UTKALMANI GOPABANDHU INSTITUTE OF ENGINEERING, ROURKELA

LECTURE NOTES

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SUBJECT- PETROLEUM REFINING & PETROCHEMICAL TECHNOLOGY

DEPARTMENT OF CHEMICAL ENGINEERING

SESSION-(2021-22)

UTKALMANI INSTITUTE OF TECHNOLOGY, ROURKELA-4

DEPARTMENT
OF
CHEMICAL ENGINEERING

SUBJECT: PETRO REFINERY&PETROCHEMICAL TECHNOLOGY
COURSE CODE: TH-3

PRESENTED BY: SATARUPA SAHU

Chapter 1-INTRODUCTION TO PETROLEUM INDUSTRIES

LESSON OBJECTIVE

The topics help the students

- To study the Growth of petrochemical industry in India**,** petrochemicals and the importance of petrochemical industry, Theories on Origin of petroleum, Transportation of crude oil for refining.

COURSE OUTCOMES:

1. Classify petroleum refining process and fractionation of crude oil.
2. Explain the Importance of 1st, 2nd, 3rd generation petrochemical, refinery products, their properties and uses.
3. Identify growth and future of petroleum refinery and petrochemical industries in India.

TOPIC TO BE COVERED:

Lecture No	Topics to be covered
Lecture 1	Development of petrochemical industry in India
Lecture 2	Growth of petrochemical industry in India
Lecture 3	Define petrochemicals & describe the importance of petrochemical industry
Lecture 4	Theories on Origin of petroleum
Lecture 5	Detection and production of petroleum
Lecture 6	Pre-treatment of oil before refining, desalting and stabilisation of crude
Lecture 7	Classification and composition of petroleum
Lecture 8	Transportation of crude oil for refining

TOOLS USED:

- Chalk and duster
- K-Yan

MODEL QUESTIONS:

1. Define Petrochemicals.
2. Differentiate between petroleum and petrochemical.
3. What are the various means for transportation of crude oil?
4. Write down the development and growth of petrochemical industry in India.
5. Describe the importance of petrochemical industry.
6. Write down the theories on origin of petroleum.
7. Write down the classification and composition of petroleum.

ASSESSMENT METHODS APPLIED:

- Class quiz
- Assignment

REFERENCES:

- Modern Petroleum Refining Process by B K B Rao, Oxford IBH Publication
- Petroleum Refining Technology by Dr. Ram Prasad, Khanna Publications.

PETROLEUM

- Petroleum (also called crude oil) is a naturally mixture of hydrocarbons, generally in the liquid state, that may also include compounds of sulfur, nitrogen, oxygen, and metals and other elements.
- Inorganic sediment and water may also be present. A petroleum product is any product that is manufactured during petroleum refining. Consequently, it is not surprising that petroleum can vary in composition properties and produce wide variations in refining behavior as well as product properties.
- Petroleum means literally rock oil and refers to hydrocarbons that occur widely in the sedimentary rocks in the form of gases, liquids, semisolids, or solids.
- From a chemical standpoint, petroleum is an extremely complex mixture of hydrocarbon compounds, usually with minor amounts of nitrogen-, oxygen-, and sulfur-containing compounds as well as trace amounts of metal-containing compounds.

DEVELOPMENT OF INDIAN PETROLEUM INDUSTRY

- In India the first oil well was dug in 1866 and the first refinery was started in 1893. Assam oil company refinery at Digboi was the only major refinery till 1954.
- The Assam Oil Company name was changed to Oil India Ltd (OIL) in 1959. Real Foundation of Oil industry took place during the second five year plan (1956 – 1961) when the government of India Lunched a planned programme of exploration, production, refining and distribution of oil.
- The Oil and Natural Gas Commission was formed in 1957 and the name was changed to Oil and Natural Gas Corporation Ltd in 1994. The ONGC has got overall responsibility for exploration, development and production of oil and gas in India.
- On-shore and Off-Shore. The OIL is especially responsible for continental north east India. Other important oil companies are Indian Oil Corporation Ltd, Hindustan Petroleum Corporation Ltd and Bharat Petroleum Corporation Ltd.
- India's sedimentary area is about 1.42 million Square Kilometers of which 0.42 million square kilometers is off shore area spread over 6000 Km coastal line and 0.4 million sq. Kilometer is available in the form of continental slope while the remaining area is land based.
- The biggest off-shore activity started with the discovery of Bombay High in 1973.Prior to this in 1963 the Adiabet, the mouth of Narmada was located, other successful areas like Rann of Kutch, Gulf of Mannar, Cambay , Coastal Kerala, Coromondel palk Bay soon followed.
- The Reliance petroleum ltd has been established by Reliance Industries Ltd. Along with the ESSAR Oil, this is the first private sector oil company to join oil refining. The RIL has a major petrochemical complex in Jamnagar near Kandla port.

Region	Crude oil reserves (in million metric tonnes)	Share of oil (%)	Natural gas reserves (in BCM)	Share of gas (%)
Arunachal Pradesh	1.52	0.25	0.93	0.07
Andhra Pradesh	8.15	1.35	48.31	3.75
Assam	159.96	26.48	158.57	12.29
Coal Bed Methane	0	0	106.58	8.26
Eastern Offshore	40.67	6.73	507.76	39.37
Gujarat	118.61	19.63	62.28	4.83
Nagaland	2.38	0.39	0.09	0.01
Rajasthan	24.55	4.06	34.86	2.70
Tamil Nadu	9.00	1.49	31.98	2.48
Tripura	0.07	0.01	36.10	2.80
Western Offshore	239.20	39.60	302.35	23.44
Total	**604.10**	**100**	**1,289.81**	**100**

PETROCHEMICAL PROCESSING SECTOR

- The annual consumption of virgin grade polymers for the year 2017-18 was 15.9 Million Tonnes.
- Demand for Plastics in India is currently growing at an average rate of 8.9% for the past 4 years (2013-14 to 2017-18).
- It is expected to reach 24 Million Ton by 2022-23 and 35 Million Ton by 2027-28.
- There are more than 50,000 processing units in organized and unorganized sector (around 33,500 are in organized segment) having 1,53,500 Plastics processing machines for producing a diverse range of plastic products.
- The processing capacity is estimated to be 45.1 Million tonnes per annum.
- This processing capacity had been growing @ 8.8% CAGR during last 4 years and the processing industry is expected to invest $10 billion during the next 5 years to enhance the capacity to 62.4 Million Ton and 86 Million Ton by 2027-28.

OPPORTUNITY

- The economic reforms initiated in 1991 brought about significant changes in the domestic petrochemical industry.
- Delicensing and deregulation allowed the market forces to determine investment and growth.
- It is now established globally that ethylene (the main building block for petrochemicals) consumption and polymer consumption in the downstream plastic articles have strong correlations with the growth of Gross Domestic Product (GDP).
- Polymer consumption has strong backward and forward linkages and an increase in polymer consumption has a multiplier effect on the GDP Growth.
- The annual consumption of virgin grade polymers for the year 2017-18 was 15.9 Million Tonnes. Demand for plastics in India is currently growing at an average rate of 8.9% for the past 4 years (2013-14 to 2017-18).
- It is expected to reach 24 Million Ton by 2022-23 and 35 Million Ton by 2027-28. There are more than 50,000 processing units in organized and unorganized sector (around 33,500 are in organized segment) having 1,53,500 Plastics processing machines for producing a diverse range of plastic products.
- The processing capacity is estimated to be 45.1 Million tonnes per annum.
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SUB-GROUP	**2012-13**	**2013-14**	**2014-15**	**2015-16**	**2016-17**
Synthetic Fiber	3124	3144	3527	3554	3595
Polymers	7509	7876	7558	8839	9163
Elastomers (S.Rubber)	96	105	172	242	285
Synthetic Detergent Intermediates	627	597	596	566	664
Performance Plastics	1691	1685	1591	1700	1799
Total	**13047**	**13406**	**13443**	**14900**	**15506**

PETROCHEMICALS

- **Petrochemicals** are chemicals derived from petroleum or natural gas. They are an essential part of the chemical industry as the demand for synthetic materials grows continually and plays a major part in today's economy and society.
- These are widely used in the production of plastics, synthetic fibres, synthetic rubber, detergents, insecticides, dyestuff, etc. Various constituents of natural gas and refinery gases are separated and used for producing petrochemicals.
- The petrochemical industry is of very recent origin and at present, it is one of the fastest growing industries.

IMPORTANCE OF PETROCHEMICAL INDUSTRY

- Petrochemicals are derived from various chemical compounds, mainly from hydrocarbons. These hydrocarbons are derived from crude oil and natural gas.
- Among the various fractions produced by distillation of crude oil, petroleum gases, naphtha, kerosene and gas oil are the main feed stocks for petrochemical industry.
- Ethane, propane and natural gas liquids obtained from natural gas are the other important feedstock used in the Petrochemicals industry.
- Petrochemical industry plays a vital role in economic growth and development of manufacturing sector. The value addition in the petrochemicals industry is higher than most of the other industry sectors.
- The first petrochemical plant in India was set up by the Union Carbide India Ltd. at Trombay in 1966.
- The Indian Petrochemicals Corporation Ltd. (IPCL) was the first public sector plant to be located at Jawaharnagar (near Vadodara) in Gujarat. It started its production in 1973.
- Petrochemical industry mainly comprise of synthetic fibre / yarn, polymers, Synthetic Rubber (elastomers), Synthetic detergent intermediates, performance plastics and plastic processing industry.
- Today, petrochemical products permeate the entire spectrum of daily use items and cover almost every sphere of life like clothing, housing, construction, furniture, automobiles, household items, agriculture, horticulture, irrigation, packaging, medical appliances, electronics and electrical etc.
- Presently there are eleven naphtha and/or/dual feed cracker complexes in operation with combined ethylene capacity of about 7.05 million tonnes per annum. In addition, there are six aromatic complexes in operation with a combined Xylene capacity of about 5.5 million tonnes.
- The Indian basic petrochemicals market (including end products market which includes polymers, synthetic fibers, elastomers and surfactants) the total petrochemical market has grown at a CAGR of 11% from USD 19.3 billion in FY11 to USD 24 billion in FY13.
- The total installed capacity of major basic petrochemicals (ethylene, propylene, butadiene, styrene, benzene & toluene) in FY13 is 12.2 million metric tons per annum (mmtpa) against the total demand of12.5 mmtpa .
- In FY12, there was a surplus capacity of ~1 mmtpa, but in the last two years overall demand has crossed the installed capacity. Imports have grown at a CAGR of 17% between FY09 and FY13, whereas the exports have grown at a higher rate of 19% in the same period.

THEORIES ON ORIGIN OF PETROLEUM

- Many theories have been proposed to this origin. Many hypotheses have been proposed to explain the origin but however these have some problem related to the origin.

i. Source material (Identification)
ii. ii. Intermediate
iii. iii. Biochemical Changes

There are basically 2 theories regarding the origin of petroleum.

1. Inorganic Origin 2. Organic origin

- Earlier ideas were in favour of inorganic origin of petroleum but modern theory point a definite finger towards the organic origin of petroleum.
- The general agreement now days is organic source material for the origin of petroleum. There are wide differences of opinion on the processes by which it form and on the nature of the organic matter from which it was derived.
  a. Whether the matter was animal or vegetal
  b. Whether it was deposited in a fresh water or saline water environment.
  c. Whether the organic source material was a decompositional residue of organic matter or a synthesis of existing hydro organic compound.
- Further differences of thought arise when an attempt is made to explain the transformation of organic source material into petroleum.
  a. Heat and pressure
  b. Bacterial action

c. Radioactive bombardment
d. Catalytic reaction

- These are possibly source of energy required for the transformation from organic source material to petroleum.

Inorganic Origin of Petroleum (Theories)

- These theories have long being abundant or discarded and in the present context are of historic importance only.
- The main reason or chief support for theories of inorganic origin lies in the fact that in laboratory the hydrocarbons methane, ethane, acetylene, benzene etc are repeatedly being made from, inorganic source.
- One aspect of the theory of the inorganic origin of petroleum cannot be over looked and that is the possibility of its accounting for some of hydrocarbon content of petroleum. Ordinary marine organic matter contains approximately 7 – 10% hydrogen whereas petroleum contains 11 – 15% hydrogen.
- Free hydrogen is not ordinarily found in sediment rock because hydrogen is the lightest of all gases and thereby it easily escape into the atmosphere. There are two serious objections to the theories of organic origin.

1. Optical Activity: also known as optic rotary power, the power to rotate the plane of polarization of polarized light is a property of most petroleum and this phenomenon is entirely confined to organic matter and is observed only where biological agencies have prevailed.
2. The serious objection to any inorganic origin is that several homogeneous series of hydrocarbon compounds containing great numbers of individual members are found in all petroleum. All known compounds of this kind are of organic origin and could hardly reformed by inorganic agencies.

Theories in support of Organic Origin of Petroleum

- Petroleum was originated from organic source called proto- petroleum- primary source material and is of organic origin.
- There still exist different opinion that proto- petroleum is plant or animal. There are 3 main evidence in support of organic origin of petroleum.

1. There is a vast amount of organic matter present in the sediments of the earth. Sufficient amount of hydrogen and carbon present in the remains of organic material.
2. The presence of porphyrin pigments and nitrogen in almost all kind of petroleum is a definite indication of its organic origin i.e more or less direct indication of the animal or vegetable origin or both of petroleum. Porphyrin is a bi- product formed from the red colouring matter of blood or from green colouring matter of plants (Cholorophyll). Nitrogen is an essential component of amino acid which infact is hydrolysed protein of all living matter.
3. Optical Rotatory Power with exception of quartz and cinnabar (HgS). It is believed that the optical activity in most oil is due to the presence of Cholestrol ($C_{26} H_{45} OH$) which is found in both vegetable and animal matter.

Stages in the Formation of Petroleum

At present most of the petroleum geologist believed in a 3 stage sequence of origin of petroleum.

1. A disseminated accumulation of organic matter in the shales, clays and other fined grained sediments occur as they are being deposited. if the hydrogen and carbon are in the form of solid organic matter of considerable chemical complexity when deposited in the shale, then we have to think of mechanism for transforming this material into petroleum either in the shale or subsequently in the porous and permeable reservoir (source rock).
2. Either the organic matter or the petroleum moves out of the shale during their compaction by overloading and into the surrounding porous and permeable, sandstone or carbonate rock. This movement from the source rock to reservoir rock is called Primary Migration . (Reservoir Rock).
3. If the source material reaches the reservoir rocks its transformation into petroleum takes place through processes not known clearly. However a subsequent secondary migration through the permeable rocks carries it to places where further movement is obstructed and pools are formed. (Reservoir Trap).

ORGANIC SOURCE MATERIAL

Organic source material required for the formation of petroleum may consist either of

- Animal remains
- Vegetable remains

- The waste material formed by organism during their life cycles. Since most petroleum deposits are closely associated with sediments deposited under marine condition.
- Most theories of organic origin hold the view that petroleum originated in sediments of marine environment. Consequently the organic matter of ocean is of prime importance.
- The marine organism that may provide organic source for petroleum may be :
  1. Plant Life : Marine fungi, bacteria , algae, dinoflagellates.
  2. Animal Life : may invlude many diverse group, such as foraminifera, radiolarian and other protozoans, the sponges, corals, warms, bryozoans etc.

DETECTION OF PETROLEUM

1. **Remote sensing electro-optical detection:**

- The method uses spectral analysis to detect and identify the presence of flammable vapors, differentiate between paraffin's and aromatics, toxic gases or obscuration conditions, as well as identify the outburst of flames at their ignition time.
- Various atmospheric conditions (fog, rain, snow) as well as false alarm stimulus (radiation sources, smoke and particles) of field scales up to 100 meters can be detected.

2. **U.V flame detection:**

- This technology utilizes the infrared emission spectrum of flames and analyzes it versus background radiation.
- The U.V spectral band because of its short-wave characteristics is absorbed in the surrounding atmosphere by air, smoke, dust, gases and various organic materials.
- Hence, U.V solar radiation dispersed in the atmosphere, especially at wavelengths shorter than 300 nm (the solar blind spectral band) being absorbed by the surrounding atmosphere, will not create false alarms for the flame detectors using this technology.
- The U.V spectral signature of the flame has a pattern that can be readily recognized over the background radiation.

PRE-TREATMENT OF OIL

- Petroleum recovered from reservoir is mixed with a variety of substances such as gases, water, chloride salts, and dirt, which contain other minerals.

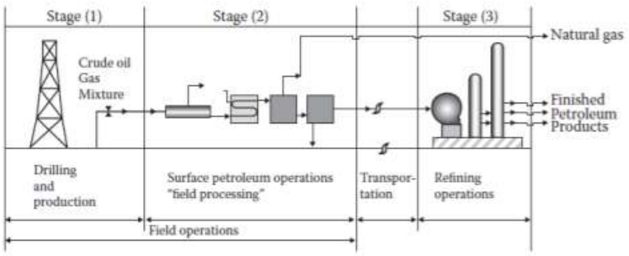

Figure 1: Main three oil operations.

- Thus, petroleum processing actually commences shortly after the production of fluids from reservoir, where pretreatment operations are applied to the crude oil prior to transportation.
- Any crude oil to be shipped by pipeline, or by any other form of transportation, must meet strict regulations in regard to water and salt content.
- Handling of crude oil mixtures, once produced, is subjected first, to what is known as surface petroleum operations (SPO).
- These field processing operations cover the myriad procedure required to handle the crude oil mixture between the well head and the delivery points for refining operations and other usages.
- The preliminary crude oil treatment, prior to the refining, involves oil dehydration followed by desalting. These two steps known as crude treatment are the main source of wastes produced within this stage (dehydration/desalting).

Refining:

- Refining breaks crude oil down into its various components, which are then selectively reconfigured into new products.
- Petroleum refineries change crude oil into petroleum products for use as fuels for transportation, heating, paving roads, and generating electricity and as feedstocks for making chemicals.
- Petroleum refineries are complex and expensive industrial facilities. All refineries have three basic steps:

1. Separation
2. Conversion
3. Treatment

Desalting:

- Salt in crude oil is in most cases found dissolved in the remnant water within the oil. It is established that the amount of salt found in crude oil is attributed to two factors:

1. The quantity of remnant water that is left in oil after normal dehydration.
2. The salinity or the initial concentration of salt in the source of this water.

- Desalting of crude oil will eliminate or minimize problems resulting from the presence of mineral salts in crude oil. In other words, one would consider the main function of the desalter is to remove salts soluble in water from the crude oil.
- However, many other contaminants such as clay, silt, rust, and other debris also need to be removed. It should be stated that the salts contain some metals that can poison catalysts used in the process of refining are dissolved in the water phase.
- These salts often deposit chlorides on the heat transfer equipment of the distillation units and cause fouling effects.
- In addition, some chlorides will decompose under high temperature, forming corrosive hydrochloric acid:

$$MgCl_2\ (aq)\ \text{High temp} \rightarrow Mg(OH)_2 + HCl$$

Stabilization:

- The stabilization process is a form of partial distillation which sweetens "sour" crude oil (removes the hydrogen sulfide) and reduces vapor pressure, thereby making the crude oil safe for shipment in tankers.
- Stabilizers maximize production of valuable hydrocarbon liquids, while making the liquids safe for storage and transport.
- Stabilization may be used to meet a required pipeline sales contract specification or to minimize the vaporization of the hydrocarbon liquid stored in an atmospheric stock-tank.
- The stabilization process also results in reducing the amount of intermediate hydrocarbon components (propane and butane) that flash to the vapor state, increasing the liquid volume.
- Thus, it results in both increasing the liquid sales and decreasing the vapor pressure of the liquid.

COMPOSITION OF PETROLEUM CRUDE OIL

- Crude oil is a multicomponent mixture consisting of more than 108 compounds. Petroleum refining refers to the separation as well as reactive processes to yield various valuable products.
- Therefore, a key issue in the petroleum refining is to deal with multicomponent feed streams and multicomponent product streams.
- Therefore, characterization of both crude, intermediate product and final product streams is very important to understand the processing operations effectively.
- The elementary composition of crude oil usually falls within the following ranges.

Element Percent by weight

1. Carbon 84–87
2. Hydrogen 11–14
3. Sulfur 0-3
4. Nitrogen 0-0.6
5. Oxygen in trace amounts

- The elements like Sulfur, Nitrogen and Oxygen are usually treated as impurities because of their inherent properties like odor, color, corrosiveness etc.

CLASSIFICATION OF PETROLEUM

The hydrocarbons in crude oil can generally be divided into following categories:

1. **Paraffins:** These can make up 15 to 60% of crude and have a carbon to hydrogen ratio of 1:2, which means they contain twice the amount of hydrogen as they do carbon.
   These are generally straight or branched chains, but never cyclic (circular) compounds.
   Paraffins are the desired content in crude and what are used to make fuels. The shorter the paraffins are, the lighter the crude is.
   Paraffins refer to alkanes such as methane, ethane, propane, n and iso butane, n and iso pentane.
2. **Napthenes:**
   Naphthenes or cycloalkanes such as cyclopropane, methyl cyclohexane are also present in the crude oil.
   These can make up 30 to 60% of crude and have a carbon to hydrogen ratio of 1:2.
   These are cyclic compounds and can be thought of as cycloparaffins. They are higher in density than equivalent paraffins and are more viscous.
3. **Aromatics:**
   Aromatics such as benzene, toluene o/m/p-xylene are also available in the crude oil.
   These can constitute anywhere from 3 to 30% of crude.
   They are undesirable because burning them results in soot. They have a much less hydrogen in comparison to carbon than is found in paraffins.
   They are also more viscous. They are often solid or semi-solid when an equivalent paraffin would be a viscous liquid under the same conditions.
4. **Asphaltics/olefins:**
   Alkenes such as ethylene, propylene and butylenes are highly chemically reactive.
   These average about 6% in most crude.
   They have a carbon to hydrogen ratio of approximately 1:1, making them very dense.
   They are generally undesirable in crude, but their 'stickiness' makes them excellent for use in road construction.
5. **Naphthalenes**
   Polynuclear aromatics such as naphthalenes consist of two or three or more aromatic rings. Their molecular weight is between 150 – 500.
6. **Organic sulphur compounds**
   Organic sulphur compounds such as thiophene, pyridine also exist in the crude oil. The basic difficulty of these organic sulphur compounds is the additional hydrogen requirements in the hydrotreaters to meet the euro III standards.
   Therefore, the operating conditions of the hydrotreaters is significantly intense when compared to those that do not target the reduction in the concentration of these organic sulphur compounds.
7. **Oxygen containing compounds**
   These compounds do not exist 2 % by weight in the crude oil. Typical examples are acetic and benzoic acids. These compounds cause corrosion and therefore needs to be effectively handled.
8. **Resins**
   Resins are polynuclear aromatic structures supported with side chains of paraffins and small ring aromatics. Their molecular weights vary between 500 – 1500. These compounds also contain sulphur, nitrogen, oxygen, vanadium and nickel.
9. **Asphaltenes**
   Asphaltenes are polynuclear aromatic structures consisting of 20 or more aromatic rings along with paraffinic and naphthenic chains. A crude with high quantities of resins and asphaltenes (heavy crude) is usually targeted for coke production.

TRANSPORTATION OF CRUDE OIL FOR REFINING:

- Getting oil to market is a process that requires various transportation and storage technologies, usually referred to as “midstream”.

- Oil is often produced in remote locations away from where it will be consumed; therefore, transportation networks have been built to transport the crude oil to refineries where it is processed and to ship the refined products to where they will be consumed (like a gas station).

1) Trucks

a) Flatbeds are open trailers that are commonly used for oil and gas equipment shipping because they let you move loads of any size and shape. Rigs, pipes, and drilling equipment are usually oversized and overweight, which makes it hard to move via any other transportation method except a specialized truck.

b) Hotshots are trailers connected to a pick-up truck that is made for moving small and urgent shipments. Whenever you need to quickly transport a piece of equipment to a remote site, hotshot is a perfect option

c) Oil tankers are special cylindrical containers connected to trucks. Tankers are adjusted to moving liquids, and they are good for moving oil as well. Although you cannot ship a large volume of oil through the truck, the vehicle can take it to any destination you need.

2) Pipelines:

This transportation method suggests that oil is gathered and then transported directly to the site or plant via a pipeline network. Despite pipeline shipping being a hot topic of discussions between industry experts, it is a fast and reliable way to distribute oil. New technology helps advance the safety of this mode, and pipelines have sensors for monitoring important indicators like temperature, pressure, etc

Pipeline transportation has its disadvantages. Firstly, it limits areas and destinations you can ship to because the pipeline infrastructure is not developed enough. Additionally, pipelines move enormous amounts of oil, so when an accident happens, the damage is very serious and it's often hard to liquidate the consequences

3) Ocean

Ships are a slow, inexpensive, reliable way to move extremely large volumes of fuel. Ocean transportation has one big advantage over other shipping methods, which is that you can transport materials globally. Despite longer transit, it is the most efficient mode for moving oil across the world. Essentially, ocean shipping is mostly used as a part of a large intermodal strategy. . A typical 30,000-barrel tank barge can carry the equivalent of 45 rail tank cars at about one-third the cost. Compared to a pipeline, barges are cheaper by 20-35%, depending on the route.

4) Rail

Rail transport was a primary way to move oil for more than 150 years. Rail transportation makes oil containers less prone to damage compared to other shipping modes. This method doesn't have enough flexibility to move oil at any point. But, when combined with other modes, rail can be extremely beneficial for a fairly fast and cost-effective way to move oil long-distance.

MODEL QUESTIONS:

8. Define Petrochemicals.
9. Differentiate between petroleum and petrochemical.
10. What are the methods used for detection of petroleum?
11. What are the various means for transportation of crude oil?
12. Define desalting of crude.
13. Define stabilisation of crude.
14. Write down the composition of crude oil by weight percentage of elements.
15. Write down the development and growth of petrochemical industry in India.
16. Describe the importance of petrochemical industry.
17. Write down the theories on origin of petroleum.
18. Write down the classification and composition of petroleum.
19. Describe the various ways of transportation of crude oil for refining.

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Chapter 2- FRACTIONATION OF CRUDE PETROLEUM OIL

LESSON OBJECTIVE

The topics help the students

- To study the Fundamental of Cracking-Principle**,** Reaction and parameters in thermal cracking, pyrolysis, vis-breaking, coking, Catalytic cracking process, different catalytic crackers.

COURSE OUTCOMES:

1. Classify petroleum refining process and fractionation of crude oil.
2. Explain the Importance of 1st, 2nd, 3rd generation petrochemical, refinery products, their properties and uses.
3. Identify growth and future of petroleum refinery and petrochemical industries in India.

TOPIC TO BE COVERED:

Lecture No	**Topics to be covered**
Lecture 9	Cracking-Principle, necessity and types of cracking
Lecture 10	Reaction and parameters in thermal cracking
Lecture 11	Reaction and parameters in pyrolysis
Lecture 12	Reaction and parameters in visbreaking
Lecture 13	Reaction and parameters in coking
Lecture 14	Reaction and parameters in coking
Lecture 15	Catalytic cracking process, parameters, process in different catalytic crackers
Lecture 16	Process in different catalytic crackers
Lecture 17	Process in different catalytic crackers
Lecture 18	Thermal reforming
Lecture 19	Catalytic reforming
Lecture 20	Polymerisation, Alkylation and isomerisation

TOOLS USED:

- Chalk and duster
- K-Yan

MODEL QUESTIONS:

1. What are the types of cracking and Conrandson Decarbonising Efficiency (CDE)?
2. What is the effect of temperature and the effect of pressure on cracking?
3. Briefly describe the process of fluid coking with flow-sheet.
4. Briefly describe the process of flex coking with flow-sheet.

ASSESSMENT METHODS APPLIED:

- Class quiz Assignment

REFERENCES:

- Modern Petroleum Refining Process by B K B Rao, Oxford IBH Publication
- Petroleum Refining Technology by Dr. Ram Prasad, Khanna Publications.

CRACKING:

- The large and relatively non-volatile hydrocarbons of otherwise practically unutilized fractions of petroleum can be broken down by suitable thermal treatment is called cracking into mixtures of smaller molecules having the desired volatility.
- Cracking is a process in which long chain hydrocarbon molecules are broken down into smaller, more useful hydrocarbon molecules.
- Cracking can be carried out to any hydrocarbon feedstock but it is usually applied for vacuum gas oil (VGO).
- Cracking can be with or without a catalyst.
- Thus cracking may be defined as the decomposition or pyrolysis of higher hydrocarbons into lower hydrocarbons at high temperature.
- Gasoline obtained by cracking of gas oil is called cracked gasoline.
- The process of Cracking is carried cut by heating high boiling fractions when the bigger molecules break up into smaller one of much lower boiling points.
- In this manner cheap oils which are much less in demand are converted into petrol or gasoline.
- The products obtained as a result of cracking depend mainly upon the structure of hydrocarbons, temperature, pressure and catalyst used.
- The main objective of cracking is the production of gasoline. There are in general three types of cracking.

1. **Catalytic Cracking:**
    - It is carried out in presence of a catalyst at high temperature and low, moderate pressure or no pressure.
    - The catalytic cracking involves enhancing the octane number of the product
    - Heavy naphthas are used are typical feed stocks.
2. **Thermal Cracking:**
    - It is carried out at high temperature under a high applied pressure.
    - Feed stock is highly olefinic, aromatic and have high sulfur.
    - Thermal cracking follows free radical mechanism.
3. **Hydrogenation Cracking:**
    - It this type of cracking heavy oils are converted to gasoline by the action of high pressure hydrogen at high temperature in presence of a catalyst.

NECESSITY FOR CRACKING

Cracking is important for the following reasons:

1. Natural gasoline and straight run gasoline, obtained from petroleum are quite insufficient is meet the demand for gasoline (petrol) as a result of rapid rise in the number of automobiles during the last few decades.
2. This deficiency is met with by the production of gasoline from less volatile products of: petroleum, i,e., heavy oil and kerosene oil by means of controlled pyrolysis or cracking.
3. It helps to match the supply of fractions with the demand for them. The supply is how much of a fraction an oil refinery produces. The demand is how much of a fraction customers want to buy.
4. Fractional distillation of crude oil usually produces more of the larger hydrocarbons than can be sold, and less of the smaller hydrocarbons than customers want. Smaller hydrocarbons, such as petrol, are more useful as fuels than larger hydrocarbons. Since cracking converts larger hydrocarbons into smaller hydrocarbons, the supply of fuels is improved. This helps to match supply with demand.
5. It produces alkenes. Alkenes are more reactive than alkanes. They are used as feedstock for the petrochemical industry.

Cracking chemistry

- Long chain paraffins converted to olefins and olefins

- Straight chain paraffins converted to branched paraffins
- Alkylated aromatics converted to aromatics and paraffins
- Ring compounds converted to alkylated aromatics
- Dehydrogenation of naphthenes to aromatics and hydrogen
- Undesired reaction: Coke formation due to excess cracking
- Cracking is an endothermic reaction. Therefore, in principle cracking generates lighter hydrocarbons constituting paraffins, olefins and aromatics.
- In other words, high boiling low octane number feed stocks are converted to low boiling high octane number products.

Effect of temperature:

- The rate of reaction increases with increasing the temperature of cracking. For example same yield of gasoline will be obtained at 400 or 500 degree C but the time for cracking is very less at high temperature i.e 720 minutes to 36 secs.
- The rate of cracking increases twice for every 10^0C rise at 400^0C, 14^0C at 500^0C and 17^0C at 600^0C.

Effect of pressure:

- Pressure has no noticeable effect on the rate of cracking and normal yield of gasoline.
- Cracking under pressure can however form the most favourable conditions for heat distribution in order to local overheating and hence provides lower yields of tars and coke and takes place most efficiently and with the least consumption of fuel.
- The productivity of the cracking plants can be increased by increasing the pressure of the process.

THERMAL CRACKING:

- This form of cracking was the earliest method used by refiners to get greater yields of light distillates from a given crude oil. High temperatures (generally above about 315°C) and residence time were the variables used to determine yields of lighter products.
- However, as temperature and residence time were increased to get greater yields of light products, the thermal cracking processes were hampered by excessive coke formation. The products of thermal cracking have very poor stability and require further treatment.
- Hence fluid catalytic cracking finds more favour at present with the refiners. However thermal cracking is employed in preparing highly aromatic thermal tar for the production of needle coke.
- This process produces gas, naphtha, middle distillates and thermal tar from every variety of charge stocks from distillates to the heaviest crudes and residual oils. The gas produced from thermal cracking contains propylene and butylenes which can be polymerized to produce polymer gasoline of high octane number.

Process Description

- A simplified flow diagram of thermal cracking process is given in Fig.
- In thermal cracking charge is heated to 970°F to 1020°F in a pipe heater under a pressure of about 1000 psi at the outlet of the heating coil so that dense phase and longer time are provided during reaction.

$$C_{1O}H_{22} \rightarrow C_5H_{12} + C_5H_{10}$$

Paraffin Olefin

- The lower molecules of paraffin and olefin thus formed may be further decomposed. They can even be fully cracked to carbon and hydrogen at a certain high temperature.

$$CH_4 \rightarrow C + 2H_2$$

- The charge is fed in the fractionator in which it is fractionated along with the cracked products from the reaction chamber.
- The vapours of gas and gasoline go out from the fractionator at the top. These vapours are condensed in a condenser to obtain gas and gasoline.

- The liquid products from the fractionator pass on to the hot oil pump which transfers these products to cracking tubes from where the heated products go to the reaction chamber. Here cracking reactions are allowed to complete.
- Vapour products from the cracked products are also separated.
- The vapour products go the fractionator, where they are fractionated into mixture of gas and gasoline and liquids. The coke left or deposited in the reaction chamber is periodically withdrawn.
- Thermal cracking yield petrol, gases and cracking remainder as its products.
- Thermal cracking is of two types: vapour liquid or liquid phase cracking and vapour phase cracking.
- Liquid phase cracking is carried out at a temperature of 470- 540°C and a pressure of 40 to 60 atms.
- The vapour phase cracking is carried out at 550°C and higher and under 2-5 atm. pressures.
- The cracking phase of liquid phase processes take place both in the liquid and the of vapour phase cracking in the vapour phase only.

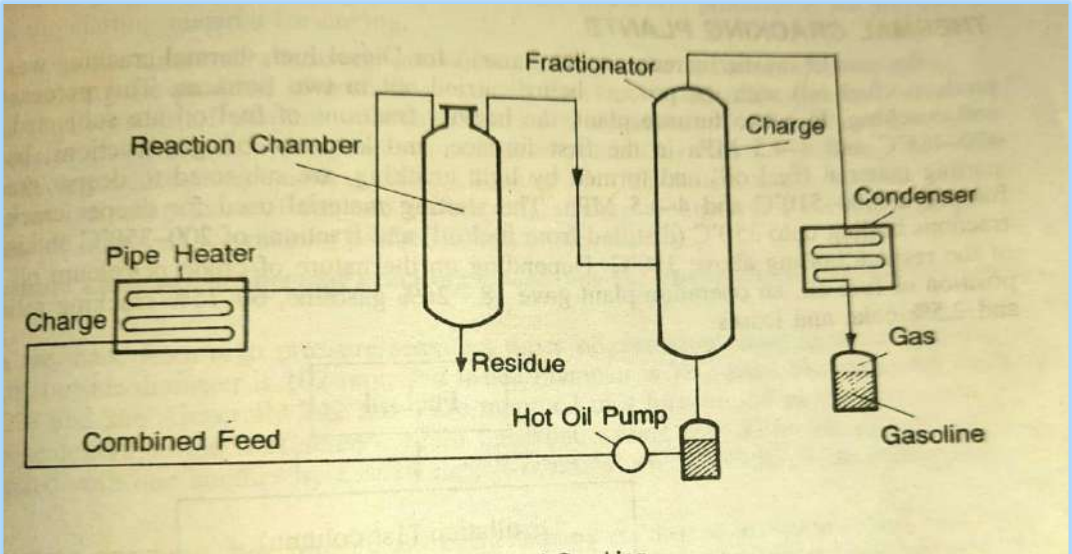


Fig. 1. Thermal Cracking.

PYROLYSIS:

- Pyrolysis of petroleum and gaseous material takes place at 650-1100 C (Higher temperature) and lower pressure than in the case of thermal cracking and coking.
- In addition to decomposition products, pyrolysis gives synthesis products such as benzene, toluene, and xylene, phenanthrene and their derivate.
- Thus pyrolysis gives a higher yield of gases with high amount of unsaturated hydrocarbons in comparison to thermal cracking or coking.
- The liquid from pyrolysis has higher amount of aromatics.
- The feedstock for chemical and petrochemical industry is mainly comprised of olefin hydrocarbons and benzene like aromatics compounds which are produced from pyrolysis process.
- Products obtained from pyrolysis of gasoline(naphtha) include pyro gas(up to C_4), pyro gasoline (C_5-190C), pyro condensate(Heavy oil, above 190C), steam.
- Modern plants of pyrolysis consists of furnaces, condensation sections, sections for absorbing H_2S and CO_2, drying and liquefaction section and group of columns for separation of fractions and hydrocarbons, quenching unit and refrigeration, heat generation unit.
- The separation of pyrogas is effected by the condensation rectification method. The process has units for the separation of :

a) H_2 at 4.5 MPa.

b) CH_4 fraction at 3.5 MPa.
c) C_2H_6- C_2H_4 fraction at 2.8-2.9 MPa.
d) C_3H_8 -C_3H_6fraction at 1.8 MPa.
e) Butylene divinyl fraction, and
f) C_5 hydrocarbon fractions.

- The ethane ethylene fraction is purified from acetylene by catalytic hydrogenation in the same plant, after which ethylene is separated from it at a low temperature and a pressure of 2 MPa.
- Ethane is used as the starting material for pyrolysis in separate furnace.
- Propylene (99.9%) can be separated from the propane propylene fraction in the similar manner, but at a higher temperature and 1.2 MPa pressure.
- Divinyl can be separated from the butylene divinyl fractions in two stage extractive rectification by an aqueous solution of acetonitryl.
- The C5 fraction can be processed for separation of isoprene and cyclopentadiene.
- In recent years, pyro gasoline can be processed to obtain benzene by two stage hydrogenation and subsequent hydro-dealkylation of benzene hydrocarbons present in hydrogenation.
- Pyro gasoline can also be fractionated to separate a high aromatic high octane component of automobile gasoline.
- The yield of ethylene, which is the main product of Pyrolysis, depends on the composition of the starting material and the conditions of the process.
- Upto 80% or C_2H_4 can be obtained by the pyrolysis of ethane.
- The yield of C_2H_4 decreases as the molecular mass of the starting material increases.
- The yield of by-products increases with increase of molecular mass of starting material.
- Pyrolysis of kerosene or other petroleum products is carried out by vapour phase cracking at about 650-720 C and at nearly atmospheric pressure.
- The high temperature used in the process results in the formation of large amounts of gaseous products rich in ethylene, other unsaturated hydrocarbons, and aromatic hydrocarbons which are a raw material for organic synthesis.
- The important disadvantages of Pyrolysis are

a. The necessity to stop the operation for burning off coke.
b. High consumption of metals, including high quality alloy steel

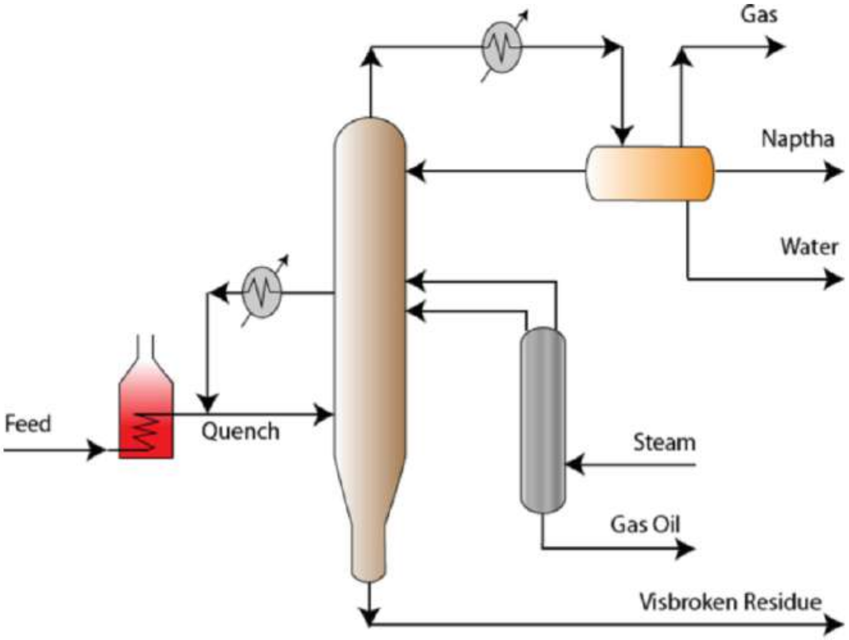
VISBREAKING

- In Visbreaking operation, a mild thermal cracking is carried out.
- Visbreaking produces Naphtha, Gasoil and a residue. The residue has lower viscosity and pour point and hence can easily meet the requirements of the fuel oil specifications in the fuel oil blending pool.
- Visbreaking basically breaks the long paraffinic side chains attached to aromatic structures. Due to this the residue pour point and viscosities are considerably reduced.
- Two classes of reactions occur during visbreaking

1. Cracking of side chained aromatic compounds to produce short chained aromatics and paraffins
2. Cracking of large molecules to form light hydrocarbons

PROCESS DESCRIPTION:

- Visbreaking is carried out either in a coil or in a soaker.
- When coil technology is used, the mild thermal cracking is carried out in the furnace coils
- When soaker technology is adopted, the cracking is carried out in a soaker unit that is kept immediately after the furnace.
- After cracking, the products are at high temperatures (480 ^{o}C for coiled furnace case or 430 ^{o}C for the soaker)
- After cracking, the products are cooled using quenching operation.



- Quenching is a direct heat transfer mechanism in which a hot stream is cooled with a hydrocarbon or water to reduce the temperature of the system drastically.
- After quenching, the mixture is fed to a distillation column supplemented with a side column and a partial condenser
- From partial condenser, water, naphtha and gas are produced. Naphtha liquid stream is sent as a reflux for the column.
- The side column is fed with steam and produces gas oil. Steam enhances hydrocarbon volatility as explained before in the lecture devoted towards crude distillation process.

COKING:

• Petroleum coke is obtained in Petroleum industry as an ultimate product of prolonged thermal cracking.
• Coking is a thermal cracking operation falling in a temperature range 500 to 650 C.
• Feed stocks otherwise not suitable to operations like thermal or catalytic cracking, are usually fed to Coking units.
• Coking is influenced by the gravity and molecular structure of the feed.
• Propensity of cracking is an outright function of Conradson carbon residue(CCR).
• An analogical term Conrandson Decarbonising Efficiency (CDE) is defined as

CDE= LIQUID PRODUCTS/ CARBON RESIDUE IN FEED STOCK
• Aromatics, asphaltenes are desirable feed stocks for good yield of coke.
• Sulfur in the feed stock increases the coke yield.
• Sulfur forms an inseparable complex with coke which is difficult to separate once coking is completed. • BIS specification of petroleum coke is IS: 8502-1994

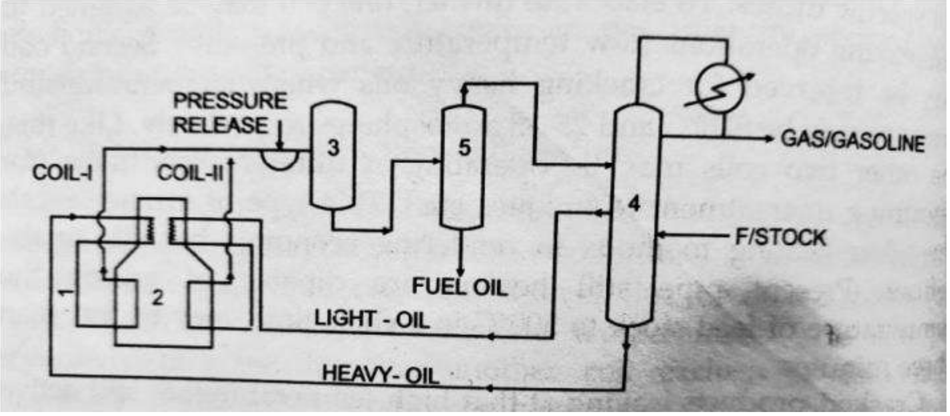
• General methods of petroleum coke production are listed below
1. Hot oven method(koppers)
2. Thermal cracking (Two coil-Dubb's)
3. Delayed coking
4. Fluid coking
5. Flex coking

Hot oven Method

- This method has no reputation in petroleum industries now a days.
- With some modifications, the byproduct coke from oven is employed for other coking petroleum stock.
- High molecular weight stocks such as asphaltenes, tars, pitches serve as raw materials to these oven
- Temperature of (1000-1200) C is required and coking time of 18 hours is most desirable.
- With pitch of CCR value 50%,coke yield shall be approximately 70%.

Thermal Cracking

- Thermal cracking and coking operations are simultaneously done in Dubb's Two coil cracking technology.
- The feed enters at the fractionator (4).
- Thermal cracking allows the heavy oil to be cracked separately and then mixed and chilled with fresh feed.
- Instead of this, in coking, the cracked products from coil 1 and 2 are allowed to complete cracking in evaporator (3).



- After evaporation, there are flash Chambers in cracking which are replaced by coke chambers(5) where the separation of fuel oil and volatile takes place.
- The lighter product escapes into fractionator (4) where gases are obtained as top product and heavy oil and light oil are obtained as bottom product.
- Coke from evaporator and coke chambers are removed by conventional techniques.

Operating Conditions:

1. Coil Temperature:520-550 C
2. Coil pressure: 30 atms
3. Coke chamber pressure:15-20 atm

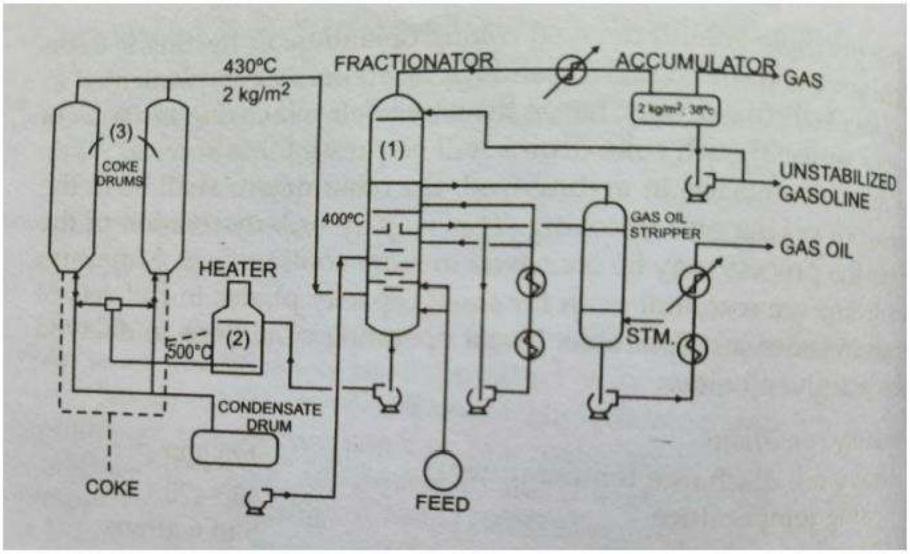
Delayed Coking:

- Delayed coking the outcome of two coil coking which has capability of handling all type of feed materials such as solvent extracts.
- The principle behind delayed coking operation, is: heating is done in a furnace to initiate cracking and the reactions are complemented in huge and tall coke drums; hence the name delayed coking is used.
- As a rule a series of such coke drums will be pressed into service. While one drum is engaged in getting feed, the other drums shall be in the process of coking and decoking.
- Minimum two drums are essential even for small capacity plants, in fact sets of drums in series are desirable.

Usual operating conditions in delayed Coker are given below:

- Recycle ratios of fresh (heavy) and light oils are adjusted to maximise yields of either liquid or solid products. An yield of 30% coke for reduced crudes or 80% for tars and pitches may be expected.
- Coke from these units contains volatile matter upto 8-15% . CDE of the plant may be reaching upto 99.8%.
- The process begins with the fresh feed entering the fractionator (1). The fractionator complies with all the assigned duties as in two coil cracking plant. Heavy oil from the bottom of fractionator passes through a heater (2) at a high velocity.
- Introduction of steam into heating coil prevents coke deposition in coil. The hot and partially vaporised mixture enters the coke drum (3).
- The coke drum is charged with hot mixture to half to two-third of the height of the drum; or to a convenient marked level.

- The level of hot mix in drums is modulated by cathode ray monitoring. Steam and volatiles escape from the coke drums and enter the fractionator. This fractionator is also known as dephlegmator.
- These vapours preferentially relinquish heat to incoming feed; and in this act stripping of volatiles from feed takes place.



- Changing of coke drums may require a time of 4 to 5 hours.
- Immediately after changing is over the drum shall be isolated from the stream. Effluents of the heater shall now be switched in to second drum.
- Coking being slow usually takes a time of 10 to 16 hours. Time of charging coke drums must balance the time of coking and decoking operations.

Operating conditions:

1. Heavy oil, discharge temperature (470-520)C
2. Coking temperature (450-470)C
3. Pressure in coke drum (5-6)atms
4. Drum diameter (4-5)M
5. Height (14-20) M
6. Thickness of drum (up to 4cm)

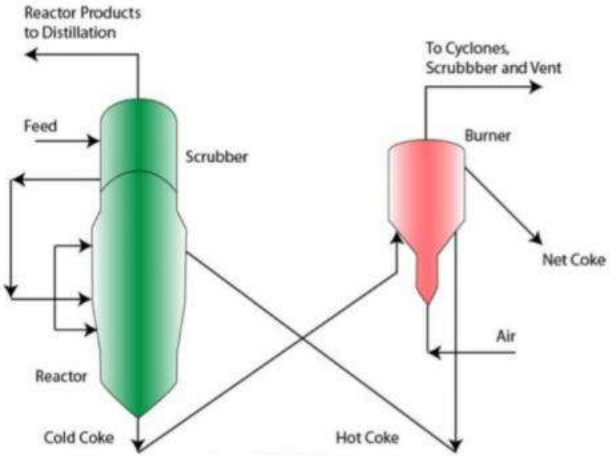
Decoking

- Coke being set and hard, much difficulty is encountered in removing.
- Decoking is a time consuming and arduous task.
- Lot of developments took place in the direction of decoking operations. Presently hydraulic jets at 150 to 200 atmospheres pressure are directed to break the coke, in place of once used mechanical breaking with hammers.
- Drilling and mild dynamiting is also allowed.
- Of late the ingenious chain pulling technique has been acclaimed and welcomed by the industry.
- The technique consists of suspending strong chains in coke drums from the hooks fixed to the thick shell of drum at the top.
- Other ends of the chains are free to fold and lie submerged under charge. After coking is over, usually steaming is done to drive off hydrocarbon vapours.
- The top flange is disconnected and the chains are pulled by cranes; this upward thrust shatters the coke to pieces,making easy for coke removal.

Fluid coking:

- The heated feed is fed to a fluidized bed where coke particles with finer particle sizes would aid fluidization.

- After coking, lighter products are withdrawn as overhead vapour and coke thus formed is removed continuously.
- The fluid coker also has an additional scrubber which will remove heavier compounds from the vapors (if any) and send them back with the feed stream. Here, the feed stream absorbs heavier hydrocarbons from the vapors generated.
- This is required as it is difficult to keep heavier hydrocarbons in the feed phase only due to pertinent high temperatures.
- The coke after coking reaction is cold coke. Therefore, to generate hot coke, a burner unit is used to heat the coke using exothermic CO2 reaction.
- The offgases from the burner are sent to cyclones, scrubbing and then to the vent. The hot coke thus obtained is recycled back to the fluidized bed or taken out as a net coke product.
- The coker products are fed to a complex distillation column i.e., main column supplemented with side columns.



- From the complex distillation column, naphtha, water, light gas oil and heavy gas oil are obtained.
- Additional complexities in the distillation unit are

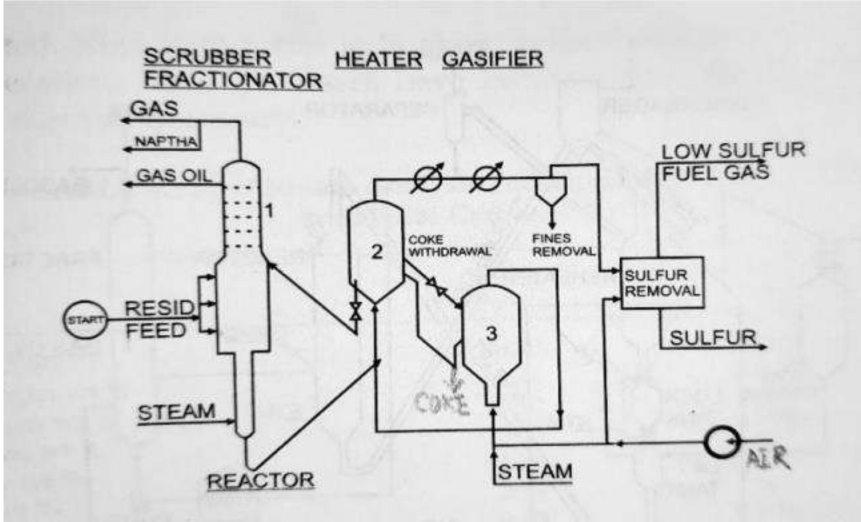
1. Feed entering the distillation column but not the coker unit: This is to facilitate the removal of light ends from the feed (if any) and don't subject them to cracking.
2. This is also due to the reason that light ends are valuable commodities and we don't want to loose them to produce cheap coke product. In this case, the bottom product from the distillation column is fed to the furnace for pre-heating and subsequent coking operation.
3. Live steam in distillation: This is to facilitate easy removal of lighter hydrocarbons in various sections.
4. Circulatory reflux (Pump around units): This is to facilitate good amount of liquid reflux in various sections of the main column.

Operating condition:

1. Reaction temperature : (480-560)C
2. Pressure : Normal 1 atm
3. Burner Temperature: (590-650)C
4. Pressure burner : about 2 atm

Flexi Coking

- Matrix of coking and gasification operations is called as flexi coking.
- This integration enables refineries to convert vacuum residuums, other heavy feed stocks into desulfurised liquids and gases. As a result 99% vacuum residuums end up as liquids or gases with less than one percent sulfur.



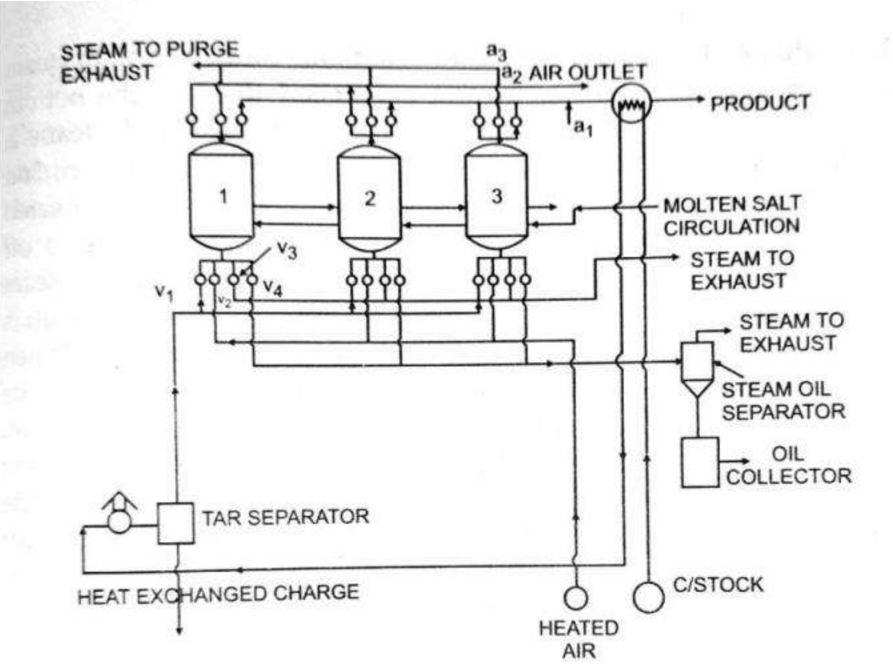
- Residuum feed is injected into reactor where thermal cracking takes place.
- Lighter products leave the reactor and enter the scrubber cum (1) fractionator. The purpose of fractionator is not only to rectify the volatiles, but also to entrap the coke fines leaving the reactor.
- Steam(admitted at the bottom reactor) stripped coke circulates into heater (2), where devolatilisation takes place; hydrocarbon gases obtained in this process are subsequently treated for purification.
- Coke formed in the heater is sent into gasifier (3), where coke is encountered with a stream of air and steam.
- Gasified products again join the main gas stream for purification.
- Part of coke may be withdrawn if necessary, at any point between heater and gasifier

CATALYTIC CRACKING:

Fixed Bed Crackers (Houdry Process)

- Figure illustrates Houdry Fixed bed process.
- At present, though no new plants based on this technology are being set up the old ones still continuing.
- There are three reactors in parallel (1, 2 & 3), in this system.
- At the bottom of each reactor there are four connections (V1, V2 V3 and V4) provided through a rotary disc.
- Only one line at a time is to be connected to the reactor; when the first reactor is on process stream, 2nd reactor will be on steam purge followed by air purge, and the 3rd reactor will be in regeneration process.
- At the start, charge oil vapor, free from tar, will enter the reactor through valve V1.
- After cracking, the vapours escape through the reactor outlet as product and go to the fractionator through line a1.
- At the top of the reactor also; same type of rotary arrangement is there, but connects only three valves; these values connect line a1 for products; a2 for air outlet and a3 forsteam purge alternatively. • Immediately the reactor is disconnected and connected with steam line (from top) through line a3 and exhausted through the bottom (V4).
- Oil vapours from this exhaust are condensed and steam is allowed to leave the separator.
- During this purging operation, 2nd reactor will be on steam.
- Soon purging operation is over, preheated air is sent into reactor 1, through valve V2 and flue gas goes off through line a2 at the top of the reactor.
- After regeneration steam purging from top to bottom is again conducted and exhaust steam is taken out through valve V3 from the bottom of reactor.
- When downward steam purging takes place, 2nd reactor has to be disconnected and 3rd reactor will be connected to main stream.
- Rotary valves with interlocking systems conducts smooth automatic cycling of the reactors.
- Molten salt is circulated to reactor, from the reactor under regeneration, to supply necessary heat.

- Molten salt maintains the heat of reaction in each reactor through extracting heat from the regenerator and supplying it.
- The valves are rotary type and interlocked so that manual error cannot result.



- Usual cyclic operation consists of the following:

1. On stream -10 minutes.
2. Downward purging of steam to recover hydrocarbons -5 min.
3. Regenerations by blowing hot air through bottom of the reactor -10 min.
4 Air purge followed by steam purge downward-5 min.

- It can be seen that on stream will be equal to regeneration period; which will be equal to the sum of steam purging periods, before and after regeneration.

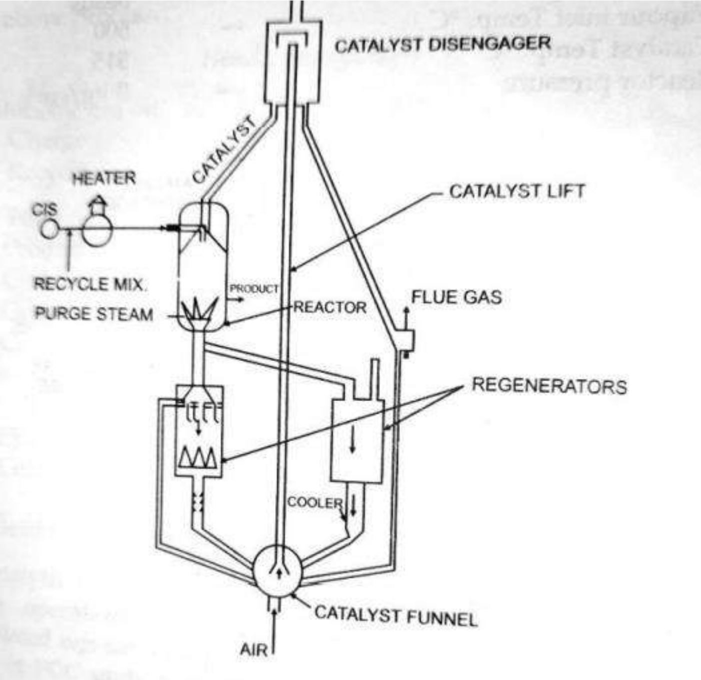
Operating conditions

- Reactor temperature 450 to 520°C
- Operating velocity (gauge) 1 to 2 kg/cm^2
- Space velocity (Liquid)-1 to 1.75 (1/Hr.)
- Regeneration temperature-upto 520°C
- Air pressure, during regeneration upto 4 kg/cm^2
- Catalyst shape- Beads/pellets
- Composition -Silica-alumina
- Vapour inlet temperature 430°C.

Moving Bed-Air lift- Thermofar catalytic cracking

- Thermofor catalytic cracking units fall into this category.
- Catalyst shape in these units may be spherical or beads.
- The shape and size of the catalyst permit free flow of catalyst in the reactor.
- Catalyst and oil move cocurrently from top to bottom in the reactor.
- Reactor is stacked directly over the regenerator as shown in Figure.
- In between reactor and regenerator there is a constriction, where steam purging is done.
- This helps firstly in removing hydrocarbons from the surface of catalyst, secondary steam prevents the reactor products from going downwards into regenerator; which is highly essential otherwise the situation may become unwanted.

- Spent catalyst is regenerated by air blowing.



Air lift T.C.C.

- The flue gas passes through cyclone separators, leaving catalyst dust, if any, in the out going stream. • At the bottom of regenerator, there is a cooling section to cool the catalyst. Such regenerators shall be in two numbers, kept below the reactor.
- The catalyst collected from the regenerator is lifted into catalyst diserngager, placed at a height more than the reactor which automatically feed the catalyst into reactor due to gravity.
- Old designs employed bucket elevators to lift the catalyst, while modern practice is to use air.
- Thus the name Air lift Thermofor catalytic cracking has been accomplished.
- Catalyst from both the regenerators is conveyed into a single funnel, from where the pneumatic conveyance can take place.
- Feed and catalyst always travel downwardly in the reactor, and products escape from the side of reactor. • Proper distribution of catalyst for good performance is essential.
- The disadvantage of this process is in low catalyst to oil ratio which increases the coke deposition on catalyst.

Operating conditions

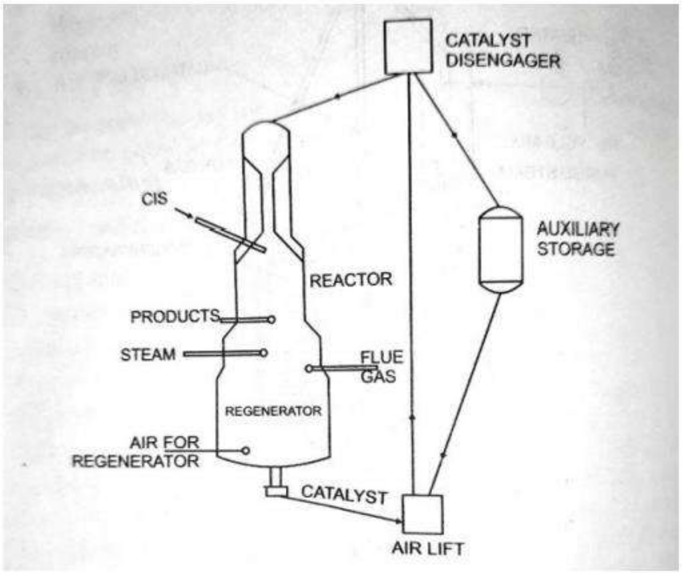
1. Regeneration Temperature-600 C
2. Recycle ratio- 0-0.5 Vol/vol
3. Catalyst to oil ratio- 2 to 7
4. Space velocity- 0.7 V/hr.V
5. Catalyst shape- beads
6. Vapour inlet Temp. °C-500
7. Catalyst Temp. °C- 515
8. Reactor pressure- 3 kg/cm2

Moving Bed- Houdri Flow Process

- Houdri flow process is distinguished from the TCC process in its

(a) ease of operation
(b) low cost of maintenance
(c) high catalytic activity (low catalyst make up costs) (d) flexibility in handling charge stocks and conversions attained.

• In this design, reactor is placed above the regenerator, in a single shell.
• The regenerated catalyst (either natural or synthetic type) is carried by pneumatic lift to disengager, from where the catalyst can either go into reactor or auxiliary storage bin.
• The system works on self-heat balance, so no additional heating or cooling of catalyst is anticipated. • Usually operations are conducted in temperature range of 450-520°C, at pressure 1.5 to 2 atmos; with a space velocity of 1.5 to 4 V/hr./V.
• Catalyst to oil ratio of 3 to 7 is maintained with high recycle ratios of 1:1.
• A conversion of 90% can be obtained with recycling, while once through cracking permits a conversion of 60%.
• The octane value of gasoline lies in the range of 85 to 90. Yield can be improved by using zeolite catalysts.



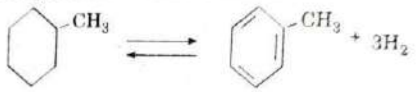
CATALYTIC REFORMING:

- Upgrading low octane gasolines catalytically is called catalytic reforming.
- Thermal reforming can also be practised but not desirable due to the inherent disadvantages.
- The octane rating improvement is accomplished chiefly by reorienting or re-forming the low octane components into high octane components by converting n paraffins to aromatics.
- The proper and worthy reaction is dehydrogenation and cyclisation of n-paraffins; that results in a tangible improvement in octane rating (n-heptane of zero octane rating-to more than 100 octane number).
- Cracking reactions produce more lighter components which have better octane quality than the heavier ones; yet the reactions are not opted due to the fear of excessive coke formation unsaturation in the products.
- Vigorous hydrocrack when the feed stock is rich in paraffins.

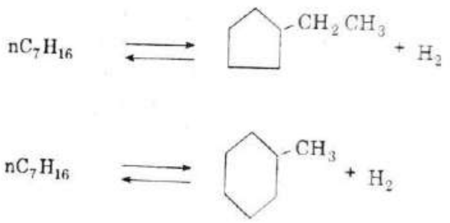
Reforming Reactions

- Straight-run naphthas are solely composed of normal and branched paraffins, five and six membered ring naphthenes, and single ring aromatics.
- In a typical teed, the carbon number ranges from five up to twelve.
- For all practical purposes, there are no olefins in hydrotreated feed for catalytic reforming unit.
- Each of these constituents of the feed can undergo several competing reactions. The main reactions involved in the catalytic reforming are given below.

(a) Dehydrogenation of naphthenes to aromatics



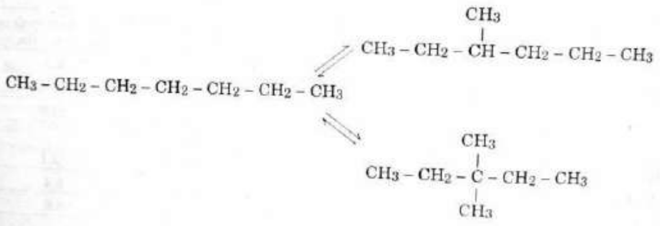
(b) Dehydrocyclization of paraffins to aromatics

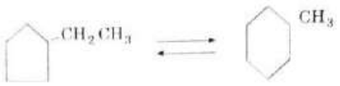


(c) Hydrocracking of high molecular weight paraffins to lower molecular weight paraffins

$nC_7H_{16} + H_2 \longrightarrow C_4H_{10} + C_3H_8$

(d) Isomerization of paraffins and naphthenes to more desirable hydrocarbons





(e) Demethylation and dealkylation/transalkylation

- Hydrogen in substantial amount is produced by the first two reactions and it is consumed in the reactions (3rd and 5th reaction).
- Isomerization of alkyl cyclo-pentanes to cyclohexane homologs is an important intermediate reaction step.
- Hydrocracking and demethylation reactions produce gaseous products, decreasing liquid reformate yield.
- De-alkylation and trans-alkylation reactions, which occur to a very minor extent, determine the final distribution of aromatic products.
- Relative reaction rates and equilibrium constraints determine the yield structure for any given reforming operation.
- Reactivity decreases with decreasing carbon number for each type of hydrocarbon.
- Dehydrogenation of cyclohexane homologs is a very rapid reaction whereas isomerization of alkyl cyclopentanes occurs much less rapidly.
- Dehydrocyclization of paraffins is the slowest of the aromatics-forming reactions

Reforming Catalysts

- Reforming catalysts are dual functional, In that they promote simultaneously reactions that are specific functions of the metal and/or acidic properties of the catalyst.
- The metal provides the hydrogenation-dehydrogenation activity of the catalyst and can function either as a simple metal or as a transition metal (one of the metal oxides or sulphides).
- The simple metal form has a dehydrogenation activity of much higher magnitude than the oxides or sulphides and is, therefore, used exclusively in today's reforming processes.
- Most of the metals in Group VII of the periodic table, such as nickel, palladium and platinum are effective dehydrogenation catalysts; however, platinum is the most active and is used in all present day commercial reforming catalysts
- A secondary metal used in bimetallic catalysts of which rhenium is the most common, is primarily used to improve catalyst stability and does not alter start of run yields.
- The acid activity of the catalysts promotes or controls all other reforming reactions and is usually supported by the addition of halogens to the catalyst base.
- Most of the commercial reforming catalysts use chlorine. The addition of silica can be used to supply the acid function of the catalyst.
- The metal and acidic components are supported on an active alumina base which does not exhibit any acidity influence on the catalyst.
- The most active alumina crystal structures are beta and gamma aluminas and all commercial reforming catalysts use one or the other or a combination of both for the catalyst support.

The advantages of bimetallic catalysts over monometallic catalysts are:

(a) Higher stable liquid yield
(b) Higher octane C_5 components
(c) Increased hydrogen production
(d) Operation at low pressures
(e)Operation at low hydrogen to feed ratio
(f) Long run between regenerations
(g) Good temperature stability

Effect of Pressure

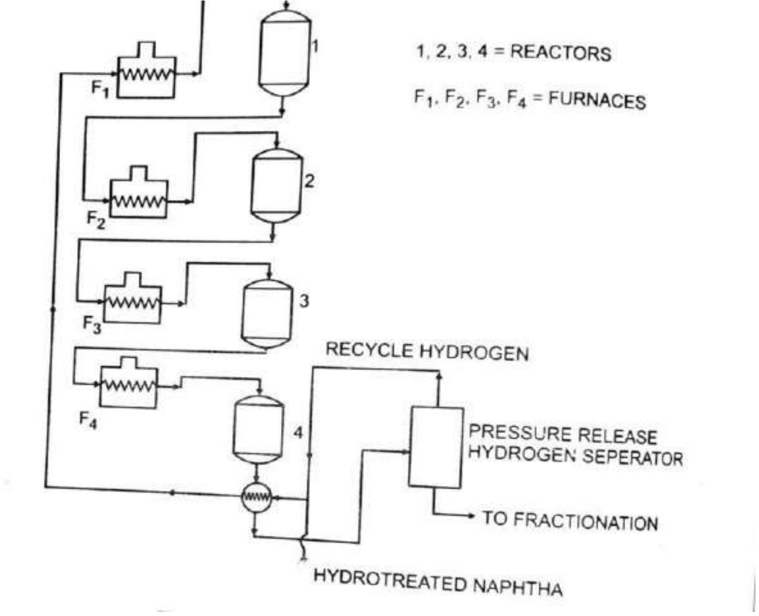
- Low pressure, encourages dehydrogenation reaction noticeable effect of pressure on isomerisation may be expected.
- Coke formation is more at low pressures. Increase in pressure causes dealkylation very much.
- Hydrocracking and elimination reactions are directly related to the partial pressure of hydrogen.

Effect of Temperature

- Except hydrogenation reactions, which are exothermic all other reactions are favoured by increasing temperature.
- With increase temperature, chances of degradation of product, and coke deposition are likely.
- For economic operations the parameters are
  1. High temperature
  2. Low pressure
  3. High hydrogen circulation.
- With increased coke deposition at low pressures, the reactors are preferably operated at 10 to 50 atms pressure.
- The temperature above 500°C promptly spoils the activity of catalyst.
- A temperature range of 450-500°C is frequently advisable and can bring about all reactions without much severe problems.

Catalytic Reforming (Platforming)

- Catalytic reforming process employs platinum and other combinations as catalysts. Hydro-treated naphtha (68-180°C) is mixed with recycle hydrogen and sent through a furnace.
- The hot vapour is sent into three catalyst cases (reactors in series). Old designs may enjoy four reactors in series: the last one is known as swing reactor.
- The outlet temperature of the vapours shall be around 500°C.

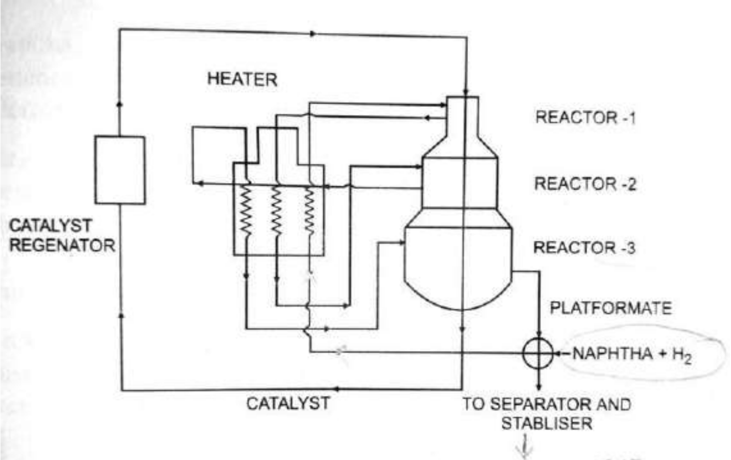


- Swing reactor comes into main stream when regeneration is attempted.
- Pressure in reactors is kept in the range of 15 to 75 atms.
- Except hydrogenation reactions, which are less prevailing, all other reactions require heat, this invites a heater to substantiate heat of reactions and placed in between two reactors.
- Cyclisation reactions are pronounced at severe conditions, hence the last reactor operates generally at higher temperature by 20 to 30°C from the preceding one.
- Catalysts are made into pellets of 3 mm size.
- Halogenation is prescribed whenever regeneration is carried out.

Platforming

- After the reforming is over the effluents are cooled and gas is separated.
- High pressure separator removes recycle gases mainly hydrogen, while low pressure separators relieve most of the light fractions.
- Hydrogen is usually produced to an extent of 2.5% by weight of feed.
- High recycling ratios prevent coke deposition and the space velocity is kept below 2 in all these operations.
- In regeneration processes, the space velocity goes upto 5.
- Continuous operation as developed by UOP is classified as platforming operation, and is presented in following figure.
- As the name suggests, continuous operation of catalyst is achieved here. Further, continuous rates ad constant quality production of reformate of high octane value and production of LPG from naphthas are some remarkable advantages in this system.
- Arrangement of the three stacked reactors one over the other forms the main difference in reactor arrangement.

- Feed and catalyst travel concurrently in all these reactors from top to bottom.
- Heating the reactants in between the reactors remain unchanged.
- The catalyst from bottom of third rector is transferred to separate regenerator.
- After regeneration the catalyst is transferred to the first reactor continuously.



. Platforming.

Types of Reforming:

1. Rhein Forming
    - Fixed bed regeneration process.
    - Rhenium-platinum catalyst combinations
    - Pressure below 20 atms.
    - Very less pressure results in increase of aromatics and hydrogen.
    - High space velocity with low recycle ratios of hydrogen (3 to 3.5)
    - Yield of hydrogen (75-84)%
    - Octane no: approx. 100
    - Products: C_1 to C_3 fractions
2. Power Forming

- Cyclic or semi-regenerative process.
- Platinum and multi-metal catalyst combination
- Octane number (85-102)
- Yield of hydrogen (11-17)%
- Products: C_1 to C_4 fractions

3. Selecto Forming:
   - Mild hydrogenation process.
   - Non nobel metals acts as catalyst(ex: zeolite)
   - High octane number and low volatile gasoline is achieved.
   - Pressure (5-40) atms.
   - Octane no-(95-100)
   - Products: $C_5{}^{+}$ fractions
4. Ultra Forming:
   - Low pressure and regenerative catalyst.
   - Combination of active nobel metals as catalyst.
   - Products: $C_5{}^{+}$ fractions
5. Rex Forming
   - Platinum, iridium and palladium as catalyst
   - Products: $C_5{}^{+}$ fractions

OLEFIN POLYMERIZATION

- ➢ Olefin polymerization to yield polymer gasoline is primarily carried out to obtain polymers with good octane numbers.
- ➢ The light gaseous hydrocarbons produced by catalytic cracking are highly unsaturated and are usually converted into high-octane gasoline components in polymerization or alkylation processes.
- ➢ In polymerization, the light olefins propylene and butylene are induced to combine, or polymerize, into molecules of two or three times their original molecular weight.
- ➢ The catalysts employed consist of phosphoric acid on pellets of kieselguhr, a porous sedimentary rock.
- ➢ High pressures, on the order of 30 to 75 bars (3 to 7.5 MPa), or 400 to 1,100 psi, are required at temperatures ranging from 175 to 230 °C (350 to 450 °F).
- ➢ Polymer gasolines derived from propylene and butylene have octane numbers above 90.
- ➢ The octane number of the polymer gasoline product is not greater than the octane number of the products produced from reforming and alkylation.
- ➢ Instead, comparatively poor quality product is obtained. But for the sake of enhancing octane number polymerization is carried out.
- ➢ On the other hand, polymer gasoline has more vapour pressure than the corresponding alkylation products. Therefore, in both ways, polymer gasoline product quality is lower than that obtained from the alkylation unit.
- ➢ Typical feedstocks for polymerization process are C_3 and C_4 olefins that are obtained from catalytic cracking - The end product from polymerization reactor is a dimer or a trimer of the olefins.

Reaction mechanism & operating conditions

Reaction mechanism comprises of four basic steps

- ➢ Carbonium ion formation (Step 1): Here, olefin reacts with acid catalyst to yield carbonium ion.
- ➢ Additon reaction (Step 2): Carbonium ion reacts with olefin to generate intermediate carbonium ion

- Regeneration (Step 3): The intermediate carbonium ion converts to the dimer and generates back the proton on the catalyst surface
- Isomerization (Step 4): Straight chain proton substituted olefins convert to isomeric carbonium ions.

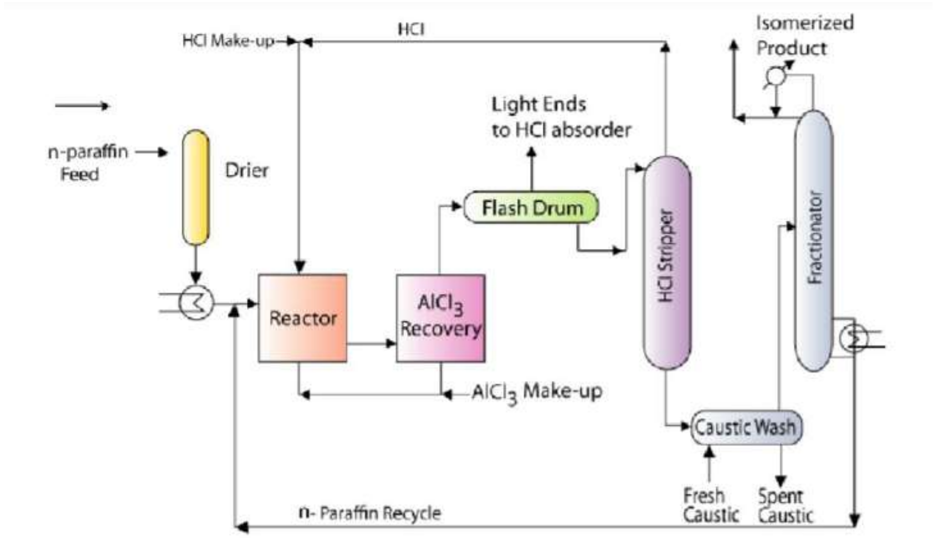
Catalysts used: Acid catalysts (H_2SO_4) are used. - Temperature: (150 – 220)^{o}C are used. Too high temperatures give tar deposits. - Pressure: 25 – 100 atms

ISOMERISATION

- The basic principle of Isomerization is to straight chain alkanes to side chain paraffins.
- This enhances the octane number substantially
- For instance, n-pentane has an octane number of 61.7 whereas iso-pentane has an octane number of 92.3
- Usually light naphtha is used as a feed stock.
- The demand for aviation gasoline became so great during World War II and afterward that the quantities of isobutane available for alkylation feedstock were insufficient.
- This deficiency was remedied by isomerization of the more abundant normal butane into isobutane.
- The isomerization catalyst is aluminum chloride supported on alumina and promoted by hydrogen chloride gas.
- Commercial processes have also been developed for the isomerization of low-octane normal pentane and normal hexane to the higher-octane isoparaffin form.
- Here the catalyst is usually promoted with platinum. As in catalytic reforming, the reactions are carried out in the presence of hydrogen.
- Hydrogen is neither produced nor consumed in the process but is employed to inhibit undesirable side reactions. The reactor step is usually followed by molecular sieve extraction and distillation.
- Though this process is an attractive way to exclude low-octane components from the gasoline blending pool, it does not produce a final product of sufficiently high octane to contribute much to the manufacture of unleaded gasoline.
-

Catalyst

- Platinum base catalysts are used
- AlCl3 is used as a promoter for the catalyst
- During reaction, part of the AlCl3 gets converted to HCl
- Therefore, completely dry conditions shall be maintained to avoid catalyst deactivation and corrosion.
- Catalytic reaction takes place in the presence of hydrogen to suppress coke formation



Process parameters

- Reactor pressure: 4 – 24 barg
- Reactor temperature: 500 – 525 ºC
- H2/Hydrocarbon molar ratio: 2 – 3

Process technology

- Light naphtha and hydrogen (make up) are totally dried and sent to an isomerisation reactor after pre-heating the feed mixture in a heat exchanger
- Reaction operating conditions: 150 – 200 ºC and 17 – 28 barg
- Typical conversions: 75 – 80 % for pentanes.
- After reaction, AlCl3 is recovered from the product using condensation or distillation
- The basic principle for AlCl3 recovery is that at the reactor operating conditions, the AlCl3 is in volatile conditions and is soluble in hydrocarbons
- After AlCl3 is recovered from the product, it is sent back to the reactor along with the make- up AlCl3
- Eventually, the product enters a flash drum where bulkly light ends along with little quantities of HCl are separated from the liquid product.
- The light ends recovered from the flash drum are sent to aHCl absorber where HCl is absorbed into caustic solution to generate the light end gases. The light end gases can be further used for other processes in the refinery.
- The bottom product then enters aHCl stripper where most of the HCl is stripped from the isomerisation product rich stream. The HCl is recycled back to the reactor to ensure good catalyst activity. Make-up HCl is added to account for losses
- Subsequently, caustic wash is carried out to remove any trace quantities of HCl
- The isoermized product rich stream is then sent to a fractionators that separates the isomerized product from the unreacted feed.
- The unreacted feed from the fractionators is sent back to the reactor.

ALKYLATION

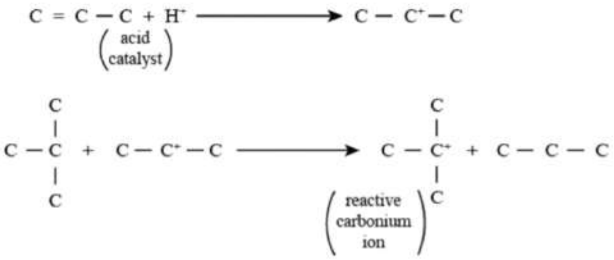
- In an alkylation process, olefins are reacted with isoparaffins to yield alkylate product.
- The basic purpose of alkylation is to enhance the octane number of the feed stock.
- For instance, octane number of butane alkylate is about 92 – 97.
- This is due to the formation of a hydrocarbon with side chain arrangement of carbon and hydrogen atoms.

- The alkylation reaction also achieves a longer chain molecule by the combination of two smaller molecules, one being an olefin and the other an isoparaffin (usually isobutane).
- During World War II, alkylation became the main process for the manufacture of isooctane, a primary component in the blending of aviation gasoline.
- Two alkylation processes employed in the industry are based upon different acid systems as catalysts.
- In sulfuric acid alkylation, concentrated sulfuric acid of 98 percent purity serves as the catalyst for a reaction that is carried out at 2 to 7 °C (35 to 45 °F).
- Refrigeration is necessary because of the heat generated by the reaction. The octane numbers of the alkylates produced range from 85 to 95.
- Hydrofluoric acid is also used as a catalyst for many alkylation units.
- The chemical reactions are similar to those in the sulfuric acid process, but it is possible to use higher temperatures (between 24 and 46 °C, or 75 to 115 °F), thus avoiding the need for refrigeration.
- Recovery of hydrofluoric acid is accomplished by distillation.

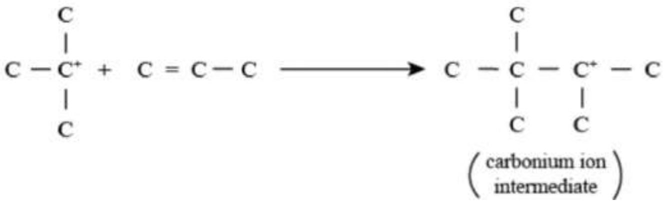
Reaction Mechanism

There are three basic reaction steps to achieve alkylation.

- **Step 1** involving Carbonium ion formation: In this reaction, alkene reacts with a proton (acid catalyst) to produce a proton substituted olefin. The proton substituted olefin reacts with isoparaffin to generate a reactive carbonium ion and alkane.



- **Step 2** involving carbonium ion intermediate formation: In this reaction, the carbonium ion formed in step 1 reacts with the olefin to produce an intermediate carbonium ion.



- **Step 3** involving regeneration of carbonium ion: In this reaction, the intermediate carbonium ion reacts with the isoparaffin to produce alkylate product and carbonium ion. Thus carbonium ion is again regenerated to take part in step 2 reactions along with other additional unreacted olefin molecules.

Reaction conditions –

1. To avoid olefin polymerization, high isobutane to olefin ratios are used.
2. Typical isobutene to olefin ratios are 5:1 to 15:1
3. Acid catalysts are used. Primarily sulphuric acid (H2SO4) or HF are used.
4. Reaction operating temperature: 10 - 20 oC using H2SO4 and 25 – 40 oC using HF
5. Reaction temperature: 4.4 bar for H2SO4 and 7.8 bar for HF
6. When H2SO4 is used refrigeration is used. - When HF is used, refrigeration is not used.

SULFURIC ACID BASED ALKYLATION PROCESS TECHNOLOGY

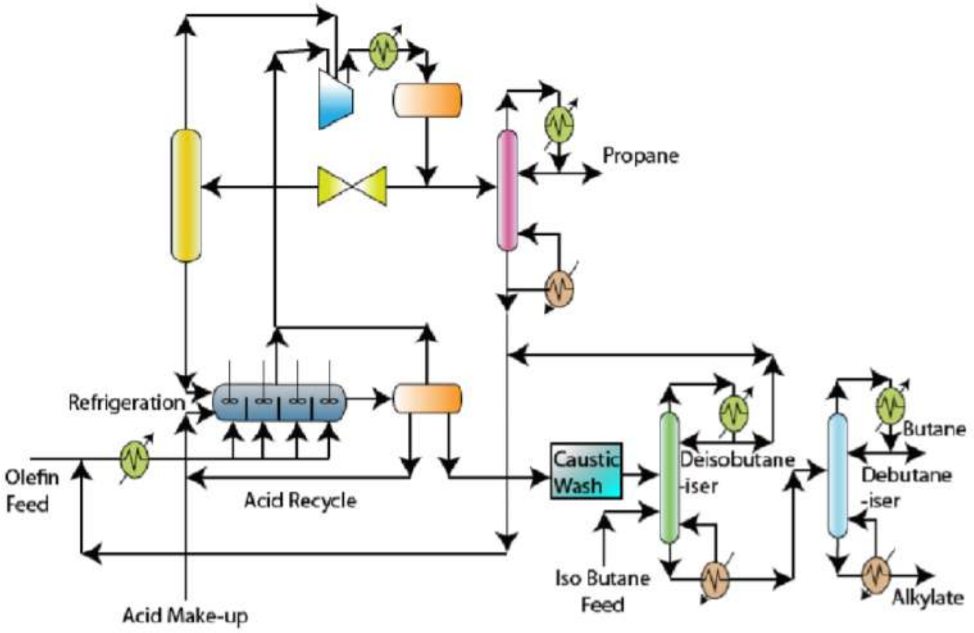


Figure 9.1 Sulphuric Acid Alkylation Unit

- **Caustic wash:** The feed mixture (olefin + C4 compounds) are first subjected to caustic wash. During caustic wash, sulphur compounds are removed and spent caustic is recycled back to the caustic wash. Fresh caustic solution is added to take care of the loss.
- **Refrigeration:** The olefin feed enters a refrigeration unit to reduce the feedstock temperature.
- **Alkylation reactor:** The reactor is arranged as a series of CSTRs with acid fed in the first CSTR and feed supplied to different CSTRs. This arrangement is for maximizing the conversion.
- In the alkylation reactor it is important to note that the olefin is the limiting reactant and isoparaffin is the excess reactant.
- The alkylator unit therefore will have two phases in due course of reaction namely the olefin + isoparaffin mixture which will be lighter and the alkylate stream which will be heavier and will be appearing as a bottom fraction if allowed to settle.
- Since excess isoparaffin is used, the isoparaffin can be easily allowed as a bypass stream.
- Eventually, the alkylate product from the last reactor will be taken out as a heavy stream.
- Thus, the alkylation reactor produces two streams. These are
  (a) isoparaffin rich organic phase and
  (b) alkylate rich phase along with acid and isobutane phases.
- These streams should be subjected to further purification.

- **Phase separator**: It so happens that the acid enters the organic rich stream and will be subjected to phase separation by settling. Similarly, the olefin/isoparaffin mixture will be also separated by gravity settling. Thus the phase separator produces three streams namely

1. olefin + isoparaffin rich phase
2. acid rich stream
3. alkylate rich stream.

- **Olefin + Paraffin processing:** The olefin + paraffin stream is first subjected to compression followed by cooling.
- When this stream is subjected to throttling and phase separation, then the olefin + paraffin rich stream will be generated.
- The propane rich stream from this stream is generated as another stream in the phase separator.
- **Propane defractionator**: The propane rich stream after cooling is fed to a fractionator where propane is separated from the olefin+isoparaffin mixture.
- The olefin+isoparaffin mixture is sent back to mix with the olefin feed.
- Caustic wash for alkylate rich stream: The caustic wash operation ensures to completely eliminate acid concentration from the alkylate.
- **Alkylate fractionation:** The alkylate is fed to a distillation column that is supplied with isobutane feed and alkylate feeds to produce isobutane as a top product and alkylate + butane mixture as a bottom product.
- **Debutanizer:** The debutanizer separates butane and alkylate using the concept of distillation.

UTKALMANI INSTITUTE OF TECHNOLOGY, ROURKELA-4

DEPARTMENT
OF
CHEMICAL ENGINEERING

SUBJECT: PETRO REFINERY&PETROCHEMICAL TECHNOLOGY
COURSE CODE: TH-3

PRESENTED BY: SATARUPA SAHU

Chapter 3-PETROLEUM REFINING

LESSON OBJECTIVE

The topics help the students

- To study the Fundamental of Crude oil distillation system- Operation in Single, Two, Three stages distillation units, Safety, storage and handling of Petrochemical Products. To be acquainted with product from a refinery, temperature range and uses of petroleum products

COURSE OUTCOMES:

1. Classify petroleum refining process and fractionation of crude oil.
2. Explain the Importance of 1st, 2nd, 3rd generation petrochemical, refinery products, their properties and uses.
3. Identify growth and future of petroleum refinery and petrochemical industries in India.

TOPIC TO BE COVERED:

Lecture No	Topics to be covered
Lecture 21	Product from a petroleum refinery
Lecture 22	Temperature range and uses of petroleum products
Lecture 23	Crude oil distillation system- Operation in Single stage distillation units
Lecture 24	Crude oil distillation system- Operation in Two stages distillation units
Lecture 25	Crude oil distillation system- Operation in vacuum distillation column
Lecture 26	Crude oil distillation system- Operation in Atmospheric distillation column
Lecture 27	Crude oil distillation system- Operation in Three stages distillation units
Lecture 28	Crude oil distillation system- Operation in Three stages distillation units
Lecture 29	Flow diagram of an integrated petroleum refinery
Lecture 30	Safety, storage of Petrochemical Products
Lecture 31	Handling of Petrochemical Products
Lecture 32	Overviews of Refineries in India

TOOLS USED:

- Chalk and duster
- K-Yan

MODEL QUESTIONS:

1. Describe the Operation in two and three stages distillation units with a neat diagram.
2. Write down the products obtained from petroleum refinery.
3. Write down the temperature range and uses of petroleum products.
4. Describe the Safety, storage of Petrochemical Products.

ASSESSMENT METHODS APPLIED:

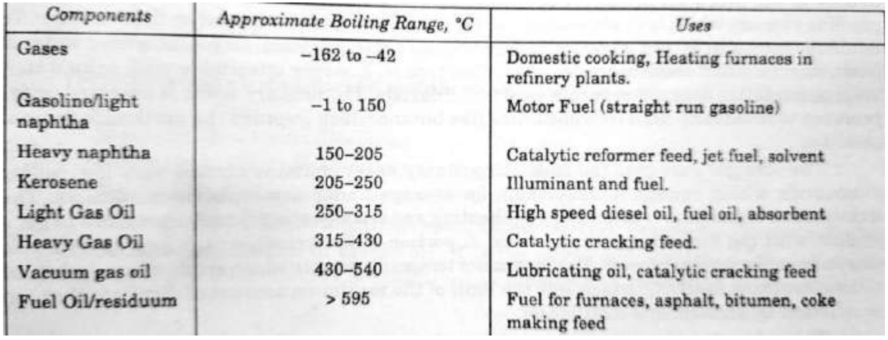
- Class quiz
- Assignment

REFERENCES:

- Modern Petroleum Refining Process by B K B Rao, Oxford IBH Publication
- Petroleum Refining Technology by Dr. Ram Prasad, Khanna Publications

Crude Oil Distillation

- Crude oil consists of a complex mixture of hydrocarbons widely differing in boiling points.
- Distillation is done to separate the crude oil into the basis fractions like motor gasoline, kerosene, gas oil, fuel oil.
- The order in which these components emerge as crude oil is distilled is given in the Table.
- The proportions of these fractions vary considerably with the source of crude oil but each fractions is identified by its boiling range.



Components	Approximate Boiling Range, °C	Uses
Gases	−162 to −42	Domestic cooking, Heating furnaces in refinery plants.
Gasoline/light naphtha	−1 to 150	Motor Fuel (straight run gasoline)
Heavy naphtha	150–205	Catalytic reformer feed, jet fuel, solvent
Kerosene	205–250	Illuminant and fuel.
Light Gas Oil	250–315	High speed diesel oil, fuel oil, absorbent
Heavy Gas Oil	315–430	Catalytic cracking feed.
Vacuum gas oil	430–540	Lubricating oil, catalytic cracking feed
Fuel Oil/residuum	> 595	Fuel for furnaces, asphalt, bitumen, coke making feed

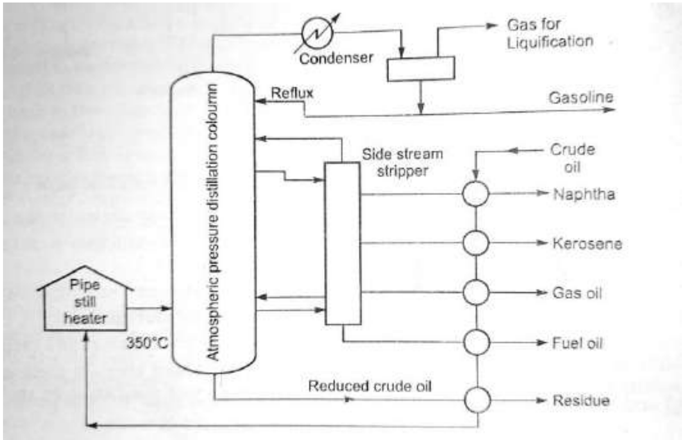
Crude oil distillation:

- The crude oil is pumped from tanker to crude oil tank where it is allowed to settle and water is drained off. As water is highly objectionable, because it increases the pressure suddenly and deposits salts on equipment.
- The crude oil is pumped from tank to primary column of the distillation column by centrifugal pumps.
- The pressure at the discharge of these pumps is maintained high enough to force the crude oil through preheat exchangers and a preheat furnace before it enters the column.
- All oil streams from the primary column like kerosene, gas oil and residue are at high temperature and their heat is transferred to the incoming crude oil in heat exchangers.
- Bulk of the heat to the crude oil is given by oil/gas burned in tube still heaters.
    - ➢ Each heater has a convection section in which oil is gradually heated by fuel gas.
    - ➢ Radiant section where tubes are exposed to radiant heat and oil is brought up to the desired temperature.
- The air for combustion in still heater is provided by blower.
- The heater outlet temperature is varied by varying the oil/ gas burnt as fuel.
- The crude oil partly vaporized enters the primary tower which is a fractionating tower with plates.
- The lighter components such as gasoline and gas rise to the top are condensed in overhead condenser and flow into an accumulator.
- The heavier components such as gas oil, and residue falls to the bottom of the column.
- In order to provide sufficient liquid flow down the column, a part of the condensed liquid from the overhead accumulator is pumped back to the column as reflux.
- Within certain limits, greater the reflux, better is the quantity of overhead product.
- The straight run gasoline from the primary tower contains certain very low boiling compounds which render it unsuitable for storage under atmospheric conditions.
- The stabilization of gasoline is effected by preheating and fractionating it under pressure to get a product with the desired vapour pressure.
- A portion of the kerosene is drawn off as a side stream from the primary tower.

- The maximum temperature up to which crude oil can be heated without cracking is 400C, which sets the limit of the maximum amount of distillate that can be collected by atmospheric distillation.
- The reduced crude at the bottom of the primary tower consists of kerosene, gas oils and residue.
- It is pumped through a furnace into the secondary tower.
- The components of reduced crude are all high boiling materials and would require very high temperature to vaporize them.
- High temperature will destroy the quality of oil by cracking it and will prove very corrosive to the material of the tower itself.
- The boiling points are therefore lowered by applying a vacuum to the tower by the use of steam jet ejectors, operation at a pressure of 300 mm. Hg absolute lowers boiling points well enough to vaporize all the oils with a heater outlet temperature of approximately 320C.
- Kerosene and light & heavy gas oils are drawn off as side streams.
- The last two liquids still contain some low boiling material which lower the flash point and render them unsafe for storage.
- They are led into columns called strippers where steam or oil heat is applied to drive away the light material.
- Steam reduces the partial pressure of oil vapour and causes the low boiling components to be driven off.
- The residue from the secondary tower is pumped away to storage or to the feed preparation unit where it is split into asphalt for bitumen manufacture and waxy distillate for catalytic cracker feed.

Single stage atmospheric distillation unit:

- A single-stage crude unit is shown in Figure. The crude feed is preheated by the outgoing streams and then enters a direct fired furnace-type heater (pipe still).
- The materials separate in the distillation column according to their boiling points, the lowest-boiling fraction leaving at the top of the column.

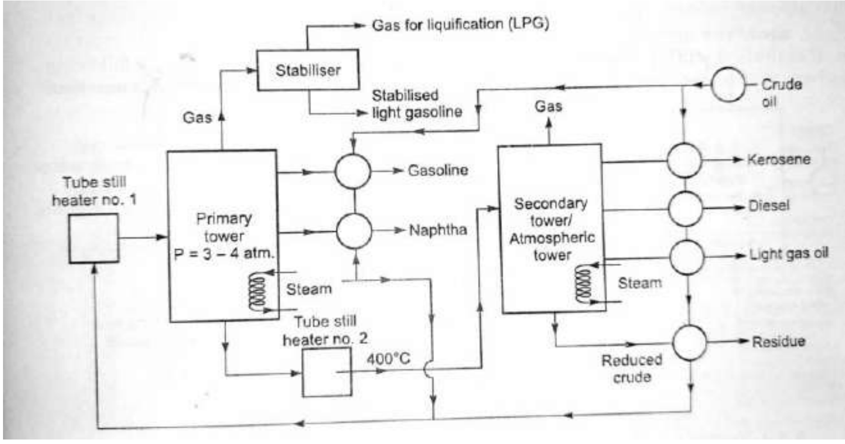


- Desired products may be withdrawn as side-streams at appropriate points on the column.
- The side-streams are further fractionated in small columns called strippers.
- Here, steam is used to free the cut from its more volatile components so that the initial boiling point of the products can be adjusted to its desired value. It is also called straight run distillation of crude oil.
- Typical yield (weight %) from atmospheric distillation of crude oil is (gas +LPG + losses)
- = 2 to 3%, (gasoline + naphtha) C5- 145°C = 8 to 15%, Kerosene (145 - 250°C) = 15 to 20%,
- High speed diesel oil (270-370°C) = 20 to 35%, reduced crude (> 370°C) = 30 to 45%.

- However capacity of single stage distillation unit for processing crude is limited which calls for addition of pressure units.
- Moreover, high boiling point products can not be separated as operating it at higher temperature may result in cracking of products.
- Therefore vacuum units are added to get the high boiling point products vaporised and separated at lower temperature.
- This is also called crude topping or atmospheric distillation of crude as the pressure in the distillation column is slightly above atmospheric.

Two stage distillation unit:

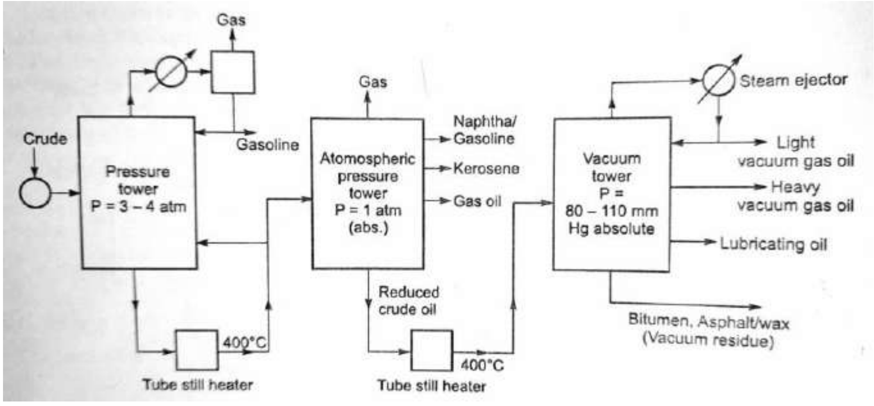
- This scheme of distillation includes a primary tower which operates at about 3-4 atmospheric pressure and a secondary tower operating at atmospheric pressure together with stabiliser.
- This scheme is used when crude is to be separated into six to ten narrow cuts (i.e. products with very close and overlapping boiling points).



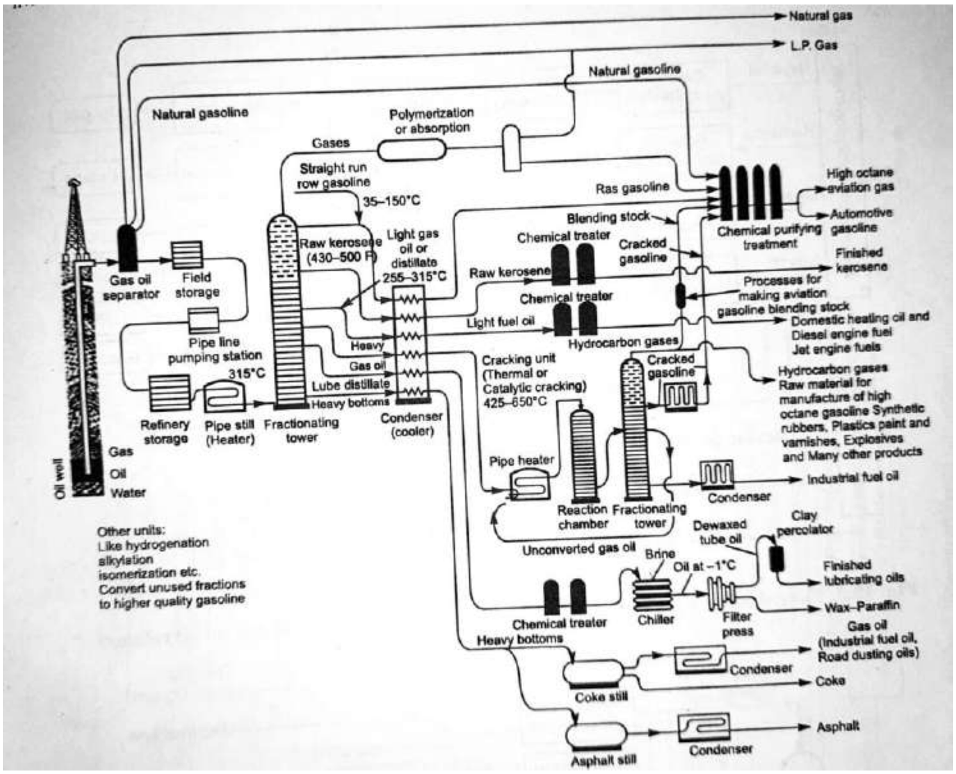
- Two/three side-streams (e.g. gasoline, naphtha) are withdrawn from primary tower while the overhead (gas) product becomes feed to stabiliser.
- Primary tower bottoms becomes the feed for secondary tower from which side-streams like kerosene, diesel, gas oil etc. are withdrawn at appropriate points after passing through strippers to remove the light components.

Three stage distillation unit:

- This system comprises of all the three i.e. pressure, atmosphere and vacuum tower.
- Because some products of crude are having very high boiling temperature or heat sensitive so that they can not be distilled at atmospheric pressure.
- Since boiling point is reduced as the pressure is lowered (i.e. vacuum is created), such materials are distilled under vacuum.
- Vacuum distillation is used for the production of lubricating oils, asphalts and feed to catalytic cracking unit (i.e. heavy gas oil).



- Hence, a vacuum tower is added to a two stage distillation unit for the production of above products thus making it a three stage unit.
- Light vacuum gas oil (LVGO) is a blending component for light diesel oil (LDO) and a feedstock for catalytic cracker/hydrocracker.
- Heavy vacuum gas oil (HVGO) is a feedstock for visbreaker and catalytic cracker/hydrocracker.
- Vacuum residue is used for bitumen production as well as is a feed component for visbreaker.
- The residue from the atmospheric tower is fed at about 425C to the vacuum tower, where pressure is maintained at 80-110 mm Hg absolute.
- The overhead gas oil fraction is removed and the side streams are withdrawn through strippers.
- The bottom product is tar or asphalt.
- Vacuum distillation units are similar to atmospheric crude distillation unit except that their diameter is larger due to larger crude vapor volumes at lower pressure (vacuum).
- 10 metre diameter vacuum columns are in operation, steam jet ejector or barometric condensers are used for maintaining desired vacuum in the vacuum tower.
- Pressurised units can handle larger throughput of crude though the pumping cost will be higher and cost of material of construction will be more.



STORAGE AND HANDING OF PETROLEUM PRODUCTS

FUEL STORAGE TANK

- Low flash point liquid fuels are stored in tanks fitted with roofs which float on the surface of the liquid and those having flash points well above room temperature (eg. Kerosene) are stored in tanks provided with fixed conical shape roofs.
- Fuel oil is stored in the storage tank erected above the ground when the capacity exceeds 70000 liters. For lower capacities, underground storage tanks are economical.
- Storage tanks are normally made of welded mild steel plates with a height to diameter ratio of about 1.5. The overhead tank is mounted on concrete blocks which provide a slight gradient of 1: 50 towards the drain valves.
- All fuel oils contain water which settles to the bottom of the tank and should be removed through a drain cock. The elimination of any air space above the fuels reduces fire hazards and evaporation losses.
- The vent pipe (gooseneck type) is located at the highest point of the storage tank to facilitate filing by venting air and oil vapor during liquid fuels filling operation.
- It should be about 5 cms in diameter and provided with a strainer at the outlet. The oil filling pipe can be located either at the top or at the bottom of the tank.
- When located at the top, the pipe must descend to the bottom of the tank to avoid free fall of oil from the top on the oil surface during tank filling causing frictional/ impact heat generation.
- The drain at the lower end bottom is used periodically to remove the accumulated water pipe located at the lower end bottom is used periodically to remove the accumulated water.
- Vertically cylindrical tanks up to 2.5 metre diameter may be erected direct on to a reinforced concrete foundation with the base having bitumen seal to prevent entry of water between tank bottom and concrete.
- One manhole at the top should be provided for tank up to 3.5 metre height. An additional manhole at the bottom should be provided if the tank height is more than 3.5 metres.
- Brass dip stick should be used to measure the tank level. Alternatively, float or remote reading gauges can be employed. Glass level indicator should not be used for level measurement in the tank.
- Oil draw off level should be above the oil heater mat and always >7.5 cms above the bottom.
- Water accumulated at the bottom of the tank should be drained regularly, otherwise it carried to the burner with oil will cause sputtering of flame and possible flame failure.
- Water should be drained from main storage tank once every 15 days and from service tank once every 7 days as fuel oil contains up to 1% water which accelerates the sludge formation.

STORAGE TANK HEATING

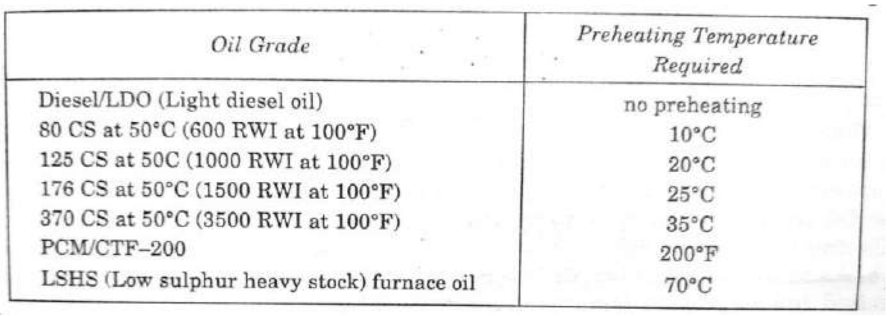
- Heating of liquid fuels in storage tank is done usually by low pressure steam coils (called mat heater) located as low as possible in the tank preferably below the level of the off take.
- Hot water heater or electrical heaters are also used which are economical for small tanks.
- Normally, lagging/insulation of these tanks is not necessary.
- Hot oil pipelines are lagged with electrical or steam tracer lines within the lagging to balance the heat loss from the pipes through the lagging.
- Temperature of the liquid fuels in storage tank should be so maintained that it will have a viscosity of about 1000 seconds (Redwood No. I).

Pumps used for oil pumping:

- The pumps used for pumping oil are normally of following three types

1. bucket type
2. reciprocating pumps
3. gear/screw type rotary pumps

- If driven by electric motors, it should be ensured that all electrical insulations are sound and no loose connections are made.



Oil Grade	*Preheating Temperature Required*
Diesel/LDO (Light diesel oil)	no preheating
80 CS at 50°C (600 RWI at 100°F)	10°C
125 CS at 50C (1000 RWI at 100°F)	20°C
176 CS at 50°C (1500 RWI at 100°F)	25°C
370 CS at 50°C (3500 RWI at 100°F)	35°C
PCM/CTF–200	200°F
LSHS (Low sulphur heavy stock) furnace oil	70°C

- The safe current carrying capacity for each pump motor should be noted. High viscosity of oil means more load on motor and high pressure drop of oil.
- Hence, correct pumping temperature of the oil is very important.
- The preheating of heavier fuels before pumping and before atomisation should be only upto the temperature required by the viscosity consideration for easy pumping and without excessive pressure drop.

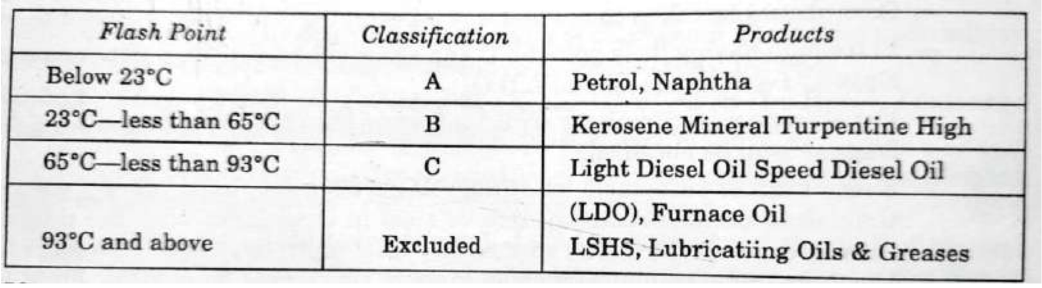
All petroleum oil storage installations should conform to the following Petroleum Rules which is statutory/safety requirement.

- The storage tank shall be electrically connected with the earth in an efficient manner by means of not less than two separate and distinct connections placed at opposite extremities of the tank.
- Every oil installation should be surrounded by a wall at least 2 metres in height.
- Storage capacity and flash point are to be written on the body of the tank.
- Provisions of firefighting equipment and adequate supply of dry sand in buckets with necessary implements for its convenient application in extinguishing petroleum fires should be made.
- The ground in the interior of the installation and protected area surrounding the storage tank should be kept clean and free from all inflammable materials and rubbish.
- Care should be taken to prevent any oil escaping into drain, sewer or public road.
- Petroleum having flash point 65° C and above but below 93°C comes under petroleum class C i.e. (Furnace oil and L.D.O.)
- For storage capacity above 45 K.L., license from the Chief Inspector of Explosives, Nagpur is to be obtained.
- Every tank or receptacle for storage of petroleum is bulk (other than a well-head tank shall be constructed of iron or steel in accordance with the relevant Indian standards or specifications approved by chief controler as per petroleum rules 1976. However underground petroleum storage tanks may be made of Fibre Reinforced Plastics (PRP) also.
- When two or more tanks are installed in one enclosure, the total capacity of the tanks in the enclosure shall not exceed 60,000 KL in case of fixed roof tanks and 1,20,000 KL in case of floating root tanks. A combination of fixed and floating head tanks can also be located in the same enclosure/premises but the total capacity should not exceed 60,000 KL.
- Height of storage tank should not exceed 1.5 times its diameter or 20 m whichever is less.

- An air space of not less 5% of the total storage capacity shall be considered while designing oil storage tank.
- All petroleum storage tanks installed above or below the ground shall be protected against Corrosion by the use of protective coating and cathodic protection.
- Cost iron valves are not permitted in oil installations.
- Tanks after erection or repair will be tested with clean water.
- All storage and handling facility shall maintain the specified distance from any other facility nearby.
- No fire water/ foam ring main shall pass through dyked enclosure.
- Tanks shall be arranged in maximum two rows so that each tank is approachable from the road/area surrounding the enclosure. However, tank having capacity of 50000 m³ and above shall be laid in a single row.
- Piping from/to any tank located in a single dyked enclosure should not pass through any other dyked enclosure. Piping within the dyked enclosure should be minimized.
- Any tank having a diameter of more than 30 metres should be separated with firewalls from other tanks.
- The minimum distance between a tank shell and inside of the dyke wall shall not be less than half of the tank diameter.
- Firewalls should be constructed by limiting the aggregate capacity of each group of tanks within 20000 m³.

Explosive Regulations on Storage of Petroleum Products:

- If any two classes of petroleum are stored together, the storage rules applicable for more dangerous product between the two shall be applicable i.e if furnace oil and LSHS are stored adjacent to each other, even the storage of LSHS which is normally excluded from the purview of the Explosive Regulations should conform to those applicable to furnace oil. The whole installation in such card will be deemed to be that of furnace oil alone.



Flash Point	*Classification*	*Products*
Below 23°C	A	Petrol, Naphtha
23°C—less than 65°C	B	Kerosene Mineral Turpentine High
65°C—less than 93°C	C	Light Diesel Oil Speed Diesel Oil
93°C and above	Excluded	(LDO), Furnace Oil LSHS, Lubricatiing Oils & Greases

- If LSHS alone is being stored in the premises, any amount of it could be stored without either the approval or a license from the Dept. of Explosives since it falls under exempted category.

UTKALMANI INSTITUTE OF TECHNOLOGY, ROURKELA-4

DEPARTMENT
OF
CHEMICAL ENGINEERING

SUBJECT: PETRO REFINERY&PETROCHEMICAL TECHNOLOGY
COURSE CODE: TH-3

PRESENTED BY: SATARUPA SAHU

Chapter 4- CHEMICAL FEED STOCK-FIRST GENERATION PETROCHEMICALS

LESSON OBJECTIVE

The topics help the students

- To understand the growth and history of Petrochemical industries globally and in India, petrochemical feed stock-category, composition, sources.
- To understand the manufacturing of Steam reforming of naphtha, cyclohexane.

COURSE OUTCOMES:

1. Classify petroleum refining process and fractionation of crude oil.
2. Explain the Importance of 1st, 2nd, 3rd generation petrochemical, refinery products, their properties and uses.
3. Identify growth and future of petroleum refinery and petrochemical industries in India.

TOPIC TO BE COVERED:

Lecture No	Topics to be covered
Lecture 33	History of Petrochemical industries globally and in India
Lecture 34	Growth of Petrochemical industries globally and in India
Lecture 35	Petrochemical feed stock- category
Lecture 36	Petrochemical feed stock- composition
Lecture 37	Petrochemical feed stock- source
Lecture 38	Process flow-sheet of Steam reforming of naphtha
Lecture 39	Process description of Steam reforming of naphtha
Lecture 40	Process flow-sheet of Separation of C4 cuts from naphtha crackers
Lecture 41	Process description of Separation of C4 cuts from naphtha crackers
Lecture 42	Industrial method of cyclohexane manufacturing

TOOLS USED:

- Chalk and duster
- K-Yan

MODEL QUESTIONS:

1. Describe the steam reforming of naphtha with a neat diagram.
2. Write down the petrochemical feed stock- category, composition and source.
3. Write down the history of Petrochemical industries globally and in India.
4. Describe the industrial method of cyclohexane manufacturing.

ASSESSMENT METHODS APPLIED:

- Class quiz
- Assignment

REFERENCES:

- Modern Petroleum Refining Process by B K B Rao, Oxford IBH Publication
- Petroleum Refining Technology by Dr. Ram Prasad, Khanna Publications

HISTORY AND GROWTH OF PETROCHEMICAL INDUSTRIES IN INDIA

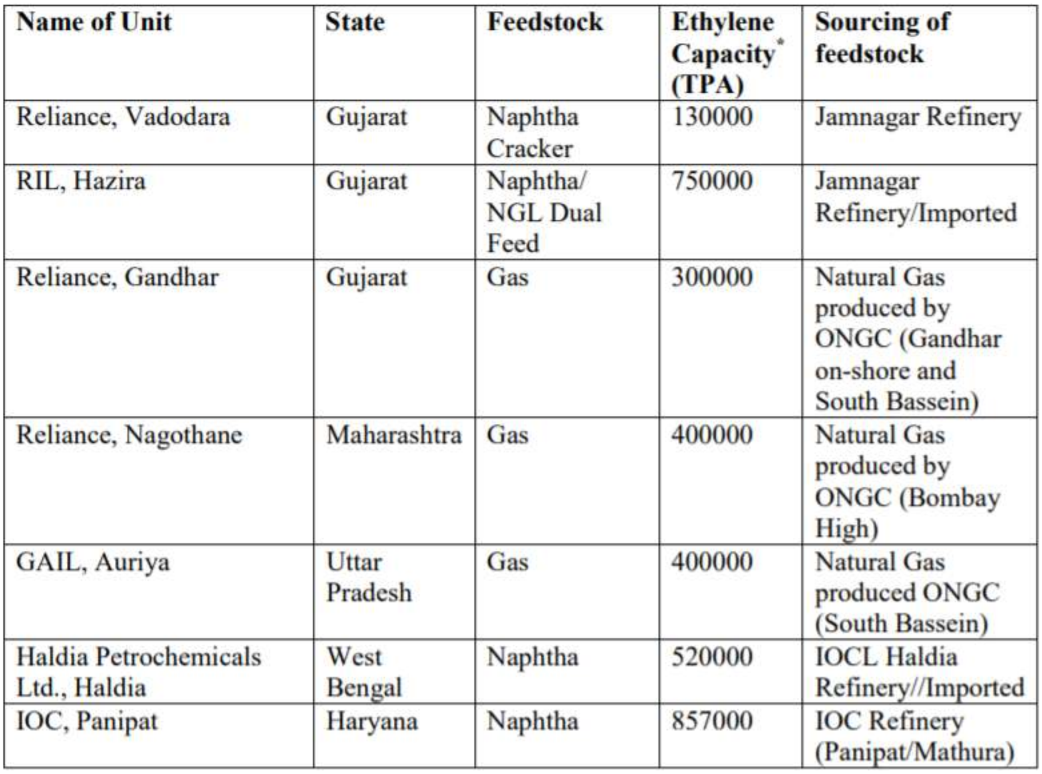
- The first petrochemical plant in India was set up by the Union Carbide India Ltd. at Trombay in 1966.
- The Indian Petrochemicals Corporation Ltd. (IPCL) was the first public sector plant to be located at Jawaharnagar (near Vadodara) in Gujarat. It started its production in 1973.
- Petrochemical industry mainly comprise of synthetic fibre / yarn, polymers, Synthetic Rubber (elastomers), Synthetic detergent intermediates, performance plastics and plastic processing industry.
- Today, petrochemical products permeate the entire spectrum of daily use items and cover almost every sphere of life like clothing, housing, construction, furniture, automobiles, household items, agriculture, horticulture, irrigation, packaging, medical appliances, electronics and electrical etc.
- Presently there are eleven naphtha and/or/dual feed cracker complexes in operation with combined ethylene capacity of about 7.05 million tonnes per annum. In addition, there are six aromatic complexes in operation with a combined Xylene capacity of about 5.5 million tonnes.
- The Indian basic petrochemicals market (including end products market which includes polymers, synthetic fibers, elastomers and surfactants) the total petrochemical market has grown at a CAGR of 11% from USD 19.3 billion in FY11 to USD 24 billion in FY13.
- The total installed capacity of major basic petrochemicals (ethylene, propylene, butadiene, styrene, benzene & toluene) in FY13 is 12.2 million metric tons per annum (mmtpa) against the total demand of12.5 mmtpa .
- In FY12, there was a surplus capacity of ~1 mmtpa, but in the last two years overall demand has crossed the installed capacity. Imports have grown at a CAGR of 17% between FY09 and FY13, whereas the exports have grown at a higher rate of 19% in the same period.
- The chemical and the petrochemical sectors together constitute around 14 percent of domestic industrial activity.
- The Indian petrochemical industry constitutes around 40 per cent of chemical sector output. According to an ASSOCHAM study, the Indian petrochemical industry, valued at $40 billion, in 2012 is expected to grow at 12-15 per cent annually over the next five years.
- At present there are three naphtha1 based, three gas based and one mixed feed cracker complexes in the country with a combined annual ethylene capacity of 3.3 MMT.
- The major players in Indian petrochemicals industry are Reliance Industries Limited, Haldia Petrochemicals and GAIL (India) Limited.
- With the commissioning of their petrochemical complex last year at Panipat, Indian Oil Corporation has also emerged as another major player.
- The location of petrochemical units is given in Table 1 along with the feedstock used.
- As is apparent from Table 1, the major feedstock used in Indian petrochemical units is naphtha and natural gas (propane and butane).
- The major intermediate products produced in the country are ethylene, propylene, butadiene, benzene, toluene and xylene.

HISTORY AND GROWTH OF PETROCHEMICAL INDUSTRIES GLOBALLY

- In 1835, Henri Victor Regnault, a French chemist left vinyl chloride in the sun and found white solid at the bottom of the flask which was polyvinyl chloride.
- In 1839, Eduard Simon discovered polystyrene by accident by distilling storax. In 1856, William Henry Perkin discovered the first synthetic dye, Mauveine.
- In 1888, Friedrich Reinitzer, an Austrian plant scientist observed cholesteryl benzoate had two different melting points.
- In 1909, Leo Hendrik Baekeland invented bakelite made from phenol and formaldehyde. In 1928, synthetic fuels were invented using Fischer-Tropsch process.
- In 1929, Walter Bock invented synthetic rubber Buna-S which is made up of styrene and butadiene and used to make car tires.

- In 1933, Otto Röhm polymerized the first acrylic glass methyl methacrylate. In 1935, Michael Perrin invented polyethylene.
- In 1937, Wallace Hume Carothers invented nylon. In 1938, Otto Bayer invented polyurethane. In 1941, Roy Plunkett invented Teflon.

Table 1: Existing Naphtha / Gas Cracker (2011)



Name of Unit	State	Feedstock	Ethylene Capacity* (TPA)	Sourcing of feedstock
Reliance, Vadodara	Gujarat	Naphtha Cracker	130000	Jamnagar Refinery
RIL, Hazira	Gujarat	Naphtha/ NGL Dual Feed	750000	Jamnagar Refinery/Imported
Reliance, Gandhar	Gujarat	Gas	300000	Natural Gas produced by ONGC (Gandhar on-shore and South Bassein)
Reliance, Nagothane	Maharashtra	Gas	400000	Natural Gas produced by ONGC (Bombay High)
GAIL, Auriya	Uttar Pradesh	Gas	400000	Natural Gas produced ONGC (South Bassein)
Haldia Petrochemicals Ltd., Haldia	West Bengal	Naphtha	520000	IOCL Haldia Refinery//Imported
IOC, Panipat	Haryana	Naphtha	857000	IOC Refinery (Panipat/Mathura)

- In 1946, he invented Polyester. Polyethylene terephthalate (PET) bottles are made from ethylene and paraxylene.
- The two most common petrochemical classes are olefins (including ethylene and propylene) and aromatics (including benzene, toluene and xylene isomers).
- Global ethylene production was 190 million tonnes and propylene was 120 million tonnes in 2019. Aromatics production is approximately 70 million tonnes.
- The largest petrochemical industries are located in the USA and Western Europe; however, major growth in new production capacity is in the Middle East and Asia. There is substantial inter-regional petrochemical trade.

PETROCHEMICAL FEED STOCK- CATEGORY, COMPOSITION AND SOURCE

Primary petrochemicals are divided into three groups depending on their chemical structure:

Olefins:

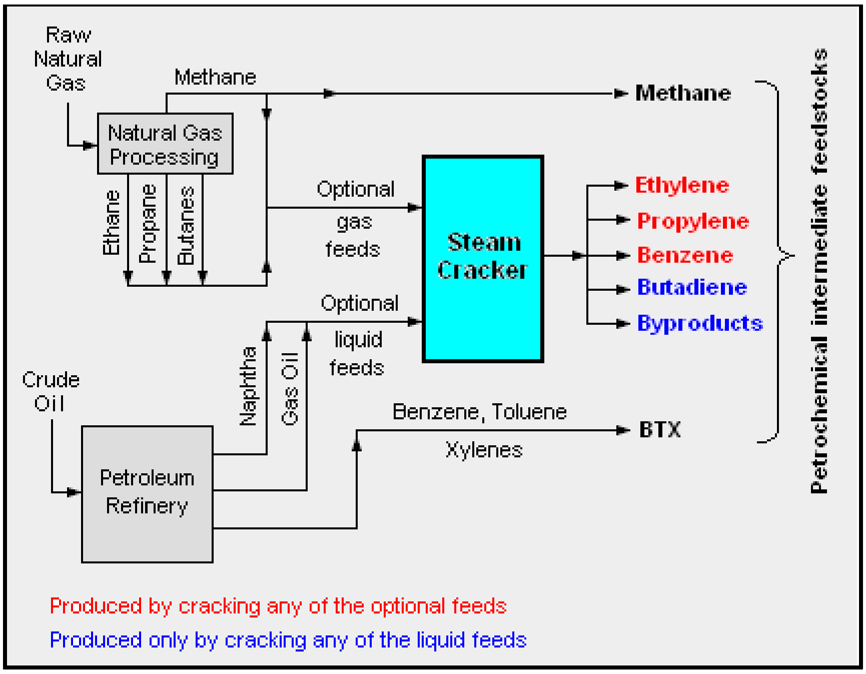
- **It** includes ethene, propene, butenes and butadiene.
- Ethylene and propylene are important sources of industrial chemicals and plastics products. Butadiene is used in making synthetic rubber.

Aromatics

- **It** includes benzene, toluene and xylenes, as a whole referred to as BTX and primarily obtained from petroleum refineries by extraction from the reformate produced in catalytic reformers using naphtha obtained from petroleum refineries.
- Alternatively, BTX can be produced by aromatization of alkanes.
- Benzene is a raw material for dyes and synthetic detergents, and benzene and toluene for isocyanates MDI and TDI used in making polyurethanes.
- Manufacturers use xylenes to produce plastics and synthetic fibers.

Synthesis gas

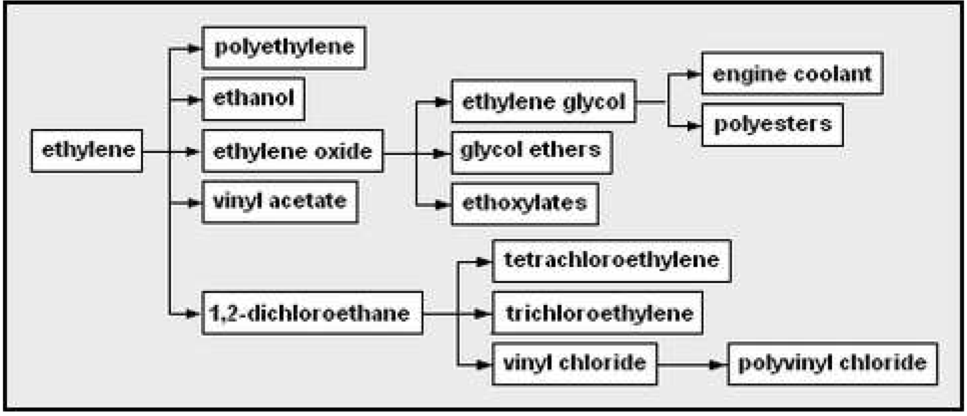
- It is a mixture of carbon monoxide and hydrogen used to make ammonia and methanol.
- Ammonia is used to make the fertilizer urea and methanol is used as a solvent and chemical intermediate.
- Steam crackers are not to be confused with steam reforming plants used to produce hydrogen and ammonia.



Petrochemical Feed Stock

Olefins

The following is a partial list of major commercial petrochemicals and their derivatives:



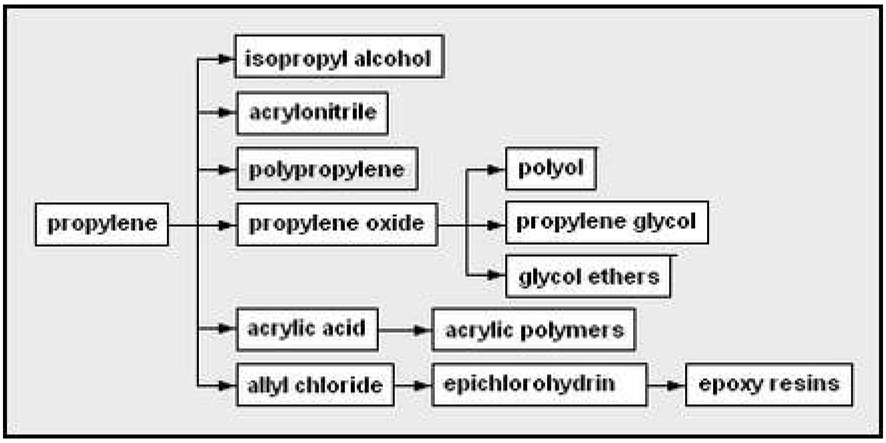
Chemicals produced from ethylene

- **Ethylene** – the simplest olefin; used as a chemical feedstock and ripening stimulant
    - polyethylene – polymerized ethylene; LDPE, HDPE, LLDPE
    - ethanol – via ethylene hydration (chemical reaction adding water) of ethylene
    - ethylene oxide – via ethylene oxidation
    - ethylene glycol – via ethylene oxide hydration
        - ➢ engine coolant – ethylene glycol, water and inhibitor mixture
        - ➢ polyesters – any of several polymers with ester linkages in the main chain
    - glycol ethers – via glycol condescension
    - ethoxylates
    - vinyl acetate: 1,2-dichloroethane
    - trichloroethylene

        - tetrachloroethylene – also called perchloroethylene; used as a dry cleaning solvent and degreaser
        - vinyl chloride – monomer for polyvinyl chloride
        - polyvinyl chloride (PVC) – a type of plastic used for piping, tubing, other things

Propylene – used as a monomer and a chemical feedstock

- isopropyl alcohol – 2-propanol; often used as a solvent or rubbing alcohol
- acrylonitrile – useful as a monomer in forming Orlon, ABS
- polypropylene – polymerized propylene
- propylene oxide
    - ➢ polyether polyol – used in the production of polyurethanes
    - ➢ propylene glycol – used in engine coolant and aircraft deicer fluid
    - ➢ glycol ethers – from the condensation of glycols
- acrylic acid
    - ➢ acrylic polymers
- allyl chloride
    - ➢ epichlorohydrin – chloro-oxirane; used in epoxy resin formation
- epoxy resins – a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine



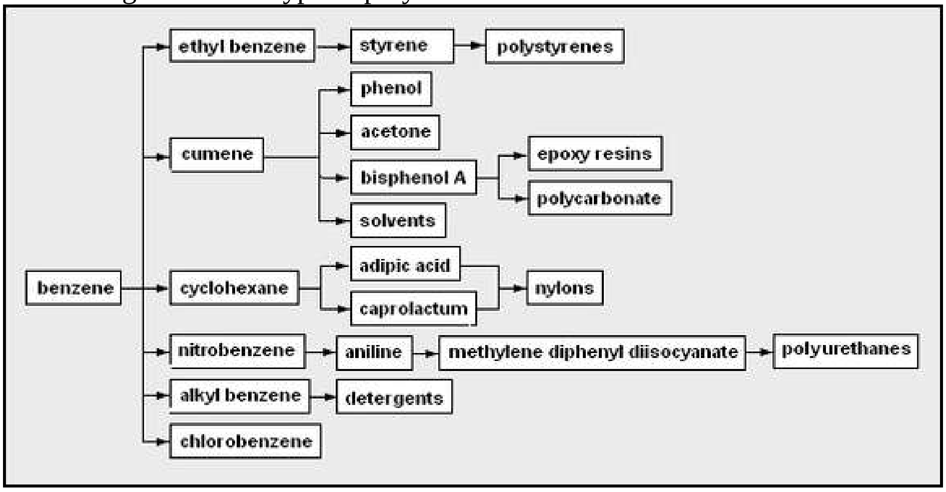
Chemicals produced from propylene

- **Butene**
    - isomers of butylene – useful as monomers or co-monomers
        - ➢ isobutylene – feed for making methyl *tert*-butyl ether (MTBE) or monomer for copolymerization with a low percentage of isoprene to make butyl rubber
    - 1,3-butadiene (or buta-1,3-diene) – a diene often used as a monomer or co-monomer for polymerization to elastomers such as polybutadiene, styrene-butadiene rubber, or a plastic such as acrylonitrile-butadiene-styrene (ABS)
        - ➢ synthetic rubbers – synthetic elastomers made of any one or more of several petrochemical (usually) monomers such as 1,3-butadiene, styrene, isobutylene, isoprene, chloroprene; elastomeric polymers are often made with a high percentage of conjugated diene monomers such as 1,3-butadiene, isoprene, or chloroprene
- **Higher olefins**
    - polyolefins – such poly-alpha-olefins, which are used as lubricants
    - alpha-olefins – used as monomers, co-monomers, and other chemical precursors. For example, a small amount of 1-hexene can be copolymerized with ethylene into a more flexible form of polyethylene.
    - other higher olefins
    - detergent alcohols

Aromatics

- **Benzene** – the simplest aromatic hydrocarbon
    - Ethylbenzene – made from benzene and ethylene
    - styrene – made by dehydrogenation of ethylbenzene; used as a monomer

- polystyrenes – polymers with styrene as a monomer
- cumene – isopropylbenzene; a feedstock in the cumene process
- phenol – hydroxybenzene; often made by the cumene process
- acetone – dimethyl ketone; also often made by the cumene process
- bisphenol A – a type of "double" phenol used in polymerization in epoxy resins and making a common type of polycarbonate

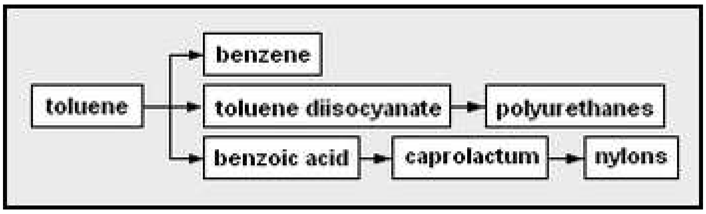


Chemicals produced from benzene

- epoxy resins – a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine
- polycarbonate – a plastic polymer made from bisphenol A and phosgene (carbonyl dichloride)
- solvents – liquids used for dissolving materials; examples often made from petrochemicals include ethanol, isopropyl alcohol, acetone, benzene, toluene, xylenes
- cyclohexane – a 6-carbon aliphatic cyclic hydrocarbon sometimes used as a non-polar solvent
- adipic acid – a 6-carbon dicarboxylic acid, which can be a precursor used as a co-monomer together with a diamine to form an alternating copolymer form of nylon.
- nylons – types of polyamides, some are alternating copolymers formed from copolymerizing dicarboxylic acid or derivatives with diamines
- caprolactam – a 6-carbon cyclic amide
- nylons – types of polyamides, some are from polymerizing caprolactam
- nitrobenzene – can be made by single nitration of benzene
- aniline – aminobenzene
- methylene diphenyl diisocyanate (MDI) – used as a co-monomer with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas
- alkylbenzene – a general type of aromatic hydrocarbon, which can be used as a precursor for a sulfonate surfactant (detergent)
- detergents – often include surfactants types such as alkylbenzene sulfonates and nonylphenol ethoxylates
- chlorobenzene

Toluene – methylbenzene; can be a solvent or precursor for other chemicals

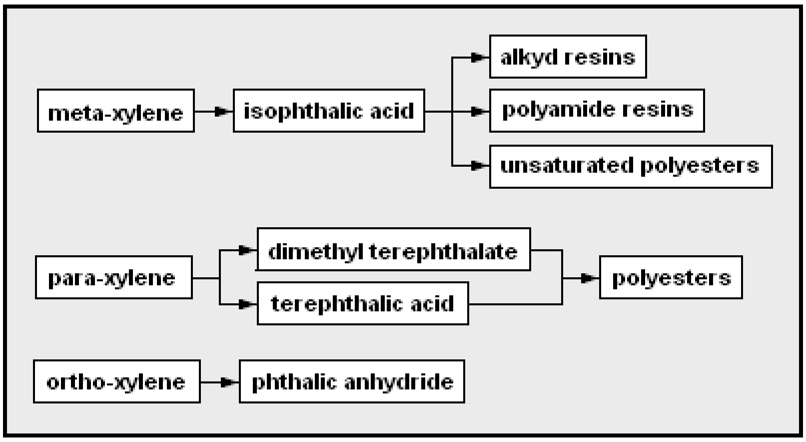
- benzene
- toluene diisocyanate (TDI) – used as co-monomers with polyether polyols to form polyurethanes or with di- or polyamines to form polyureas polyurethanes
- benzoic acid – carboxybenzene
  - caprolactam



Chemicals produced from toluene

Mixed xylenes – any of three dimethylbenzene isomers, could be a solvent but more often precursor chemicals

- *ortho*-xylene – both methyl groups can be oxidized to form (*ortho*-)phthalic acid
  - ➢ phthalic anhydride
- *para*-xylene – both methyl groups can be oxidized to form terephthalic acid
  - ➢ dimethyl terephthalate – can be copolymerized to form certain polyesters
    - ▪ polyesters – although there can be many types, polyethylene terephthalate is made from petrochemical products and is very widely used in petrol stations
  - ➢ purified terephthalic acid – often copolymerized to form polyethylene terephthalate
    - ▪ polyesters
- *meta*-xylene
  - ➢ isophthalic acid
    - ▪ alkyd resins
    - ▪ polyamide resins
    - ▪ unsaturated polyesters



Chemicals produced from xylenes

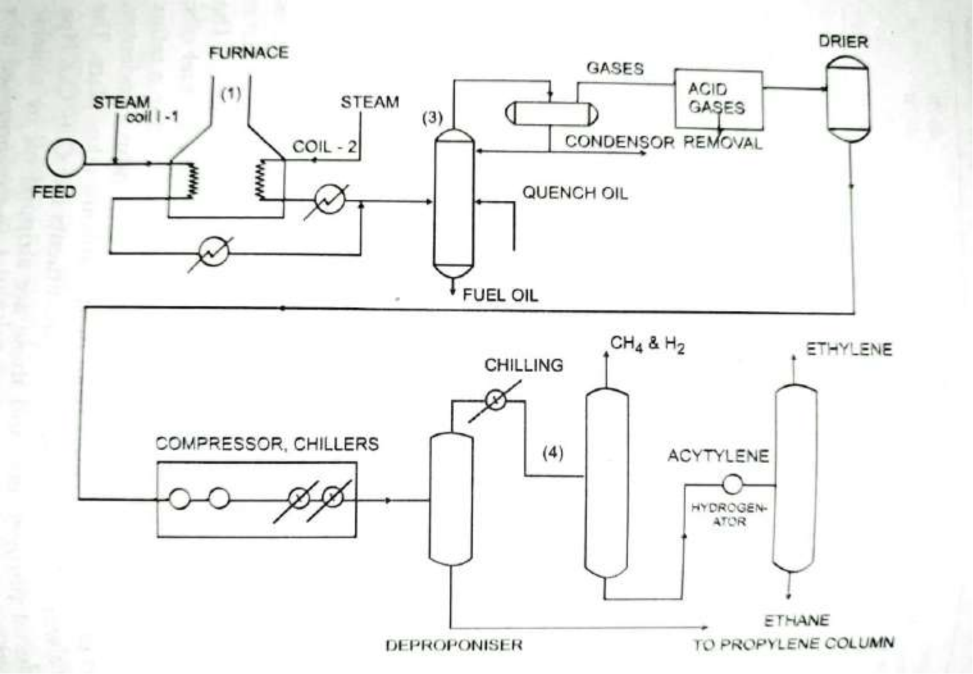
STEAM CRACKING OF NAPHTHA

- In almost all parts of the world, naphtha cracking is appropriated to produce olefins, mainly ethylene and propylene.
- In fact any petroleum stock is suitable and is in a position to replace naphtha, which is preferentially reserved for steam reforming process.
- Alternatively olefins and diolefins can be produced by dehydrogenation of paraffins of suitable range.
- As an example, propane and ethane can be cracked/dehydrogenated to yield corresponding olefins as given by the following reactions:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$
$$C_3H_8 \rightarrow C_2H_4 + CH_4$$
$$\rightarrow C_3H_6 + H_2$$
$$C_4H_{10} \rightarrow C_2H_4 + C_2H_6$$
$$\rightarrow C_3H_8 + H_2$$
$$\rightarrow C_4H_6 + 2\,H_2$$

- Dehydrogenation reactions are quite fast, hence it is wise to choose the feed stock (mole, weight) as close as possible to the required olefin.

- For cracking lighter stocks the temperature of cracking has to be increased.
- When ethane and propane are chosen as feed stocks, the following points must be pondered.
  1. Methane: It enjoys a free ride in the reactor hence it increases the burden in the system.
  2. Propane and Butanes: Both produce olefins of same carbon atom range in the beginning; for alkylation and polymer gasoline these can be used comfortably.
  3. Carbon dioxide: This is always present up to 20 ppm in all cracked stocks. It should be removed before the feed is cracked.
  4. Hydrogen Sulfide: Mostly present in all feed stocks; one way it is beneficial, as it inhibits coke formation.
  5. Oxygen: It is a dangerous component as it leads to explosion. Nitrogen and other inerts: No problem.
- Naphtha cracking for olefins is schematically presented in Fig. The hydrocarbon feed stock is preheated and cracked in presence of steam in a tubular furnace (1).
- The furnace is maintained at a high temperature such that the effluents record a temperature of 800 to 850°C as soon as the furnace effluents emerge out of furnace, they are cooled in a transfer line heat exchanger (2), which is set apart for production of high pressure steam (100-120 Kgf/cm^2)



- Still hot, the products are rapidly quenched by showering with feed stock or with circulating oils. Direct quenching with water is also practised in some cases.
- Quenching with oils is done in a pyrolysis fractionator (3) where fractionation is also carried out simultaneously.
- The bottom product of this fractionator shall be heavy oils or fuel oils; mostly polymer products.
- The lighter fractions are cooled in a reflux condenser, at the top of the fractionator. In the reflux condenser, separation of gaseous products from light distillates takes place.
- The gases are always infested with acidic constituents like CO_2, CO, H_2S, SO_2, oxides of nitrogen etc. and these are stripped off by suitable solvents.
- The acid free gases are new cooled and compressed to a pressure of 30 to 40 atmospheres whereby propane and higher components are liquefied.
- The mixture is separated into propane and gases in depropaniser unit.
- The top gases of deproponiser mainly contain un-condensable such as H_2, CH_4, and C_2 fractions.
- Further chilling will liquefy C_2 fractions, from where CH_4 and H_2 steams can be easily driven off, this is done in demetnaniser (4).

- The demethaniser bottoms are given mild hydrogen treatment to convert acetylene, which is always present in cracking operations (max 1%) into ethylene. Ethane-ethylene fractionation is done in a column (5).
- Propane, from deproponiser is again processed for propane, propylene and butane fractions.
- Ethane and propane are again routed through furnace, but through a second coil, operating at much severer conditions than the other coil. The effluents are later joined with the main stream products.
- Proper selection of cracking conditions and rapid quenching achieve high yields of desired olefins, and failure of proper selection results in undesirable coproducts like methane and polymers.

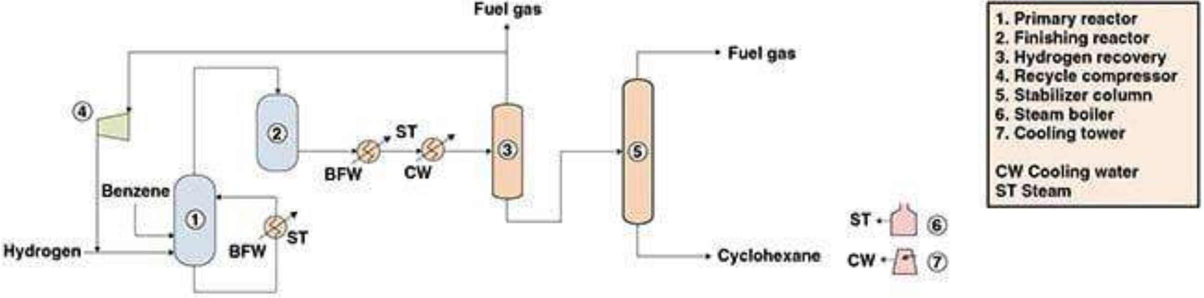
INDUSTRIAL METHOD OF CYCLOHEXANE MANUFACTURING

INTRODUCTION

- Cyclohexane is a relatively stable cycloalkane, present in crude oils in concentrations of 0.1–1.0%.
- This cycloparaffin is a colorless, flammable liquid, widely used as an intermediate in nylon manufacturing.
- On a commercial scale, cyclohexane production is almost entirely based on the catalytic hydrogenation of benzene, which can be conducted in the liquid or vapor phase in the presence of hydrogen.

PROCESS DESCRIPTION

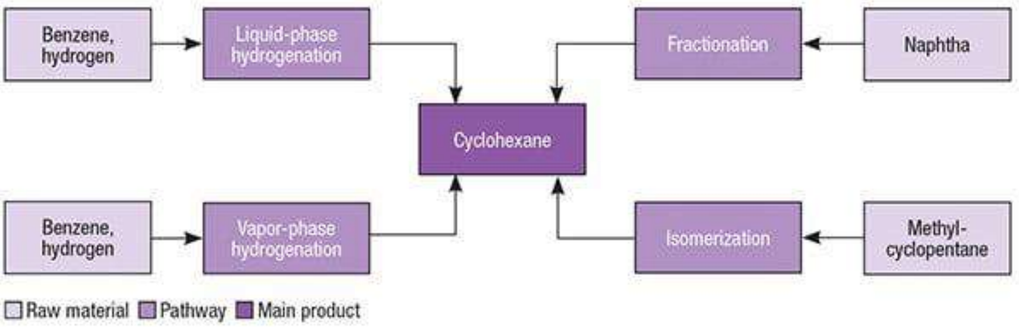
- The process for the production of cyclohexane from benzene and hydrogen involves liquid-phase hydrogenation of benzene in the presence of a nickel-based catalyst. Figure 1 presents a simplified flow diagram of the process.



- ***Reaction:***
  - Initially, benzene is fed to the primary reactor along with fresh and recycled hydrogen.
  - The hydrogenation reaction is carried out in a bubble column reactor, in the presence of a nickel catalyst.
  - The catalyst is maintained in a suspension with the aid of an external circulation loop.
  - Most of the heat of reaction is removed by the vaporization of the product stream, which is further recovered via a top stream within the reactor.
  - The remaining reaction heat is removed in the external loop, by passing the reactor reflux stream through a heat exchanger against boiler feedwater, producing low-pressure steam.
  - Most of the benzene feed is converted in this step. The top gaseous product stream is directed to a fixed-bed reactor, where the remaining benzene content is converted to cyclohexane.
  - The finishing hydrogenation reaction is conducted in the presence of a solid nickel-based catalyst supported on alumina.
- ***Hydrogen recovery:***
  - The product stream is fed to a knock-out drum operated at high pressure.
  - Most of the cyclohexane in the feed condenses, producing two streams: one gaseous hydrogen-rich stream and a liquid cyclohexane-rich stream.
  - The hydrogen stream is routed to the recycle compressor, where it is compressed to the pressure of the primary reactor and recycled.
- ***Purification:***

- In a distillation column, the liquid cyclohexane-rich stream that is recovered is stripped of lighter contaminants, such as methane, ethane and soluble hydrogen.
- Light-ends recovered from column’s top are used for fuel, while a cyclohexane stream with a residual benzene content lower than 100 ppm is obtained from column’s bottom.

- **PRODUCTION PATHWAYS**
  - Cyclohexane has been primarily manufactured by the hydrogenation of benzene, which can be carried out in both liquid and gaseous phases, in the presence of different metal-based catalysts.
  - This chemical may also be obtained from naphtha fractionation, or by isomerization of methyl-cyclopentane.



UTKALMANI INSTITUTE OF TECHNOLOGY, ROURKELA-4

DEPARTMENT
OF
CHEMICAL ENGINEERING

SUBJECT: PETRO REFINERY&PETROCHEMICAL TECHNOLOGY
COURSE CODE: TH-3

PRESENTED BY: SATARUPA SAHU

Chapter 5- SECOND GENERATION PETROCHEMICALS

LESSON OBJECTIVE

The topics help the students

- To study the manufacturing of methanol from synthesis gas, ethanol from synthesis gas, vinyl monomer (vinyl acetate), Polyester monomer (Terephthalic acid), Phthalic Anhydride.

COURSE OUTCOMES:

1. Classify petroleum refining process and fractionation of crude oil.
2. Explain the Importance of 1st, 2nd, 3rd generation petrochemical, refinery products, their properties and uses.
3. Identify growth and future of petroleum refinery and petrochemical industries in India.

TOPIC TO BE COVERED:

Lecture 43	Process flow-diagram for manufacturing of methanol from synthesis gas
Lecture 44	Process description for manufacturing of methanol from synthesis gas
Lecture 45	Manufacturing of ethanol from synthesis gas
Lecture 46	Manufacturing of vinyl monomer(vinyl chloride)
Lecture 47	Manufacturing of vinyl monomer(vinyl acetate)
Lecture 48	Manufacturing of vinyl monomer(Acrylonitrile)
Lecture 49	Manufacturing of Polyester monomer(Terephthalic acid)
Lecture 50	Process flow-diagram for Manufacturing of Phthalic Anhydride
Lecture 51	Process description for Manufacturing of Phthalic Anhydride
Lecture 52	Revision of the chapter

TOOLS USED:

- Chalk and duster
- K-Yan

MODEL QUESTIONS:

1. Describe the manufacturing of methanol from synthesis gas with a neat diagram.
2. Describe the manufacturing of vinyl monomer (vinyl chloride) with flow-sheet.
3. Describe the manufacturing of vinyl monomer (Acrylonitrile) with flow-sheet.
4. Describe the manufacturing of vinyl monomer (vinyl acetate) with flow-sheet.
5. Describe the manufacturing of ethanol from synthesis gas with flow-sheet.

ASSESSMENT METHODS APPLIED:

- Class quiz
- Assignment

REFERENCES:

- Modern Petroleum Refining Process by B K B Rao, Oxford IBH Publication
- Petroleum Refining Technology by Dr. Ram Prasad, Khanna Publications

MANUFACTURE OF METHANOL FROM SYNTHESIS GAS

Introduction - Synthesis gas is $H_2 + CO$

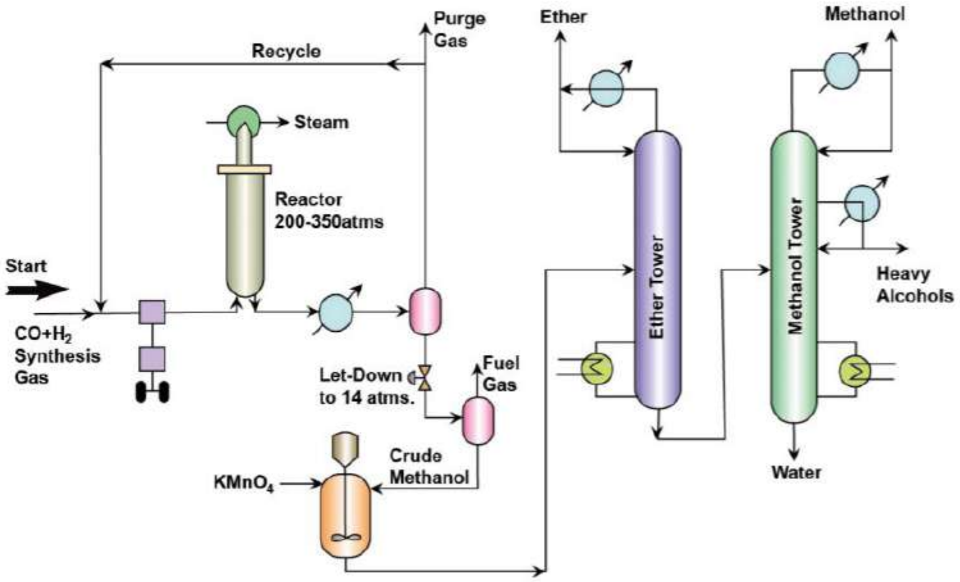
- When synthesis gas is subjected to high pressure and moderate temperature conditions, it converts to methanol.
- Followed by this, the methanol is separated using a series of phase separators and distillation columns.
- The process technology is relatively simple

Reactions

- Desired: $CO + 2H_2 \rightarrow CH_3OH$
- Side reactions: $CO + 3H_2 \rightarrow CH_4 + H_2O$
  $2CO + 2H_2 \rightarrow CH_4 + CO_2$
- All above reactions are exothermic
- Undesired reaction: $zCO + aH_2 \rightarrow$ alchohols + hydrocarbons
- Catalyst: Mixed catalyst made of oxides of Zn, Cr, Mn, Al.

PROCESS DESCRIPTION:

- ✓ H_2 and CO adjusted to molar ratio of 2.25
- ✓ The mixture is compressed to 200 – 350 atms
- ✓ Recycle gas (Unreacted feed) is also mixed and sent to the compressor
- ✓ Then eventually the mixture is fed to a reactor. Steam is circulated in the heating tubes to maintain a temperature of 300 – 375 °C
- ✓ After reaction, the exit gases are cooled
- ✓ After cooling, phase separation is allowed. In this phase separation operation methanol and other high molecular weight compounds enter the liquid phase and unreacted feed is produced as the gas phase.



- ✓ The gas phase stream is purged to remove inert components and most of the gas stream is sent as a recycle to the reactor.
- ✓ The liquid stream is further depressurized to about 14 atms to enter a second phase separator that produces fuel gas as the gaseous product and the liquid stream bereft of the fuel gas components is rich of the methanol component.
- ✓ The liquid stream then enters a mixer fed with $KMnO_4$ so as to remove traces of impurities such as ketones, aldehydes etc.
- ✓ Eventually, the liquid stream enters a distillation column that separates dimethyl ether as a top product.

- ✓ The bottom product from the first distillation column enters a fractionator that produces methanol, other high molecular weight alcohols and water as three different products.

MANUFACTURING OF VINYL CHLORIDE FROM ETHYLENE

Introduction

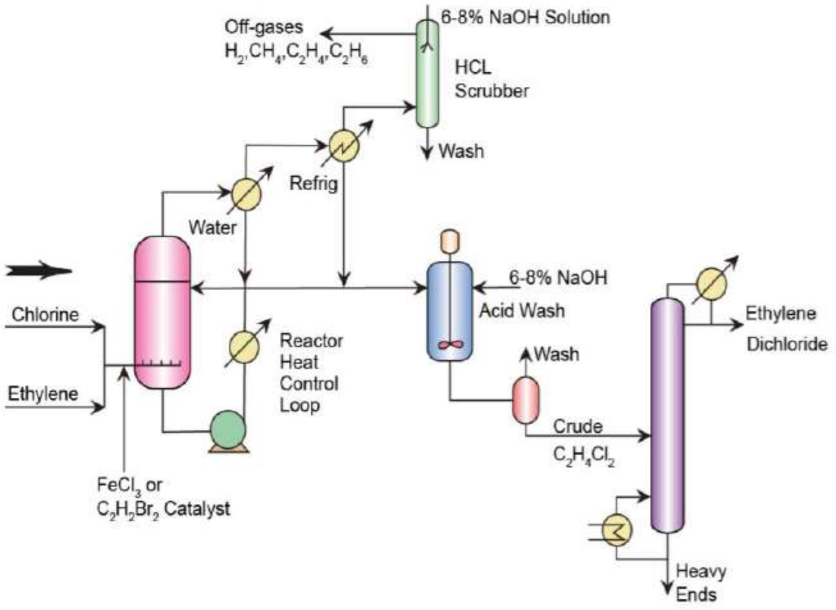
- Vinyl chloride is produced in a two-step process from ethylene
- Ethylene first reacts with Chlorine to produce Ethylene dichloride
- The purified Ethylene dichloride undergoes selective cracking to form vinyl chloride
- We first present the process technology associated to Ethylene Chloride

Ethylene dichloride

- ✓ Desired Reactions

  $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$
- ✓ Undesired products:

  Propylene dichloride and Polychloroethanes
- ✓ Reaction occurs in a liquid phase reactor with ethylene dichloride serving as the liquid medium and reactants reacting the liquid phase
- ✓ Catalyst is $FeCl_3$ or Ethylene dibromide



Product Description

- ✓ C_2H_4 and Cl_2 are mixed and sent to the liquid phase reactor.
- ✓ Here, the feed mixture bubbles through the ethylene dichloride product medium
- ✓ Reactor operating conditions are 50 °C and 1.5 – 2 atms.
- ✓ The reaction is exothermic. Therefore, energy is removed using either cooling jacket or external heat exchanger
- ✓ To facilitate better conversion, circulating reactor designs are used.
- ✓ $FeCl_3$ traces are also added to serve as catalyst
- ✓ The vapour products are cooled to produce two products namely a vapour product and a liquid product. The liquid product is partially recycled back to the reactor to maintain the liquid medium concentration.
- ✓ The vapour product is sent to a refrigeration unit for further cooling which will further extract ethylene dichloride to liquid phase and makes the vapour phase bereft of the product.
- ✓ The liquid product is crude ethylene dichloride with traces of HCl.
- ✓ Therefore, acid wash is carried out first with dilute NaOH to obtain crude ethylene dichloride.
- ✓ A settling tank is allowed to separate the spent NaOH solution and crude $C_2H_4Cl_2$ (as well liquid).

- ✓ The crude ethylene dichloride eventually enters a distillation column that separates the ethylene dichloride from the other heavy end products.
- ✓ The vapour phase stream is sent to a dilute NaOH solution to remove HCl and produce the spent NaOH solution. The off gases consist of H_2, CH_4, C_2H_4 and C_2H_6.

MANUFACTURING OF VINYL ACETATE

Introduction

- Vinyl acetate is an organic compound with the formula $CH_3CO_2CH=CH_2$.
- This colorless liquid is the precursor to polyvinyl acetate, an important industrial polymer.
- Traditional process involves the reaction of acetylene and acetic acid

$$C_2H_2 + CH_3COOH \rightarrow CH_3COOCH=CH_2$$

Process Description

- The process is centered on the reaction between ethylene, oxygen and acetic acid in order to produce vinyl acetate and water.
- There is a second unwanted reaction in the process based on the ethylene oxidization to produce water and carbon dioxide.
- The gaseous effluents from the reactor are cooled trying to have a partial condensation of the stream.
- Next, the gas is separated from the liquids in a phase separator. The gas is washed with acetic acid from a recycle stream.
- This helps to recover the vinyl acetate in the absorber. Afterwards, there is a process to eliminate the CO_2 from the gas phase and recycle it back in to the reactor the Ethylene is necessary.
- The liquids that come out from the separator and the acetic acid used in the washing process enter an azeotropic distillation tower.
- In this part of the process, the main objective is to separate the acetic acid (bottoms) form the water and vinyl acetate mixture (distillate).

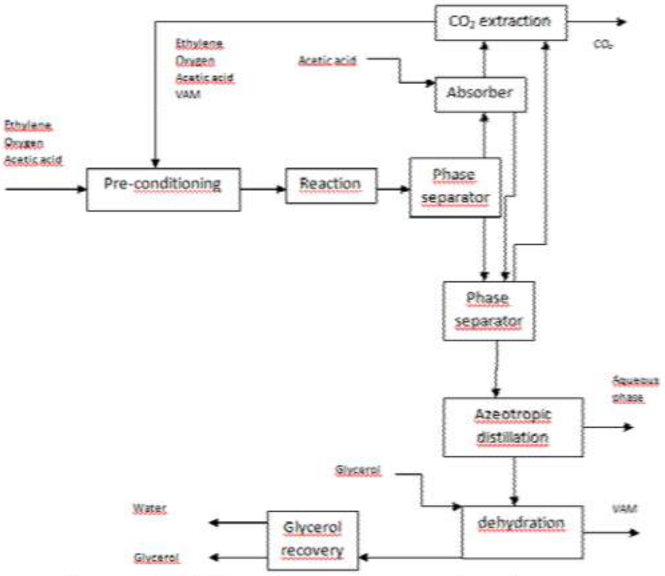


Figure 1. VAM production process flow diagram.

- The distillate enters to a decantation process in which its organic product (mainly vinyl acetate) divides into a reflux stream that heads back to the distillation column and another stream that enters a separation train process where the proper concentration level of vinyl acetate is achieved to comply with the wanted specifications.
- The aqueous stream from the decanter is discarded.
- A portion of the bottoms stream from the distillation column (mainly acetic acid) is used in the washing process in the absorber, while the other portion of the bottom stream is mixed with pure acetic acid from the feed streams to later on enter to an evaporation process.

- The gaseous acetic acid obtained is mixed with the recycle gas, oxygen and ethylene to form the feed to the reactor.

Reaction system

- The reaction that produces the vinyl acetate takes place in reactor where a gaseous mixture of ethylene, acetic acid, and air (with small presence of CO_2 and water from the recycle streams) are fed to the reactor.
- The concentration of oxygen must be kept below 8 % molar because at higher concentrations it breaches the explosive limit of the mixture.

$$\mathbf{C_2H_4+C_2H_4O_2+0.5\ O_2 \rightarrow C_4H_6O_2+H_2O}$$
$$\mathbf{C_2H_4+3O_2 \rightarrow 2CO_2+2H_2O}$$

- These reactions are highly exothermic and the standard heat of reaction for the first reaction is 42.1 Kcal per mol of vinyl acetate, while the heat of reaction for the second reaction is -316Kcal per mol of ethylene.
- The heat of reaction is removed by generating vapor in the shell section of the tubes. This vapor is used in other part of the process.
- This is the same for the reaction catalyzed by palladium and gold supported by silica.
- The temperature must be below 200ºC because at this temperature the catalyst suffers irreversible mechanical damages.
- The catalyst is activated with a temperature over 140º C. This allows to take an inferior operation limit temperature of 150ºC.

MANUFACTURING OF ACRYLONITRILE BY AMMOXIDATION OF PROPYLENE

INTRODUCTION

- A typical acrylonitrile plant consists of reactor section, acrylonitrile recovery section, acrylonitrile purification section and HCN purification section.
- Propylene, ammonia and air are fed to fluidised bed catalytic reactor where ammoxidation of propylene – a highly exothermic reaction occurs.

Reactions:

Formation of acrylonitrile occurs by the following reaction:

$$CH_2{=}CH{-}CH_3 + O_2 \longrightarrow CH_2{=}CH{-}CHO + H_2O$$
$$CH_2{=}CH{-}CHO + NH_3 \longrightarrow CH_2{=}CH{-}CH{=}NH + H_2O$$
$$CH_2{=}CH{-}CH{=}NH + \tfrac{1}{2} O_2 \longrightarrow CH_2{=}CH{-}CN + H_2O$$

Overall reaction:

$$CH_2{=}CH{-}CH_3 + NH_3 + 3/2\ O_2 \longrightarrow CH_2{=}CH{-}CN + 3\ H_2O\ \Delta H \cong -515 kJ / mol$$

Side reactions:

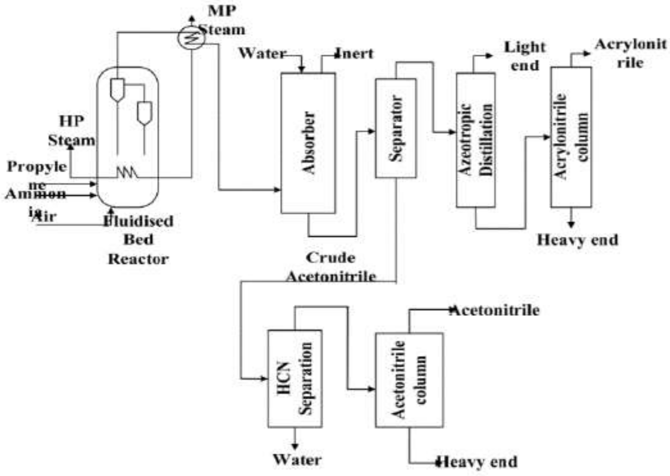
$$2\ CH_2{=}CH{-}CH_3 + 3\ NH_3 + 3\ O_2 \rightarrow 3\ CH_3CN + 6\ H_2O$$
$$CH_2{=}CH{-}CH_3 + 3\ NH_3 + 3O_2 \longrightarrow 3\ HCN + 6\ H_2O$$
$$CH_2{=}CH{-}CH_3 + 3\ O_2 \longrightarrow 3\ CO + 3\ H_2O$$
$$2\ CH_2{=}CH{-}CH_3 + 9\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O$$

PROCESS DESCRIPTION:

Process steps involve are

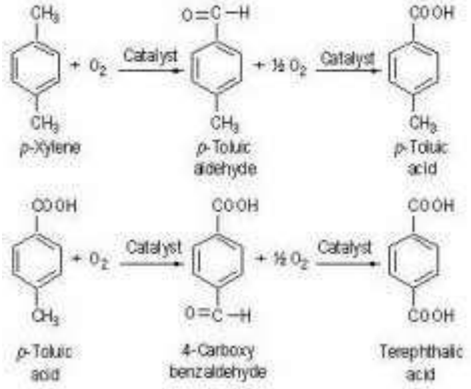
- Catalyst preparation: bismuth and molybednum
- Mixing of propylene, ammonia and oxygen in 1:1:6
- Reaction section: Macrylonitrile acetonitrile, hydrogen cyanide, unreacted mixture of propylene, ammonia and oxygen are fed to fluidised bed reactor.
- Various product from reactor are and oxygen.
- Reaction is highly exothermic.
- Removal of ammonia

- Absorption of absorbable component from ammonia free gas in water to separate the non-condensable and unconverted propylene, propane, nitrogen, CO and CO_2.
- Stripping of organic components and separation of HCN
- Separation of Acrylonitrile and acetonitrile which are close boiling compounds. And are separated by extractive distillation using water as solvent. A dilute solution of acrylonitrile is separated which is recovered and concentrated
- Purification of acetonitrile
- Final purification of acrylonitrile

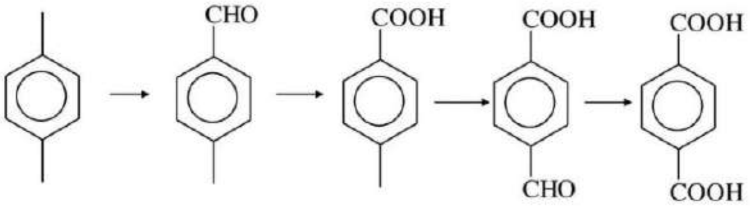


MANUFACTURING OF TEREPHTHALIC ACID

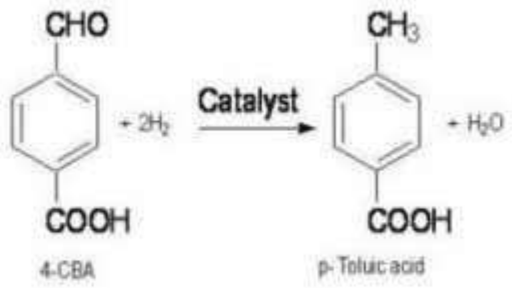
- To produce PTA oxidation of Paraxylene accomplished in Acetic Acid in presence of metal catalyst like (Mn^{+2}), initially (CTA) crude Terephthalic Acid was obtained and then purified.
- So the product is called Purified Terephthalic Acid.
- In manufacturing technology wise there would be change but general outline is same for all the technology providers.
- The reactions of importance are shown in the following chemical equations



The sequence of oxidation:

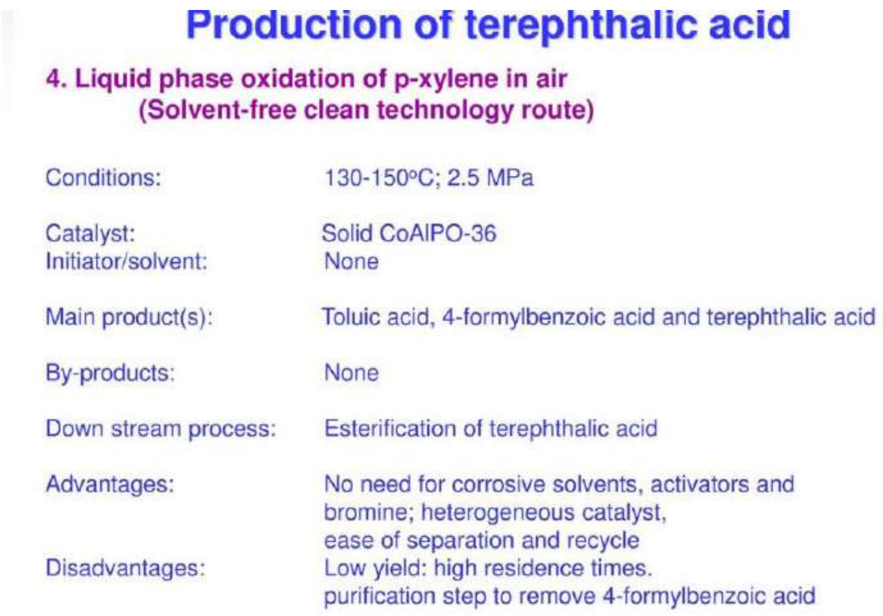


- Purification of Crude Terephthalic Acid requires at least one chemical step in addition to the physical procedures (e.g. crystallization, washing).
- One of the major impurities, 4-carboxybenzaldehyde (4-CBA), is quite difficult to remove by physical means but can be converted to para-toluic acid by catalytic hydrogenation in an aqueous solution as shown in the following equation:



The technology consists of the following major processing steps:

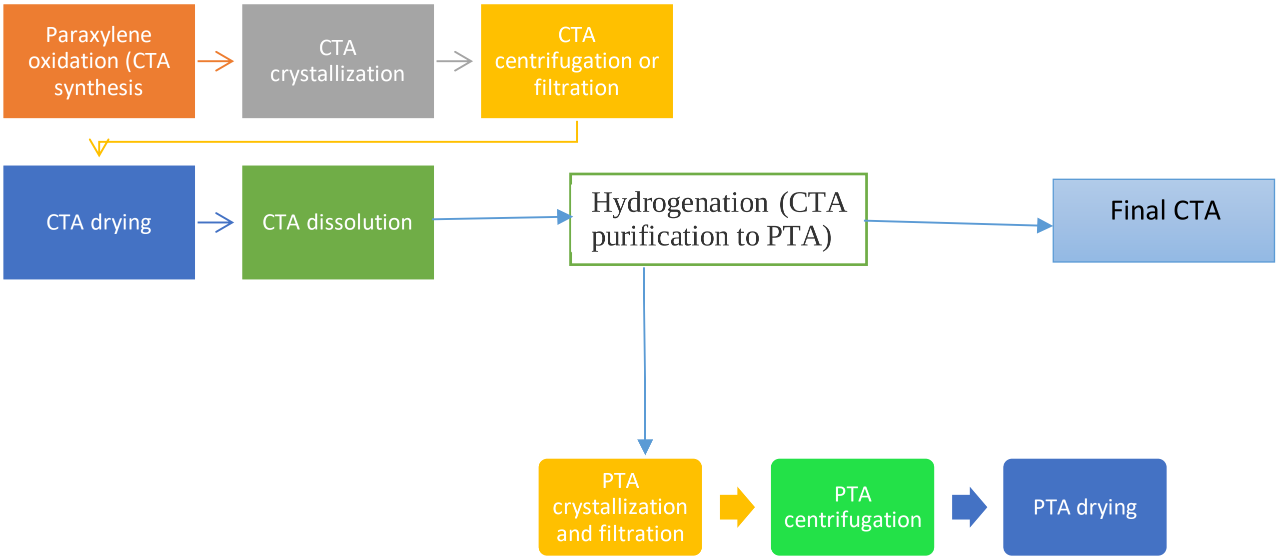
- Paraxylene oxidation (CTA synthesis)
- CTA crystallization
- CTA centrifugation or filtration
- CTA drying
- CTA dissolution
- Hydrogenation (CTA purification to PTA)
- PTA crystallization and filtration
- PTA centrifugation
- PTA drying



Production of terephthalic acid

4. Liquid phase oxidation of p-xylene in air
(Solvent-free clean technology route)

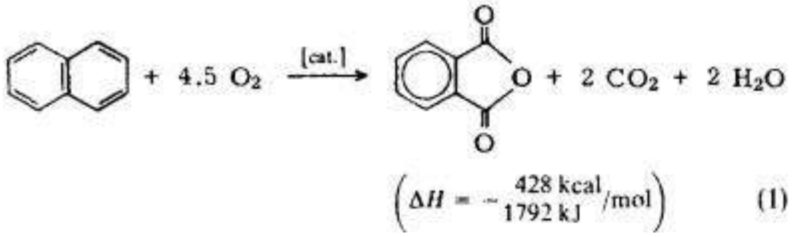
Conditions:	130-150°C; 2.5 MPa
Catalyst:	Solid CoAlPO-36
Initiator/solvent:	None
Main product(s):	Toluic acid, 4-formylbenzoic acid and terephthalic acid
By-products:	None
Down stream process:	Esterification of terephthalic acid
Advantages:	No need for corrosive solvents, activators and bromine; heterogeneous catalyst, ease of separation and recycle
Disadvantages:	Low yield: high residence times. purification step to remove 4-formylbenzoic acid



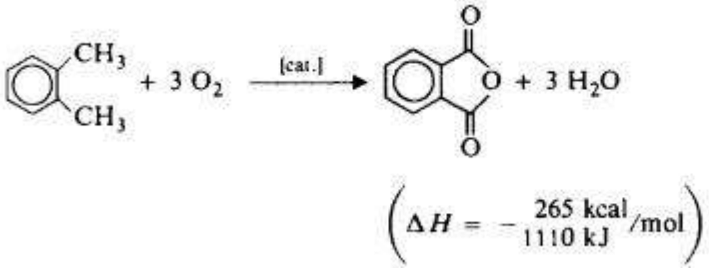
PHTHALIC ANHYDRIDE MANUFACTURING

Oxidation of Naphthalene and/or O-xylene:

(a) Naphthalene Oxidation



(b) O-xylene oxidation



(c) Major side reactions

$C_{10}H_8$ + 12 O_2 (Air) → 10 CO_2 + 4H_2O

C_8H_{10} + 10.5 O_2 (Air) → 8CO_2 + 5H_2O

(d) Minor side reaction

$C_{10}H_8$ + 9 O_2 (Air) → $C_4H_5O_3$ (maleic anhydride) + 6 CO_2 + 3H_2O

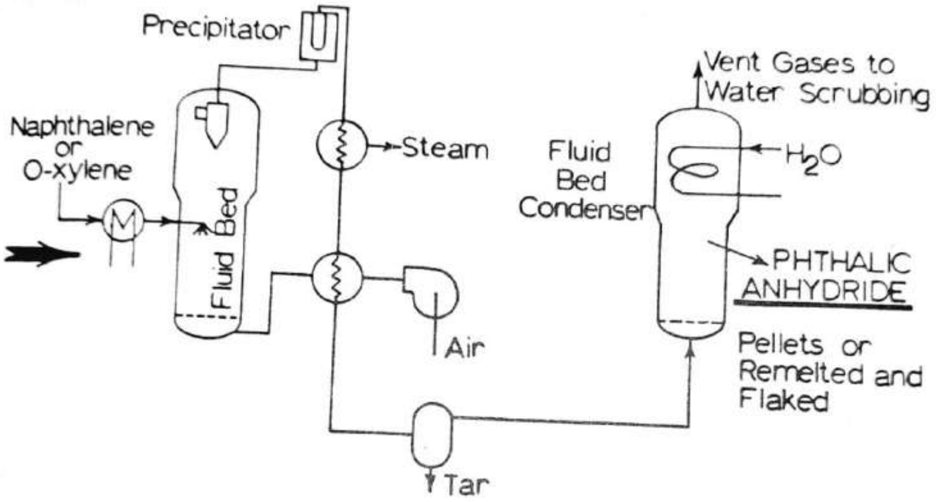
$C_{10}H_8$ + 7.5 O_2 (Air) → $C_4H_2O_3$ (maleic anhydride) + 4 CO_2 + 4H_2O

All side reactions are endothermic than primary reactions.

Process Description:

- Naphthalene, o-xylene or mixture are melted and vaporized by bubbling by preheated air through the molten material.

- Secondary air to make up the air/feed requirement is added downstream and the reacting mixture is passed through a preheater to a fixed bed converter.
- This is a multi-tubular catalytic reactor filled with support V_2O_5.



- The exothermic heat of reaction is removed from the outside of the tubes by a molten salt circulating system. Conditions for oxidation within the converter are 380°-450°C, contact time of 0.1 to 0.4 sec.
- Reacted effluent gases are passed through a waste-heat steam boiler and then to a preheater where the final temperature is dropped to a few degrees above the dew point of phthalic anhydride.
- Condensation of the solid product can be effected by pairs of switching fin-tube condensers, a cyclone, a fluidized bed condenser, or a water scrubber.
- The crude solid product is melted, distilled under vacuum, and condensed with a flaking or pelletizing operation completing the production scheme.
- The major impurity is maleic anhydride in 0.2-0.4% quantities.
- Maleic anhydride and an easily converted derivative, fumaric acid, can be recovered in 3-5% yield from the off-gas scrubbing liquor of the crude phthalic anhydride condensers.
- A process modification which is competitive is the substitution of a fluid bed catalytic reactor for the fixed bed multitubular reactor.
- Conditions at the head end are somewhat different. The molten naphthalene and/or o-xylene is sprayed directly into the air-fluidized catalytic reactor which operates at 600°C.
- The reacted gases rise upwards through the dense phase into a wider calming-settling zone and thence through the internal cyclone to dust filters.
- Condensation is the same as above, but no vacuum distillation is required.
- A comparison of reactor conditions for the two cases shows that the fluid bed process operates at 140-220°C higher, a longer contact time of 10 sec versus 0.1 to 0.4 sec, a lower air-feed ratio of 15 kg air/kg feed.
- The yields are equivalent (75-80%) and almost no maleic acid is produced, thus giving a very high purity phthalic anhydride product.

Major engineering problems

1. Explosion hazards-minimized by adding excess air to stay below the lower explosive limit
2. Fixed bed tubular reactor design -tube size and heat transfer must be considered to avoid too high a center temperature within each catalytic tube
3. Process alternatives-fixed bed versus fluid bed, the latter required more development to get into the competitive position it now holds
4. Catalyst development for high specificity of oxidation
5. Choice of coolant for fixed bed converters-mercury and diphenyl are also used

UTKALMANI INSTITUTE OF TECHNOLOGY, ROURKELA-4

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SUBJECT: PETRO REFINERY&PETROCHEMICAL TECHNOLOGY
COURSE CODE: TH-3

PRESENTED BY: SATARUPA SAHU

Chapter 6- THIRD GENERATION PETROCHEMICALS

LESSON OBJECTIVE

The topics help the students

- To study the manufacturing of formaldehyde, acetaldehyde, Acetic acid, Benzene, Toulene and Xylene, Aniline and Melamine.

COURSE OUTCOMES:

1. Classify petroleum refining process and fractionation of crude oil.
2. Explain the Importance of 1st, 2nd, 3rd generation petrochemical, refinery products, their properties and uses.
3. Identify growth and future of petroleum refinery and petrochemical industries in India.

TOPIC TO BE COVERED:

Lecture 53	Manufacturing of formaldehyde
Lecture 54	Manufacturing of acetaldehyde
Lecture 55	Manufacturing of Acetic acid
Lecture 56	Manufacturing of BTX(Benzene)
Lecture 57	Manufacturing of BTX(Toluene)
Lecture 58	Manufacturing of BTX(Xylene)
Lecture 59	Manufacturing of Aniline
Lecture 60	Manufacturing of Melamine

TOOLS USED:

- Chalk and duster
- K-Yan

MODEL QUESTIONS:

1. Describe the manufacturing of formaldehyde from synthesis gas with a neat diagram.
2. Describe the manufacturing of acetaldehyde with flow-sheet.
3. Describe the manufacturing of Acetic acid with flow-sheet.
4. Describe the manufacturing of Benzene, Toulene and Xylene with flow-sheet.
5. Describe the manufacturing of Aniline with flow-sheet.
6. Describe the manufacturing of Melamine with flow-sheet

ASSESSMENT METHODS APPLIED:

- Class quiz
- Assignment

REFERENCES:

- Modern Petroleum Refining Process by B K B Rao, Oxford IBH Publication
- Petroleum Refining Technology by Dr. Ram Prasad, Khanna Publications

MANUFACTURING OF FORMALDEHYDE

Introduction

- Production technology for formaldehyde and chloromethanes.
- Formaldehyde is produced from methanol
- Chloromethanes are produced from methane by chlorination route.

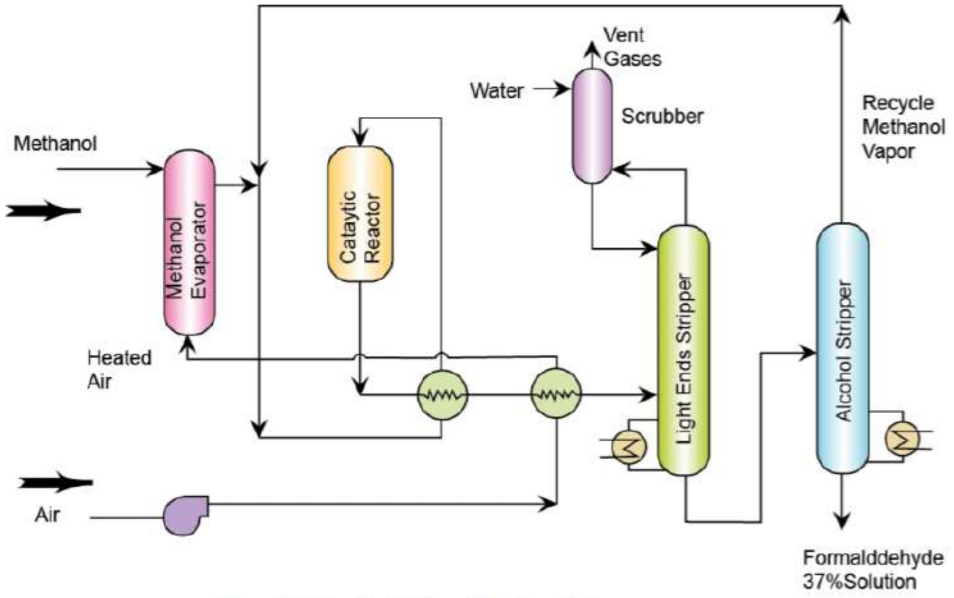
Formaldehyde production

Reactions

- Oxidation: $CH_3OH + 0.5\ O_2 \rightarrow HCHO + H_2O$
- Pyrolysis: $CH_3OH \rightarrow HCHO + H_2$
- Undesired reaction: $CH_3OH + 1.5\ O_2 \rightarrow 2H_2O + CO_2$
- In the above reactions, the first and third are exothermic reactions but the second reaction is endothermic.
- The reactions are carried out in vapour phase. Catalyst: Silver or zinc oxide catalysts on wire gauge are used.
- Operating temperature and pressure: Near about atmospheric pressure and 500 – 600 ^{O}C

Process description:

- Air is sent for pre-heating using reactor outlet product and heat integration concept.
- Eventually heated air and methanol are fed to a methanol evaporator unit which enables the evaporation of methanol as well as mixing with air. The reactor inlet temperature is 54 ^{o}C.
- The feed ratio is about 30 – 50 % for $CH_3OH: O_2$



- After reaction, the product is a vapour mixture with temperature 450 – 900 ^{o}C
- After reaction, the product gas is cooled with the heat integration concept and then eventually fed to the absorption tower.
- The absorbent in the absorption tower is water as well as formaldehyde rich water.
- Since formaldehyde rich water is produced in the absorption, a portion of the rich water absorbent solution from the absorber is partially recycled at a specific section of the absorber.
- From the absorber, HCHO + methanol rich water stream is obtained as the bottom product.
- The stream is sent to a light end stripper eventually to remove any light end compounds that got absorbed in the stream.
- The vapors from the light end unit consisting of light end compounds can be fed at the absorption unit at specific location that matches with the composition of the vapors in the absorption column.

- Eventually, the light end stripper bottom product is fed to a distillation tower that produces methanol vapour as the top product and the bottom formaldehyde + water product (37 % formaldehyde concentration).

ACETALDEHYDE, CH_3CHO

- Acetaldehyde can be manufactured from acetylene by the following three methods.

1. By hydration of acetylene in the liquid phase using a mercury-iron catalyst.
2. By hydration of acetylene in the vapour phase over a solid catalyst.
3. By hydrolysis of simple vinyl ethers.

- In addition, acetaldehyde is also made by partial catalytic oxidation of ethyl alcohol and by catalytic oxidation of ethylene.
- Production of acetaldehyde by hydration of acetylene in the liquid phase using mercury-iron catalyst is carried out in the industry.
- Carefully purified acetylene together with recycle gas at 1.5 to 2.5 atm pressure is continuously passed in a hydrator through a liquid catalyst containing a solution of Hg(II) sulphate in H_2SO_4.
- The Hg (II) is reduced to Hg(I) and then to Hg because acetaldehyde is a reducing agent.

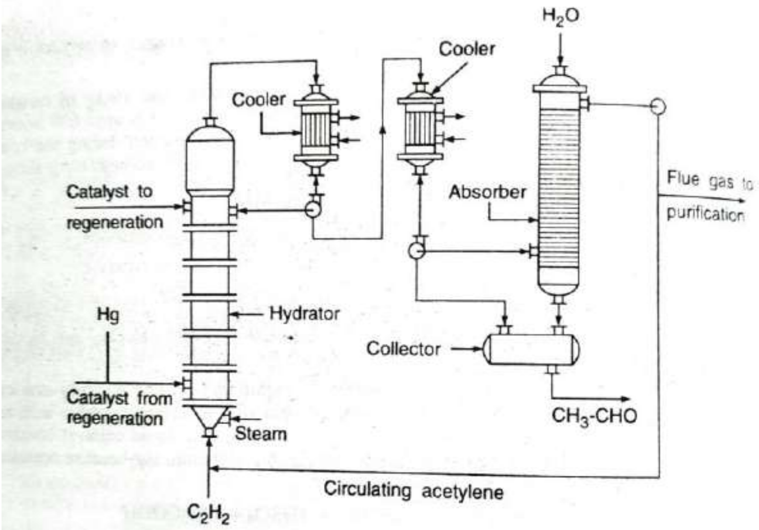
$$2Hg_2S0_4 + H_20 + CH_3CHO \rightarrow Hg_2SO_4 + H_2SO_4 + CH_3COOH$$

$$Hg_2S0_4 + H_20 + CH_3CHO \rightarrow 2Hg + H_2SO_4 + CH_3COOH$$

- In order to maintain the necessary composition of the catalyst liquid, Hg metal and an oxidising agent are added which in the presence of H2SOsq transform the mercury metal to Hg(II) sulphate required for the hydration of acetylene.

$$2Hg + Fe_2(SO_4)_3 \rightarrow Hg_2SO_4 + 2FeSO_4$$

$$Hg_2S0_4 + Fe_2(SO_4)_3 \rightarrow 2HgSO_4 + 2FeSO_4$$



- Hg metal is periodically introduced. It is sprayed into the reactor through a funnel at the top (about 0.1 kg of Hg is lost per ton of CH_3CHO produced). Under these conditions 50-60% of C_2H_2 is hydrated.

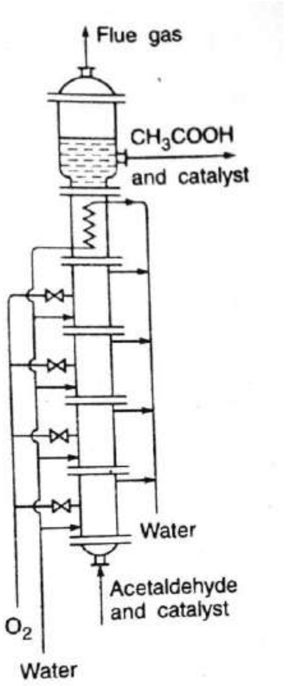
$$CH\equiv CH + H_20 \rightarrow CH_3CHO + I51\ kJ$$

- The hydrator is a column with a conical bottom and a widened top. It is made of ferrosilicon or of stainless steel. Each of the bubbler trays of the hydrator operates in accordance with a model which is closer to complete mixing then to plug flow both w.r.t. the gas and the liquid.
- The gas and liquid move through the tray in cross flow.
- Since there is a large number of trays in the tower process calculations can be carried out for counter current plug flow through the tower.
- The temperature in the hydrator is maintained at 80-100°C by introducing live steam.
- The steam gas mixture leaving at the top of the hydrator contain acetaldehyde, acetylene and water vapours with other impurities and this mixture is passed through Coolers.

- In the first cooler, water vapour condenses, the condensate being transferred to the hydrator.
- In second cooler acetaldehyde and water condense together and the solution is collected in tank.
- The uncondensed gases are fed to an absorber, where the remaining acetaldehyde is removed by spraying water in which acetaldehyde dissolves.
- It is cooled to 10°C and unreacted acetylene is recycled to the head of the process. About 10% of the gas is continuously purged to remove N_2 and CO_2 and prevent their excessive accumulation in the recycle gas.
- Pure acetaldehyde is produced by consecutive distillation and rectification.
- The catalyst liquid flows out of the hydrator to a settling tank for recovery of Hg and from it goes to a Regeneration tank.
- The Catalyst liquid contains approx. 200g/L of H_2SO_4, 0.5- 0.6g/L mercuric Oxide and 40 g/L iron oxides. The yield of acetaldehyde w.rt. acetylene reacted is about 90-95%.
- One ton of acetaldehyde can be produced from 680 kg of acetylene, 0.1 kg of Hg, 3 tonnes of steam and some amount of H_2SO_4, HNO_3 and iron sulphate.
- Since mercury is toxic, oxides of Zn, Mg, Ni, Fe, Co, Cr and other metals have also been suggested as catalysts.
- Heterogeneous catalytic processes of this type can be carried out by using a fluidised bed of the catalyst. The yield of acetaldehyde is 88- 90% of the converted C_2H_2.
- The degree of conversion per pass is 90%.

ACETIC ACID, CH_3COOH

- Acetic acid is manufactured for a very long time by dry distillation of wood and fermentation.
- Now acetaldehyde is processed into acetic acid by its liquid phase oxidation by the oxygen of the air at 60-70°C in presence of a catalyst, a solution of Manganese acetate, $Mn(CH_3COO)_2$ in acetic acid.



- The unstable peracetic acid is formed as an intermediate product of oxidation.

$$CH_3CHO + O_2 \rightarrow CH_3COOOH$$

- The peracetic acid reacts with a second molecule of acetaldehyde to form a peroxide compound that decomposes into two molecules of acetic acid.

$$CH_3COOOH + CH_3CHO \rightarrow CH_3CO.O.O.CHOH.CH_3 \rightarrow 2CH_3COOH$$

- Accumulation of peracetic acid in the apparatus may cause an explosion.

- To prevent this, the gas vapour mixture is diluted with nitrogen and the temperature is maintained between 60-75°C.

- The use of mangasese salts as catalyst promotes the reduction of peracetic acid to acetic acid.
- The process is carries out in tray type oxidising tower similar to that used in making acetaldehyde.
- The industrial process consists of three stages:
  1. Oxidation of acetaldehyde.
  2. Absorption of acetaldehyde from the discharged gases.
  3. Separation of acetaldehyde from acetic acid
- The oxidising reactor is column assembled from aluminium sheet drums with cooling coils.
- A solution of acetaldehyde and catalyst is introduced into the lower part of the column.
- The oxygen is fed in along the entire height of the column. The vapour gas mixture leaving the reactor contains acetic acid, unreacted acetaldehyde and by-products of the reaction.
- The mixture is cooled, the acetaldehyde is recycled to the reactor, while the crude acetic acid is distilled.
- The yield of acetic acid is 90%.
- Acetic acid is semi product of organic synthesis for the production of chemical fibres and plastics, solvents, lacquers and varnishes, fragrant substances, and many other products. Its salts are used as mordants and medicines.

BTX MANUFACTURING

There are three steps in manufacturing of BTX.

1. Catalytic reforming process
2. Separation of aromatics from reformate
3. Separation of BTX

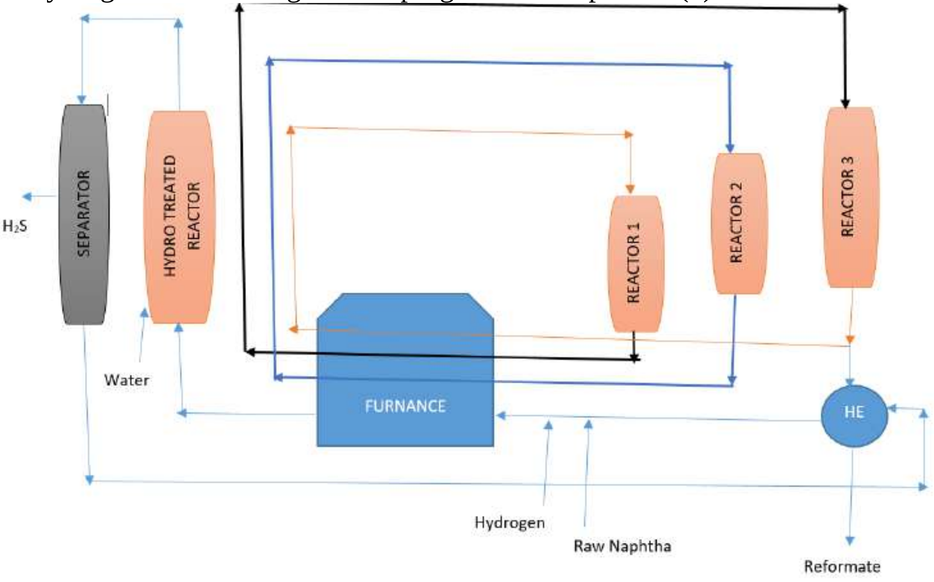
Step 1: Catalytic Reforming Process

Operating condition

- Feed: Raw Naphtha with hydrogen
- Catalyst: Alumina and Rhenium
- Temperature: 500 °C
- Pressure: 20 atm
- H_2 recycle ratio: 1:10

Process Description:

- Raw naphtha is mixed with hydrogen and sent through furnace (3).
- The mixture is desulhurised by hydro treating in reactor (1) which eliminates sulfur in the form of hydrogen sulfide and gases are purged out in separator (2).

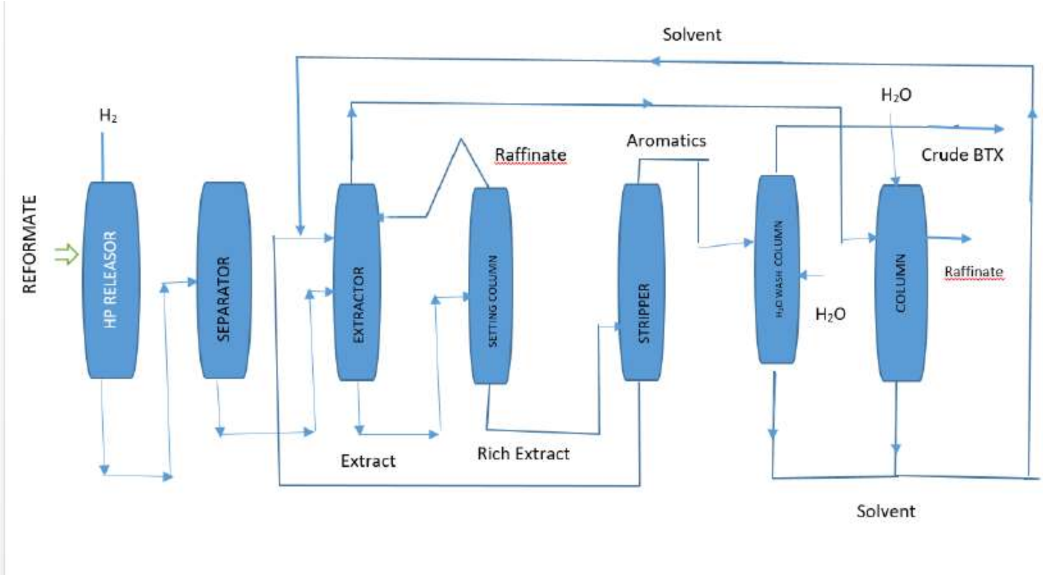


- The sulfur free naphtha is mixed with recycle hydrogen and pass through a process heat exchanger.
- The feed along with the naphtha and hydrogen is heated to 500°C in furnace (3) and vaporized feed is sent to reactor R_1-R_3 with intermediate pressure.
- Catalyst used in 3 mm size pellet and one furnace maintains all the reaction temperature.

Step 2: Separation of Aromatics from Reformate

Process Description:

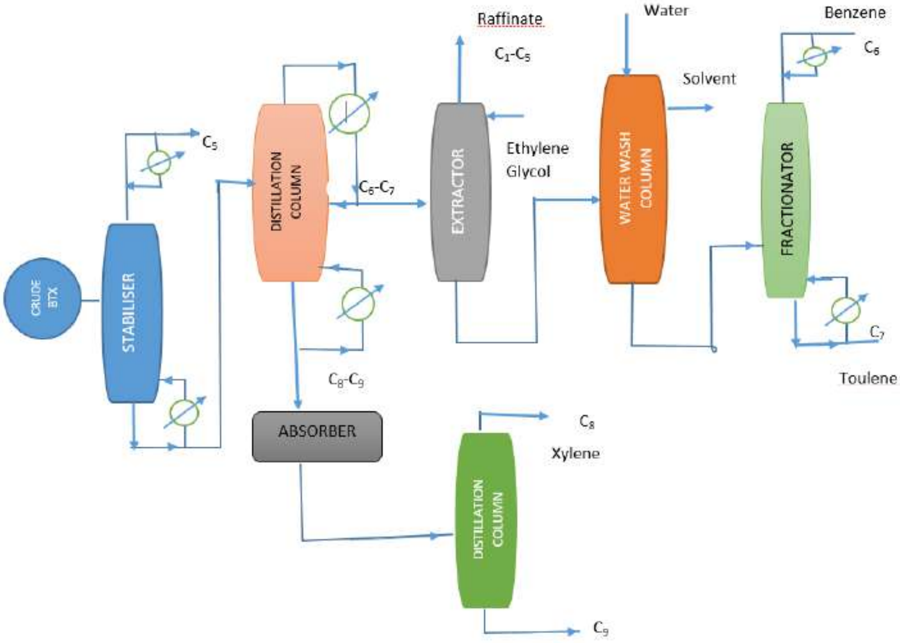
- Reformate from catalytic reforming process is sent to the high pressure releaser where hydrogen gas is liberated out.
- The liquid product is stabilized at a pressure of (5-7) bar by driving off the low boiling components as well as dissolved gas in separator.
- The solvents used are dimethyl formate, dimethyl sulphoxide, ethylene glycol which are good for extraction of light aromatics.
- Extractor consists of plate column where the fed is introduced at the bottom and solvent is fed counter currently.
- The temperature of the extractor is kept around (40-50) ^{O} C.
- The extract is the desired product and collected at the bottom and sent to settling column (4) along with the extra amount of raffinate.
- Rest of the raffinate is returned to extractor from setting column.
- The extract from the bottom of settling column is sent to stripper where solvent is collected at bottom and aromatics at top.
- The aromatics is sent to water wash column to separate solvent and crude BTX at the top.
- The solvent from stripper is recycled to extractor.
- The raffinate separated from extractor is purified by washing with water in column.
- The top product results non-aromatics raffinate which can be further processed by mixing with incoming naphtha.
- The solvent washing is purified and sent to extractor.



Step 3: Separation of BTX

- The feed BTX is first stabilized in stabilizer to remove fractions up to C_5.
- The bottom product of the column is sent to distillation column where C_6-C_7 fraction is collected overhead product and C_8-C_9 fraction is collected at the bottom.
- Benzene, toluene is separated by ethylene glycol solution as solvent in extractor.

- The top product contains lighter hydrocarbon (C_1-C_5) and bottom contains benzene, toluene which are water washed in water wash column.
- In fractionator, benzene (C_6) is recovered as top and toluene (C_7) as bottom product.
- C_8-C_9 fractions are sent to distillation column where C_8 (Xylene) is separated as top and C_9 as bottom product.



MANUFACTURING OF ANILINE

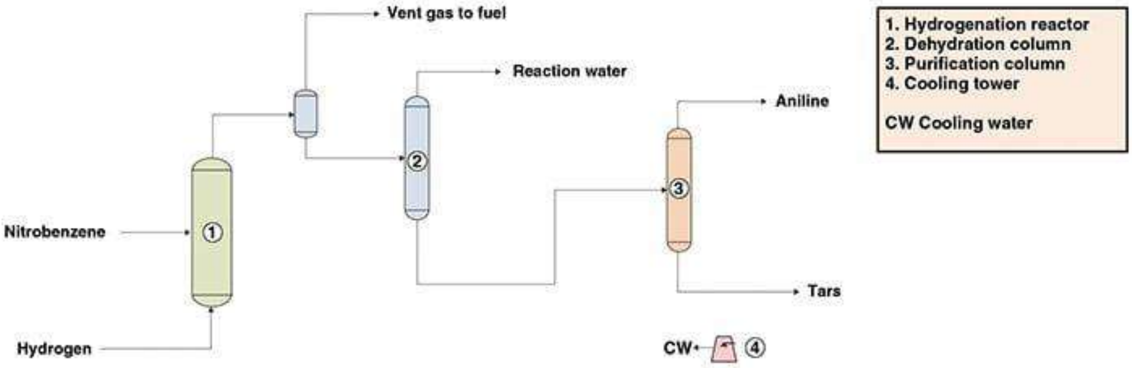
Introduction

- Aniline, also known as amino benzene or benzenamine, is an aromatic amine with the formula $C_6H_5NH_2$.
- It is mainly used as a raw material in the production of methylene diphenyl diisocyanate (MDI), an intermediate in polyurethane manufacture.
- Aniline is also used as an intermediate for dyes and pigments, explosives, agricultural chemicals and pharmaceuticals.

Process Description

- The following paragraphs describe aniline production from nitrobenzene via a liquid-phase hydrogenation process, similar to the one owned by DuPont (Wilmington, Del.; www.dupont.com).
- The process can be divided into three main parts: nitrobenzene hydrogenation, dehydration and purification.
- **Nitrobenzene hydrogenation.** Nitrobenzene (mononitrobenzene or MNB) is fed with hydrogen into a plug-flow tubular reactor containing a noble metal catalyst supported on carbon.
- The hydrogenation is carried out in the liquid phase and the nitrobenzene conversion to aniline is near 100% in a single pass.
- **Dehydration.** The reactor effluent is virtually free of nitrobenzene due to the high conversion of the reaction.
- The hydrogen excess is separated from the reactor effluent and the liquid product is directed to a dehydration column.
- In this column, the water generated is removed as the overhead product and the bottoms stream is sent to the purification area.
- **Purification.** In the purification area, heavy impurities (tars) are separated from the crude aniline stream by the bottom of a distillation step.

- The final product obtained as the distillate of the column is high-quality aniline, with purity above 99.95 wt.% and containing less than 0.1 parts per million (ppm) of nitrobenzene by weight.



MANUFACTURING OF LINEAR ALKYL BENZENE(LAB)

Introduction

- Linear alkylbenzenes (sometimes also known as LABs) are a family of organic compounds with the formula $C_6H_5C_nH_{2n+1}$.
- Typically, n lies between 10 and 16, although generally supplied as a tighter cut, such as C_{12}-C_{15}, C_{12}-C_{13} and C_{10}-C_{13}, for detergent use.
- The C_nH_{2n+1} chain is unbranched. They are mainly produced as intermediate in the production of surfactants, for use in detergent.

Production

- Hydrotreated kerosene is a typical feedstock for high purity linear paraffins (n-paraffins), which are subsequently dehydrogenated to linear olefins:

$$\mathbf{C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2}$$

- Alternatively, ethylene can be oligomerized (partially polymerized) to produce linear alkenes. The resulting linear mono-olefins react with benzene in the presence of a catalyst to produce the LABs.
- Hydrogen fluoride (HF) and aluminium chloride ($AlCl_3$) are the two major catalysts for the alkylation of benzene with linear mono-olefins.
- The HF-based process is commercially dominant; however, the risk of releasing HF (a poisonous substance) into the environment became a concern particularly after the Clean Air Act Amendment. In 1995, a solid catalyst system (the DETAL process) became available.
- The process eliminates catalyst neutralization and HF disposal. Consequently, most LAB plants built since then have utilized this process.

Production Details

- Given the large scale applications of LAB-derived detergents, a variety routes have been developed to produce linear alkylbenzenes.
- The HF/n-paraffins process involving dehydrogenation of n-paraffins to olefins, and subsequent reaction with benzene using hydrogen fluoride as catalyst.
- This process accounts for the majority of the installed LAB production in the world.
- It includes a PACOL Stage where n-paraffins are converted to mono-olefins (typically internal mono-olefins), a DEFINE Unit whose primary function is to convert residual diolefins to mono-olefins, a PEP Unit which is essentially an aromatic removal unit - introduced before the alkylation step to improve LAB yield and quality, an alkylation step where mono-olefins, both internal and alpha olefins, are reacted with benzene to produce LAB in the presence of HF catalyst.
- The DETAL process involving dehydrogenation of n-paraffins to olefins, and subsequent reaction with benzene using a fixed bed catalyst.
- This is newer technology and has several of the stages depicted in the HF/n-paraffins process, but it is principally different in the benzene alkylation step, during which a solid-state catalyst is

employed. There is a developing transalkylation (TA) stage to the Detal process wherein any higher alkylated benzenes (HAB) are contacted with additional benzene over a transalkylation catalyst.

- The Friedel-Crafts alkylation process involves chlorination of n-paraffins to monochloroparaffins followed by alkylation of benzene using aluminum chloride ($AlCl_3$) catalyst. This method is one of the oldest commercial routes to LABs.
- Each process generates LAB products with distinct features. Important product characteristics include the bromine index, sulfonatability, amount of 2-phenyl isomers (2-phenylalkane), the tetralin content, amount of non-alkylbenzene components, and the linearity of the product.
- The production of n-paraffins often occurs as part of an integrated LAB plant where the producers start from kerosene as raw material.
- The UOP process for producing normal paraffin includes a kerosene prefractionation unit, a hydrotreating unit and a Molex unit.
- The ExxonMobil Chemical technology includes a recovery process and can produce LAB grade n-paraffins from most medium to low sulfur kerosene without the use of a hydrotreater stage upstream. A desulfurization process is needed to reduce the sulfur content of some n-paraffins

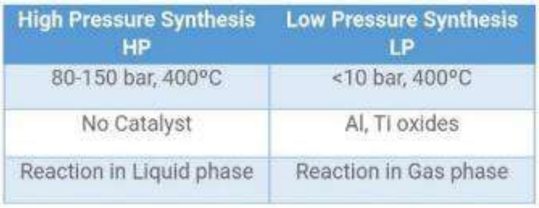
Melamine Manufacturing Process

• Melamine is a white powder organic base which is mainly used to form resins with formaldehyde (MF) and formaldehyde-urea (MUF), extensively used as coatings for furniture, textiles and paper or as plastizers.

• Melamine is obtained from Urea in two stages: First the urea decomposition to form isocyanic acid and ammonia, and afterwards a formation step yielding melamine and carbon dioxide. The overall process is endothermic.

• Since urea is the feedstock for melamine manufacturing process, and ammonia by-product is obtained in the latter, the recycle of the off-gas to the Urea plant is arranged for efficient feedstock use:

• The main characteristics of the continuous processes actually employed are listed in the following table:

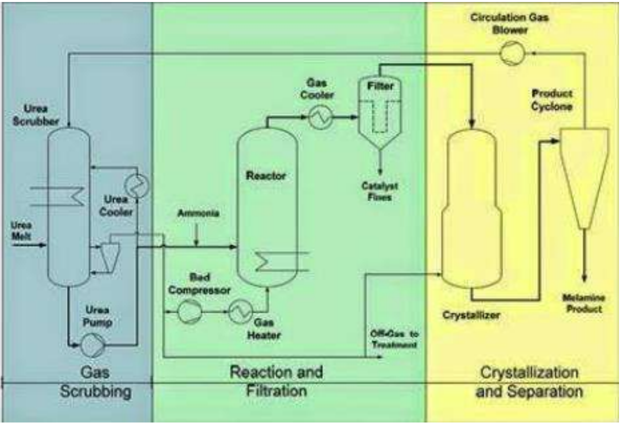


High Pressure Synthesis HP	Low Pressure Synthesis LP
80-150 bar, 400°C	<10 bar, 400°C
No Catalyst	Al, Ti oxides
Reaction in Liquid phase	Reaction in Gas phase

Low Pressure Synthesis

• The LP process in vapour phase is a catalytic process in which the decomposition of molten urea and the synthesis of melamine takes place in a fluidized catalytic reactor.

• The effluent is quenched with water (recovering the product in a slurry) or with cold gas, and the off gas is sent to the recovery and treatment unit.



• The slurry (in case of liquid quenching) is driven through a filter (to remove catalyst fines) and finally to a crystallization equipment, where the final product is obtained after a centrifuge and a dryer with a purity above 99.8%.

- In the following process flow diagram by Lurgi, the quenching is carried out with gas and therefore there is no drying unit:

High Pressure Process

- The HP process in liquid phase (or Shortened Liquid Phase SLP) requires no catalyst, reaches similar purities as in LP, and consists of a high pressure section, in which molten urea is converted to Melamine in the reactor followed by a quenching step and the recovering of the off gas through a stripper.
- In the low pressure section the hydrolyser and filtration lead to a crystallization unit from which the Melamine slurry is dried and stored.
- The figure below shows schematically these steps