit.

4.8.3 Carbon Burn

1. Conditions of carbon :
    a. 400˚C (750˚F) reactor inlet temperatures and 454˚C (850˚F) maximum reactor outlet temperatures .
    b. Maximum pressure consistent with air supply and equipment.
    c. Maximum recycle circulation consistent with equipment.
    d. 0.6 to 0.8 mole % oxygen at the compressor discharge
2. Maintain chloride addition at 20: 1 mole ratio of water: chloride at the inlet of reactor 1. Also hold 30: 1 mole ratio of water: chloride at the inlet of the last reactor when the last reactor is being burned in parallel.
3. Maintain corrosion control (caustic or carbonate circulation through the air cooler – separator).
4. Hold carbon burn conditions until the reactor outlet temperatures have remained at their base levels for four hours.

4.8.4 Oxidation

1. Conditions of oxidation:
    a. 510˚C (950 ˚F) reactor inlet temperatures.
    b. 5 mole % oxygen in circulating gas.
2. Hold a 20: 1 mole ratio of water: chloride for eight hours.
3. Stop chloride injection.
4. Flash and drain separator: Drain all low points thoroughly before stopping heater firing.

4.8.5 Cool down

1. Stop heater firing continues maximum gas circulation.
2. Maintain 5 mole % oxygen in the circulating gas throughout the cool down.
3. Continue gas circulation until all reactor outlet temperatures are below 204 ˚C (400 ˚F).

4.8.6 Nitrogen purge

1. Purge in reverse from the first reactor inlet unit the oxygen level is less than 0.3 mole % and the carbon dioxide level is less than 0.1 mole % at the compressor discharge.
2. Purge forward from the first reactor inlet until the oxygen level is less than 0.3 mole % and the carbon dioxide level is less than 0.1 mole % at the compressor suction.
3. Measure the sulfur dioxide level in the purge gas. Hold purges until the sulfur dioxide level has peaked, and declined to a low level (less than 50 ppm).

4.8.7 Reduction

1. Purge 10 catalyst volumes of hydrogen through the plant, purging all lines.
2. Pressure the unit to a minimum of 7 kg / cm^2 absolute (100 psia) with grade hydrogen.
3. Begin maximum gas circulation. Increase inlet temperatures at 55 ^{0}C / hour to 427 ^{0}C (100^{0}F / hours to 800 ^{0} F) for all catalysts except R – 30 series which will be 480 ^{0}C (900 ^{0}F) .
4. Hold required reactor outlet temperatures for one hour.

5. During the heat – up, water should be frequently drained from the separator and system low points and the circulating gas hydrogen sulfide content should be monitored.
6. After we holding required reactor outlet temperatures for one hour , reduce heater firing and begin cooling to 371 ^{0}C (700 ^{0}F) reactor inlet temperatures in preparation for cut in.

4.8.8 Sulfate Removal

1. If a sulfate removal step is to be used, complete the regeneration through step G – 4 of the Reduction. The oxidation hold period, step D – 2, can be shortened to four hours. The reduction may also be done with catalyst reformer hydrogen of 75% minimum purity.
2. At the 510 ^{0}C (950^{0}F) conditions of step G-4 of reduction, start chloride injection at 20:1 mol ratio water: chloride, maintain a circulating water pH of 7.5 to 8.0.
3. Maintain 510 ^{0}C (950 ^{0}F) and 7.0 kg/cm^2 absolute (100 psia) hydrogen partial pressure and all reactor effluent hydrogen sulfide concentrations are below 5 ppm .
4. When 5 ppm hydrogen sulfide concentration is reached at all reactor outlets, stop chloride injection, flush and drain the separator, and reduce heater firing.
5. Continue gas circulation until all reactor outlet temperatures are below 400 ^{0}C (750^0 F) .
6. Depressurize and nitrogen purge the unit .
7. Re-establish the conditions of the carbon burn , step C . when the proof burn is complete , continue with the procedure through the oxidation , cool down , purge reduction , and startup steps as outlined

4.8.9 Start-up

1. Pressure to 8.8 kg/cm^2 (125 psia) minimum hydrogen partial pressure.
2. Start naphtha charge at 371 ^{0}C (700 ^{0}F) reactor inlet temperatures .
3. Follow programmed chloride addition.
4. Hold the reactor temperatures at reduced levels until the water and sulfur specification are met.

CH.5

Catalytic Reforming Parameters

5.1 INTRODUCTION

Catalytic reformers are designed for flexibility in operation, whether for motor fuel production or to produce aromatics such as benzene, toluene, and xylenes (BTX). To meet these drastically varying demands, the reforming catalyst must respond to change in unit operating condition. The variables, which affect the performance of the catalyst and change the yield and quality of reformat are; feedstock properties, reaction temperature, space velocity, reaction pressure and hydrogen to hydrocarbon mole ratio.

5.2 TEMPERATURE

The operator has very little freedom to act on an industrial unit in normal operation. In fact temperature is the only operating variable he can use to adapt changes in feed quality or to produce reformats of different quality.

Reformers are generally designed with three or more reactors in usually series each of them contain different quantity of catalyst so there are changes of temperature as feed flow through the catalyst from one reactor to another.

Reaction temperatures are chosen to balance the advantage of increased reformats quality (research octane number) and disadvantage of increased deactivation rate as temperature increased.

T (SOR) or start of run temperature is the reactor inlet temperature, which yields the required octane number at full capacity at the beginning of the run, and its related to the RON under certain condition is shown in figure (5.1).

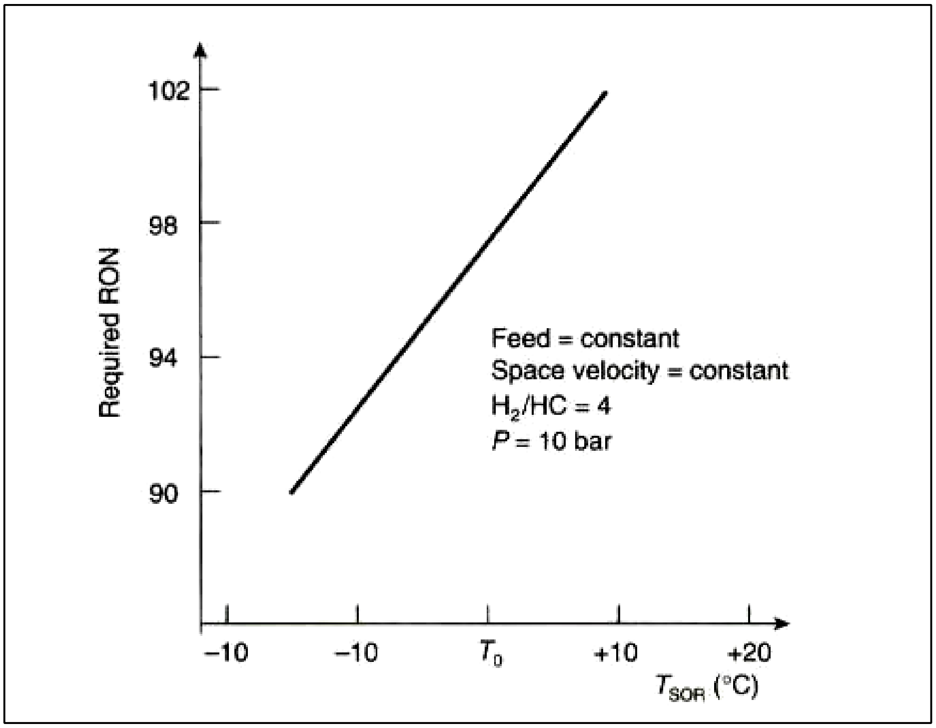


Figure (5.1), Variation in octane number versus T_{SOR}.

Also temperature variation curve with time depends on the severity of an operating and naturally on the catalyst quality. Platinum catalyst alone or bimetallic Pt-Re catalyst will allow the required octane number to be achieved at the same starting temperature but the variation will be much faster with monometallic catalyst. As shown in figure (5.2).

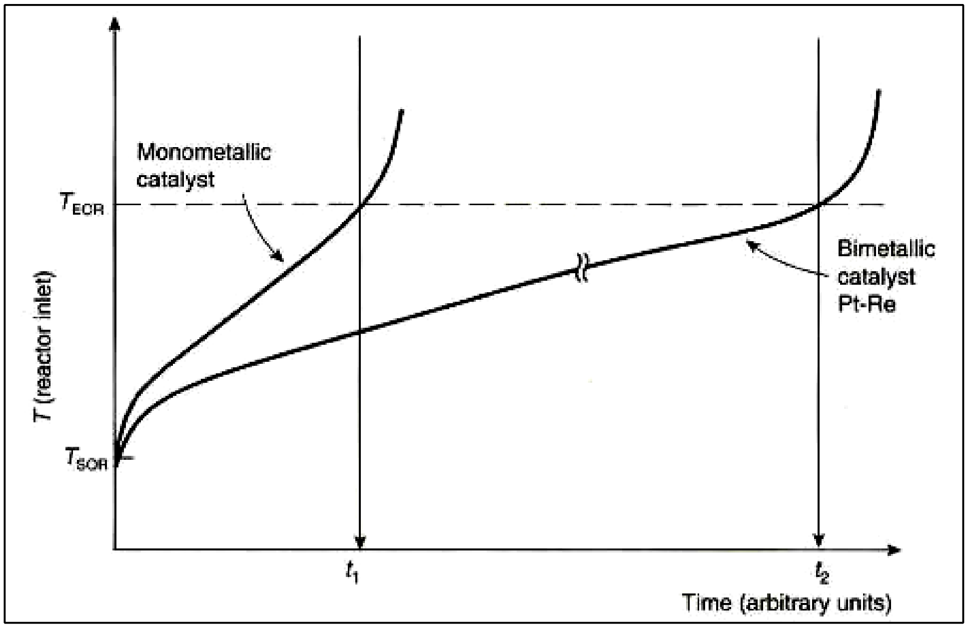


Figure (5.2), Variation in temperature during a run.

Yield doesn't vary in the same way. Monometallic catalyst shows a drop in yield as soon as the temperature rises. While bimetallic C5+ selectivity remains the same, until the end of the run as shown in figure (5.3).

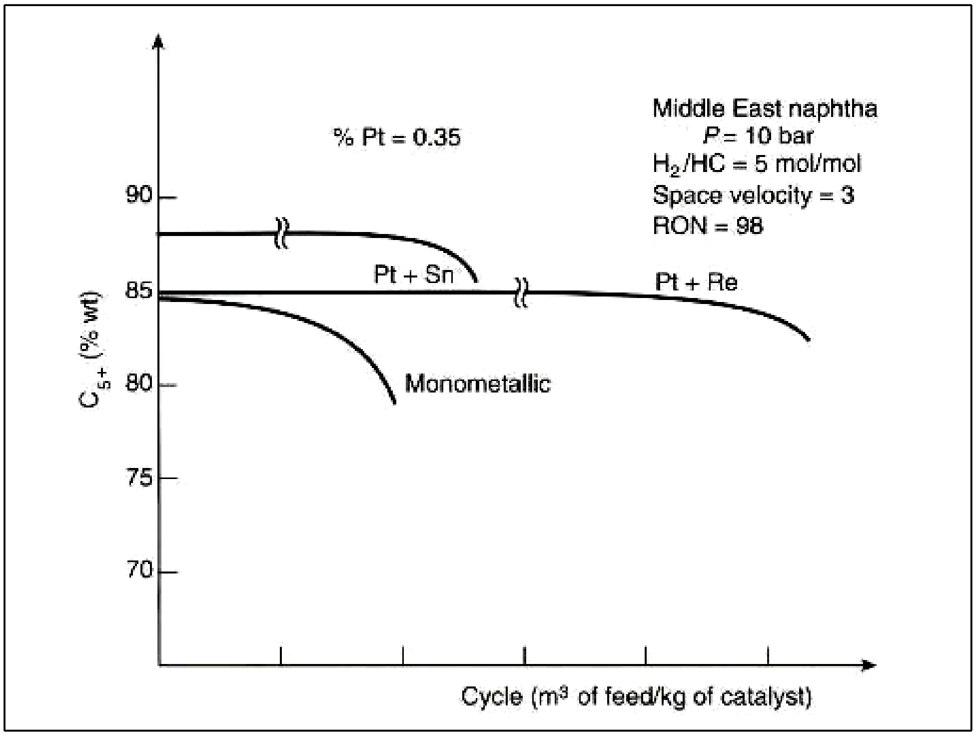


Figure (5.3), Variation in C_{5+} during the run.

Another important parameters is (ΔT) across each reactor which give indication about the reaction occur as well as the H_2/H.C ratio used. In the first reactor there are negative (ΔT) due to the dehydrogenation reaction that take place in this reactor. But positive (ΔT) observed in last reactor due to the hydrocracking that takes place in this reactor as dehydrogenation is endothermic reaction but hydrocracking is exothermic reaction.

5.3 REACTION PRESSURE

The reformer units in 1950 typically operated in the pressure higher than that operated nowadays .Reformers have three or more reactors usually in series and the pressure is different in each reactor. It is preferable to use the average reactor pressure, if it is available, for estimating yields and cycle length.

The pressure under which reforming take place affect on yields and cycle length. Decreasing pressure increase the production of aromatics and hydrogen by dehydrogenation of naphthenes and dehydrocyclization of paraffins and reducing hydro cracking as shown in figure (5.4).

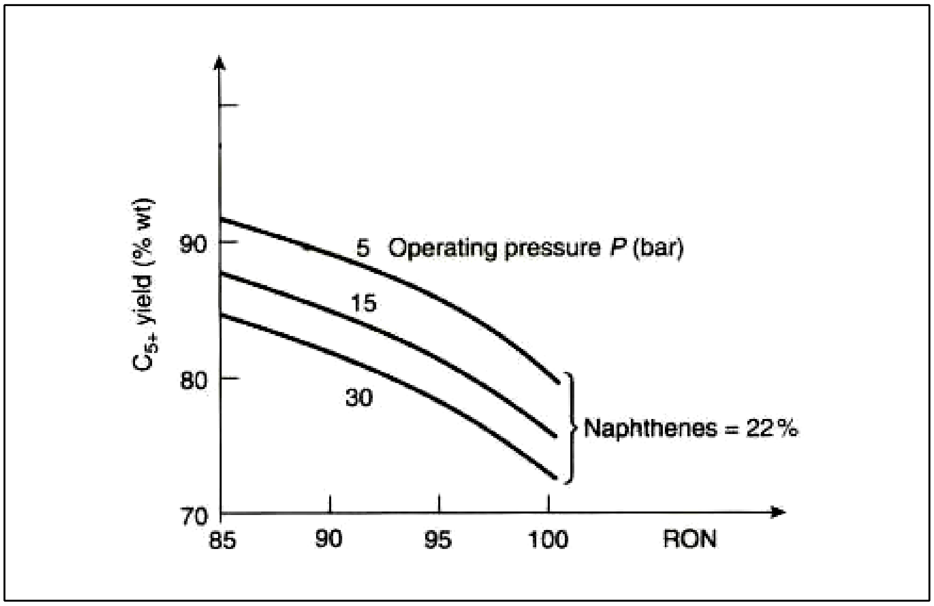


Figure (5.4), Influence of P and the feed on C_{5+} yield.

The disadvantages of increasing pressure are:

- increased catalyst coking;
- reduce the product yield and;
- shorter cycle length.

Notes

At 100 RON there is an increase in percent yield of reformat from 79.7 to 83.5 by a reduction in pressure from 300 to 100 psig.

5.4 HYDROGEN TO HYDROCARBON RATIO

In catalytic reformers hydrogen is recycled in order to maintain a certain ratio of H_2/H.C and high partial pressure.

The advantage of increasing H_2/H.C ratio is the hydrogen react with coke precursors, removing them from the catalyst before they form significant amount of polycyclic aromatics and deactivation the catalyst also reduce catalyst deactivation rate. The disadvantage of increasing H_2/H.C ratio it affects aromatization and increases hydro cracking.

A lower hydrogen partial pressure favors dehydrogenation of naphthenes and dehydrocyclization of paraffins. However, it affect on the catalyst life due to increasing density to form coke.

Monometallic catalyst in seventies worked at high ratio (7-8) to achieve stability comparable to the modern catalyst with H_2/H.C=4 as shown in figure (5.5).

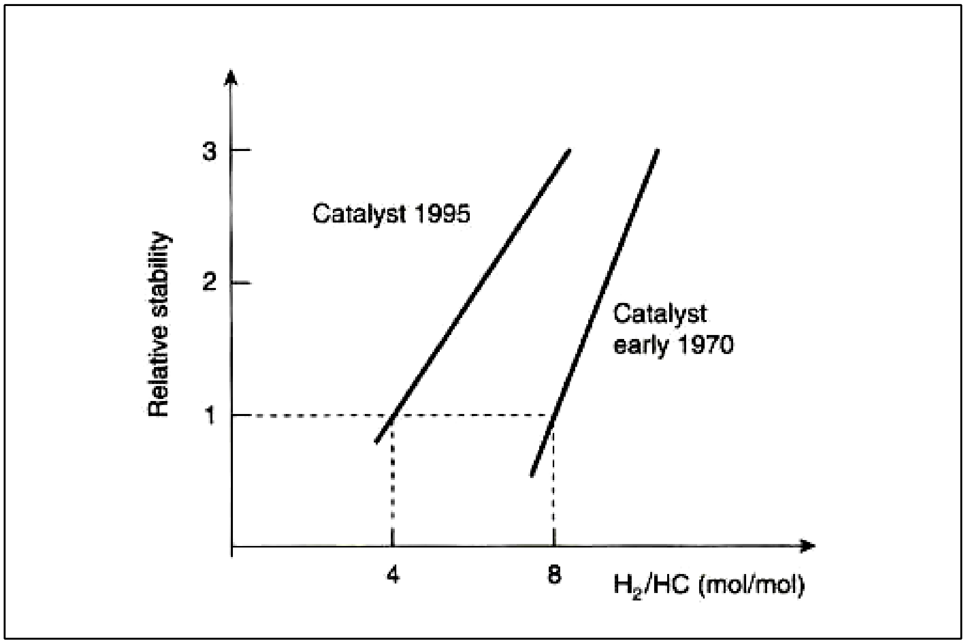


Figure (5.5), Catalyst stability versus H_2/H.C.

Notes

By reducing H2/H.C from 8 to 4 and 4 to 2 the carbon on catalyst is increased by a factor of 1.75 and 3.6 respectively. By reducing H2/H.C ratio from 5 to 4 shorten cycle length about 20%.

5.5 SPACE VELOCITY

It is a measure of the contact time between the reactants and the catalyst and expressed as liquid hourly space velocity or weight hourly space velocity.

LHSV = volume per hour of reactor charge / vol. of catalyst.

WHSV = weight per hour of reactor charge/weight of catalyst.

The choice represents a compromise between allowable hydro cracking and desired dehydrocyclization. Aromatization and isomerzation aren't affected by changes in space velocity because these reaction approach equilibrium even at high space velocity.

Modern reformers usually operate between from 1.0 to 2.0 h^{-1} (LHSV). As below 1.0 h^{-1} undesired side reaction, increased hydro cracking and reducing reformat yield.

Figure (5.6) show that beginning with space velocity=2 to 3 requires raising the reactor inlet temperature by 8 degree centigrade to maintain reformat octane number, in contrast a drop of 1.5 allow the inlet temperature to be lowered by 6 degree centigrade. These values may vary little depending on the operating condition and catalyst used.

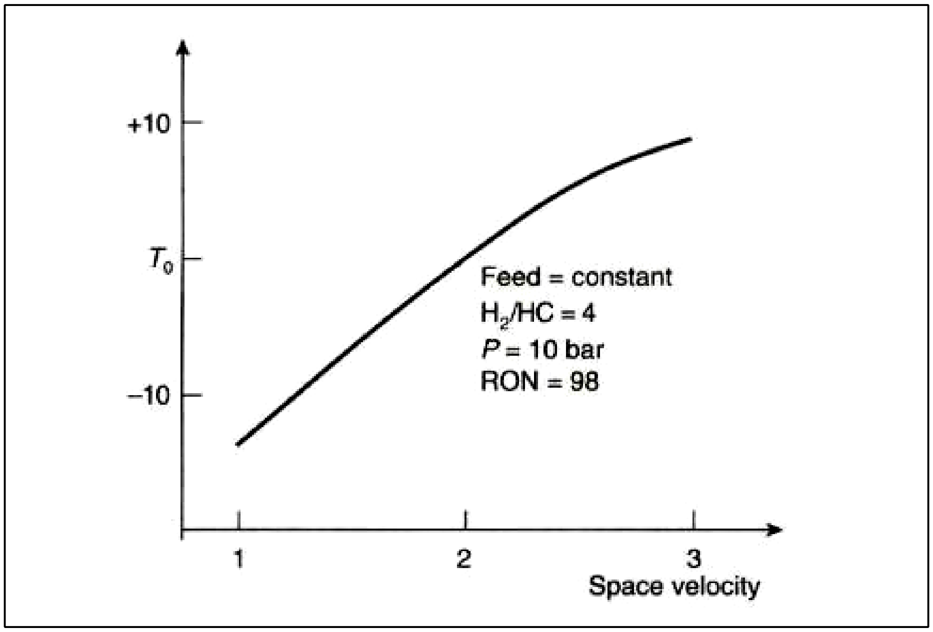


Figure (5.6), Influence of Space Velocity on Octane Number.

5.6 FEEDSTOCK PROPERTIES

In reforming operation, the feed properties are parameters which can significantly influence the performance of the catalyst such as:

- Straight run naphtha generally constitutes the major feedstock for reformers. Feedstock containing an appreciable concentration of unsaturated hydrocarbons such as thermal cracked, cat-cracked, coker and pyrolysis naphtha must usually be hydro-treated before reforming in order to prevent undue hydrogen consumption in the reformer and excessive catalyst deactivation. In addition to being high in sulfur and nitrogen, these stocks contain substantial amount of mono-olefins. These olefinic species are undesirable in reformer feed for several reasons. First, in a reformer reactor, olefins hydrogenate, consuming hydrogen that might be needed for hydro-treating other stocks. Second, hydrogenation of olefins markedly lowers their octane numbers, resulting in lower octane reformat. The third is increasing the tendency to polymerize and form coke on the reforming catalyst.

- Sulfur in the feed poisons the metal and organic nitrogen compounds, which can form ammonia, poisons the acid function, of the catalyst, so concentration must be maintained at less than about 1 PPM by hydro-treating before reforming.

- Water and chlorine compounds as they alter the acidity of the support, and their concentration must be carefully controlled to maintain the proper catalyst acidity.

- Metal such as As, Pb and Cu must be kept at low concentration, because they deposit on the Pt component and deactivate it.

Table (5.1) summarizes the effects of cut points on the different variables. The temperature T (SOR) increases if the initial boiling points are low. The run duration is shortened by low initial boiling points due to the higher operating temperature, and by high end point due to the presence of coke precursors.

Initial boiling points are too low, indicating the presence of a lot of C_6, cause a large amount of benzene to be produced. Since light paraffins are hard to convert, the desired octane will be achieved only by production more C_{7+} aromatics. High endpoints reduce benzene production, but can cause substitute naphthalene to be produced, which it run cause rapid catalyst coking.

Figure (5.7) show that the difference between the amount of naphthenes on the yields, higher naphthenes give higher amount of yields.

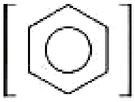
Variable	T_{SOR}	**Run duration**		**Total aromatics**
IBP ↘ IBP < 100°C	↗	↘	↗	↗
EP ↗ EP < 180°C EP > 180°C	↘ ↘	→ ↘	↘ ↘	→ Presence of naphthalenes

Table (5.1), Influence of IBP and EP at constant space velocity and RON.

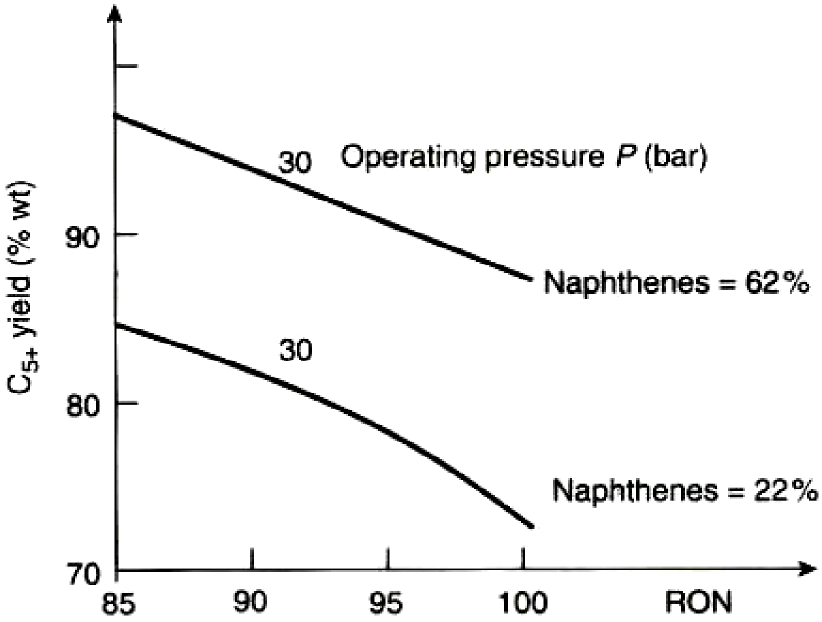
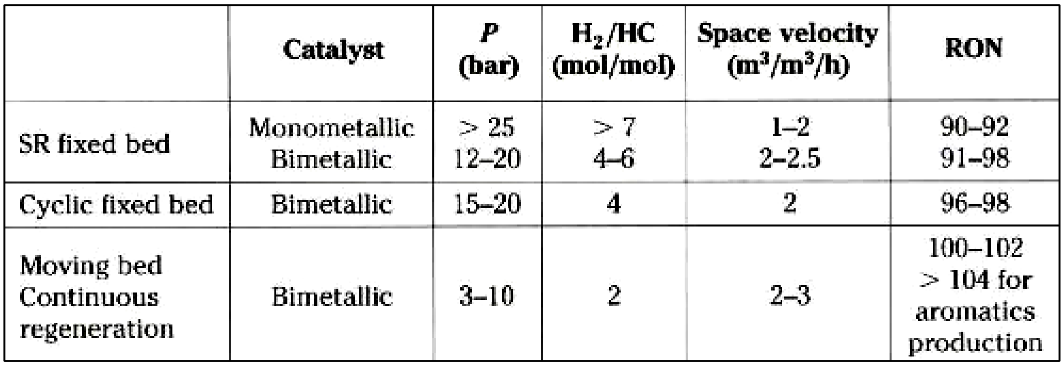


Figure (5.7), Influence of P and the feed on C_{5+} yield.

Operating pressure for present day processes is summarized in table (5.2) to have a possible yield with a possible quality with different type of catalyst (monometallic and bimetallic catalysts).



	Catalyst	***P*** **(bar)**	**H_2/HC (mol/mol)**	**Space velocity ($m^3/m^3/h$)**	**RON**
SR fixed bed	Monometallic Bimetallic	> 25 12–20	> 7 4–6	1–2 2–2.5	90–92 91–98
Cyclic fixed bed	Bimetallic	15–20	4	2	96–98
Moving bed Continuous regeneration	Bimetallic	3–10	2	2–3	100–102 > 104 for aromatics production

Table (5.2), Operating conditions for present-day processes.

CH.6

Hazard Assessment

Hazard

[1] Chemical and catalyst handling:

A. Labels and Other Forms of Warning:

All portable containers of hazardous chemicals must have a large, readable label or tag which states:

- Name and address of manufacturer
- Name of chemical
- Numerical hazard warning or other appropriate warning supplied by manufacturer

Labels can be color coded according to following:

- Orange Carcinogen Hazard (ie benzene)
- Red Chemical Burn Hazard (ie acids, bases)
- Yellow Toxic Vapor Hazard (ie H_2S)
- White All Others

B. Material safety data sheet (MSDS):

Chemical manufacturers, importers and distributors are required to provide MSDSs to purchasers of hazardous chemicals.

Although format of MSDS can vary, they must include following information:

- Chemical and common name
- Ingredient information
- Physical and chemical characteristics
- Physical hazards - potential for reactivity, fire and/or explosion
- Health hazards
- Symptoms of exposure
- Primary route of likely entry into body on exposure
- OSHA permissible exposure levels
- Precautions for use
- Waste disposal
- Protective measures and equipment, including during spills and maintenance
- Emergency and first-aid procedures
- Date of MSDS preparation and last revision
- Emergency contact of manufacturer or distributor

[2] Hydrogen sulfide poisoning:

Hydrogen sulfide is both an irritant and an extremely poisonous gas. Many natural and refinery gases contain more than 0.10 mol-percent H_2S. Current OSHA permissible exposure limits are 20 mol-ppm ceiling concentration and 50 mol-ppm peak concentration for maximum ten minute exposure.

Any unit processing gases containing H_2S can be operated safely, provided ordinary precautions are taken and poisonous nature of H_2S is recognized and understood.

A-Acute hydrogen sulfide poisoning:

Breathing air or gas containing more than 500 mol-ppm H_2S can cause acute poisoning and may be fatal.

B-Symptoms of acute hydrogen sulfide poisoning:

Symptoms of acute H2S poisoning are muscular spasms, irregular breathing, lowered pulse, odor to breath and nausea. Loss of consciousness and suspension of respiration quickly follow.

After victim recovers, there is still risk of edema (excess accumulation of fluid) of lungs which may cause severe illness or death in 8 to 48 hours.

C- First aid treatment of acute hydrogen sulfide poisoning:

Move victim at once to fresh air. If breathing has not stopped, keep victim in fresh air and keep quiet.

If possible, put him to bed. Secure a physician and keep patient quiet and under close observation for about 48 hours for possible edema of lungs.

If victim has become unconscious and breathing has stopped, artificial respiration must be started at once. Speed in beginning artificial respiration is essential. Do not give up. Men have been revived after more than four hours of artificial respiration.

If other persons are present, send one for a physician. Others should rub patient's arms and legs and apply hot water bottles, blankets or other sources of warmth to keep him warm.

After patient is revived, he should be kept quiet and warm, and remain under observation for 48 hours for appearance of edema of lungs.

D-Sub acute hydrogen sulfide poisoning:

Breathing air or gas containing H_2S anywhere between 10 to 500 mol-ppm for an hour or more may cause sub acute or chronic hydrogen sulfide poisoning.

E- Symptoms of sub acute poisoning:

Symptoms of sub acute H_2S poisoning are headache, inflammation of eyes and throat, dizziness, indigestion, excessive saliva, and weakness. Edema of lungs may occur.

F- Treatment of sub acute poisoning

Keep patient in dark to reduce eyestrain; have a physician treat inflamed eyes and throat. Watch for possible edema.
Where sub acute poisoning is suspected, atmosphere should be checked repeatedly for presence of H_2S.

G-Prevention of hydrogen sulfide poisoning:

Best method for prevention of H_2S poisoning is to stay out of areas known or suspected to contain it.

Fresh air masks or gas masks suitable for use with hydrogen sulfide must be used in all work where exposure is likely to occur. Masks are checked frequently to make sure they are not exhausted.

Persons who must work on or in equipment containing appreciable concentrations of H2S, must wear fresh air masks and work in pairs so that one may effect a rescue or call for help should other be overcome.

As mentioned above, atmosphere in which people work should be checked from time to time for appreciable concentrations of H_2S.

[3] Precautions for entering contaminated or inert atmosphere:

Nitrogen is non-toxic. However in vessels or areas where there is a high nitrogen concentration, there is also a deficiency of oxygen for breathing. Breathing an atmosphere deficient in oxygen will rapidly result in dizziness, unconsciousness, or death depending on length of exposure.

Do not enter or even place your head into a vessel which has a high concentration of nitrogen.
Do not stand close to a valve where nitrogen is being vented from equipment at a high rate which may temporarily cause a deficiency in oxygen close to valve.

Refinery personnel who must enter a contaminated or inert atmosphere follow all prescribed standard safety precautions and regulations which apply for refinery.

It is important to emphasize that if a person has entered a vessel and become unconscious, no individual should go in to help him without first donning a fresh air mask.

A. Safe Vessel Entry

Precautions apply equally to entry into all forms of vessels, including enclosed areas which may not normally be considered vessels. Examples include:

Reactors
Fractionators
Receivers
Fired Heaters
Neutralizing Basins
API Separators
Separators
Drums
Pumps
Storage Tanks
Water Treatment Basins

(1) General precautions:

- Vessel must be positively isolated.
- Safe access to vessel must be assured.
- Man way and internals must be provided.
- Personnel entering vessel must be provided with safety harnesses.
- Two persons must be available outside vessel to assist personnel inside.

- Safety of atmosphere inside vessel must be confirmed by checks for toxic gases (eg H_2S), oxygen content, and explosive gases.
- A supply of fresh air must be available for people who will rescue personnel entering vessel in event they encounter difficulty.
- A vessel entry permit must be obtained and registered with responsible persons.

(2) Positive isolation:

Every line connecting to a nozzle on vessel to be entered must be blinded.

Area around vessel man ways is surveyed for possible sources of dangerous gases which may enter vessel while person is inside. Any hazards found during survey are isolated or removed.

(3)Vessel access:

Proper access is provided both to exterior and interior of vessel to be entered. Exterior access should be a solid, permanent ladder and platform or scaffolding strong enough to support people and equipment who are involved in work to be performed.

Access to interior must be strong and solid. Scaffolding is preferred when vessel is large enough to permit its use.

(4) Safety harness:

Any person entering a vessel should wear a safety harness with attached safety line.

Minimum of one harness for each person entering vessel and at least one spare harness for persons watching at man way should be provided.

(5)Man way watch:

Before a person enters a vessel, there should be minimum two people available outside vessel; one of whom is specifically assigned responsibility to observe activity of people inside vessel.

These people should not leave their post until those inside vessel have safely exited.

A communication system must be provided for man way watch so that they can quickly call for help in event personnel inside vessel encounter difficulty. Radio, telephone, or public address system is necessary for that purpose.

(6) Fresh air:

Vessel must be purged completely free of any noxious or poisonous gases and inventoried with fresh air before permitting anyone to enter. Safety department must test atmosphere within vessel for toxic gases, oxygen and explosive gases before entry. This must be repeated every 4 hours while there are people inside vessel. Each point of entry and any dead areas inside vessel, such as receiver boots or areas behind internal baffles where there is little air circulation, should be checked.

Fresh air can be circulated through vessel using an air mover, fan, or, in cases where moisture is a concern, vessel can be purged using dry certified instrument air from a hose or hard piped connection.

When instrument air is used, a check of supply header is made to ensure it is properly lined up and there are no connections where nitrogen can enter system (nitrogen improperly used as backup for instrument air by some refiners). Fresh air purge should be continued as long as people are inside vessel.

Minimum one fresh air mask for each person entering vessel and at least one spare mask for manhole watcher should be provided at vessel entry. Each mask must have backup air supply completely independent of main supply. It must also be independent of electrical power. Auxiliary supply must have an alarm that alerts user he is on backup supply, and should be sufficiently large to give user five minute autonomy to escape from danger.

(7) Vessel entry permits:

Before entering vessel, a vessel entry permit must be obtained. Vessel entry permit ensures that all responsible parties know that work is being conducted inside vessel and establishes safe preparation procedure to follow in order to prevent mistakes which can result in an accident. Permit is typically issued by safety engineer or shift supervisor.

(8) Checkout prior to startup:

Risk of exposure to hydrocarbons, toxic or poisonous gases, and catalyst dust is low during new unit checkout. Primary danger is nitrogen. Vessel entry procedure must be rigorously followed during checkout of new unit.

Oxygen content of atmosphere inside vessel is checked before every entry and vessel is blinded.

Independent blinds at each vessel nozzle are preferred.

(9)Turnaround inspections:

In turnaround inspections, possibility that vessels contain dangerous gases is much higher. Equipment which has been in service must be thoroughly purged before entry. Vessel should have been steamed out (unless steam presents hazard to internals), then fresh air circulated through it until all traces of hydrocarbons are gone. If liquid hydrocarbon remains or if odors persist afterwards, repeat purging procedure until vessel is clean.

In a turnaround inspection, every vessel nozzle must be blinded with no exceptions. Blinds must all be in place before vessel is purged.

Another factor to be cautious of is heat stress especially if entering a vessel immediately after unit has been shut down.

B. Aromatic Hydrocarbons:

i. Benzene:

Benzene is extremely toxic.

Special instruction: If clothing (including gloves, shoes) becomes contaminated with benzene, it should be removed immediately. Wash any skin areas exposed to benzene with soap and water.

Take complete bath if body area is wetted with benzene. Do not wear clothing that has been wet with benzene until garment is decontaminated by washing or dry cleaning.

Wearing clothing that has been wet with benzene almost guarantees that person will inhale benzene vapors over a long period of time, resulting in potential health hazards.

Avoid draining benzene to concrete or into sewers where it can vaporize and create health hazard. Do not use hot water or steam which aggravates vaporization of benzene.

If you must enter an area of high benzene vapor concentration resulting from a spill, wear appropriate respiratory protection such as self-contained breathing apparatus, or air mask with external supply.

ii. Toluene, xylenes and heavier aromatics:

These compounds are moderately toxic and are believed not to have destructive effects on blood forming organs as does benzene. If clothing (including gloves, shoes, etc) becomes wet with such aromatics, remove clothing, bathe, and put on fresh clothing. Avoid breathing aromatic vapors.

iii. Minimizing exposure to aromatics:

Operating and laboratory personnel involved in obtaining samples wear chemical-type safety goggles or shield, protective apron or laboratory coat, solvent-resistant gloves, and approved respiratory protective equipment where ambient concentrations exceed allowable limits.

This protective equipment is not, however, substitute for safe working conditions, proper ventilation, good personal practices, and proper maintenance of operating and safety equipment.
In all cases, skin contact (Especially eyes) and inhalation must be minimized.

Sampling liquid hydrocarbons requires some care to limit personal exposure and release to atmosphere.

To minimize vaporization, hot hydrocarbon streams must be routed through a cooler before drawing a sample. In all sampling situations, personnel are instructed to remain at arm's length from sample container and to situate themselves upwind of container if possible. These simple precautions greatly minimize exposure to hydrocarbon vapors.

iv. Medical attention:

U.S. NIOSH/OSHA guidelines for toluene, xylene and ethylbenzene set forth recommendations for medical monitoring of personnel working in environments where exposure to these materials can occur.

All new or current employees should be alerted to early signs and symptoms resulting from exposure to aromatics, and any workers experiencing such symptoms must seek professional medical attention.

C. Safety Information for UOP Platforming Catalysts:

It is during periods of opening and cleaning equipment or in sampling that bodily exposure to UOP Platforming catalyst can occur and caution must be exercised.

Material Safety Data Sheets should be obtained from UOP at the time of catalyst supply and should be available to the operating personnel.

Major constituent of UOP Platforming catalyst is alumina, which is not currently listed by OSHA as a hazardous substance. These catalysts do contain other constituents, in lesser amounts, which might present hazards to human health and/or the environment if handled or disposed of improperly. It is the purpose of this safety section to provide information and recommendations which will allow safe handling and proper disposal of these catalysts.
Only following fresh catalysts (R-11, R-12, R-14, R-16, R-18, R-19, R-50, R-51, R-55, R-60, R-62) contain hydrogen sulfide.

Spent Platforming catalysts may also contain additional hazardous chemicals, such as: arsenic, carbon, hydrocarbons, iron pyrites, iron sulfide, lead, and vanadium. The toxic properties and exposure limit of the most hazardous of these chemicals follow:

i. Hydrogen sulfide:

Hydrogen sulfide is both an irritant and an asphyxiant. Current OSHA permissible exposure limits are 20 ppm ceiling concentration and 50 ppm peak concentration for a maximum 10 minute exposure.

ii. Arsenic:

Arsenic is a recognized carcinogen and can cause acute and chronic toxicity. Symptoms of acute toxicity are somewhat dependent upon route of contact and can include (for ingestion or inhalation): irritation of the stomach and intestines, with nausea, vomiting and diarrhea; liver damage; kidney damage; blood disturbances; and allergic reactions. The OSHA 8-hour time weighted average exposure limit to inorganic arsenic compounds is 10 micrograms per cubic meter of air.

Greatest potential for human exposure to catalyst materials comes from catalyst dust during reactor loading and from dust, fumes, and vapors during catalyst unloading operations.

For the unprotected worker, hazardous dust, fumes, and vapors may be inhaled, ingested, or contaminate the eyes and skin.

• Handling Catalyst spills and Deposited Catalyst Dust:

Always wear NIOSH-approved self-contained breathing apparatus or combination of toxic dust respirator-rubber frame eye goggles, protective clothing, and gloves. Avoid cleaning methods which raise dust. Dispose of all catalyst wastes properly in containers, which should then be labeled as to the contents and hazards.

Do not dispose of catalyst wastes in a public water system or in the normal solid waste. Return material to supplier for metal recovery.

• Handling UOP Catalysts Safely:

UOP believes that OSHA exposure limits to catalyst chemicals will not be exceeded if proper handling procedures and worker protective clothing/safety devices are used.

UOP recommends that the following minimum safety procedures be established and adhered to:

- Handle catalysts only in a well ventilated area. In areas where natural ventilation is insufficient, use local mechanical exhaust ventilation

- Wear a NIOSH-approved toxic dust respirator with full face-piece, protective clothing, and gloves for normal catalyst handling operations

- Reactor loading and unloading operations present extraordinary health risks, especially to personnel working in the reactor. During loading operations, large quantities of catalyst dust may be generated. During unloading, the hazards may include inert (nitrogen) atmosphere, toxic feedstock, product, or purge materials present with the catalyst, or toxic forms of catalyst chemicals. Personnel working in reactors should wear a supplied air respirator with a hood or helmet, operated in a pressure-demand or other positive-pressure mode, or in a continuous flow mode (NIOSH Respirator Code SAFE: PD, PP, CF). This respirator should have a primary, secondary, and emergency supply of air. In addition, personnel in the reactor should be equipped with safety harnesses and safety lines for rescue and a means for visual, voice or signal line communication with standby personnel, who should be strategically located with suitable rescue equipment. The OSHA regulations concerning use of respirators (29 CFR, Subpart 1, Section1910.134) should be read and thoroughly understood before undertaking to place personnel in reactors during catalyst loading and unloading operations.

- Protective clothing and all safety devices should be thoroughly decontaminated after each use. Worn-out, broken or defective safety equipment and clothing should be removed from service and repaired or replaced. Good personal hygiene after handling a catalyst or being exposed to catalyst dust is an essential part of a responsible catalyst safety program. Do not eat, drink, or smoke in areas where the catalyst is being handled or where exposure to catalyst dust is likely

National Fire Protection Association Identification of Color Coding:

Color Blue: Type of possible injury

- Materials which on very short exposure may cause death or major residual injury even though prompt medical treatment was given

- Materials which on short exposure may cause serious temporary or residual injury even though prompt medical treatment was given

- Materials which on intense or continued exposure may cause temporary incapacitation or possible residual injury unless prompt medical treatment is given.

- Materials which on exposure cause irritation but only minor residual injury even if no treatment is given.
- Materials which on exposure under fire conditions offer no hazard beyond those of ordinary combustible materials.

Color Red: Susceptibility of material burning

- Materials which will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or which are readily dispersed in air and which will burn readily.
- Liquid and solids that can be ignited under almost all ambient temperature conditions.
- Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur.
- Materials that must be preheated before ignition can occur.
- Materials that will not burn.

Color Yellow: Susceptibility of release of energy

- Materials which in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperature and pressure

- Materials which in themselves are capable of detonation or explosive reaction but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water

- Materials which in themselves, are normally unstable and readily undergo violent chemical change but do not detonate. Also materials which may react violently with water or which may form potentially explosive mixtures with water

- Materials which in themselves are normally stable, but which may become unstable at elevated temperatures and pressures or which may react with water with some release of energy but not violently

- Materials which in themselves are normally stable, even under fire exposure conditions and which are not reactive with water

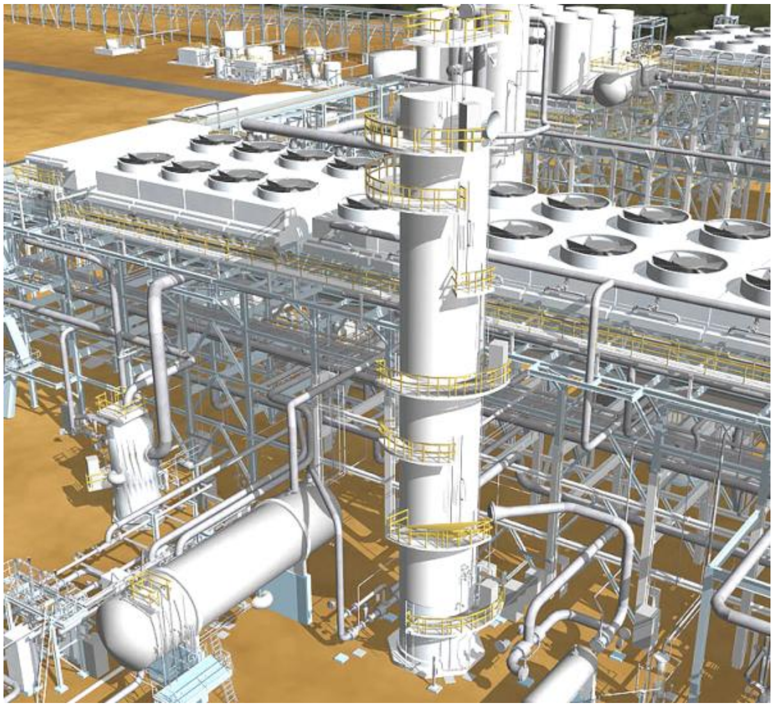
Hazardous materials:

List of attached material safety data sheets:

- Naphtha
- Reformate
- LPG, sweetened
- Hydrocarbons, (C1-C4)
- Hydrogen
- Hydrogen Sulfide
- Benzene
- Toluene
- Xylene
- Phosphate
- DMDS
- Caustic Soda
- UOP Platforming Catalyst

CH.7

Plant Design



PLANT LOCATION

The final choice of the plant site usually involves a presentation of the economic factors for several equally attractive sites. The exact type of economic study of plant location will vary with each company making a study.

Factors Affecting Plant Location

1. Raw materials supply

The location of the raw materials of an industry contributes more toward the choice of plant site than any other factor. This is especially noticeable in those industries in which the raw material is inexpensive and bulky and is made more compact and obtains a high bulk value.

2. Markets and transportation

The existence of transportation facilities has given rise to many of the greatest trade centers of the world.

A location should be chosen, if possible which has several competition will help to maintain low rates and given better service.

3. Markets for Finished products

The large oil refiners are located along the seacoast or near large cities where a market exists for the finished products.

Crude oil is easily pumped by pipelines or shipped from the oil well sin the interior.

Cheap rates are thus secured for a crude low-priced commodity.

Consumed in large quantities while the finished products are made in the center of the market in order to lower the distribution cost.

4. Power and fuel supply

The fuel best plan is to locate near large coal field if coal is the primary fuel or to tie up by long contracts sufficient gas and /or oil to ensure the continuity of operation over a long term.

Sources of power:

Power for chemical industry is primarily from coal water and oil. The turbines or engines used to generate electricity can be operated non condensing and supply exhaust steam for processing purposes.

5. Water Supply

Water for industrial purposes can be obtained from two general sources; the plants own source or principle supply if the demands for water are large. It is more economical for the industry to supply its own water such a supply may be obtained from drilled will rivers, lakes, damned streams

before a company enters up on any project, it must ensure it self of as insufficient supply of water for all industrial. Sanitary and fire demands both present and future.
Water natural quality is as diverse as the sites and regions from which it is. Water temperature and chemical characteristics such as organic and inorganic contaminants, the relative price are of greatest economic importance in determining the value of water to the chemical industry. The relative importance of each of these depends upon the service for which the water is wanted.

6. Climate

Chemical plants as general rules are rather difficult to insulate or to provide with artificial heat or conditional air.
Essentially a process must be designed for production of a commodity or commodities under the most economic conditions, if out side plant climate does not fit into the picture of production, then process and process equipment.

7. Labor

Before locating an industry in any particular location a careful study of the supply of available labor must be made.
Factors to be considered in labor studies are supply. Kind, diversity, intelligence, wage scale, regulations, efficiency and costs.

8. Community and site characteristics

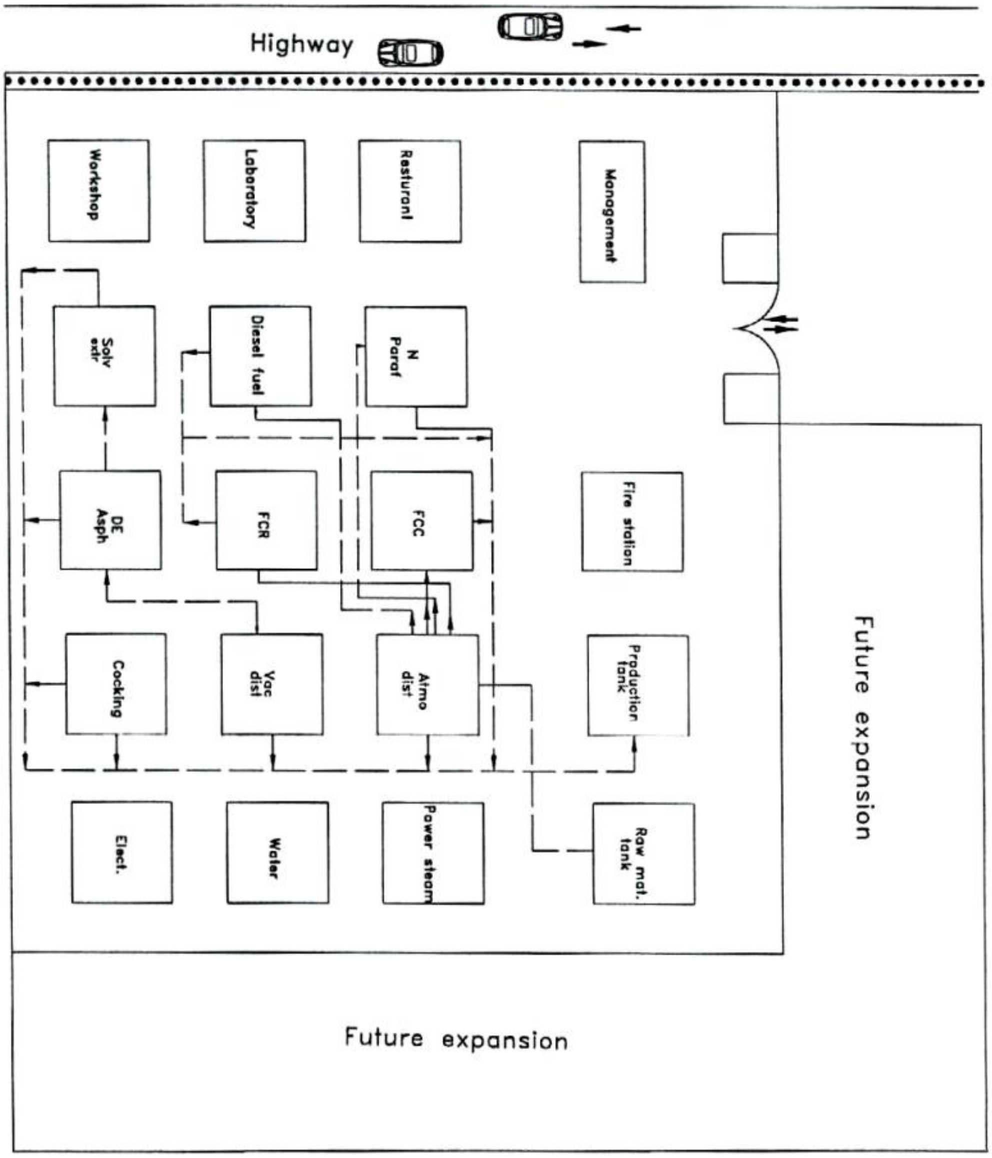
In the selection of a definite plant site in a designated area there are many minor factors to which some attention should be given. The chemical industry is usually of minor importance. Of great importance is a nature of the subsoil the need of piling or other expensive foundations can materially affect construction costs. Also the site information is essential in the selection of apian location.

PLANT LAYOUT

For marketing, many factors must be considered such as:

1. New sites development or addition previously development.
2. Future expansion.
3. Economic distribution of services-water process steam, power and gas.
4. Weather condition are they amenable to out door construction.
5. Safety consideration possible hazards of fire explosion and fumes.
6. Building code requirements.
7. Waste disposal problems.
8. Sensible use of floor and elevation space.

The layout will bed one by the use of (unite areas) concept method which are particularly well adopted to large plant layout. Unite areas are often delineated by means of distant process phase and operational producers by reasons of contamination and by safety consideration requirement. Thus the delineation of the shape and extent of a unite area and of interrelation ships of each area in a master plot plan is one of the first take of layout planning.



CH.8

Design

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 lb_{mol} /hr

By using catalytic reforming yield correlations at (K =11.7, R.O.N.C.=98):-

1) From fig. (6-3): [C_5^+ vol% =82%]
2) From fig. (6-4): [C_4 vol% = 6.4%]
3) From fig. (6-5): [($C_1 + C_2$) wt% = 2.25%,C_3 wt% = 3%]
4) From fig. (6-6): [H_2 wt% = 2.8%]

From Kern by t_{mean} = 40 * 1.8 + 32 = 104 f°
$\rho_{Naphtha}$ = 0.71 * 62.4 = 44.3 lb/ft^3

Volume flow rate of Naphtha = 60125 / 44.3 = 1357.22 ft^3/hr

Volume flow rate of C_{5+} = 0.82 * 1357.22 = 1112.92 ft^3/hr

At t_{mean} = 104 f° ,and 45° API:
ρ_{C5+} = 0.787 * 62.4 = 49.11 lb/ft^3

Mass flow rate of C_{5+} = 49.11 * 1112.92 = 54655.5 lb/hr

Mass flow rate of ($C_1 + C_2$) = 0.0225 * 60125 = 1352.81 lb/hr

Mass flow rate of C_3 = 0.03 * 60125 = 1803.75 lb/hr

Mass flow rate of H_2 = 0.028 * 60125 = 1683.5 lb/hr

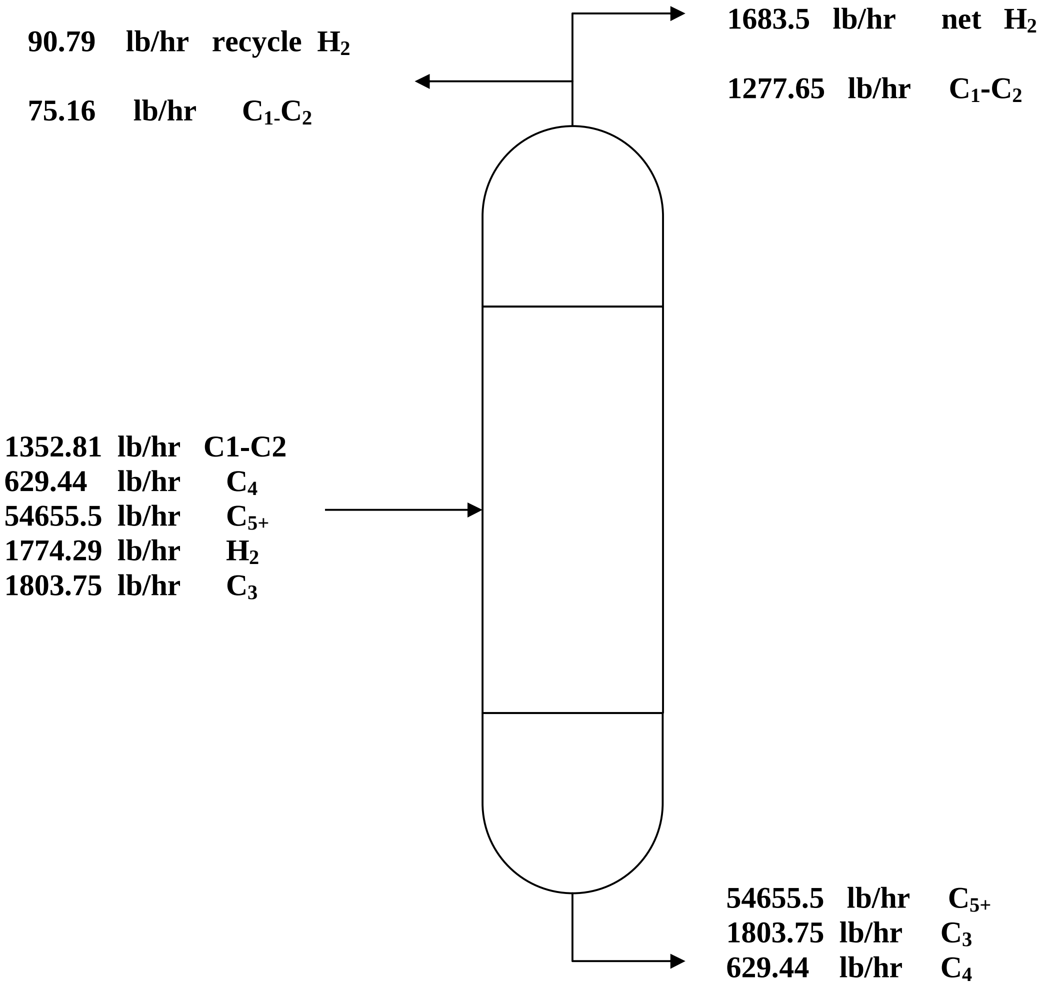
Mass flow rate of C_4 =
60125 – (54655.5+1352.81+1803.75+1683.5) =629.44 lb/hr

Assume recycle ratio of H_2 = 8000 Scf /bbl
= 0.00151 lb H_2/lb Naphtha

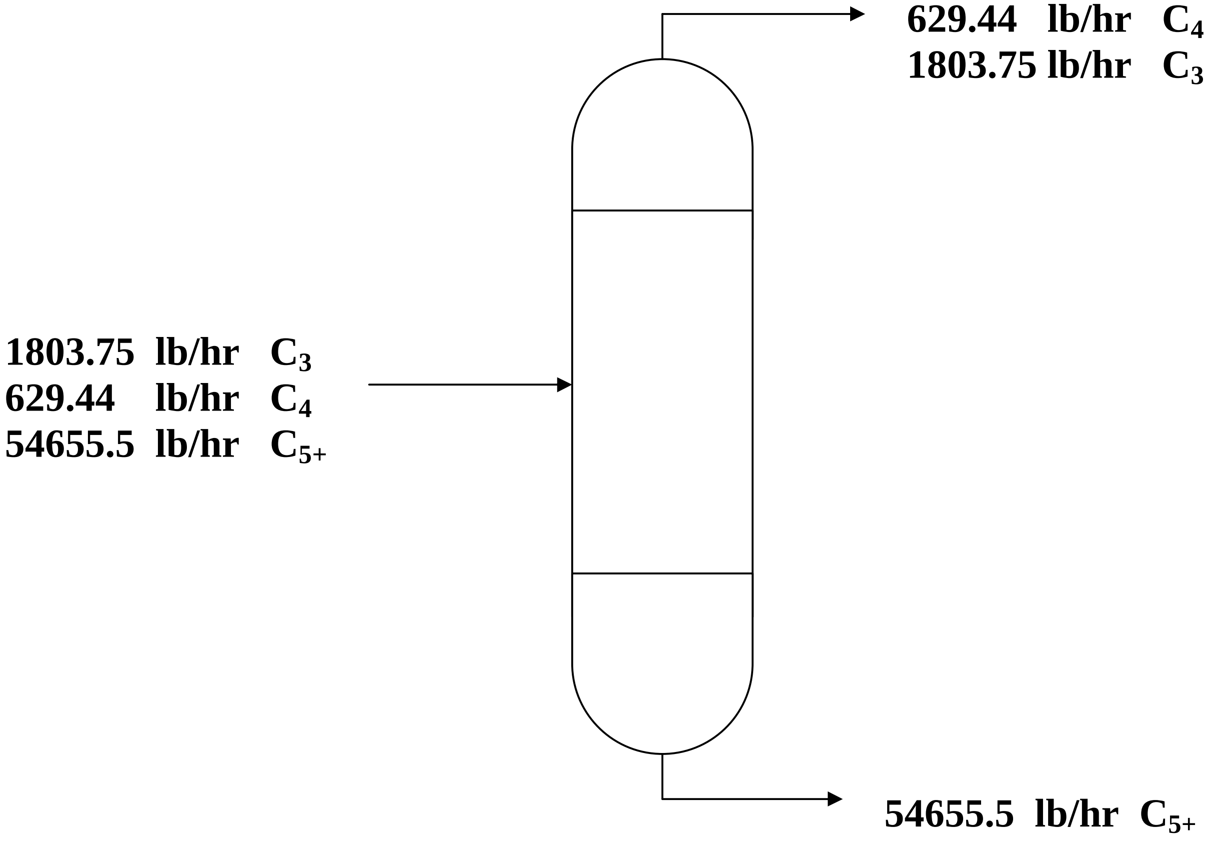
Mass flow rate of recycled H_2 = 60125 * 0.00151 = 90.79 lb/hr

Mass flow rate of total H_2 = 1683.5 + 90.79 = 1774.29 lb/hr

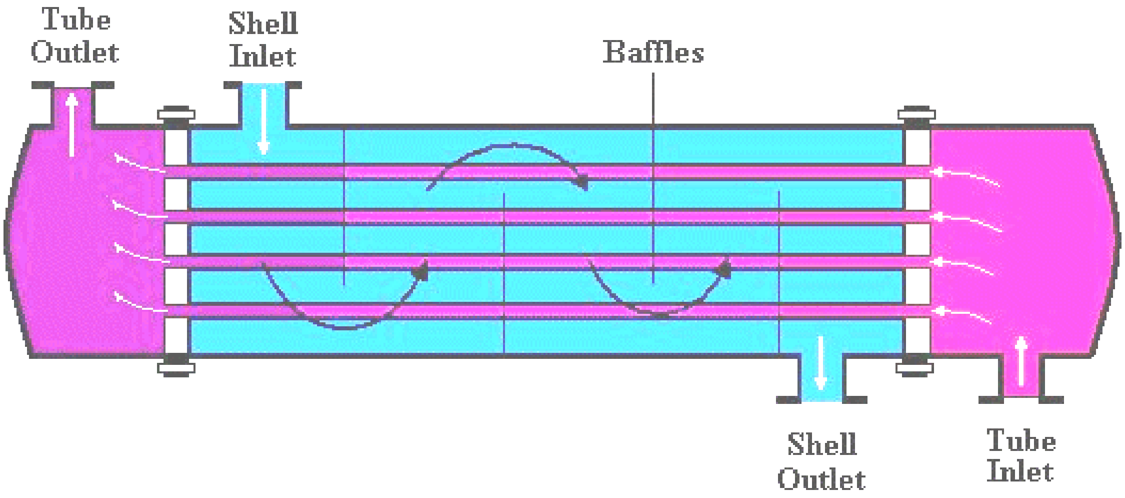
Material balance on flash drum:-



Material balance on stabilizer:-



Heat Exchanger Design



Shell and tube exchangers:

Heat Exchanger:

Heat exchangers are devices build for efficient heat transfer from one fluid to another .they are used widely in refinery industry to cooled products or preheat feed.

Role of heat exchanger in chemical processing:

- Heat or cool a stream flowing from item of equipment to another. The stream may be:
  - -A liquid.
  - -A gas.
  - -A multiphase mixture.
- To vaporize a liquid stream.
- To condense a vapor stream.

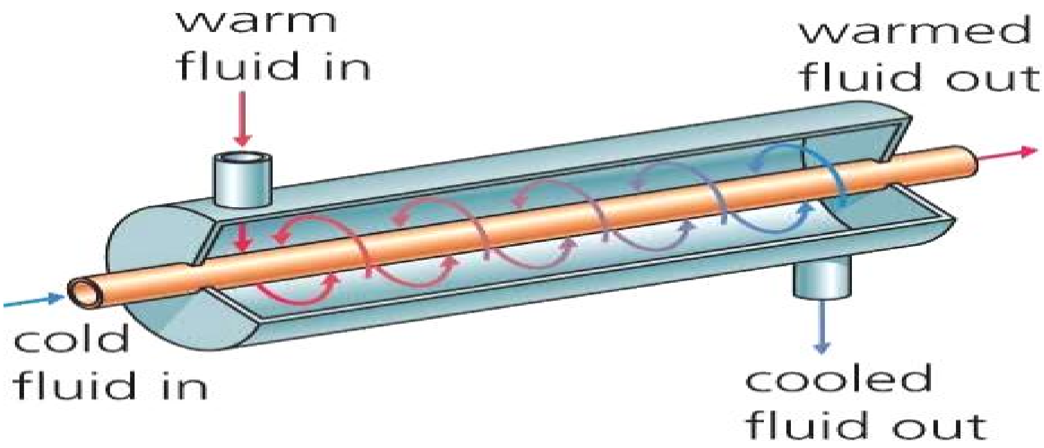
Types of heat exchangers:

1-parallel flow heat exchanger:

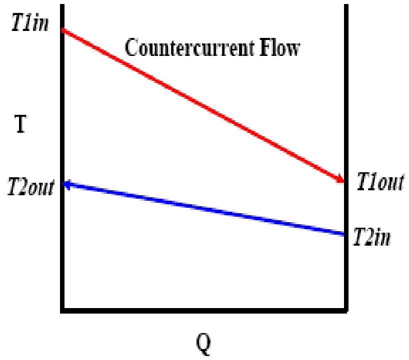
In this type of heat exchanger the two fluids flow in the same direction .If we assume that specific heat capacity is constant ,so

A.Counter flow heat exchanger:

In counter-flow heat exchanger fluids flow in opposite direction.



So rate of heat transfer between two fluids will be
$dQ/dT= U*A*dT_{lm}$



where:

U : overall heat transfer coefficient.
A : area of tubes
$dT_{lm} = (dt_1-dt_2)/Ln\ (dt_1/dt_2)$.

B.Cross flow heat exchanger:

In it the direction of fluids are perpendicular to each other .the required surface area for this heat exchanger is calculated from tables it's between surface area for counter flow and parallel flow.

Preparation of design heat exchanger:

1. A phase change involved in the system: A quick look at the boiling points compared with the entrance and exit temperatures.

2. The flow rates and operating pressures:

This information is critical in establishing the mass and energy balance around the exchanger. Operating pressures are particularly important for gases as their physical properties vary greatly with pressure.

3. The physical properties of the streams involved:

you should get the physical properties for each zone separately to ensure accuracy, but in some cases it is acceptable to use an average value. Physical properties that you will want to collect for each phase of each stream will include: heat capacity, viscosity, thermal conductivity, density, and latent heat (for phase changes). These are in addition to the boiling points of the streams at their respective pressures.

4. The allowable pressure drops and velocities in the exchanger:

Pressure drops are very important in exchanger design (especially for gases). As the pressure drops, so does viscosity and the fluids ability to transfer heat. Therefore, the pressure drop and velocities must be limited.

The velocity is directly proportional to the heat transfer coefficient which is motivation to keep it high, while erosion and material limits are motivation to keep the velocity low.

Typical liquid velocities are (3-10 ft/s). Typical gas velocities are (50-100 ft/s). Typical pressure drops are (5-8 psi) on the tube side and (3-5 psi) on the shell side.

5. The Heat duty of the system:

This can be calculated by a simple energy balance from one of the streams.

6. The Area of the exchanger:

These can be found in most textbooks dedicated to the subject. Once you've estimated the overall heat transfer coefficient, use the equation $Q=U\ A\ dT_{lm}$ to get your preliminary area estimate.

7. Prepare layout for my exchanger:

selecting a shell diameter, tube sheet layout, baffle and tube spacing, then check your velocity and pressure drop requirements to see if they're being met. Some guidelines may be as follows: 3/4 in. and 1.0 in. diameter tubes are the most popular and smaller sizes should only be used for exchangers needing less than 30 m^2 of area. If your pressure drop requirements are low, avoid using four or more tube passes as this will drastically increase your pressure drop.

Other Considerations:

- Materials of Construction
- Ease of Maintenance
- Cost of Exchanger
- Overall Heat Integration

The tubular element:

The full filament of many industrial services requires the use of large number of double pipe hairpins (double pipe heat exchangers).

Double pipe exchanger:

Heaters are used primarily to heat process fluid; steam is usually employed for this purpose, although in oil refineries hot recalculated oil serves the same purpose.

- Water is the main cooling medium.
- The principal parts are two sets of concentric pipes, two connecting, tees and a return head and a return bend.
-The inner pipe is supported within the outer pipe by packing glands.
-The return bends which is usually exposed and does not provide effective - heat transfer surface - Hairpins are useful as inexpensive heat - transfer surface.

Double pipe exchanger fittings:

Outer pipe , IPS	Inner pipe , IP
2	$1\ ^{1}/_{2}$
$2\ ^{1}/_{2}$	$1^{1/4}$
3	2
4	3

- Double pipe exchangers are usually assembled in 12 , 15 or 20ft effective length .

- The use of a large number of double pipe hairpins consumes I considerable ground area and also entail a large number of points at which leakage may occur.
- They can best be obtained by means of shell and tube equipment.
- Shell and tube equipment involves expanding a tube into a tube sheet and forming a seal which does not leak under reasonable conditions.

- In some industrial uses it is desirable to install tubes in a tube sheet so that they can be removed easily.

-The tubes actually packed in the tube sheet by means of ferrules using a soft metal packing ring.

Heat exchanger tubes:

The outside diameter of heat exchanger or condenser tubes is the actual outside diameter in inches with in a very strict tolerance.

- Heat exchanger tubes are available in a verity of metals which include steel, copper, admiralty, brass, 70 – 30 copper - nickel, aluminum bronze, aluminum, and the stainless steels.
- They are obtainable in a number of different wall thickness defined by Birmingham wire gage, which is usually referred to as BWG or gage of the tube. The most common diameters arc % and 1 inch O.D.

Tube pitch:

Tube holes can not be drilled very close together, the shortest distance between two adjacent tube holes is the' clearance or ligament, and these are now fairly standard. I1 Tubes are laid out on cither square or triangular pattern

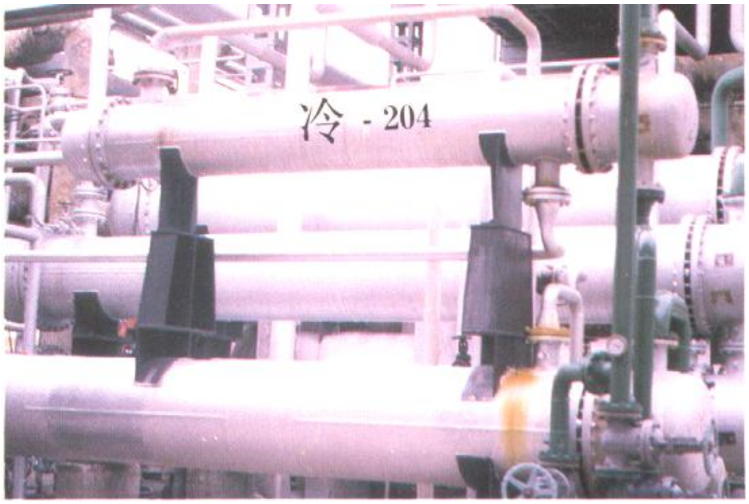
Shells:

Shells are fabricated from steel pipe with nominal IPS diameters up to 12 in above 12 in the actual outside diameter and the nominal pipe diameter are the same.

The standard wall thickness for shells with inside diameters from 12 to 24 inch inclusive is 3/8 inch , which is satisfactory for shell-side operating pressure up to 300 psi.

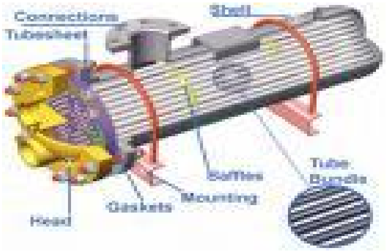
Baffles:

It is apparent that higher heat - transfer coefficients result when a liquid is maintained in a state of turbulence to include turbulence outside the tube it's customary to employ baffles which cause the liquid to how through the shell at right angles o the axes of the lubes. The center - to - center distance between baffles is called balled pitch or baffle spacing.



Heat exchanger design:

Choosing heat exchanger which used to exchange heat between the hot vapor from third reactor and naphtha feed need to preheated before enter the furnace.



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:
   - a- From fig.(5) C_P= 0.545 Btu/lb.˚ f
   - b- From Fig.(1) K= 0.082 Btu/hr.ft.˚f
   - c- From fig.(14) μ= 0.14*2.42=0.3388 lb/hr.ft
   - d- From fig.(6) 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˚

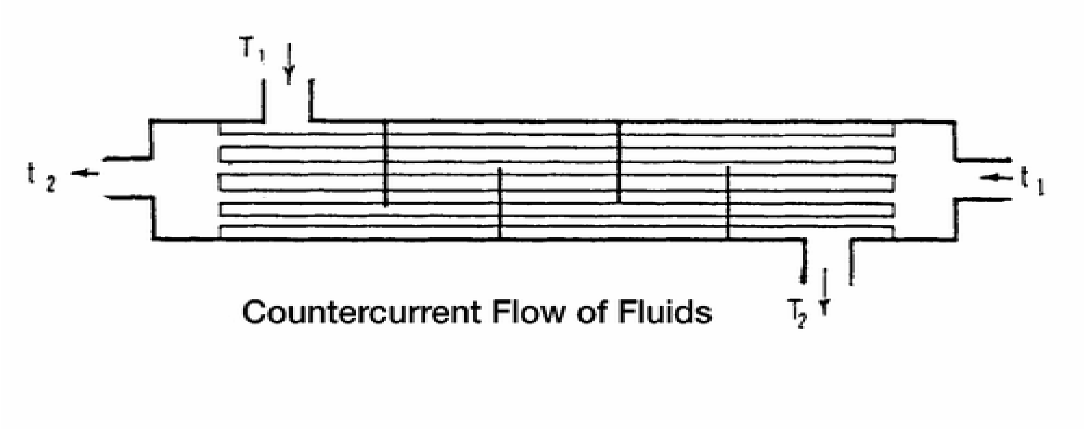
From Kern Book:

- 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

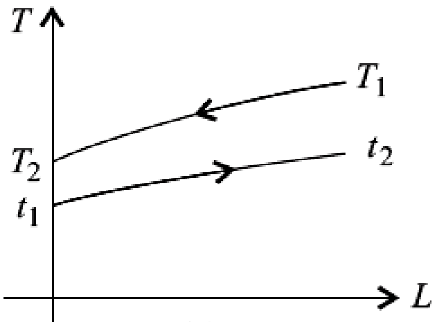
Step (3): L.M.T.D:

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

From fig. (10-34)A **[1shell pass and 2 or more tube passes]**

We found **f=0.9**

LMTD $_{\text{corrected}}$ = 0.9*180.55=162.5 ˚f

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

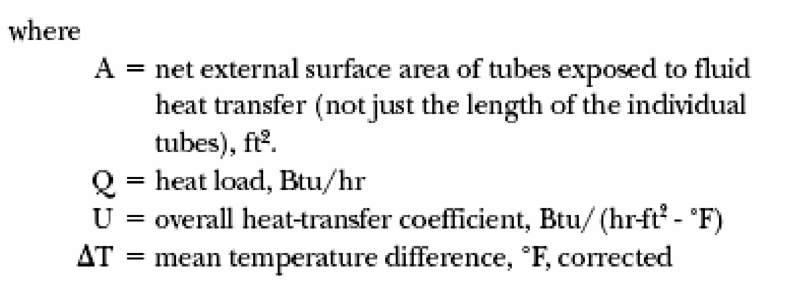
From table (10-17)

U Range= (40-75) Btu/ft^2.˚f.hr

Assume **U=57** Btu/ft^2.˚f.hr

Step (5): Area calculation

A= Q /U*ΔT_{lm}



where

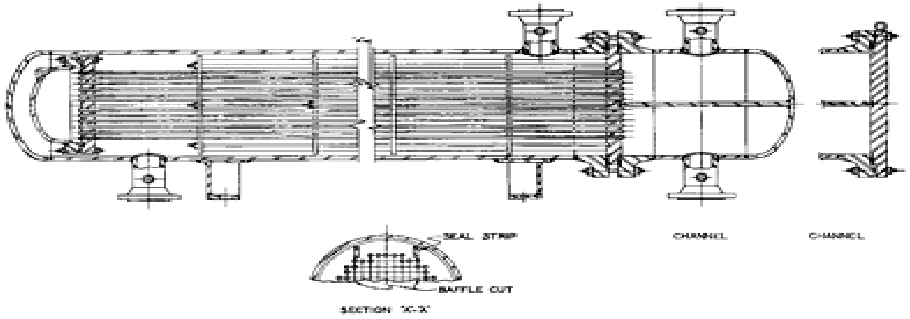
A = net external surface area of tubes exposed to fluid heat transfer (not just the length of the individual tubes), ft².
Q = heat load, Btu/hr
U = overall heat-transfer coefficient, Btu/(hr-ft² - °F)
ΔT = mean temperature difference, °F, corrected

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 (10-10)E

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*$N_{tubes/pass}$*0.00379

= 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 $=G_t*D_i/\mu_c$

=547038.486*0.0965/0.7502

=50692.23

4- L/D_i=16/0.069=230

5- from fig(10-46) 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 fig. (10-54) 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 table (10-12)

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 fig. (10-140) 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 fig (10-138) 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.

Furnace Design

FURNACE DESIGN

A fired heater is necessary for heating the feed to the desired temperature (Process temperature). This heating is made by burning the fuel and use the heat liberated from this operation to heat the feed to the wanted temperature.

In the study of furnace we will choose some items help in knowledge of its performance, and these are as follow:

1- Furnace start up

2- Heat transfer and combustion

3- Furnace equipment

First: furnace start up

This is made by 5 steps

1- Inspection: the pilots inspect the furnace before it starts so as to ensure its stable performance

2-purging the furnace

3- Lighting pilots: protection of pilots by wearing the safety clothes while working

4- Lighting furnace: slowly open the gas valve then start lighting procedure

5- Normal operations

Second: heat transfer and combustion

- Heat transfer:

Heat is produced by the combustion of fuel in the burners, this heat is circulated around the tube of the furnace (in which the liquid exists) in heater.

Heat transfer has two methods in furnace Radiation & Convection

In radiation section: heat is transferred to the tubes (Radiant tubes) by radiation

In convection section: flue gases carry heat to the tubes (convection tubes), and this increase furnace efficiency by allowing more heat to be used before it leaves through the stack

-Combustion:

To make the combustion there must be three factors present in the same time ➔ fuel + air + ignition source

fuel: it could be natural gas or fuel oil (mazot) or both , but in industry we prefer natural gas as it has some advantage like

- More cleaner
- Gives a more amount of heat
- Less expensive
- Don't cause problems with environmental laws

* Air: in furnace we use air with specified ration to fuel and it is as follow

20 % excess air ➔ in case of natural gas

25 % ➔ in case of mazot

air is used to give the Oxygen necessary for complete combustion because incomplete combustion doesn't make the best benefit of fuel heat it also produces Co which cause conflicts with environmental laws , incomplete combustion also leaves some fuel in furnace which accumulated causing bad furnace performance .

Air also is used to keep the flame temperature in its range because if it increased it causes No_x production which causes cancer.

As air help in complete combustion it helps in utilizing the maximum amount of heat in the fuel.

Third: furnace equipment

1- Radiant tubes: in which the fluid pass in the radiation section .

2- Fire box: it produces the flames to heat the fluid

Note that: the flame doesn't touch the tube this is called flame impingement it destroys the tubes, and doesn't permit any air to enter the combustion zone

3- A covering material covers the floor and walls of the furnace this material:

- reduces heat losses
- reflects heat back into the tubes

4- Chock bank: bank of tubes between convection section and radiation section. These tubes rows are usually being subjected to the highest heat-transfer rates in the fired heater, so they are termed as (shield), or (shock) tubes

5- Convection section

6- Draft: for the pass of flame gases organizing

7- Damper: control the flow of hot gases out of the furnace

8- Burner: it mixes fuel with air in a
manner to keep stable combustion and it
differs according to the fuel type.

Classification of furnce:-

The principal classification of fired heaters relates to the orientation of the heating coil in the radiant section, whether the tubes are vertical or horizontal.

Types of vertical fired heaters:-

1-Vertical-cylindrical, all radiant:

Here the tube coil is placed vertically along the walls of the combustion chamber. Firing is also vertical, from the floor of the heater.

Properties:-

1-heaters of this type represent a low-cost.

2-low efficiency design.

3- it requires a minimum of plot area .

4-typical duties are 0.5 to 20 million Btu/hr.

2-Vertical-cylindrical, helical coil:

The coil is arranged helically along the walls of the combustion chamber, and firing is vertical from the floor.
Properties:
1-This design also represents low cost.
2- Low efficiency.
3-requires a minimum of plot area.
4-one limitation on these units is that generally only one flow path is followed by the process fluid.
5-heating duties run from 0.5 to 20 million Btu/hr.

3-Vertical-cylindrical, with cross flow convection:

These heaters, also fired vertically from the floor, feature both radiant and convection sections. The radiant-section tube coil is disposed in a vertical arrangement along the walls of the combustion chamber.The convection section tube coil is arranged as a horizontal bank of tubes positioned above the combustion chamber. This configuration provides an economical, high-efficiency design that requires a minimum of plot area. Typical duties are 10 to 200 million Btu/hr.
So we will include vertical furnace design in our study.

4- Vertical-cylindrical, with integral convection:

Although this design is rarely chosen for new installations, the vast number of existing units of this type warrants its mention in any review of fired heaters.
This design is likewise vertically fired from the floor, with its tube coil installed in a vertical arrangement along the walls. The distinguishing feature of this type is the use of added surface area on the upper reaches of each tube to promote convection heating. This surface area extends into the annular space formed between the convection coil and a central baffle sleeve. Medium

efficiency can be achieved with a minimum of plot area. Typical duties are 10 to 100 million Btu/hr.

5- Arbor or wicket:

The radiant heating surface is provided by U-tubes connecting the inlet and outlet terminal manifolds. This type is especially suited for heating large flows of gas under conditions of low pressure drop. Typical applications are found in petroleum refining, where this design is often employed in the catalytic-reformer charge heater, and in various reheat services. Firing modes are usually vertical from the floor, or horizontal between the riser portions of the U-tubes.
In addition, a cross flow convection section is normally installed to provide supplementary heating capacity for chores such as stream generation. Typical duties for each arbor coil of this design are about 50 to 100 million Btu\hr.

6- Vertical-tube, double fired:

Vertical radiant tubes are arranged in a single row in each combustion cell (there are often two cells) and are fired from both sides of the row. Such an arrangement yields a highly uniform distribution of heat-transfer rates (heat flux) about the tube circumference.
Another variation of these heaters uses multilevel side-wall fired, which gives maximum control of the heat-flux profile along the length of the tubes. Multilevel side-wall fired unites are often employed in fired-reactor services and in critical reactor-feed heating services.
Single-cell models are available for smaller duties. As a group, these represent the most-expensive fired heater configuration. The typical duty range for each cell runs from about 20 to 125 million Btu/hr.

Types of horizontal fired heaters:-

1- Horizontal tube cabin:

The radiant-section tube coils of these heaters are arranged horizontally so as to line the sidewalls of the combustion chamber and the sloping roof or "hip." .the convection-section tube coil is positioned as a horizontal bank of tubes above the combustion chamber. Normally the tubes are fired vertically from the floor, but they can also be horizontally fired by sidewall-mounted burners located below the tube coil.
This economical, high-efficiency design currently represents the majority of new, horizontal-tube, fired-heater installations. Duties run 10 to 100 million Btu/hr.

2- Two-cell horizontal tube box:

Here the radiant section tube coil is deployed in a horizontal arrangement along the sidewalls and roof of the two combustion chambers. The convection section tube coil is arranged as a horizontal bank of tubes positioned between the combustion chambers. Vertically fired from the floor, this is again an economical, high-efficiency design. Typical duties range from 100 to 250 million Btu/hr. for increased capacity, the basic concept can be expanded to include three or four radiant chambers.

3- horizontal tube-cabin with dividing bridge wall:

The radiant-section tube coil is arranged horizontally along the sidewalls of the combustion chamber, and along the hip. The convection-section tube coil takes the form of a horizontal bank of tubes positioned above the combustion chamber. A dividing bridge wall between the cells allows for individual firing control over each cell in the combustion chamber. Available options permit horizontal firing with sidewall-mounted burners or vertical firing from the floor along both sides of the bridge wall. A typical duty range for this design is 20 to 100 million Btu/hr.

4- End-fired horizontal tube box:

The radiant-section tube coil is disposed in a horizontal arrangement along the sidewalls and roof of the combustion chamber. The convection-section tube coil is arranged as a horizontal bank of tubes positioned **above the** combustion chamber. These furnaces are horizontally fired by burners mounted in the end walls. A typical duty range for this design is 5 to 50 million Btu/hr.

5- End-fired horizontal tube box with side-mounted convection section:

Here the radiant section tube coil is disposed in a horizontal arrangement along the sidewalls and roof of the combustion chamber. The convection-section coil is arranged as a horizontal bank of tubes positioned along side the chamber. The unit is horizontally fired from burners mounted on the end wall. These furnaces are found in many older installations, and occasionally in new facilities that burn particularly poor grades of fuel oil containing a high ash concentration. This relatively expensive design provides duties ranging from 50 to 200 million Btu/hr.

6- horizontal-tube, double-fired:

Horizontal radiant tubes arranged in a single row and are fired from both sides to achieve a uniform distribution of heat-transfer rates around the tube circumference. Such heaters are normally fired vertically from the floor. They are often selected for critical reactor-feed heating services. For increased capacity, the concept can be expanded to provide for a dual combustion chamber. A typical duty range for each cell of this design is about 20 to 50 million Btu/hr.

In industry we prefer the vertical furnace as it has some advantage than the horizontal.

Which are:

- Little space used
- Easy maintenance
- Less expensive
- Better draft

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.

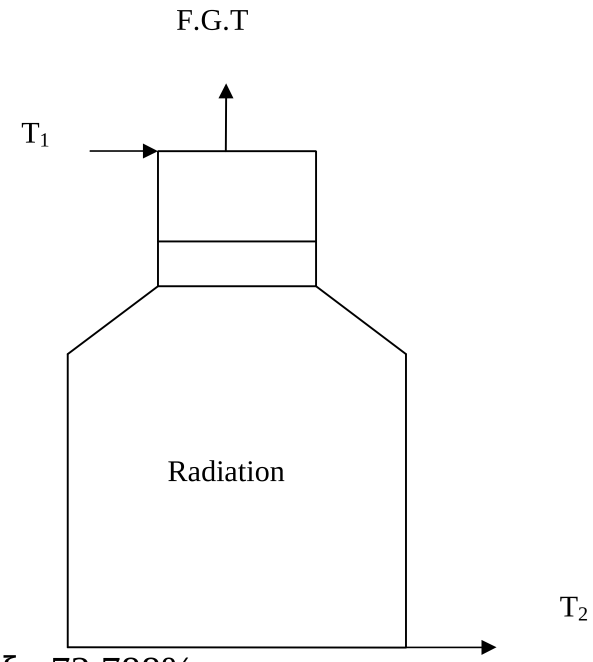
Excess air, 15%

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:

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

5- Radiant section average tube metal temperature:

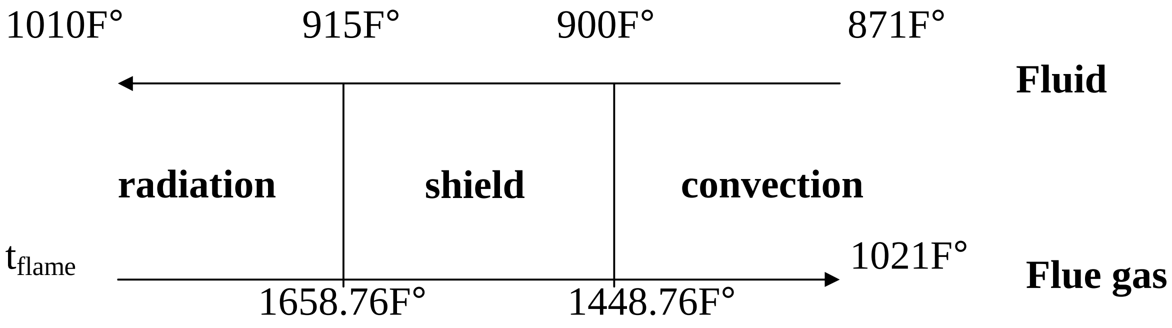
t_m= 962.5 + 75 = 1037.5 F°

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- $ETL_{shield\ bank} = 5.093 - 1 = 4.093$ 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

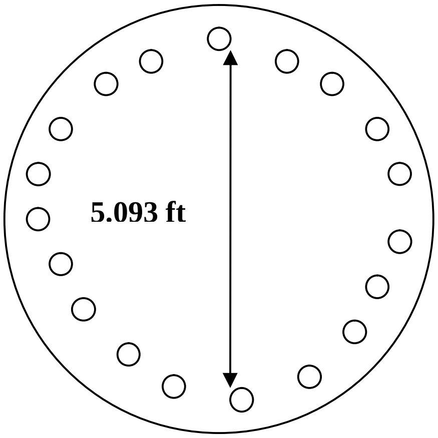
7- $g_{flue\ gas}$= 8569.863 / (3600 * 7.175) = 0.332 lb/s/ft^2

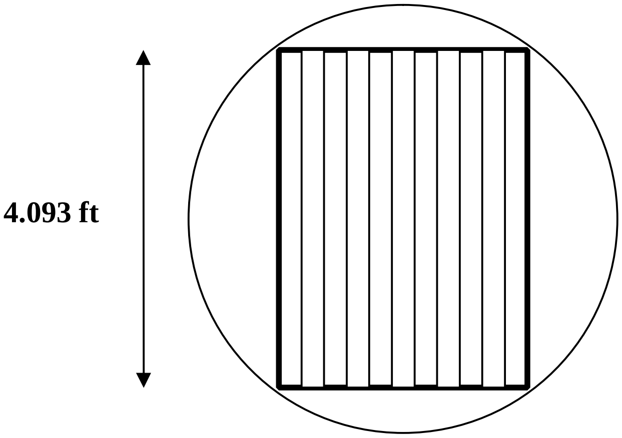
8-surface area of one shield row = 6 * 4.1 * π * (4.5 / 12) = 28.981 ft^2

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)
vertical tube radiant length = 15.672 ft

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



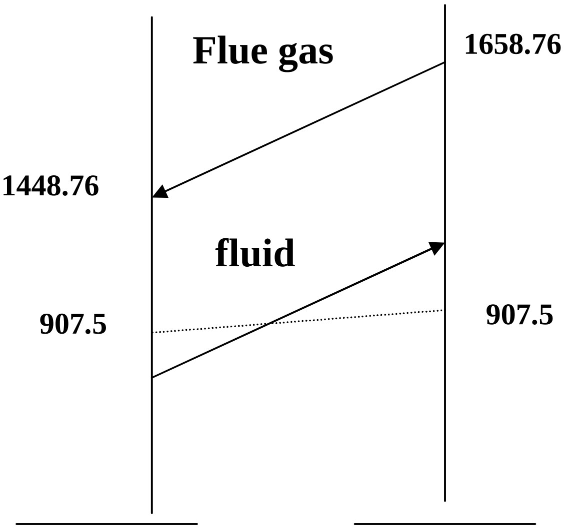


Step 4:- Shield bank

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

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

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



ΔT_{min}=541.26

ΔT_{max}=751.26

4-

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

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

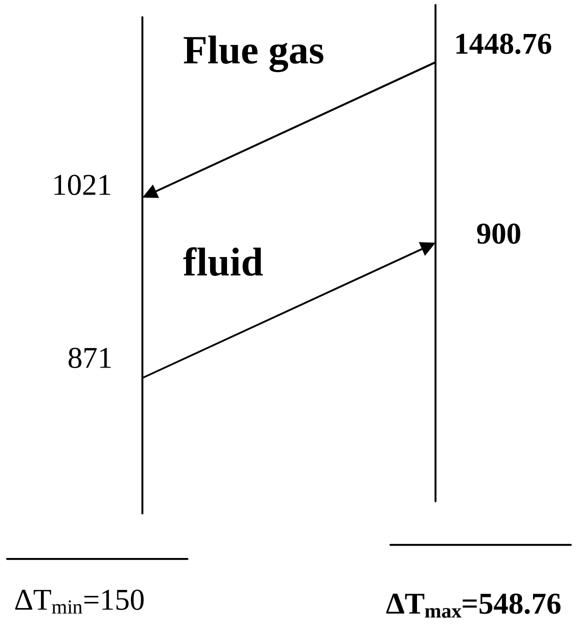
13- Check of flue gas temperature above shield bank
$H_{a,shield}$= [(4721071.361 + 499814.158) / 4721071.361] * 10790
= 11932.324 Btu/lb
By $H_{a,shield}$=11932.324 Btu/lb and excess air=15%
From fig.(3) Berman
T_{sh}=1475 F°
O.k. □ (BWT - 210) = 1448.76 F°

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

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 $\dfrac{Btu}{ft^2 F^{O} hr}$

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

$\therefore$ R_t = 0.2071 + 0.02087 + 0.005087 = 0.23305

$\therefore$ $U_{conv.}$ = (1 / 0.23305) = 4.291 $\dfrac{Btu}{ft^2 F^{O} hr}$

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

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

$\therefore$ 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°
Assume stack-exit gas temperature = 871 f°
Draft under arch = 0.05 in

At $t_{avg.}$ = 1553.76 f° 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° 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,
ρ_{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,
ρ_{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

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

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

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- $$\mathrm{Re} = \frac{4.026 \times 63.15 \times 3600}{12 \times 0.0726} = 1050586.364$$

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

Reactor Design

Reactor Design

Assumptions to ease Design Procedure

1. The reactor is an ideal plug flow reactor.
2. The reactor is iso-thermal, as heat is constantly supplied.
3. The reactor is a one-phase reactor and neglecting the presence of catalyst, for its very small and negligible volume compared to the volume of voids.
4. Feed is pure ethyl cyclohexane with recycle hydrogen and is only subjected to the dehydrogenation reaction due to the high rate of this reaction and its high equilibrium state which lead to that the reaction nearly goes to equilibrium in the first reactor.
5. Optimum conversion is as high as 60%.

Derivation of the Plug-Flow Reactor Formula

$$\tau_p = \left(\frac{C_{Ao} V}{F_{Ao}} \right) = C_{Ao} \int_0^{X_A} \frac{dX_A}{-r_A}$$

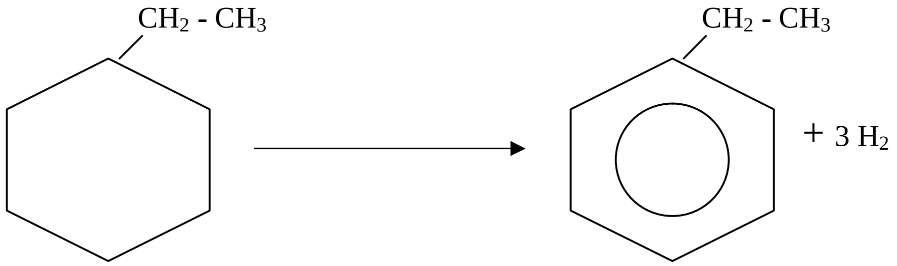
$$= \frac{1}{k\, C_{Ao}^{\,n-1}} \int_0^{X_A} \frac{(1+\varepsilon_A X_A)^n \, dX_A}{(1-X_A)}$$

Where;

C_{Ao} = concentration at XA=0 (mol/m^3).
V = volume of reactor without catalyst.
F_{Ao} = molar flow rate in (mol/hr).
X_A = conversion at the end of reactor.
$-r_A$ = rate of disappearance of reactant A
k = rate constant of dehydrogenation reaction. (50 hr^{-1})

n = order of reaction.

ε = fractional volume change = $\dfrac{V_{X_A = 1} - V_{X_A = 0}}{V_{X_A = 0}}$



$$\Theta \; - r_A = k \; C_A{}^{1}$$

$$\therefore \; n = 1$$

Then Performing the integration, and substituting with (n = 1)

$$\tau_p = \frac{1}{k\,C_{A_o}{}^{0}} \left. \right|_{0}^{0.6} \frac{(1 - X_A)\varepsilon_A + (1 + \varepsilon_A X_A)}{(1 - X_A)^2}$$

$$= \frac{1 + \varepsilon_A}{k}\left[\frac{1}{(1 - X_A)^2} - 1\right]$$

Setting:

Conversion $X_A = 0.6$ and

Rate constant k = 50 hr^{-1} (Calculated Analytically)

$$\therefore \tau_p = \frac{C_{A_o} V}{F_{A_o}} = 0.105\,(1 + \varepsilon_A)$$

$$V = 0.105\,(1 + \varepsilon_A)\,\frac{F_{A_o}}{C_{A_o}} \qquad \text{..................} \; \textbf{(*)}$$

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 x 217717 = 874271 mol

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

$$\varepsilon_A = \mathbf{2.95} \quad \text{……………………………………………(2)}$$

<u>* Volume at X_A=0 (T=798 °K and P=30 atm)</u>

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

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

Hence, $V = 482.61 \ \ m^3$

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

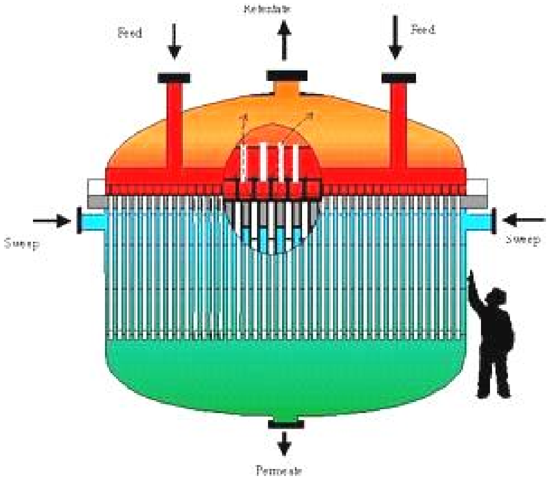
From **(1), (2), (3), I n (*)**

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

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)

Stabilizer Design

Tower design:

Design data:

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 °C.
- Top temperature = 86 °C .
- Bottom temperature = 243 °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.

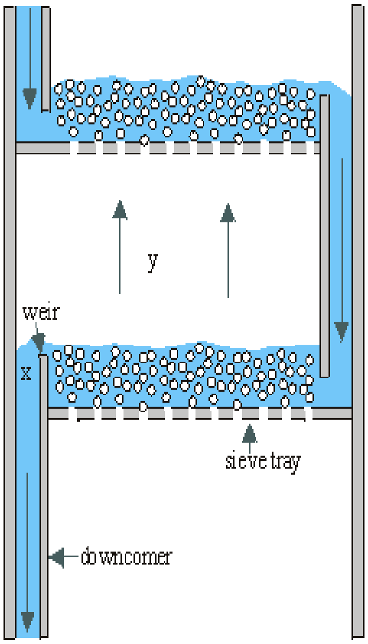
Step(2):

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 ($R_{min.}$)

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

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

Where :-

x_{if} = The values for each component in the feed.

x_{id} = The values for each component in the distillate.

α = the relative volatility of component (i) with respect to the heavy key component.

q = the feed thermal condition .

θ = the underwood's constant.

<u>Solution :-</u>

θ =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 η =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 η =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 , $T_D=86^oC$.

$V_D = 359 * (460+86)/(460+32)* 1/1$

$V_D = 398.4$ ft3 /lb_{mol}

$V_D = 398.4 * 259.84=103520\ ft^3$ / hr.

L =RD

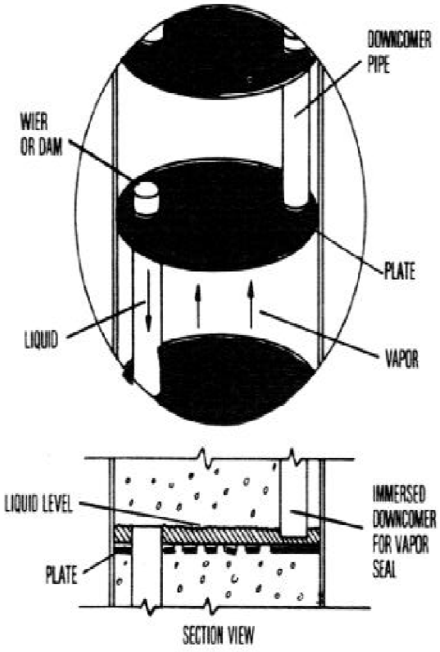
$V = D (R + 1) = 259.84\ ft^3$ /hr.

$\rho_L =48.1$ Ib / ft^3

$\rho_v = 0.8$ Ib / ft^3

$V_{c.s} =K ((\rho_1 - \rho_v) /\rho_v)^{1/2}$

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}
$D = (4A / \pi)^{½} = 5.85$ 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 :

$A_{df} / A_T = 20\%$
$A_{dc} / A_T = 10\%$
$A_{dc1} / A_T = 0.05$
$A_T = \pi/4\ D^2$
$A_T = 28.274$ 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

$D_n' = D - 2\alpha$

$=12*6-2(2)$

$D_n' = 68$ 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 :

$A_{dis} = 2(Lw_1 *5/12)+2(LW_2*5/12)$

$=2(3.54*5)+2(67.796*5)$

$A_{dis} = 890.36\ in^2 = 6.183\ ft^2$

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 (β) :

assume $\beta = 12.8\ \%$ (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}) :

   $h_{dt} = 0.003\ f_s^2 * (\rho_w / \rho_l)\ ((1-\beta^2) / c_o^2)$

   $= 5.476 * 10^{-3}\ f_{smin}^2$

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-$h_{dt} = 5.476*10^{-3}\,F^2_{s\,max}$

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

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

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

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

$V_{o\,design} = F_s\ /\ \rho_v^{\,1/2} = 32/0.8^{1/2}$

$= 35.78$ ft/sec

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

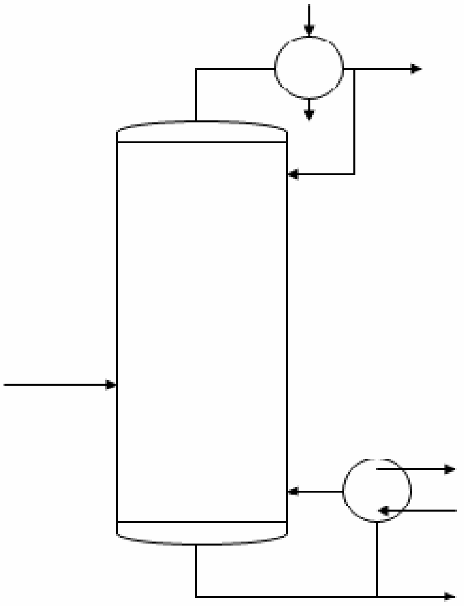
$V = N*(\pi/4)*(d_o^{\,2}/144)*v_0$

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) :-

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

$h_{dt} = 5.476 * 10^{-3}\,f_s^{\,2}$

$h_t = h_{dt} + 1.5$

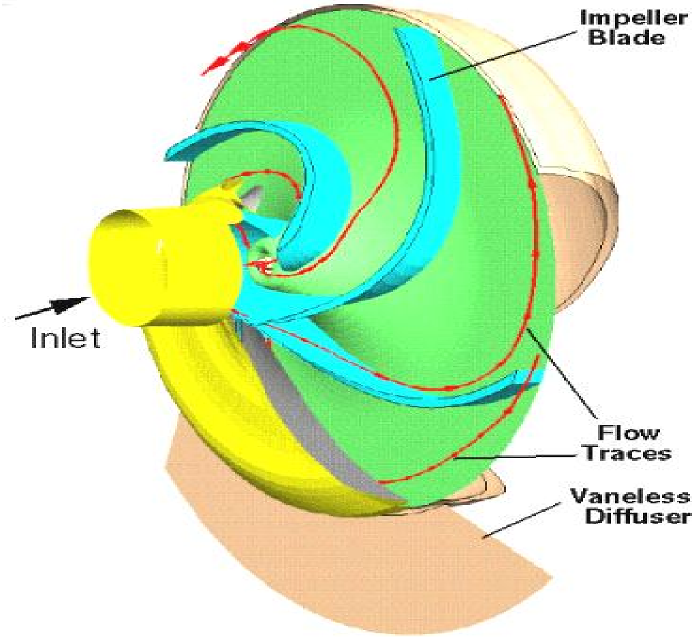
$= 6.81$ in. liq

[15] Pressure drop for tray (Δ p) :

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

$= 0.189$ psi < 0.2 psi

Pump Design



Pump Design:

Here we will design the pump which pumping feed at the first of the catalytic reforming process.

DEFINITION OF SYMBOLS USED IN DESIGN:-

V_{f1}	: inlet absolute velocity	ft / sec
V_{f2}	: outlet absolute velocity	ft / sec
U_1	: inlet tangential velocity	ft / sec
U_2	: outlet tangential velocity	ft / sec
V_{r1}	: Relative inlet velocity	ft / sec,
V_{r2}	: Relative outlet velocity	fl / sec
V_{W2}	: Residual portion of outlet tangential velocity	ft / sec
D_1	: inlet diameter.	in standard
D_2	: outlet diameter .	in standard
B_1	: Blade inlet width .	
B_2	: Blade outlet width .	
H	: Head .	Ft
N_s	: specified speed .	r.p.m
N	: impeller speed .	r.p.m
Q	: flow Rate .	G.P.M.
HP	: Hoarse power required .	
ψ	: Flow ratio ,	(0.15-0.3)
Φ	: speed ratio .	$< 0.25°$
α	: Blade outlet angle .	$< 90°$
θ	: Blade inlet angle .	(20 - 45°)
β	: Absolute outlet angle .	(10-30°)
η_{over}	: over all efficiency .	
η_{mano}	: manometric efficiency.	
η_{mec}	: mechanical efficiency .	

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 %

- $\eta_{man} = \eta_{overall} / \eta_{mech} *100$

= 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

- $Q = \pi * B_1 *D_1 * V_{F1}$

$1357/3600 = \pi * (0.1\ D_1) * D_1 * 15.28$

$D_1 = 0.28$ 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)

- $Q = \pi * B_2 * D_2 * V_{F2}$

  $B_2 = 1357 / (\pi * 0.756 * 15.28 * 3600)$

  $= 0.01$ 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})

- $V_{W1} = \text{zero}$

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

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

  $= 52.5$ 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) : -

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

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

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

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

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

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

$= 19.8^{o}$ 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) $N_{MIN} < N_{ASSUMED}$: -

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

$= 2645$ 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)

Compressor design

Compressor design

Here we will design the compressor which compresses air for regeneration.

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 (ΔP)= 5 psia
- cooling water temperature (T_w) = 90˚F

Design steps:-

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

$R_{Ct} = P_2/P_1$

$= 205/14.7$

$= 13.9 \quad >> 5$

- 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 $k_{air} = 1.4$

$\mathbf{T_F}= T_1 * R_C^{(K-1)/K}$

$= (85+460) * 3.9^{(1.4-1)/1.4}$

$= 804$ ˚R = 344˚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

$EV\% = 100 - 3.9 - 14.5\,(3.9^{1/1.4} - 1)$

$= 72.3\ \%$

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

$= 297\ CFM$

PDEV 297 CFM; so we can use it.

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

Tank Design

Tank design

Here we will design the tank which used to storage reformate.

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}) : -

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

$= (\pi * 140^2 * 54) / 4$

$= 831,265.42 \text{ ft}^3$

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

$\sum t_n = 0.25 + 0.25 + 0.35 + 0.47 + 0.6 + 0.72 + 0.84 + 0.96 + 1.03$
$= 5.47$ in

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

$$V_{steel} = \pi * D_{st} * 6 * (\sum t_n / 12)$$
$$= \pi * 140 * 6 * (5.47 / 12)$$
$$= 1202.9 \ ft^3$$

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)
$= 2 * 320.7$
$= 641.4 \ ft^3$

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