



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 1- CLASSIFICATION OF CRUDE AND REFINING SCHA3002

UNIT I INTRODUCTION

Petroleum, along with oil and coal, is classified as a fossil fuel. Fossil fuels are formed when sea plants and animals die, and the remains become buried under several thousand feet of silt, sand or mud. Fossil fuels take millions of years to form and therefore petroleum is also considered to be a non-renewable energy source.

Petroleum is formed by hydrocarbons (a hydrocarbon is a compound made up of carbon and hydrogen) with the addition of certain other substances, primarily sulphur. Petroleum in its natural form when first collected is usually named crude oil, and can be clear, green or black and may be either thin like gasoline or thick like tar.

In 1859 Edwin Drake sank the first known oil well, this was in Pennsylvania. Since this time oil and petroleum production figure grew exponentially.

Originally the primary use of petroleum was as a lighting fuel, once it had been distilled and turned into kerosene. When Edison opened the world's first electricity generating plant in 1882 the demand for kerosene began to drop. However, by this time Henry Ford had shown the world that the automobile would be the best form of transport for decades to come, and gasoline began to be a product in high demand. World War I was the real catalyst for petroleum production, with more petroleum being produced throughout the war than had ever been produced previously. In modern times petroleum is viewed as a valuable commodity, traded around the world in the same way as gold and diamonds.

USES OF PETROLEUM OTHER THAN FUEL PURPOSE

Most people tend to believe that petroleum is mostly used to power internal combustion engines in the form of gasoline or petrol. They may even conjure up images of jet fuel, but most will rarely consider the other unexpected places that petroleum by-products show up in modern life. Because crude oil contains a vast number of different hydrocarbons, various refined products have found their way into everything from plastics to pharmaceuticals.

The industry that uses petroleum to produce other chemicals is referred to as the petrochemical industry. It is estimated that a citizen in an industrialized nation currently consumes petrochemical products at a rate of three and a half gallons of oil per day. That means that, excluding fuel oil, modern life results in each citizen of an industrial nation using over 1,200 gallons of oil per year.

Agriculture

One of the most important uses of petroleum is in the production of ammonia to be used as the nitrogen source in agricultural fertilizers. Agriculture also depends on the use of pesticides to ensure consistent, healthy crop yields. Pesticides are almost all produced from oil. In essence, from running farm machinery to fertilizing plants, agriculture is one of the largest users of petroleum based products.

Plastics

Plastic is a staple of modern life. From computer monitors to nylon to Styrofoam, plastics are integral aspects of many manufactured products. Polystyrene, from which Styrofoam is made, and polyvinyl chloride (PVC) were both products of post-World War II industrialization. Nylon, which is in everything from dresses to mechanical gears and even in car engines, is the most successful petroleum-based plastic to date. Most plastics come from olefins, which include ethylene and propylene.

Pharmaceuticals

Mineral oil and petrolatum are petroleum by-products used in many creams and topical pharmaceuticals. Tar, for psoriasis and dandruff, is also produced from petroleum. Most pharmaceuticals are complex organic molecules, which have their basis in smaller, simpler organic molecules. Most of these precursors are petroleum by-products.

Dyes, Detergents, and Other

Petroleum distillates such as benzene, toluene, xylene, and others provide the raw material for products that include dyes, synthetic detergents, and fabrics. Benzene and toluene are the starting materials used to make polyurethanes, which are used in surfactants, oils, and even to varnish wood. Even sulphuric acid has its origins in the sulphur that is removed from petroleum.

PETROLEUM CHEMISTRY

Petroleum Chemistry is made of a mixture of different hydrocarbons. A hydrocarbon is an organic compound composed of two elements, hydrogen and carbon. A large part of the composition of petroleum is made up of hydrocarbons of varying lengths. The smallest hydrocarbon, methane, is composed of a single carbon atom and four hydrogen atoms. However, hydrocarbons can literally consist of hundreds or thousands of individual atoms that are linked together in any number of ways, including chains, circles, and other complex shapes.

The most prolific hydrocarbons found in the chemistry of petroleum are alkanes, these are also sometimes known as branched or linear hydrocarbons. A significant percentage of the remaining chemical compound is made up of aromatic hydrocarbons and cycloalkanes. Additionally petroleum chemistry contains several more complex hydrocarbons such as asphaltenes.

Alkanes

The primary forms of hydrocarbons in the chemistry of petroleum are the alkanes, which are also often named paraffins. These saturated, branched or straight run hydrocarbons can make up 15 to 60% of crude. They have the general formula C_nH_{2n+2} . The paraffins are very pure hydrocarbons and contain only hydrogen and carbon; it is the alkanes which give petroleum chemistry its combustible nature.

Depending upon the type of alkanes present in the raw petroleum chemistry it will be suitable for different applications.

For fuel purposes only the alkanes from the following groups will be used: Pentane and Octane will be refined into gasoline, hexadecane and nonane will be refined into kerosene or diesel or used as a component in the production of jet fuel, hexadecane will be refined into fuel oil or heating oil. The exception to this are the petroleum molecules which have less than five carbon atoms, these are a form of natural petroleum gas and will either be burned away or harvested and sold under pressure as LPG (Liquid Petroleum Gas).

Alkene

Alkenes are not saturated, which means they contain at least one carbon-to-carbon double bond. They are also called olefins. Like alkanes, this can be confusing because there is also an olefin material. As in the case of paraffin wax and alkanes, olefin is just a type of fiber that is made from alkenes. Olefin is often made from polypropylene or polyethylene and is used in everything from rope to car interiors. It is useful because it is strong without being heavy, resistant to sunlight, and relatively easy to produce.

The double bond structure of alkenes changes their chemistry in comparison to alkanes. First, alkenes are more acidic than alkanes. They are also more reactive than alkanes and easily undergo polymerization reactions, which makes them highly valuable in industrial applications. General chemical formula cycloalkanes would be C_nH_{2n} .

Alkynes

In order to be considered an alkyne (also called acetylenes), a hydrocarbon must possess at least one triple bond between two carbons. A single triple bond results in a hydrocarbon molecule with the general formula of C_nH_{2n-2} . In following the general trend where alkenes were more reactive than alkanes, alkynes are more reactive than alkenes, making them the most reactive of the three basic hydrocarbon classes.

Cycloalkanes

The cycloalkanes, which are also often referred to as the naphthenes are classed as a saturated form of hydrocarbon. These can make up 30 to 60% of crude. By saturated we mean the molecule contains either one or several carbon rings with atoms of hydrogen attached to them. Cycloalkanes are similar to alkanes in their general physical properties, but they have higher boiling points, melting points, and densities than alkanes. This is due to stronger London forces because the ring shape allows for a larger area of contact. General chemical formula cycloalkanes would be C_nH_{2n} .

Aromatics

Aromatic hydrocarbons, also called arenes, are a unique class of carbon molecules in which carbon atoms are connected by alternating double and single bonds. These can constitute anywhere from 3 to 30% of crude. The aromatic hydrocarbons are another form of unsaturated hydrocarbon and having the general formula as C_nH_{2n-6} . The specific difference between the other hydrocarbons in the petroleum molecule is that the aromatic hydrocarbons will contain benzene rings, with atoms of hydrogen attached to them. Aromatic hydrocarbons tend to produce far more emissions when combusted, many will have a sweet, sickly smell to them, hence the name aromatic hydrocarbons.

The quantity and percentages of the specific types of hydrocarbons in raw petroleum chemistry can be determined by testing in a laboratory. The process involves extracting the molecules using some form of solvent and then separating them using a gas chromatograph. Finally an instrument such as a mass spectrometer will be used to examine the separate molecules in the chemical compound of the sample.

PETROLEUM COMPOSITION

The exact molecular composition varies widely from formation to formation but the proportion of chemical elements vary over fairly narrow limits as follows

Element	Composition (Weight%)
---------	-----------------------

Carbon	83 to 85%
Hydrogen	10 to 14%
Nitrogen	0.1 to 2%
Oxygen	0.05 to 1.5%
Sulfur	0.05 to 6.0%
Metals	< 0.1%

The actual overall properties of each different petroleum source are defined by the percentage of the four main hydrocarbons found within petroleum as part of the petroleum composition. The percentages for these hydrocarbons can vary greatly, giving the crude oil a quite distinct compound personality depending upon geographic region. These hydrocarbons are typically present in petroleum at the following percentages:

Composition (Weight%)

Hydrocarbon	Average	Range
Alkanes (paraffins)	30%	15 to 60%
Naphthenes	49%	30 to 60%
Aromatics	15%	3 to 30%
Asphaltic	6%	remainder

CLASSIFICATION OF PETROLEUM

For several decades now the crude oil or petroleum industry has classified the raw crude geographic region. Further classification of petroleum, derived from the density of the raw petroleum (API gravity) and its various non-hydrocarbon components (especially sulphur), is then added to the geographic designation.

In general, if the crude oil contains high levels of sulphur the petroleum classification is termed 'sour', if it has relatively low levels of sulphur the petroleum classification is termed 'sweet'. If the raw petroleum is of a high density then the petroleum classification is termed 'heavy' and if it is of a low density the petroleum classification is termed 'light'. Density of

oil is determined by the length of the hydrocarbons it contains. If it contains a great deal of long-chain hydrocarbons, the petroleum will be denser. If it contains a greater proportion of short-chain hydrocarbons it will be less dense.

The API gravity is used to classify oils as light, medium, heavy, or extra heavy. As the “weight” of oil is the largest determinant of its market value, API gravity is exceptionally important. The API values for each “weight” are as follows:

Classification	API Value
Light	API > 31.1
Medium	22.3 < API < 31.1
Heavy	API < 22.3
Extra Heavy	API < 10.0

PRODUCTS OF PETROLEUM

Liquefied Petroleum Gas

Liquefied Petroleum Gas or LPG is a flammable liquid that is a combination of various hydrocarbons. It is used in heating appliances, in vehicles, as a refrigerant, for cooking purposes etc. The most common forms of LPG are propane and butane. It is also produced by refining crude oil. Its boiling range is less than 25 °C.

Petrochemicals

Petrochemicals as the name suggests are chemical products obtained from petroleum. Petrochemicals are classified as olefins and aromatics. These sub classes are obtained by the catalytic cracking of petroleum fractions. Its boiling range is between 30 °C to 200 °C. Petrochemicals are produced by the fractional distillation of crude oil and natural gas. Petrochemicals are used in fertilizers, wax, polish, detergents, food additives, synthetic shoes, dyes, plastic bottles and so on.

Gasoline

Gasoline is also referred to as Petrol and is a transparent liquid obtained from the fractional distillation of crude oil. It consists of organic compounds and is mainly used in internal combustion engines. It is widely used across the globe and its consumption is so high that its prices have also soared and are continuously

changing as per increase in demand. Gasoline is obtained by the fractional distillation of crude oil between 40 °C (104 °F) and 205 °C (401 °F), which is its boiling range. Gasoline is used in vehicles, electrical generators, compressors etc.

Jet fuel

Jet fuel is sometimes called Aviation Turbine Fuel (ATF) and is primarily used for aircraft. This fuel is a combination of various hydrocarbons. The most common types of Jet fuel are Jet A and Jet A-1. The boiling range for Jet fuel (similar to Kerosene) is between 150 °C to 275 °C.

Kerosene

Kerosene, also called paraffin, is a combustible liquid containing hydrocarbons. Kerosene is used to power jet engines, for cooking, heating, lighting fuels and toys. Kerosene lamps are extremely popular. The boiling range for Kerosene is between 150 °C to 275 °C. Other applications of Kerosene are as a pesticide, as a solvent, lubricant, x-ray crystallography and so on.

Diesel

Diesel fuel or petro-diesel is a derivative of petroleum. Diesel fuel most commonly used today is the Ultra-Low Sulphur Diesel as it contains reduced amounts of sulphur in it comparatively. Diesel is obtained by fractional distillation of crude oil with a boiling range of 250 °C (392 °F) and 350 °C (662 °F) at atmospheric pressure. The quality of diesel fuel is measured in terms of Cetane numbers. Diesel is comparatively easier to refine from petroleum than gasoline. Diesel is mainly used as a vehicle fuel and engines using diesel are considered to be more energy efficient and have better fuel economy than for example, gasoline. Diesel is also used in gas turbines and external combustion engines.

Lubricating oils

Lubricants are mainly used to reduce friction between surfaces. A good lubricant has a high boiling point and viscosity. It is found to have thermal and hydraulic stability as well as a low freezing point. Lubricants contain 90 percent base oil and less than 10 percent additives. The boiling range for lubricants is between 300 °C (572 °F) to 370 °C (700 °F). Lubricants are also used as motor oils, transmit power, transfer heat, prevent corrosion and rusting etc.

Paraffin wax

Paraffin is a waxy solid that is used as a lubricant. It is typically a solid at room temperature. Its boiling point is greater than 370 °C. Paraffin wax is mostly used in candle making,

waxing materials such as paper or cloth, sealant, crayons, propellant for rocket motors, waxing surfboards, floors, cosmetics such as Vaseline and so on.

Fuel oils

Fuel oils are obtained from distillation of petroleum. Fuel oil is the heaviest fuel that can be obtained from refining crude oil. It is produced by the fractional distillation of crude oil between 370 °C (700 °F) and 600 °C (1112 °F) boiling range. Fuel oils have many applications such as heating homes, offices and for the usage of trucks, ships and automobiles. It is also used as a back up in power plants and electrical generators etc.

Asphalt

Asphalt is commonly called Bitumen. Asphalt is a black and thicker version of petroleum that is obtained both naturally and as a refined product. It is also classified as pitch. Its viscosity is the same as cold molasses. Asphalt is obtained by fractional distillation of crude oil at 525 °C (977 °F). Asphalt is primarily used to lay roads. Other uses are for waterproofing products meant to seal roofs etc.

Tar

Tar is obtained by the process called destruction distillation using several organic compounds. It can be manufactured from coal, petroleum, wood or peat. The end product is a combination of various hydrocarbons and free carbon. The boiling point for tar is greater than 600 °C. Tar has several uses such as a disinfectant, to seal roofs, hulls of ships etc. Wood tar is used as a flavor, spice, scent for spas, cosmetics, anti-dandruff shampoos and so on.

CHARACTERIZATION OF CRUDE

Crude of petroleum is very complex except for the low-boiling components, no attempt is made by the refiner to analyze for the pure components that contained in the crude oil. Relatively simple analytical tests are run on the crude and the results of these are used with empirical correlations to evaluate the crude oils as feedstocks for the particular refinery. Each crude is compared with the other feedstocks available and, based upon the operating cost and product realization, is assigned a value. The useful properties are discussed.

API Gravity

API stands for the American Petroleum Institute, which is the major United States trade association for the oil and natural gas industry. One of the most important standards that the API has set is the method used for measuring the density of petroleum. This standard is called the API gravity.

Specific gravity is a ratio of the density of one substance to the density of a reference substance, usually water. The API gravity is nothing more than the standard specific gravity used by the oil industry, which compares the density of oil to that of water through a calculation designed to ensure consistency in measurement. Less dense oil or “light oil” is preferable to more dense oil as it contains greater quantities of hydrocarbons that can be converted to gasoline.

API gravity is calculated using the specific gravity of an oil, which is nothing more than the ratio of its density to that of water (density of the oil/density of water). Specific gravity for API calculations is always determined at 60 degrees Fahrenheit.

Though API values do not have units, they are often referred to as degrees. Specific gravity of Crude oil may vary from less than 10°API to over 50°API but most crudes fall in the 20 to 45°API range. API gravity always refers to the liquid sample at 60°F (15.6°C).

Sulphur Content, wt%

Sulphur content and API gravity are two properties which have the greatest influence on the value of crude oil, although nitrogen and metals contents are increasing in importance. The sulphur content is expressed as per cent of sulphur by weight and varies from less than 0.1% to greater than 5%. Crudes with greater than 0.5% sulphur generally require more extensive processing than those with lower sulphur content.

Pour Point

The pour point of the crude oil, in °F or °C, is a rough indicator of the relative paraffinicity and aromaticity of the crude. The lower the pour point, the lower the paraffin content and the greater the content of aromatics.

Carbon Residue

Carbon residue is determined by distillation to a coke residue in the absence of air. The carbon residue is roughly related to the asphalt content of the crude and to the quantity of the lubricating oil fraction that can be recovered. In most cases the lower the carbon residue, the more valuable the crude. This is expressed in terms of the weight percent carbon residue by either the Ramsbottom (RCR) or Conradson (CCR) .

Salt Content

If the salt content of the crude, when expressed as NaCl, is greater than 10 lb/ 1000 bbl, it is generally necessary to desalt the crude before processing. If the salt is not removed, severe corrosion problems may be encountered. If residua are processed catalytically, desalting is desirable at even lower salt contents of the crude. Although it is not possible to have an accurate conversion unit between lb/1000 bbl and ppm by weight because of the different densities of crude oils, 1 lb/1000 bbl is approximately 3 ppm.

Characterization Factors

There are several correlations between yield and the aromaticity and paraffinicity of crude oils, but the two most widely used are the UOP or Watson **characterization factor** (KW) and the U.S. Bureau of Mines **correlation index** (CI).

Nitrogen Content, wt%

High nitrogen content is undesirable in crude oils because organic nitrogen compounds cause severe poisoning of catalysts used in processing and cause corrosion problems. Crudes containing nitrogen more than 0.25% by weight require special processing to remove the nitrogen.

Distillation Range

The boiling range of the crude gives an indication of the quantities of the various products present. The most useful type of distillation is known as a true boiling point (TBP) distillation and generally refers to a distillation performed in equipment that accomplishes a reasonable degree of fractionation. There is no specific test procedure called a TBP distillation, but the U.S. Bureau of Mines Hempel and ASTM D-285 distillations are the tests most commonly used. Neither of these specify either the number of theoretical plates or the reflux ratio used and, as a result, there is a trend toward using the results of a 15:5 distillation (D- 2892) rather than the TBP. The 15:5 distillation is carried out using 15 theoretical plates at a reflux ratio of 5: 1. The crude distillation range has to be correlated with ASTM distillations because product specifications are generally based on the simple ASTM distillation tests like D-86 and D-1160 etc.

Metals Content, ppm

The metals content metals (nickel, vanadium, and copper) of crude oils vary from a few parts per million to more than 1000 ppm. Minute quantities of some of these metals can severely affect the activities of catalysts and result in a lower value product distribution. Vanadium concentrations above 2 ppm in fuel oils can lead to severe corrosion to turbine blades and deterioration of refractory furnace linings and stacks. Distillation concentrates the

metallic constituents of crude in the residues, but some of the organometallic compounds are actually volatilized at refinery distillation temperatures and appear in the higher-boiling distillates. The metallic content may be reduced by solvent extraction with propane or similar solvents as the organometallic compounds are precipitated with the asphaltenes and resins.

DESALTING PROCESS

Crude oil often contains water, inorganic salts, suspended solids, and water-soluble trace metals. As a first step in the refining process, to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning the catalysts in processing units, these contaminants must be removed by desalting (dehydration).

The two most typical methods of crude-oil desalting, chemical and electrostatic separation use hot water as the extraction agent. In chemical desalting, water and chemical surfactant (demulsifiers) are added to the crude, heated so that salts and other impurities dissolve into the water or attach to the water, and then held in a tank where they settle out. Electrical desalting is the application of high-voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank. Surfactants are added only when the crude has a large amount of suspended solids. Both methods of desalting are continuous. A third and less-common process involves filtering heated crude using diatomaceous earth.

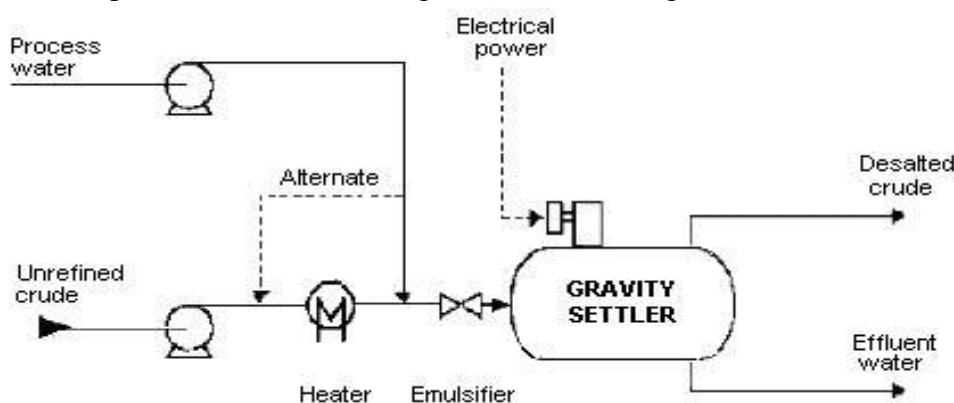


Figure 1.1 Electrostatic Desalting Flow Chart

The feedstock crude oil is heated to between 150° and 350°F to reduce viscosity and surface tension for easier mixing and separation of the water. The temperature

is limited by the vapor pressure of the crude-oil feedstock. In both methods other chemicals may be added. Ammonia is often used to reduce corrosion. Caustic or acid may be added to adjust the pH of the water wash. Wastewater and contaminants are discharged from the bottom of the settling tank to the wastewater treatment facility. The desalted crude is continuously drawn from the top of the settling tanks and sent to the crude distillation (fractionating) tower.

Safety Considerations

The potential exists for a fire due to a leak or release of crude from heaters in the crude-desalting unit. Low boiling point components of crude may also be released if a leak occurs.

Because this is a closed process, there is little potential for exposure to crude oil unless a leak or release occurs. Where elevated operating temperatures are used when desalting sour crudes, hydrogen sulfide will be present. There is the possibility of exposure to ammonia, dry chemical demulsifiers, caustics, and/or acids during this operation.

Depending on the crude feedstock and the treatment chemicals used, the wastewater will contain varying amounts of chlorides, sulfides, bicarbonates, ammonia, hydrocarbons, phenol, and suspended solids. If diatomaceous earth is used in filtration, exposures should be minimized or controlled. Diatomaceous earth can contain silica in very fine particle size, making this a potential respiratory hazard.

Corrosion Considerations

Inadequate desalting can cause fouling of heater tubes and heat exchangers throughout the refinery. Fouling restricts product flow and heat transfer and leads to failures due to increased pressures and temperatures. Corrosion, which occurs due to the presence of hydrogen sulfide, hydrogen chloride, naphthenic (organic) acids, and other contaminants in the crude oil, also causes equipment failure. Neutralized salts (ammonium chlorides and sulfides), when moistened by condensed water, can cause corrosion. Over-pressuring the unit is another potential hazard that causes failures.

ATMOSPHERIC DISTILLATION PROCESS

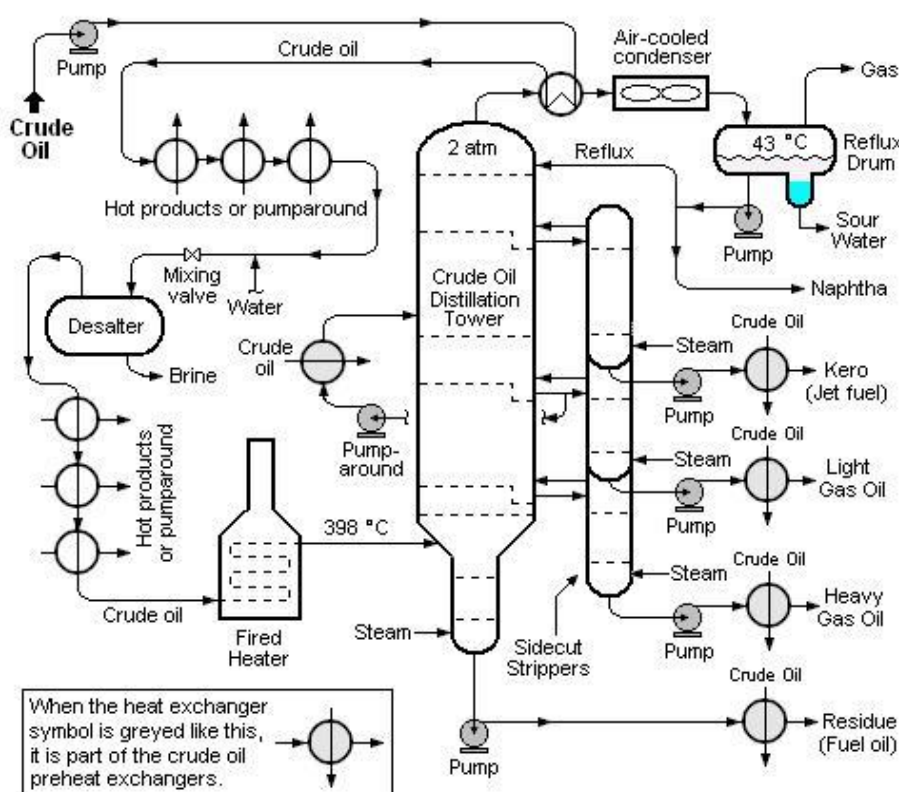
Desalting is the first separation process that takes place at the front end of a petroleum refinery. Its primary objective is to prevent corrosion and fouling of downstream lines and equipment by reducing the oil's salt content significantly. The main separation step in any crude oil refinery is atmospheric or primary distillation. Atmospheric distillation fractionates the crude oil into various distillates, fractions, or cuts of hydrocarbon compounds based on molecular size and boiling point range [e.g., light ends, propane, butanes, straight-run naphthas (light and heavy), kerosene, straight-run gas oils (light and heavy), and atmospheric residue] (Figure 1.2).

Figure 1.2 Atmospheric Distillation Unit

The term atmospheric distillation is used because the unit operates slightly above atmospheric pressure. Separation is carried out in a large tower, which contains a number of trays where hydrocarbon gases and liquids interact. The heated desalted crude enters the fractionation tower in a lower section called the flash zone. The unvaporized portion of the crude oil leaves the bottom of the tower via a steam stripper section, while the distillate vapors move up the tower countercurrent to a cooler liquid reflux stream. The cooling and condensing of the distillation tower overhead is provided partially by exchanging heat with the incoming crude oil and partially by either an air- or a water-cooled condenser. Additional heat is removed from the distillation column by a pump-around system, which is simply an internal condenser that ensures a continued reflux stream flow. The overhead distillate fraction from the distillation column is naphtha, which is allowed to leave the top of the

tower to be condensed and collected in the overhead drum. A portion of this stream is returned as reflux, while the rest is delivered to the lightend processes for stabilizing and further distillation. The other fractions removed from the side of the distillation column [i.e., from selected trays (draw-off trays)] at various points between the column top and bottom are jet fuel, kerosene, light gas oil, and heavy gas oil, which are steam stripped, cooled by exchanging heat with the incoming crude oil, and sent to other treatment areas and/or to storage. The heavier material (i.e., atmospheric residue oil) is withdrawn from the bottom of the tower.

Each stream is converted further by changing the size and structure of the molecules through crackg, reforming, and other conversion processes. The



converted products are then subjected to various treatment and separation processes to remove undesirable constituents or impurities (e.g., sulfur, nitrogen) and to improve product quality (e.g., octane number, cetane number). Atmospheric distillation is a crucial step, since it routes the molecules to the appropriate conversion units in the refinery. The cut point of the atmospheric residue depends on the prevailing fuel specifications and crude slate used. The

atmospheric residue leaves the bottom of the unit and is processed further in the vacuum distillation unit.

It is important not to subject crude oil to temperatures above 370 to 380°C because the high-molecular-weight components will undergo thermal cracking and form coke. The coke, by operating the distillation units at a high temperature, would result in plugging the tubes in the furnace that heats the crude oil fed to the distillation column. Plugging would also occur in the piping from the furnace to the distillation column as well as in the column itself.

VACUUM DISTILLATION PROCESS

Vacuum distillation is the distillation of liquids performed at a pressure lower than atmospheric pressure to take advantage of the fact that reducing the pressure lowers the boiling point of liquids.

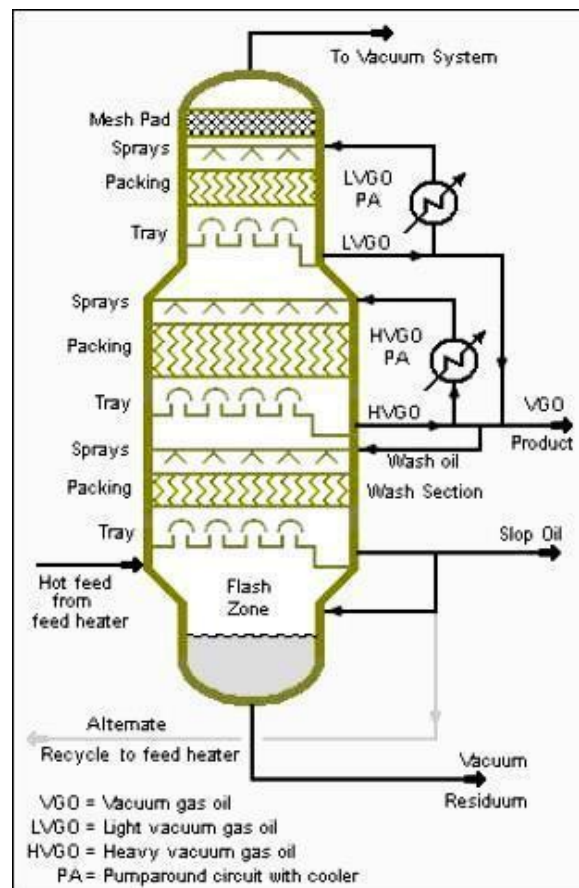


Figure 1.3 Vacuum Distillation Unit



Figure 1.4 Atmospheric and Vacuum Distillation Unit in a Crude Oil Refining Plant

The residual oil from the atmospheric distillation unit, is distilled at absolute pressures as low as 10 to 40 mmHg (also referred to as torr) so as to limit the operating temperature to less than 370 to 380 °C.

The 10 to 40 mmHg absolute pressure in a vacuum distillation column increases the volume of vapor formed per volume of liquid distilled. The result is that such columns have very large diameters.[5] Vacuum distillation columns, such those in Images 1 and 2, may have diameters of 15 meters or more, heights ranging up to about 50 meters, and feed rates ranging up to about 25,400 cubic meters per day (160,000 barrels per day).

The vacuum distillation column internals must provide good vapor-liquid contacting while, at the same time, maintaining a very low pressure increase from the column top to the column bottom. Therefore, refinery vacuum columns often use distillation trays only where withdrawing products from the side of the column (referred to as side draws). The remainder of the column uses packing material for the vapor-liquid contacting because such packing has a lower pressure drop than distillation trays. This packing material can be either structured sheet metal or randomly dumped packing such as Raschig rings.

The absolute pressure of 10 to 40 mmHg in a refinery vacuum distillation column is most often achieved by a vacuum system using multiple stages of steam jet ejectors.

Many industries, other than the petroleum refining industry, use vacuum distillation on a much smaller scale.

REFERENCE BOOKS:

1. Nelson, W.L., Petroleum Refinery Engineering, 4th Edition., McGraw Hill, New York, 1985
2. Bhaskara Rao B. K., Modern Petroleum Refining Processes, 2nd Edition., Oxford and IBH Publishing Company, New Delhi, 1989.
3. Hobson G. D and Pohl. W., Modern Petroleum Technology, 2nd Edition, Gulf Publishers, 1986.



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL ENGINEERING
DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 2-CRACKING AND REFORMING SCH3002

UNIT II CRACKING AND REFORMING

CRACKING

The “bottom of the barrel” has become more of a problem for refiners because heavier crudes are being processed and the market for heavy residual fuel oils has been decreasing. Historically, the heavy residual fuel oils have been burned to produce electric power and to supply the energy needs of heavy industry, but more severe environmental restrictions have caused many of these users to switch to natural gas. Cracking units convert large hydrocarbon molecules into smaller and more useful bits.

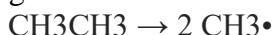
Cracking is the process whereby complex long chain hydrocarbons are broken down into simpler molecules such as light hydrocarbons, by the breaking of carbon-carbon bonds in the precursors. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst. The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum). These fractions are obtained from the distillation process as liquids, but are re-vaporised before cracking. There isn't any single unique reaction happening in the cracker. The hydrocarbon molecules are broken up in a fairly random way to produce mixtures of smaller hydrocarbons, some of which have carbon-carbon double bonds.

Reactions

A large number of chemical reactions take place during the cracking process, most of them based on free radicals. The main reactions that take place include

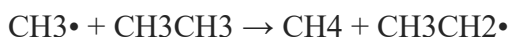
Initiation

In these reactions a single molecule breaks apart into two free radicals. Only a small fraction of the feed molecules actually undergo initiation, but these reactions are necessary to produce the free radicals that drive the rest of the reactions. In steam cracking, initiation usually involves breaking a chemical bond between two carbon atoms, rather than the bond between a carbon and a hydrogen atom.



Hydrogen abstraction

In these reactions a free radical removes a hydrogen atom from another molecule, turning the second molecule into a free radical.



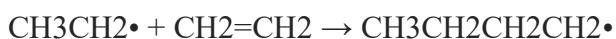
Radical decomposition

In these reactions a free radical breaks apart into two molecules, one an alkene, the other a free radical. This is the process that results in alkene products.



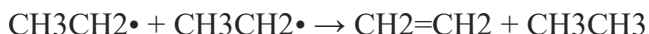
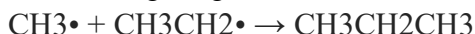
Radical addition

In these reactions, the reverse of radical decomposition reactions, a radical reacts with an alkene to form a single, larger free radical. These processes are involved in forming the aromatic products that result when heavier feedstocks are used.



Termination

In these reactions two free radicals react with each other to produce products that are not free radicals. Two common forms of termination are recombination, where the two radicals combine to form one larger molecule, and disproportionation, where one radical transfers a hydrogen atom to the other, giving an alkene and an alkane.



Cracking Methodologies

1. Thermal methods
 - a. Thermal cracking
 - b. Steam cracking
2. Catalytic methods
 - a. Fluid Catalytic cracking
 - b. Hydrocracking

THERMAL CRACKING

Breaking down large molecules by heating at high temperature and pressure is termed as thermal cracking. Thermal cracking process for upgradation of heavy residue has been used since long and still it is playing an important role in the modern refinery through upgradation of heavy residue and improving the economics of the refinery through the production of lighter distillate and other valuable product like low value fuel gas and petroleum coke.

VISBREAKING

Visbreaking is essentially a mild thermal cracking operation at mild conditions where in long chain molecules in heavy feed stocks are broken into short molecules thereby leading to a viscosity reduction of feedstock. Now all the new visbreaker units are of the soaker type. Soaker drum utilizes a soaker drum in conjunction with a fired heater to achieve conversion. Visbreaking is a non-catalytic thermal process. It reduces the viscosity and pour point of heavy petroleum fractions so that product can be sold as fuel oil. It gives 80 - 85% yield of fuel oil and balance recovered as light and middle distillates. The unit produces gas, naphtha, heavy naphtha, visbreaker gas oil, visbreaker fuel oil (a mixture of visbreaker gas oil and visbreaker tar).

A given conversion in visbreaker can be achieved by two ways:

1. High temp., low residence time cracking: Coil Visbreaking.
2. Low temp., high residence time cracking: Soaker visbreaking.

Coil cracking uses higher furnace outlet temperatures [885–930°F(473–500°C)] and reaction times from one to three minutes, while soaker cracking uses lower furnace outlet temperatures [800–830°F (427–443°C)] and longer reaction times. The product yields and properties are similar, but the soaker operation with its lower furnace outlet temperatures has the advantages of lower energy consumption and longer run times

before having to shut down to remove coke from the furnace tubes. Run times of 3–6 months are common for furnace visbreakers and 6–18 months for soaker visbreakers. This apparent advantage for soaker visbreakers is at least partially balanced by the greater difficulty in cleaning the soaking drum

The feed is introduced into the furnace and heated to the desired temperature. In the furnace or coil cracking process the feed is heated to cracking temperature (474– 500°C) and quenched as it exits the furnace with gas oil or tower bottoms to stop the cracking reaction. In the soaker cracking operation, the feed leaves the furnace between 800 and 820°F (427–438°C) and passes through a soaking drum, which provides the additional reaction time, before it is quenched. Pressure is an important design and operating parameter with units being designed for pressures as high as

750 psig (5170 kPa) for liquid-phase visbreaking and as low as 100–300 psig (690– 2070 kPa) for 20–40% vaporization at the furnace outlet. For furnace cracking, fuel consumption accounts for about 80% of the operating cost with a net fuel consumption equivalent of 1–1.5 wt% on feed. Fuel requirements for soaker visbreaking are about 30–35% lower. Many of the properties of the products of visbreaking vary with conversion and the characteristics of the feedstocks. However, some properties, such as diesel index and octane number, are more closely related to feed qualities; and others, such as density and viscosity of the gas oil, are relatively independent of both conversion and feedstock characteristics.

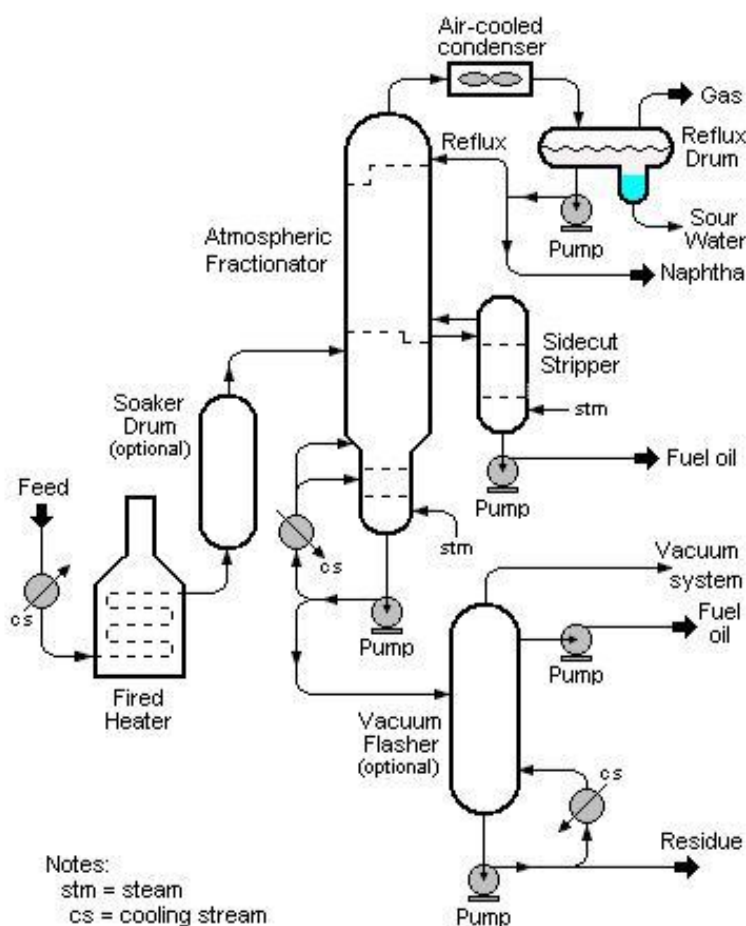


Figure 2.1 Visbreaking

CATALYTIC CRACKING

Catalytic cracking is the most important and widely used refinery process for converting heavy oils into more valuable gasoline and lighter products. Originally cracking was accomplished thermally but the catalytic process has almost completely replaced thermal cracking because more gasoline having a higher octane and less heavy fuel oils and light gases are produced. The light gases produced by catalytic cracking contain more olefins than those produced by thermal cracking.

The cracking process produces carbon (coke) which remains on the catalyst particle and rapidly lowers its activity. To maintain the catalyst activity at a useful level, it is necessary to regenerate the catalyst by burning off this coke with air. As a result, the catalyst is continuously moved from reactor to regenerator and back to reactor. The cracking reaction is endothermic and the regeneration reaction exothermic. Some units are designed to use the regeneration heat to supply that needed for the reaction and to heat the feed up to reaction temperature. These are known as “heat balance” units.

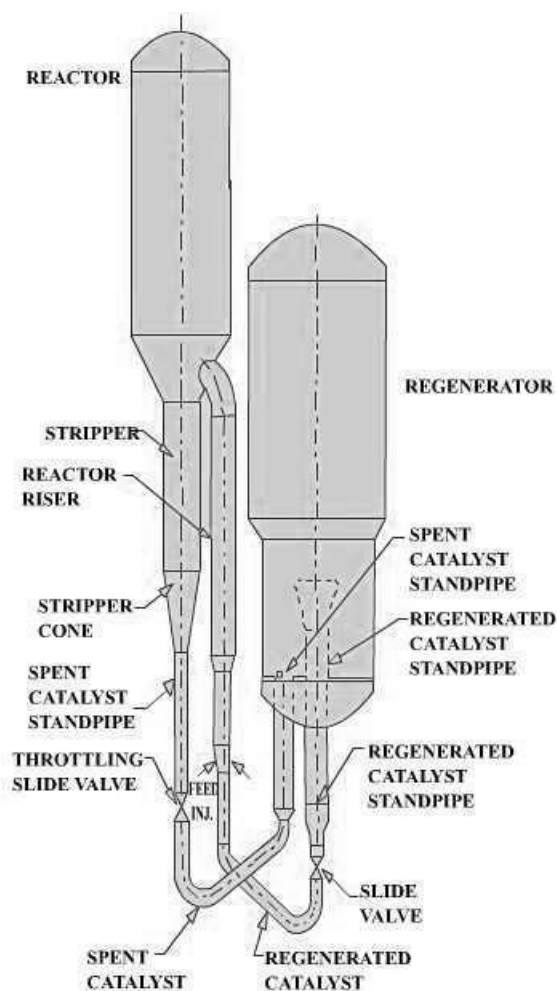


Figure 2.2 Exxon FLEXCRACKING IIIR FCC unit

Average riser reactor temperatures are in the range 900 to 1000°F (480–540°C), with oil feed temperatures from 500 to 800°F (260–425°C) and regenerator exit temperatures for catalyst from 1200 to 1500°F (650–815°C).

The catalytic-cracking processes in use today can all be classified as

- ☐ Moving-bed units
- ☐ Fluidized-bed units.

There are several modifications under each of the classes depending upon the designer or builder, but within a class the basic operation is very similar. The Thermoform catalytic cracking process (TCC) is representative of the moving-bed units and the fluid catalytic cracker (FCC) of the fluidized-bed units. There are very few TCC units in operation today and the FCC unit has taken over the field. The FCC units can be classified as either bed or riser (transfer line) cracking units depending upon where the major fraction of the cracking reaction occurs.

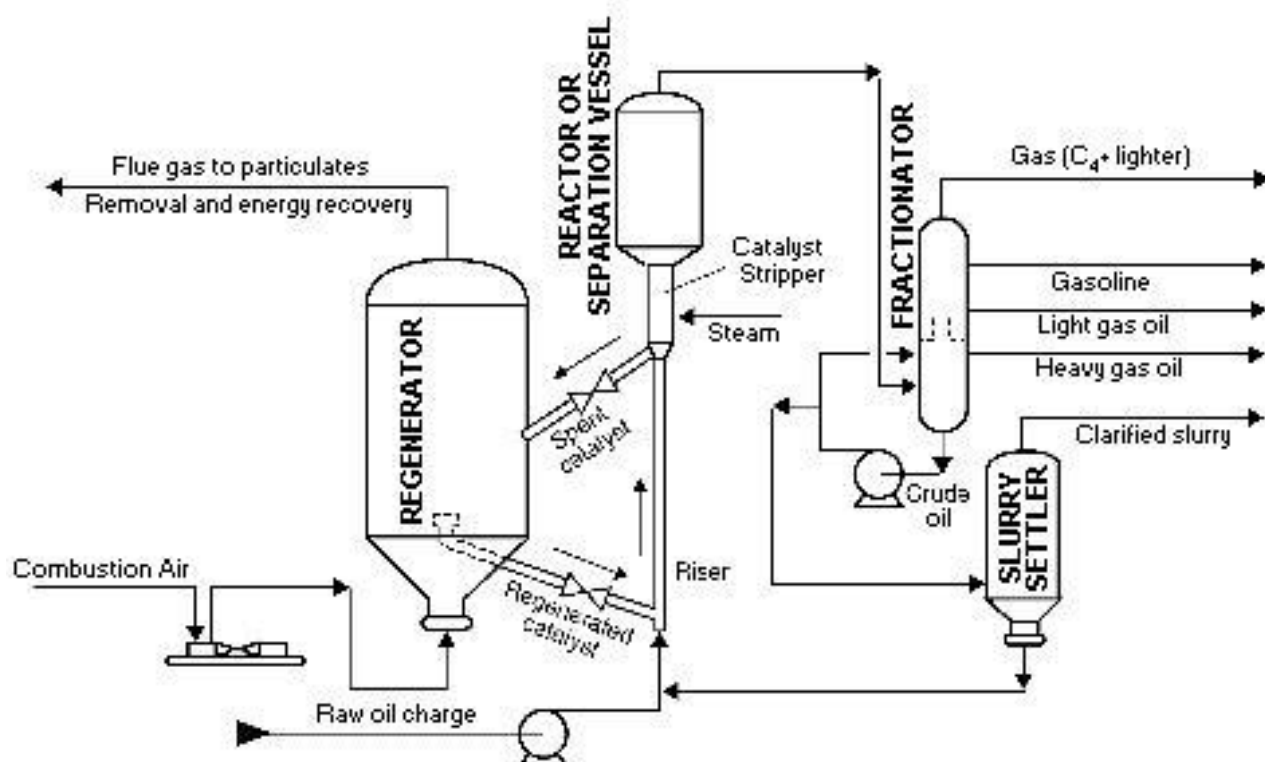


Figure 2.3 Schematic Flow Diagram of FCCU

The process flows of both types of processes are similar. The hot oil feed is contacted with the catalyst in either the feed riser line or the reactor. As the cracking reaction progresses, the catalyst is progressively deactivated by the formation of coke on the surface of the catalyst. The catalyst and hydrocarbon vapors are separated mechanically, and oil remaining on the catalyst is removed by steam stripping before the catalyst enters the regenerator. The oil vapors are taken overhead to a fractionation tower for separation into streams having the desired boiling ranges. The spent catalyst flows into the regenerator and is reactivated by burning off the coke deposits with air. Regenerator temperatures are carefully controlled to prevent catalyst

deactivation by overheating and to provide the desired amount of carbon burn-off. This is done by controlling the air flow to give a desired CO₂/CO ratio in the exit flue gases or the desired temperature in the regenerator. The flue gas and catalyst are separated by cyclone separators and electrostatic precipitators. The catalyst in some units is steam-stripped as it leaves the regenerator to remove adsorbed oxygen before the catalyst is contacted with the oil feed.

The moving-bed catalytic cracking process is similar to the FCC process. The catalyst is in the form of pellets that are moved continuously to the top of the unit by conveyor or pneumatic lift tubes to a storage hopper, then flow downward by gravity through the reactor, and finally to a regenerator. The regenerator and hopper are isolated from the reactor by steam seals. The cracked product is separated into recycle gas, oil, clarified oil, distillate, naphtha, and wet gas.

Cracking Catalysts

Commercial cracking catalysts can be divided into three classes:

- (1) acid-treated natural aluminosilicates,
- (2) amorphous synthetic silica-alumina combinations, and
- (3) crystalline synthetic silica-alumina catalysts called zeolites or molecular sieves.

The advantages of the zeolite catalysts over the natural and synthetic amorphous catalysts are:

1. Higher activity
2. Higher gasoline yields at a given conversion
3. Production of gasolines containing a larger percentage of paraffinic and aromatic hydrocarbons
4. Lower coke yield (and therefore usually a larger throughput at a given conversion level)
5. Increased isobutane production
6. Ability to go to higher conversions per pass without overcracking

Process Variables

Within the limits of normal operations, increasing

1. Reaction temperature
2. Catalyst/oil ratio
3. Catalyst activity
4. Contact time

results in an increase in conversion, while a decrease in space velocity increases conversion. It should be noted that an increase in conversion does not necessarily mean an increase in gasoline yield, as an increase in temperature above a certain level can increase conversion, coke and gas yields, and octane number of the gasoline but decrease gasoline yield.

HYDROCRACKING

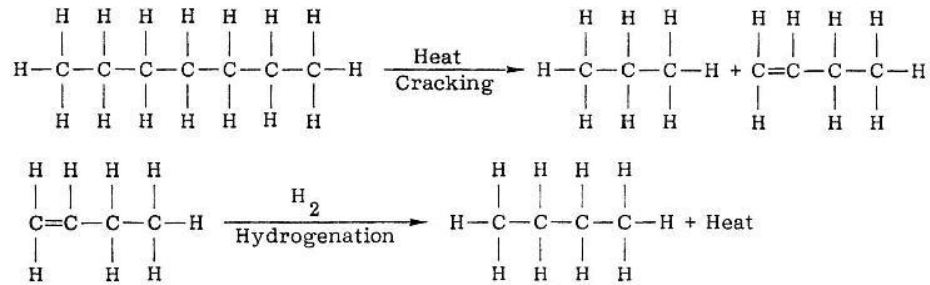
Although hydrogenation is one of the oldest catalytic processes used in refining petroleum, only in recent years has catalytic hydrocracking developed to any great extent in this country. This interest in the use of hydrocracking has been caused by several factors, including

- (1) the demand for petroleum products has shifted to high ratios of gasoline and jet fuel compared with the usages of diesel fuel and home heating oils,

- (2) by-product hydrogen at low cost and in large amounts has become available from catalytic reforming operations, and
- (3) Environmental concerns limiting sulfur and aromatic compound concentrations in motor fuels have increased.

Reactions

Although there are hundreds of simultaneous chemical reactions occurring in hydrocracking, it is the general opinion that the mechanism of hydrocracking is that of catalytic cracking with hydrogenation superimposed. Catalytic cracking is the scission of a carbon–carbon single bond, and hydrogenation is the addition of hydrogen to a carbon–carbon double bond. An example of the scission of a carbon–carbon single bond followed by hydrogenation is the following:



The hydrocracking process may require either one or two stages, depending upon the process and the feed stocks used. The shown process is a fixed-bed regenerative process employing a molecular-sieve catalyst impregnated with a rare-earth metal. The process employs either single-stage or two-stage hydrocracking with typical operating conditions ranging from 660 to 785°F and from 1000 to 2000 psig (350–420°C and 6900–13,800 kPa). The temperature and pressure vary with the age of the catalyst, the product desired, and the properties of the feedstock.

The decision to use a single- or two-stage system depends upon the size of the unit and the product desired. For most feedstocks the use of a single stage will permit the total conversion of the feed material to gasoline and lighter products by recycling the heavier material back to the reactor. The process flow for a two-stage reactor is shown in Figure 2.4. If only one stage is used, the process flow is the same as that of the first stage of the two-stage plant except the fractionation tower bottoms is recycled to the reactor feed.

The fresh feed is mixed with makeup hydrogen and recycle gas (high in hydrogen content) passed through a heater to the first reactor. If the feed has not been hydrotreated, there is a guard reactor before the first hydrocracking reactor. The guard reactor usually has a modified hydrotreating catalyst such as cobalt-molybdenum on silica-alumina to convert organic sulfur and nitrogen compounds to hydrogen sulfide, ammonia, and hydrocarbons to protect the precious metals catalyst in the following reactors. The hydrocracking reactor(s) is operated at a sufficiently high temperature to convert 40 to 50 vol% of the reactor effluent to material boiling below

400°F (205°C). The reactor effluent goes through heat exchangers to a high-pressure separator where the hydrogen-rich gases are separated and recycled to the first stage for mixing both makeup hydrogen and fresh feed. The liquid product from the separator is sent to a distillation column where the C4 and lighter gases are taken off overhead, and the light and heavy naphtha, jet fuel, and diesel fuel boiling range streams are removed as liquid sidestreams. The fractionator bottoms are used as feed to the second-stage reactor system. The unit can be operated to produce all gasoline and lighter products or to maximize jet fuel or diesel fuel products.

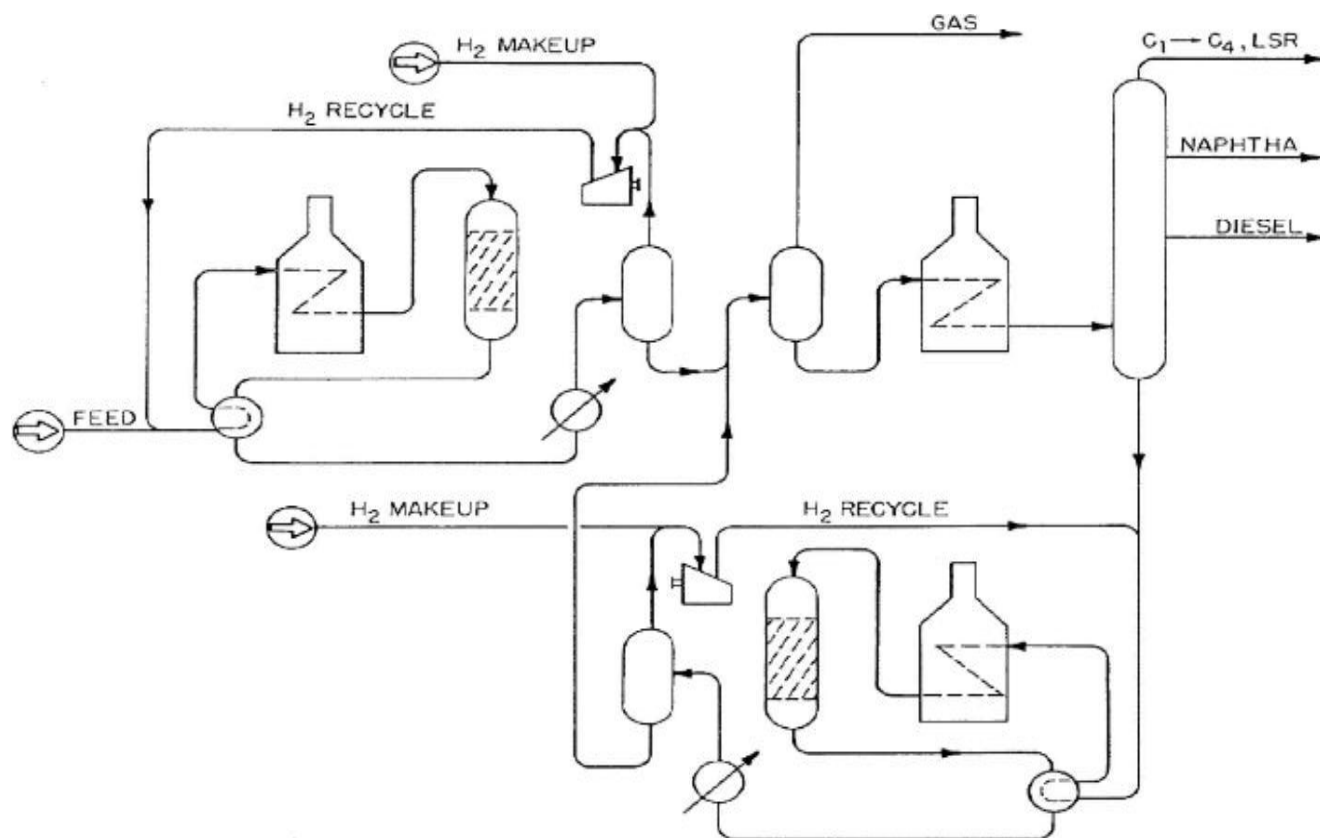


Figure 2.3 Two Stage Hydrocracker

The bottoms stream from the fractionator is mixed with recycle hydrogen from the second stage and sent through a furnace to the second-stage reactor. Here the temperature is maintained to bring the total conversion of the unconverted oil from the first-stage and second-stage recycle to 50 to 70 vol% per pass. The second-stage product is combined with the first-stage product prior to fractionation.

Both the first- and second-stage reactors contain several beds of catalysts. The major reason for having separate beds is to provide locations for injecting cold recycled hydrogen into the reactors for temperature control. In addition, redistribution of the feed and hydrogen between the beds helps to maintain a more uniform utilization of the catalyst.

When operating hydrocrackers for total conversion of distillate feeds to gasoline, the butane-and-heavier liquid yields are generally from 120 to 125 vol% of fresh feed.

Hydrocracking Catalyst

There are a number of hydrocracking catalysts available and the actual composition is tailored to the process, feed material, and the products desired. Most of the hydrocracking catalysts consist of a crystalline mixture of silica-alumina with a small uniformly distributed amount of rare earths contained within the crystalline lattice. The silica-alumina portion of the catalyst provides cracking activity while the rare-earth metals promote hydrogenation. Catalyst activity decreases with use, and reactor temperatures are raised during a run to increase reaction rate and maintain conversion.

Process Variables

The primary reaction variables are reactor temperature and pressure, space velocity, hydrogen consumption, nitrogen content of feed, and hydrogen sulphide content of the gases.

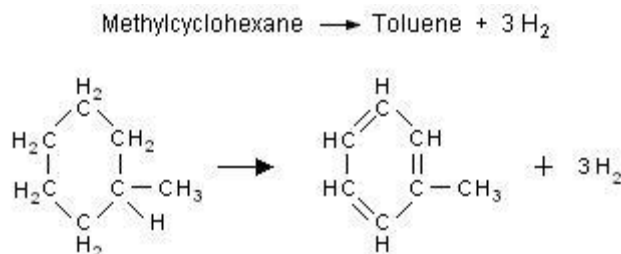
CATALYTIC REFORMING

The demand of today's automobiles for high-octane gasolines has stimulated the use of catalytic reforming. In catalytic reforming, the change in the boiling point of the stock passed through the unit is relatively small as the hydrocarbon molecular structures are rearranged to form higher-octane aromatics with only a minor amount of cracking. Thus catalytic reforming primarily increases the octane of motor gasoline rather than increasing its yield; in fact, there is a decrease in yield because of hydrocracking reactions which take place in the reforming operation.

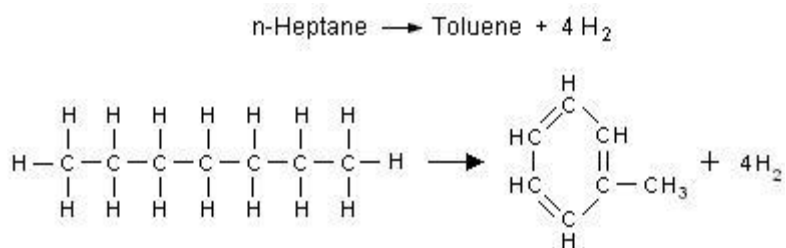
The typical feedstocks to catalytic reformers are heavy straight-run (HSR) gasolines and naphthas [180–375°F (82–190°C)] and heavy hydrocracker naphthas. These are composed of the four major hydrocarbon groups: paraffins, olefins, naphthenes, and aromatics (PONA).

There are four major reactions that take place during reforming. They are:

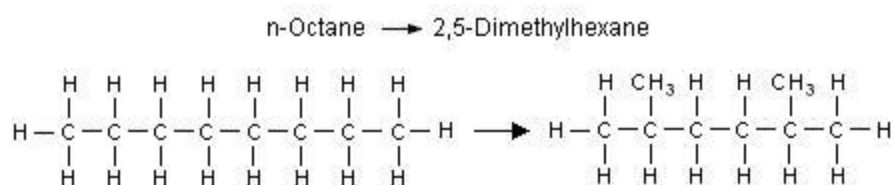
- (1) The dehydrogenation of naphthenes to aromatics



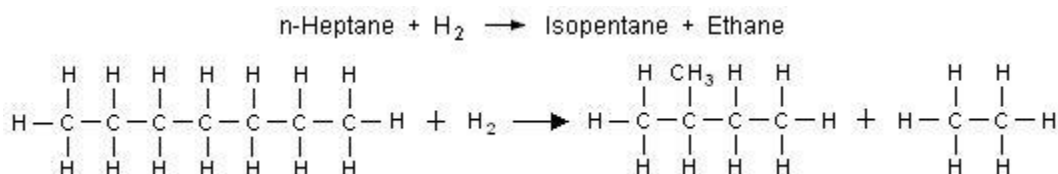
(2) The dehydrocyclization of paraffins to aromatics



(3) The isomerization of normal paraffins to isoparaffins



(4) The hydrocracking of paraffins into smaller molecules



The hydrocracking of paraffins is the only one of the above four major reforming reactions that consumes hydrogen. The isomerization of normal paraffins does not consume or produce hydrogen. However, both the dehydrogenation of naphthenes and the dehydrocyclization of paraffins produce hydrogen. The overall net production of hydrogen in the catalytic reforming of petroleum naphthas ranges from about 50 to 200 cubic meters of hydrogen gas (at 0 °C and one atmosphere) per cubic meter of liquid naphtha feedstock. In many petroleum refineries, the net hydrogen produced in catalytic reforming supplies a significant part of the hydrogen used elsewhere in the refinery (for example, in hydrosulfurization processes).

Process description

The most commonly used type of catalytic reforming unit has three reactors, each with a fixed bed of catalyst, and all of the catalyst is regenerated in situ during routine catalyst regeneration shutdowns which occur approximately once each 6 to 24 months. Such a unit is referred to as a semi-regenerative catalytic reformer (SRR).

Some catalytic reforming units have an extra spare or swing reactor and each reactor can be individually isolated so that any one reactor can be undergoing in-situ regeneration while the other reactors are in operation. When that reactor is

regenerated, it replaces another reactor which, in turn, is isolated so that it can then be regenerated. Such units, referred to as cyclic catalytic reformers, are not very common. Cyclic catalytic reformers serve to extend the period between required shutdowns.

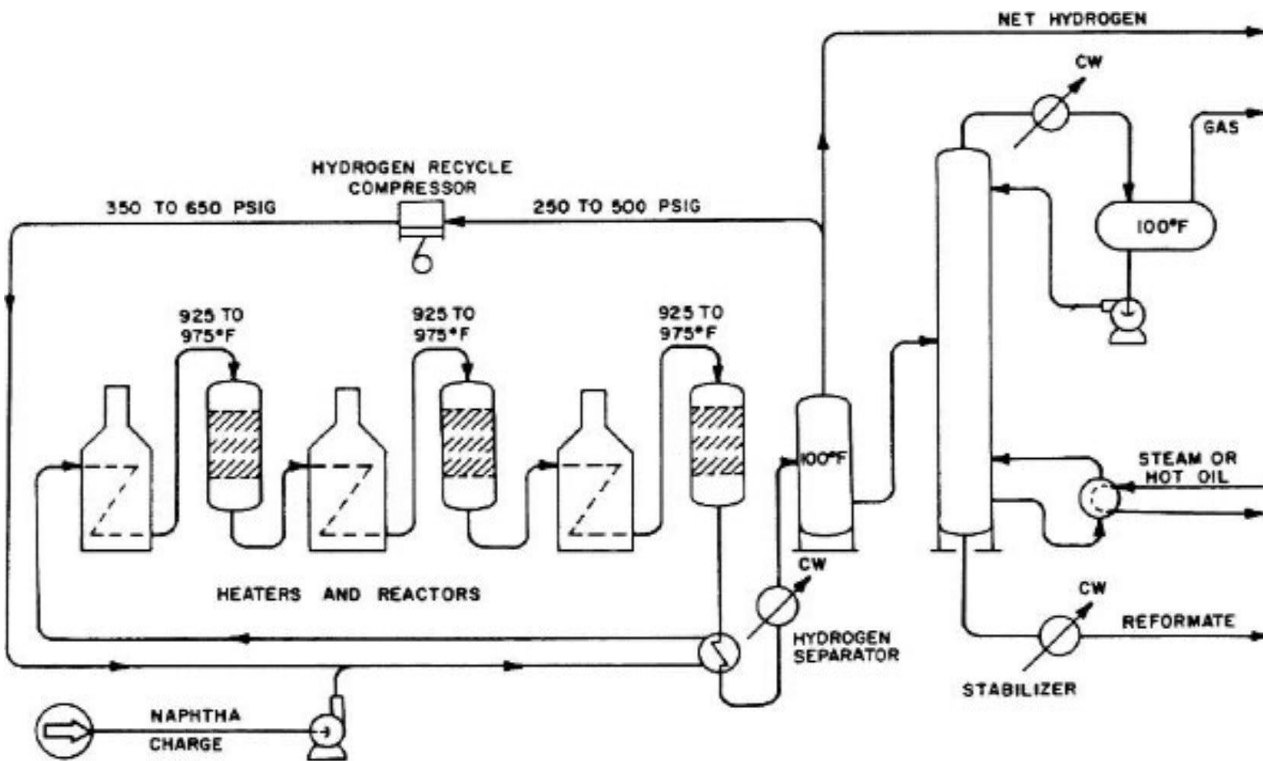


Figure 2.4 Process flow diagram of semi-regenerative catalytic reforming unit

The pretreated feed and recycle hydrogen are heated to 925 to 975°F (498–524°C) before entering the first reactor. In the first reactor, the major reaction is the dehydrogenation of naphthenes to aromatics and, as this is strongly endothermic, a large drop in temperature occurs. To maintain the reaction rate, the gases are reheated before being passed over the catalyst in the second reactor. As the charge proceeds through the reactors, the reaction rates decrease and the reactors become larger, and the reheat needed becomes less. Usually three or four reactors are sufficient to provide the desired degree of reaction and heaters are needed before each reactor to bring the mixture up to reaction temperature. In practice, either separate heaters can be used or one heater can contain several separate coils.

The reaction mixture from the last reactor is cooled and the liquid products condensed. The hydrogen-rich gases are separated from the liquid phase in a drum separator, and the liquid from the separator is sent to a fractionator to be debutanized.

The hydrogen-rich gas stream is split into a hydrogen recycle stream and a net hydrogen by-product which is used in hydrotreating or hydrocracking operations or as fuel.

The reformer operating pressure and the hydrogen/feed ratio are compromises among obtaining maximum yields, long operating times between regeneration, and stable operation. It is usually necessary to operate at pressures from 50 to 350 psig (345– 2415 kPa) and at hydrogen charge ratios of 3–8 mol H₂/mol feed (2800–7600 scf/bbl). Liquid hourly space velocities in the area of 1 to 3 are in general use.

The original reforming process is classified as a semiregenerative type because catalyst regeneration is infrequent and runs of 6 to 24 months between regeneration are common. In the cyclic processes, regeneration is typically performed on a 24- or 48-hour cycle, and a spare reactor is provided so that regeneration can be accomplished while the unit is still on-stream. Because of these extra facilities, the cyclic processes are more expensive but offer the advantages of low pressure operation and higher yields of reformate at the same severity.

Reforming Catalyst

All of the reforming catalyst in general use today contains platinum supported on an alumina base. In most cases rhenium is combined with platinum to form a more stable catalyst which permits operation at lower pressures.

Process Variables

The yield of aromatics is increased by:

- (1) High temperature (increases reaction rate but adversely affects chemical equilibrium)
- (2) Low pressure (shifts chemical equilibrium “to the right”)
- (3) Low space velocity (promotes approach to equilibrium)
- (4) Low hydrogen-to-hydrocarbon mole ratios (shifts chemical equilibrium “to the right,” however, a sufficient hydrogen partial pressure must be maintained to avoid excessive coke formation).

Alkylation unit, is one of the conversion processes used in the petroleum refineries. It is used to convert isobutane and low-molecular-weight alkenes (primarily a mixture of propene and butene) into alkylate, a high octane gasoline component. The process occurs in the presence of a strong acting acid as catalyst. The acid can be either sulfuric acid or hydrofluoric acid (HF). Depending on the acid used as catalyst the unit takes the name of SAAU (Sulphuric Acid Alkylation Unit) or HFAU (Hydrofluoric Acid Alkylation Unit). Since crude oil generally contains only 10 to 40 percent of hydrocarbon constituents in the gasoline range, refineries use a fluid catalytic cracking unit (FCCU) process to convert high molecular weight hydrocarbons into smaller and more volatile compounds, which are then converted into liquid gasoline-size hydrocarbons. Alkylation processes transform low molecular-weight alkenes and iso-paraffin molecules into larger iso-paraffins with a high octane number. The product of the unit, the alkylate, is composed of a mixture of high-octane, branched-chain paraffinic hydrocarbons (mostly isoheptane and isooctane). Alkylate is a premium gasoline blending stock because it has exceptional antiknock properties and is clean burning. The octane number of the alkylate depends mainly upon the kind of alkenes used and upon operating conditions. For example, isooctane results from combining butylene with isobutane and has an octane rating of 100 by definition. There are other products in the alkylate effluent, so the octane rating will vary accordingly.

Catalyst requirement to build an alkylation unit:

The availability of a suitable catalyst is also an important factor in deciding whether to build an alkylation plant. If sulfuric acid (HSO₂) is used, significant volumes are

2 4

needed. Access to a suitable plant is required for the supply of fresh acid and the disposition of spent acid. If a sulfuric acid plant must be constructed specifically to support an alkylation unit, such construction will have a significant impact on both the initial requirements for capital and ongoing costs of operation. Alternatively it is possible to install a WSA Process unit to regenerate the spent acid. No drying of the gas takes place. This means that there will be no loss of acid, no acidic waste material

and no heat is lost in process gas reheating. The selective condensation in the WSA condenser ensures that the regenerated fresh acid will be 98% weight, even with the humid process gas. It is possible to combine spent acid regeneration with disposal of hydrogen sulfide by using the hydrogen sulfide as a fuel.

The second main option is to use hydrofluoric acid (HF) as catalyst. In typical alkylation plants, rates of consumption for acid are much lower than for sulfuric acid. The small amount of organofluorine side products are continuously removed from the reactor and the consumed HF is replenished. HF acid plants can process a wider range of feedstocks with propylenes and butylenes. These plants also produce alkylate with better octane rating than do sulfuric plants. However, due to its hazardous nature, HF acid is produced at very few locations and transportation must be managed rigorously.

Feed to the alkylation unit:

The olefin feed to an alkylation unit generally originates from a FCCU and contains butene, isobutene, and possibly propene and/or amylenes. The olefin feed is also likely to contain diluents (such as propane, n-butane, and n-pentane), noncondensables (such as ethane and hydrogen) and contaminants. Diluents in principle have no effect on the reaction of alkylation but occupy a portion of the reactor and can influence the yield of secondary reactions of polymerisation and of undesired organofluorine side products. Incondensables are from a chemical perspective similar to diluents but they do not condense at the pressure and temperature of the process, and therefore they concentrate to a point that must be vented. Contaminants are compounds that react with and/or dilute the sulfuric acid catalyst. They increase acid consumption and contribute to produce undesirable reaction products and increase polymer formation. Common contaminants are water, methanol and ethanol.

The isobutane feed to an alkylation unit can be either low or high purity. Low purity makeup isobutane feedstock (typically < 70% vol isobutane) usually originates from the refinery (mainly from the reformer) and need to be processed in the deisobutanizer (DIB). High purity feedstock (> 95% vol isobutane) normally originates from an external

DIB and is fed directly to the alkylation unit reaction zone. The isobutane feed does not normally contain any significant level of contaminants.

Operating variables:

Many variables impact the product quality and operating costs of an alkylation unit.

Isobutane Concentration:

In order to promote the desired alkylation reactions, which are those involving isobutane and olefins, it is necessary to maintain a high concentration of isobutane in the reaction zone. Low isobutane-olefin ratios increase the likelihood of olefin-olefin polymerization that will result in lower octane. Polymerization reactions also have a higher rate of production of acid soluble oils, resulting in higher acid consumption.

Temperature:

Typically, alkylation is carried out in the neighborhood of 20 °C. Higher reaction temperatures dramatically favor polymerization reactions that will dilute the acid. Equipment corrosion will also increase with higher reaction temperatures. Low reaction temperatures slow the settling rate of the acid from the alkylate. Lower temperature than ambient cannot be achieved as the coldest possible temperature is that of the cooling fluids (air and water). Seasonal factors influence the production of polymerization reactions, therefore in summer the consumption of acid is higher, especially in HFAU.

Acid strength:

As the concentration of the acid catalyst is reduced, the rate of production of acid soluble polymers increases. Feeds that contain high amounts of propylene have a much higher rate of increase in acid consumption over the normal spending range. High acid concentration must be maintained in order to minimize polymerization and red oil production. When concentrations are too low catalyst activity is substantially decreased and polymerization enhanced to the point that it is difficult to maintain acid strength. This condition is known as acid runaway. In HSAU recent studies have found that both butylenes and amylenes can be spent to a lower acid concentration

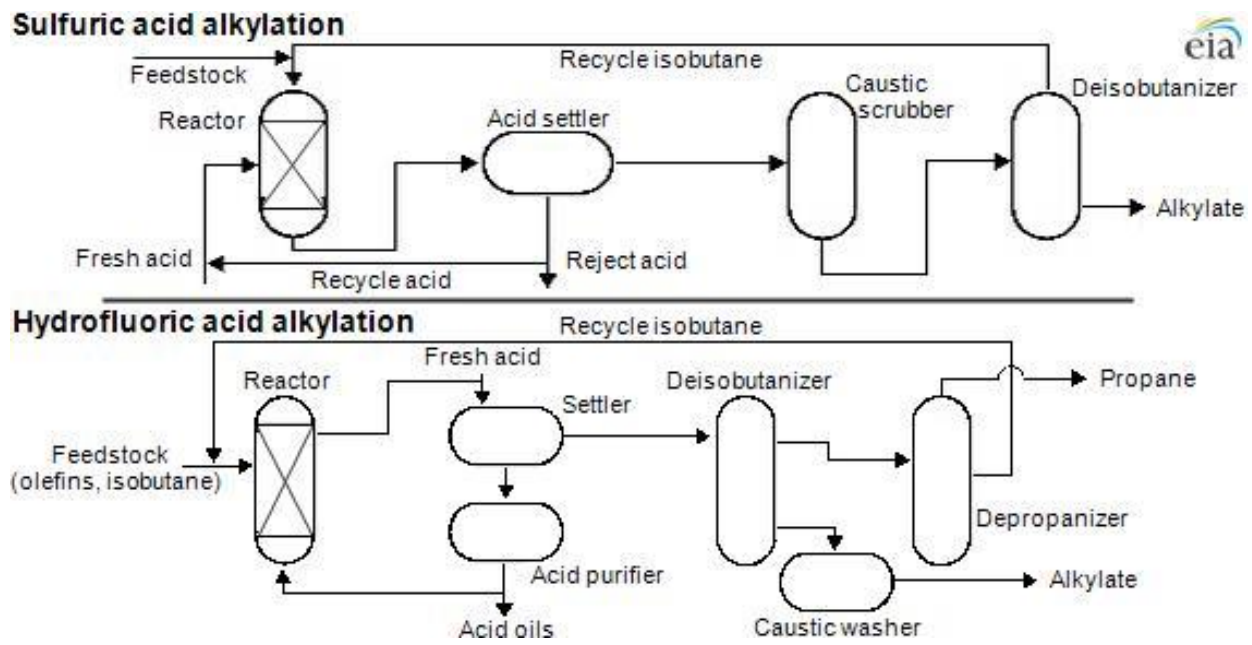
without entering into a runaway condition. While the economics of alkylating both butylenes and amylenes will benefit from lowering the acid spending strength, the acid consumption of amylenes has a greater response than that of butylenes. Also the expected decrease in octane of alkylates produced at lower acid concentrations is less for amylenes than butylenes.

Olefin space velocity:

Olefin space velocity is defined as the volume of olefin charged per hour divided by the average volume of sulfuric acid in the contactor reactor. In general, higher olefin space velocities tend to increase sulfuric acid consumption rates and decrease alkylate octane.

Mixing:

Mixing is an important parameter, especially in HSAU because the alkylation reaction depends on the emulsion of the hydrocarbon into the sulfuric acid. This is an acid continuous emulsion and it is presumed that the reaction occurs at the interface of acid and hydrocarbon. The better the emulsion, the finer the droplets and the better the reaction.

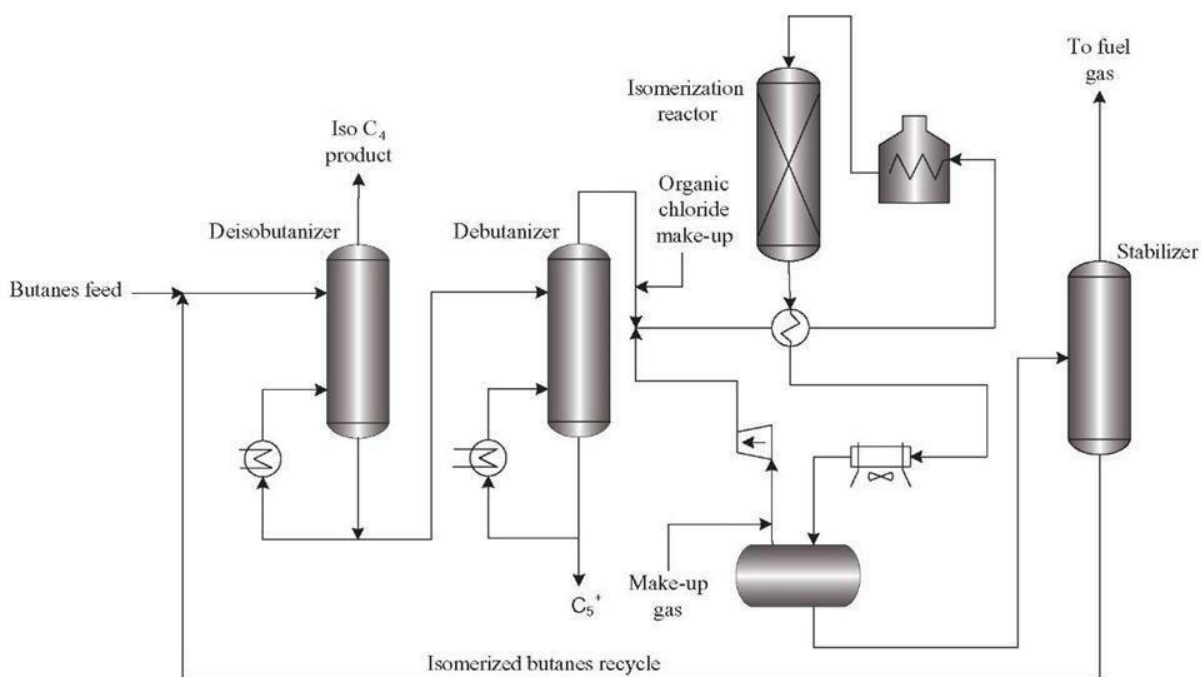


ISOMERIZATION PROCESS:

There are two distinct isomerization processes, butane (C) and pentane/hexane

(C/C) Isomerization is a process in petroleum refining that converts n-butane,
5 6

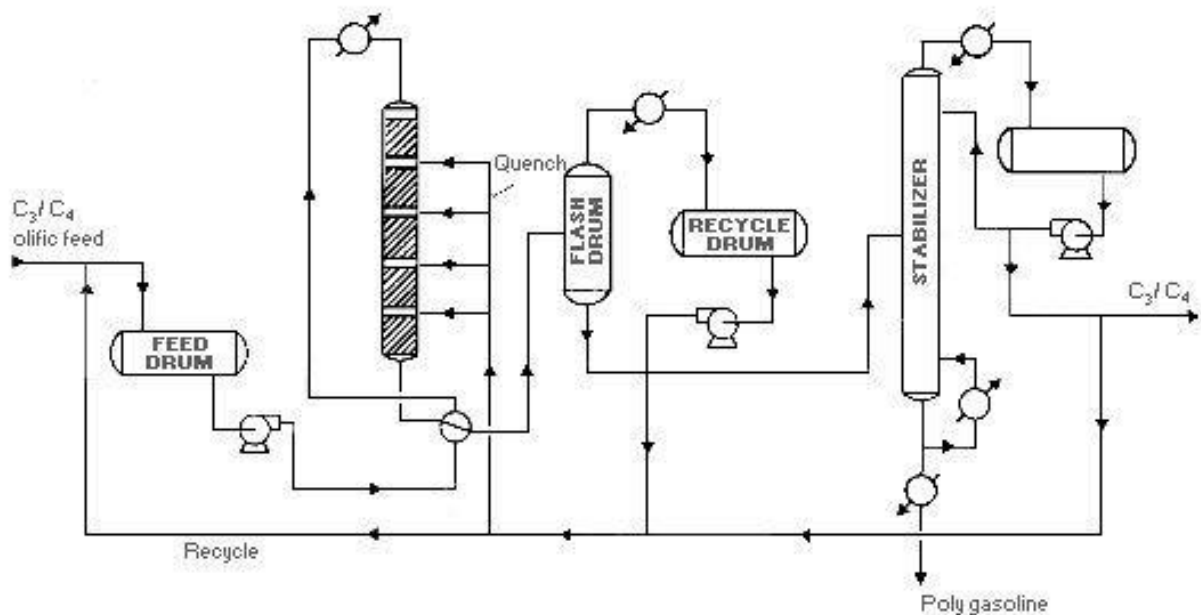
n-pentane and n-hexane into their respective isoparaffins of substantially higher octane number. The straight-chain paraffins are converted to their branched-chain counterparts whose component atoms are the same but are arranged in a different geometric structure. Isomerization is important for the conversion of n-butane into isobutane, to provide additional feedstock for alkylation units, and the conversion of normal pentanes and hexanes into higher branched isomers for gasoline blending. Isomerization is similar to catalytic reforming in that the hydrocarbon molecules are rearranged, but unlike catalytic reforming, isomerization just converts normal paraffins to isoparaffins.



Butane isomerization produces feedstock for alkylation. Aluminum chloride catalyst plus hydrogen chloride are universally used for the low-temperature processes. Platinum or another metal catalyst is used for the higher-temperature processes. In a typical low-temperature process, the feed to the isomerization plant is n-butane or mixed butanes mixed with hydrogen (to inhibit olefin formation) and passed to the reactor at 230°-340° F and 200-300 psi. Hydrogen is flashed off in a high-pressure separator and the hydrogen chloride removed in a stripper column. The resultant butane mixture is sent to a fractionator (deisobutanizer) to separate n-butane from the isobutane product.

Pentane/hexane isomerization increases the octane number of the light gasoline components n-pentane and n-hexane, which are found in abundance in straight-run gasoline. Desulfurized feedstock is mixed with a small amount of organic chloride and recycled hydrogen, and then heated to reactor temperature. It is then passed over supported-metal catalyst in the first reactor where benzene and olefins are hydrogenated. The feed next goes to the isomerization reactor where the paraffins are catalytically isomerized to isoparaffins. The reactor effluent is then cooled and subsequently separated in the product separator into two streams: a liquid product (isomerate) and a recycle hydrogen-gas stream. The isomerate is washed (caustic and water), acid stripped, and stabilized before going to storage.

POLYMER GASOLINE:



A product of polymerization of normally gaseous hydrocarbons to form high octane liquid hydrocarbons boiling in the gasoline range.

Polymer distillate, a high octane component of fuels for piston engines with spark ignition. Polymer gasoline is produced by catalytic polymerization of the propane-propylene and butylene fractions of gases from petroleum cracking and reforming. The onset of boiling for polymer gasoline is not below 70°C, and the termination of boiling is not above 225°C.

The content of unsaturated hydrocarbons is 20-90 percent, with a relatively low content of paraffin, naphthene and in particular, aromatic hydrocarbons. The octane number of hydrogenated polymer gasoline with 3.3 tetraethyl lead per kilogram is not less than 104. Inhibitors (antioxidants) are added to stabilize polymer gasolines and commercial fuels containing this component.

REFERENCE BOOKS:

1. Nelson, W.L., Petroleum Refinery Engineering, 4th Edition., McGraw Hill, New York, 1985
2. Bhaskara Rao B. K., Modern Petroleum Refining Processes, 2nd Edition., Oxford and IBH Publishing Company, New Delhi, 1989.
3. Hobson G. D and Pohl W., Modern Petroleum Technology, 2nd Edition, Gulf Publishers, 1986.



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 3 TREATMENT TECHNIQUES-SCHA3002

UNIT-3 TREATMENT TECHNIQUES

- 3.1 Treatment techniques for removal of objectionable gases and to improve performance
- 3.2 Treatment of gasoline,
- 3.3 Treatment of kerosene,
- 3.4 Treatment of lubes.
- 3.5 Extraction of aromatics and olefins

3.1 Treatment techniques for removal of objectionable gases and to improve performance

The essential purpose of the primary processes is to produce the required amounts of the various products from the available crude. The products obtained are, as a general rule, unsuitable as such for immediate use, for the following reasons :

- 1) Inadequate performance, 2) Instability in storage, and 3) Objectionable odor and appearance and contamination with water or particulate matter. Secondary refining processes (finishing or treating processes), are required to give the products acceptable with respect to the above criteria.

Main Finishing Processes

- a) The removal of the objectionable gases (Acid gas removal).
 - b) The removal of the objectionable odors.
 - c) The improvement in storage stability.
 - d) The improvement in performance characteristics.
 - e) The removal of water and particulate matter.
- a)The removal of the objectionable gases

Hydrogen sulphide : Has to be removed from products because :

a) toxic, b) foul smelling, c) corrosive, d) traces of it may seriously contaminate regenerative treating solvents such as a solutizer used for final sweetening of the products.

A) Scrubbing with caustic soda : It is still the most widely used process for the removal of H_2S , mainly because it simultaneously removes other constituents such as CO_2 , carbonyl sulphide, lower aliphatic mercaptans, phenols fatty acids and naphthenic acids.

The disadvantage of this processes is that there is no known cheap method of regenerating the spent soda, and if H_2S is present in gross amounts, as is frequently in crude gases, especially the C_2 - C_3 fractions , a regenerative method of extraction such as the girbotol method is more generally used. This method is more economical than caustic washing but caustic washing may still be required as a final cleaning-up operation for the removal of the last traces of H_2S . The combination of the two processes not only provides a very low H_2S content economically but also safe guards against high sulfur contents in the treated products should there be a temporary failure of the regenerative treating plant.

In the caustic washing of gases rather weak solutions of 2-10%wt $NaOH$ have to be used to prevent the deposition of sodium sulphide crystals. The reaction proceeds almost to the complete conversion of $NaOH$ to $NaHS$. Traces of H_2S often appear in fractions much heavier than C_2 - C_3 fraction because of a slight breakdown of sulfur compounds owing to pyrolysis during re-distillation or a similar operation. Caustic soda may be employed for its removal.

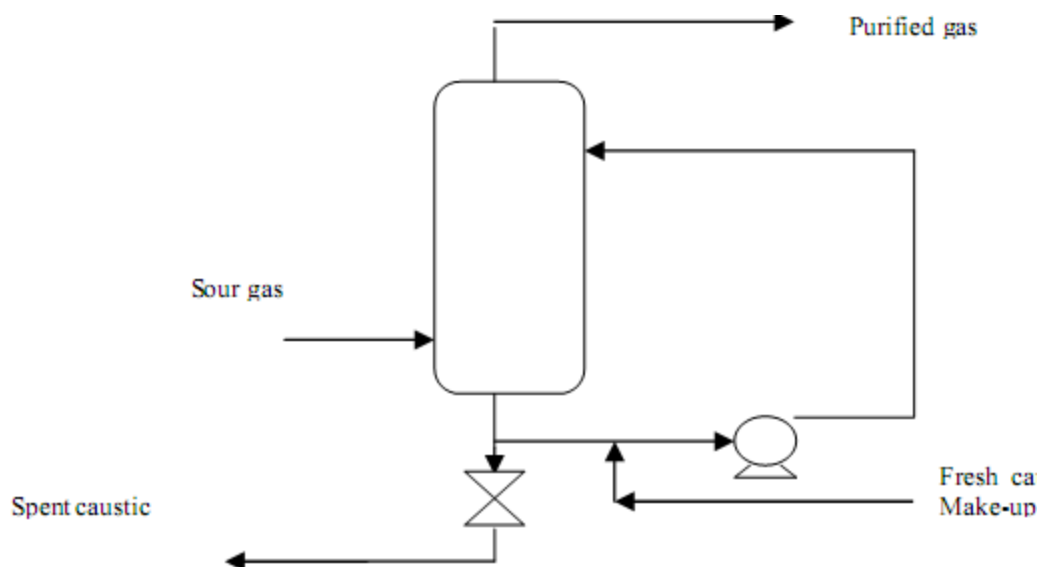
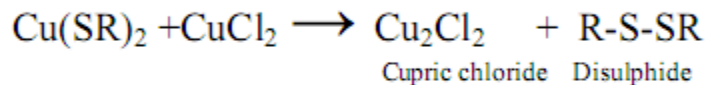
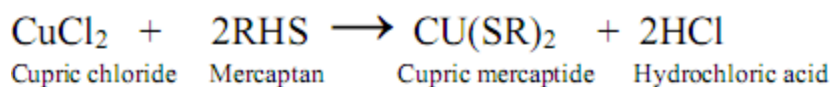


FIGURE. H₂S removal from gases by caustic washing

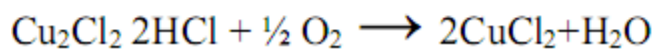
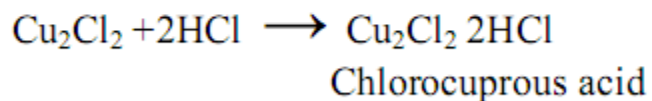
1) Copper Chloride Process

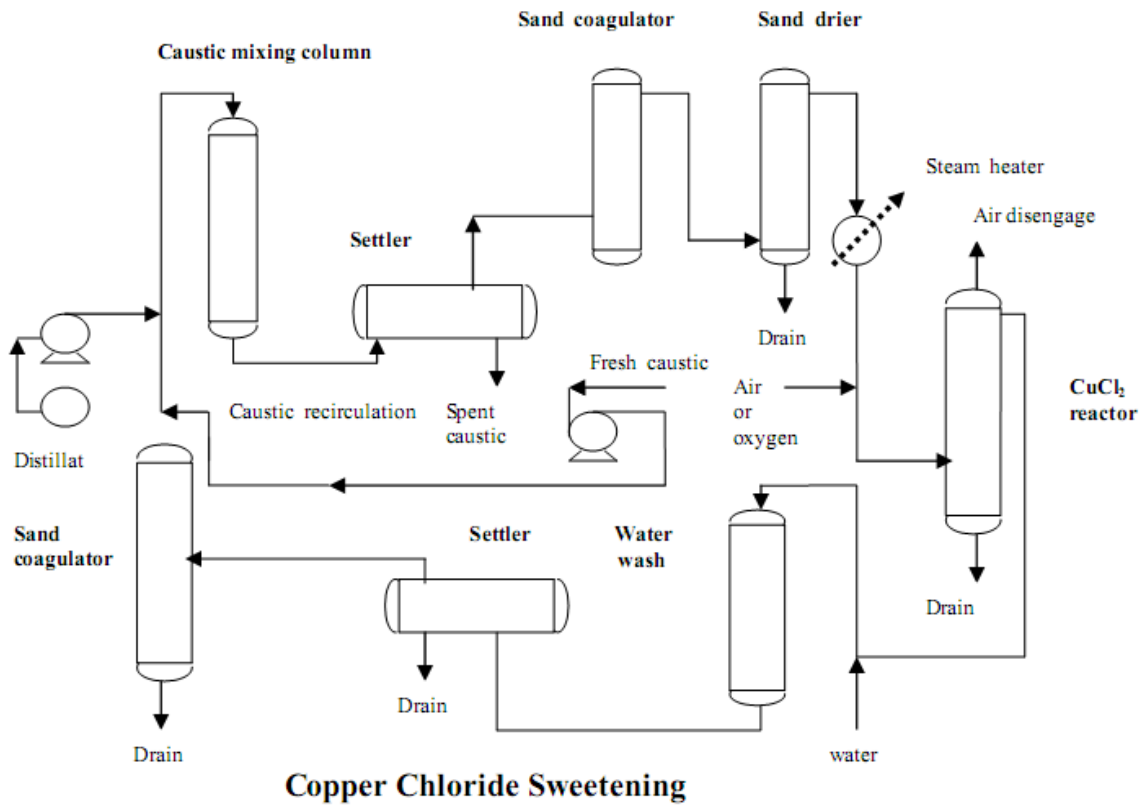
The copper chloride process is used to sweeten gasolines and kerosenes by the direct oxidation of mercaptans to disulphides, using cupric chloride as the oxidizing agent. The basic reactions of the process may be expressed as follows :

Sweetening



Regeneration





1) The sour charge is caustic washed to remove traces of hydrogen sulphide which would otherwise deactivate the cupric chloride.

2) It then pass :

A) firstly through a sand coagulator to remove any caustic and / or water haze

B) secondly through a rock salt drying lower to ensure complete removal of free water, which would adversely affect the water balance in the reactor.

3) After passing through a pre-heater to raise the temperature sufficiently to dissolve the water formed during the process, air or oxygen is injected into the line, and the dried and oxygenated feed flows upwards through the reactor which contains a bed of fullers earth impregnated with cupric chloride.

4) The sweetened product is water washed to remove traces of acidity, clarified from water haze in an up-flow sand coagulator and passed to storage.

2) Merox Process :

The Merox process, Developed by UOP (Universal Oil Products), is combination of mercaptan extraction and sweetening. The combined process is applicable to all gasoline and lighter boiling range fractions; the sweetening process is applicable to many jet fuel and kerosenes.

A) Merox Extraction:

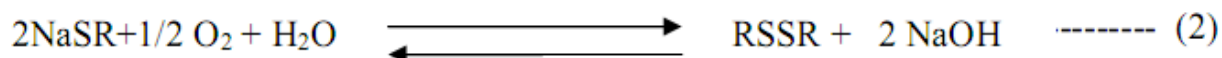
1- The mercaptans are extracted by an aqueous solution of caustic soda according to

the reaction :

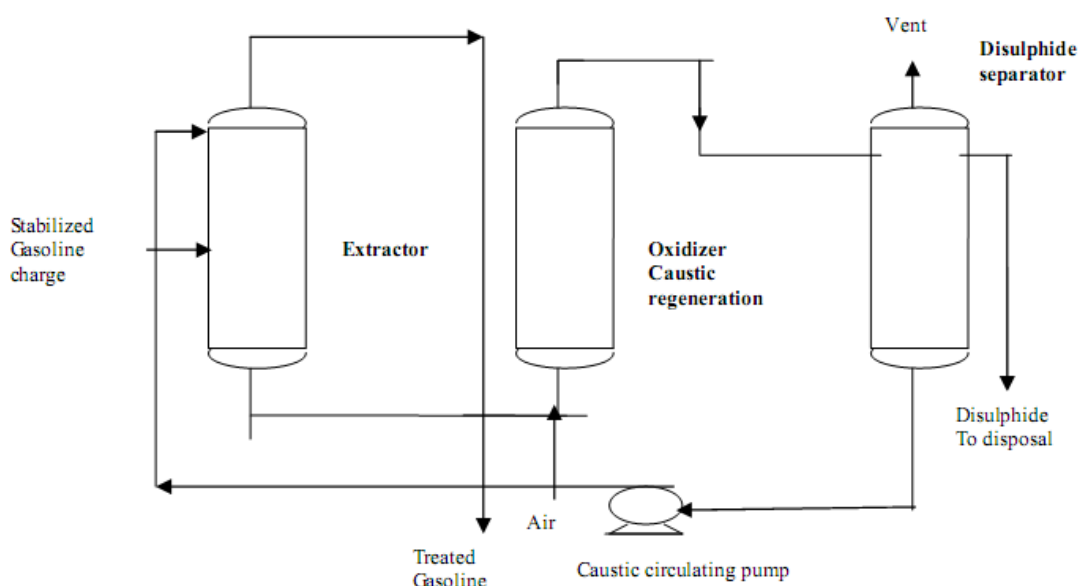


Since the reaction is reversible it is impossible to get complete removal of mercaptans by extraction without the use of an excessive amount of caustic soda solution. The forward reaction is favored by low temperature, low molecular weight of mercaptan and high caustic concentration. It is also promoted by the use of compounds that increase the solubility of the mercaptan in the aqueous phase, of these methanol, isobutyric acid and cresols.

2- The caustic is generated ,after separation from hydrocarbons by blowing with air in the presence of a catalyst at ambient temperature the reaction proceeding according to the reaction :



The disulphide so formed are insoluble in caustic soda and are removed in a gravity separator, the caustic is being re-circulated for further use. The catalyst which consists of an iron group metal chelate, may be in solution in the caustic, in which case the caustic and air are brought into contact in a reactor such as an orifice column, a mechanically stirred reactor or some other type of gas/liquid contactor. Alternatively the catalyst may be supported on a carrier, in which case the caustic and air are passed together over a packed bed.



Merox Extraction

B) Merox Sweetening

Sweetening is achieved by blowing a caustic hydrocarbon mixture with air in the presence of the catalyst where by disulphide are formed according to equation (2), and dissolve in the material being treated. As in the above mentioned regeneration process, the catalyst may be in solution in the caustic or held on carrier, and the process is carried out as described.

C) Combined Operation

The combined extraction/ Sweetening operation is carried out by a combination of the extraction and sweetening processes.

c) Removal of Water and Particulate Matter In the Refinery

- 1) Water and particulate matter in the fuel can have disastrous effects on gas turbine blades.
- 2) Free water may cause corrosion through out a fuel distribution system.
- 3) Particulate matter may block filters or the fine orifices of fuel injection and burner.

Water may be removed by :

- 1) Physically 2) Chemically 3) Electro- statically

Particulate matter may be removed by:

- 1) Water washing 2) Filtration

Processes:

1) Salt Dryers: Used to remove water from water primary distillation products and to control the water content both before and after secondary processing. The product is passed through a vertical drum filled with suitably graded rock salt. Rock salts are not powerful desiccants; it will remove the free water but not dissolved water. If more dissolved water has to be removed it is usual to use calcium chloride in the dryer.

2) Electrostatic Coalescers : Uses electrical coalescing for the removal of free water and sodium chloride or calcium chloride for the removal of any residual traces of water. The process is used

for the dehydration of heating oil, kerosene, jet fuel, diesel fuel and solvents. The dehydration product contains no free water but may contain some dissolved water.

3) Sand Coagulators and Filters : Vertical drums filled with fine sand are used for removal of particulate matter and water, this process have the advantage over salt dryers is not involving the use of chemicals. Down flow through the bed and up flow through a water separator will remove gross water but not haze. For this purpose the oil must pass upward through the bed with a bottom water drain so that it can emerge clear , and bright from the top of the drum, 5 micron peculator filter may be needed for turbo jet fuel.

4) Vacuum Flashing : Where difficulties might be met in the removal of water from high-boiling or viscous products by the previous methods, water may be removed by passing the product through a vessel at a sufficiently reduced pressure to cause the water to evaporates , it is used sometimes for the clarification of lubrication oil.

Improvement in Storage Stability

Owing to their complex composition and the presence of small amounts of N₂, S, organic acids, and oxygen, most petroleum products are subjected to deterioration in storage. This storage instability may be noticed by a darkening in color, the formation of gums, and in some cases a significant deterioration in those characteristics that control the performance of the products.

Instability may be accompanied by a marked degree of corrosiveness due to the presence of organic and/ or inorganic acids.

Caustic Extraction

In addition to the use of caustic soda for the removal of acidic gases and malodorous compounds as described earlier , it is widely used for the removal of substances which cause instability and corrosion.

e) Improvement in Performance

The performance characteristics of products from primary refining processes are seldom in keeping with the demands of modern machinery and engines. It is therefore often necessary to subject the products to secondary refining processes to remove those compounds that have an adverse effect on performance.

Performance improvement processes

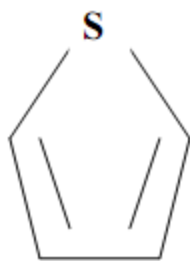
1) SO₂ Extraction : Liquid SO₂ is very selective solvent for removal of aromatic hydrocarbons . SO₂ treatment removes aromatics and some polar compounds, including sulfur , gum and color constituents , as well as olefins. The process is used in the manufacture of premium kerosene the removal of aromatics leads to better burning properties.

2) H₂SO₄ Treatment : This process is used for the removal of sulfur and thiophene from aromatic streams . It is less applicable now a days as other treating methods are available . This process may be applicable for the pretreatment of straight run naphtha that are to be reformed.

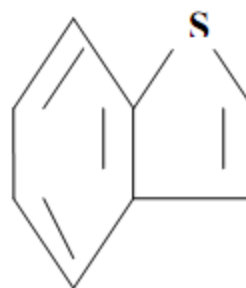
3) Hydrodesulphurization : Hydrodesulphurization is the most modern and effective processes for the removal of sulfur from oil products and for general improvement in the quality of refinery streams, including the pretreatment of catalytic reformer feed. The process convert S to H₂S by reaction with hydrogen in the presence of catalyst. This process is used mainly for the processing of straight run and cracked medium and heavy distillates, while vapor phase hydrotreating is used for the processing of light distillates it operates at lower pressure.

Thiophen

Thiophen and mono-methyl thiophens have been isolates from gasoline: alkyl-thiophens and benzo-hiophens have been isolates from keroscience. In gas oil range substituted thiophens, benzo-hiophens and higher polycyclic thiophens are present



Thiophen



Benzo thiophen

Two general methods of reducing the amount of sulfur have been developed, those which involve

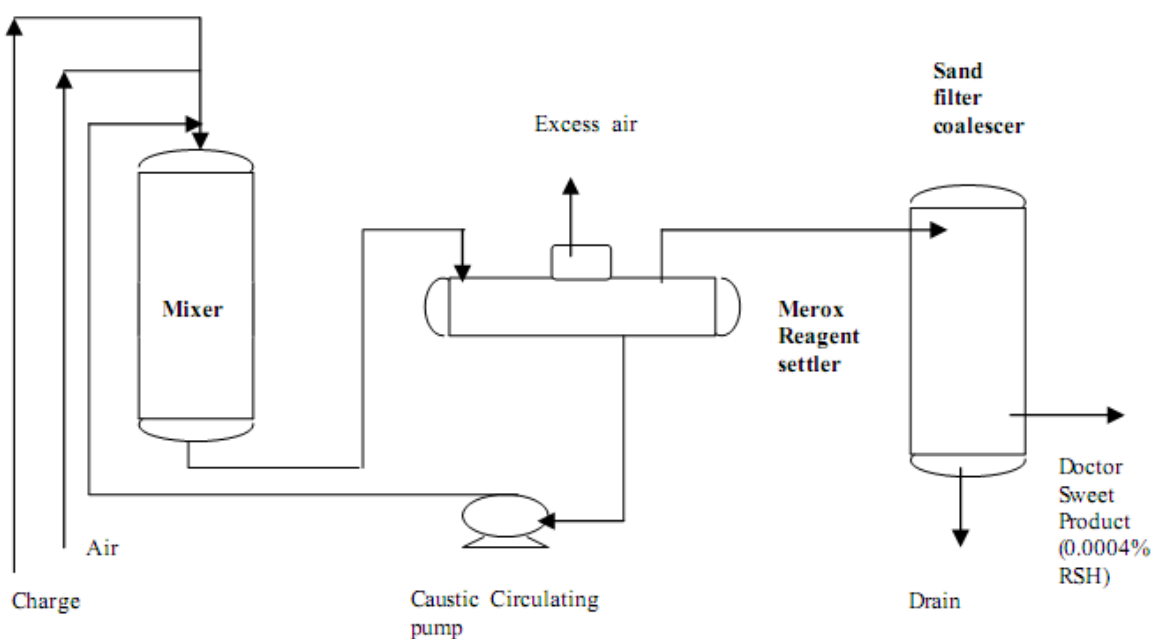
- 1) solvent extraction of the sulfur compounds and
- 2) those by which most of the sulfur compounds are decomposed by the use of a catalyst into hydrogen sulfide and the remaining hydrocarbon part of the molecule.

The solvent extraction processes are not cheap or effective as the catalytic processes in the removal of sulfur because they remove the entire sulfur bearing molecule and at the same time certain hydrocarbons, particularly those with aromatic rings. This when the removal of aromatic hydrocarbons as well as sulfur is desirable, the solvent process may be superior. H_2SO_4 , HF are an effective solvent, but SO_2 and furfural are more frequently used. The solvent process tends to raise the pour point and moderately improve the Diesel Index, but the catalytic processes of desulphurization do not materially affect either of these properties. Yields by the catalytic processes may exceed 100% especially if outside hydrogen is used.

By the addition of H_2 from outside sources more vigorous reaction (decomposition) and hydrogenation can be undertaken, and in the extreme, whole crude oils and residues can be desulphurized. Desulphurization is a mild selective hydrogenation, so mild that aromatic are not usually hydrogenated to naphthenes. Sulfur is removed as H_2S and the remaining part

of the molecule is hydrogenated. Mild decomposition result in an evolution of hydrogen which can be recycled for hydrogenation reactions but if higher boiling or refractory stocks are being treated, extra H_2 must be introduced from outside sources to maintain a higher concentration of hydrogen during the reaction. The decomposition leads to products of slightly lower boiling range than that of the parent material slightly API gravities.

Efficiency of desulphurization depends upon the charge stock and severity of treatment, ranging from as low as 50 to 60 % for mild operation to 80 to 99 % and 95 to 98% is not uncommon.



Merox Sweetening

3.2 Treatment of gasoline,

3.2 Treatment of Gasoline

Gasoline Treatment

Offending compounds in gasoline are doctored by contacting with different chemicals. In fact gasoline sweetening is done by all available techniques. Despite lead free gasolines command premium, it may not be possible to supply lead free gasoline always. When TEL is to be added, severe sweetening actually harms the product, so a meticulous balance should be maintained to give improved lead susceptibility. Odourous methyl and other mercaptans, and thiophenols are kept at less than 0.002 ppm in gasoline to give a negative doctor test, for jet fuels, the figure is kept at 20 ppm to give a satisfactory copper strip corrosion test (3 hrs at 50°C).

COPPER CHLORIDE PROCESS

Please refer the above pages

3.3 Treatment of Kerosene

For kerosenes (illuminating oils) a single treatment technique like desulfurisation is not sufficient; as the illuminating quality of kerosene is not improved in this operation. Smoke point improvement is achieved by removing smoke causing ingredients, namely aromatics. Formulations of good kerosene touch a maximum limit of 20% aromatics. Aromatics in the kerosene range are preferably of single ring structures with side chains. Oldest process for the removal of aromatics is liquid sulfur dioxide extraction invented by Edeleanu (1905), since that time it continues to enjoy a commanding position

Liquid sulfur dioxide extraction is carried out at a temperature of -14°C , the extract of which contains normally copious amounts of solvent. Aromatics from extract can be freed, just by self evaporation of solvent. The selectivity of anhydrous liquid sulfur dioxide is excellent for aromatic constituents. Although a good number of solvents are pressed into service, still the universal replacement of the old process has not been ventured.

3.4 Treatment of lubes.

Manufacturing of Lubricating Oils

The large number of natural lubricating and specialty oils today are produced by blending a small number of lubricating oil base stocks and additives. The lube oil base stocks are prepared from selected crude oils by distillation and special processing to meet the desired qualifications. The additives are chemicals used to give the base stocks desirable characteristics which they lack or to enhance and improve existing properties.

The properties that considered important :1) Viscosity, 2) Viscosity index, 3) Pour point, 4) Oxidation resistance, 5) Flash point, 6) Boiling temperature, and 7) Acidity (Neutralization number)

Lubricating oil Processing

1) Separation of the individual fractions : according to viscosity and boiling range specifications in crude oil distillation units. The heavier lubricating oil row stocks are included in the vacuum fractionating tower bottoms with the asphaltenes resin, and other undesirable materials.

2) Removal of components which have undesirable characteristics

a) Reduce carbon- and sludge forming tendencies (Solvent deasphalting)

b) Improve viscosity index (Solvent extractions + Hydrocracking)

c) Lower Cloud and pour points (Solvent De-waxing + Selective hydrocracking)

d) Improve color and oxygen stability (Hydrotreating)

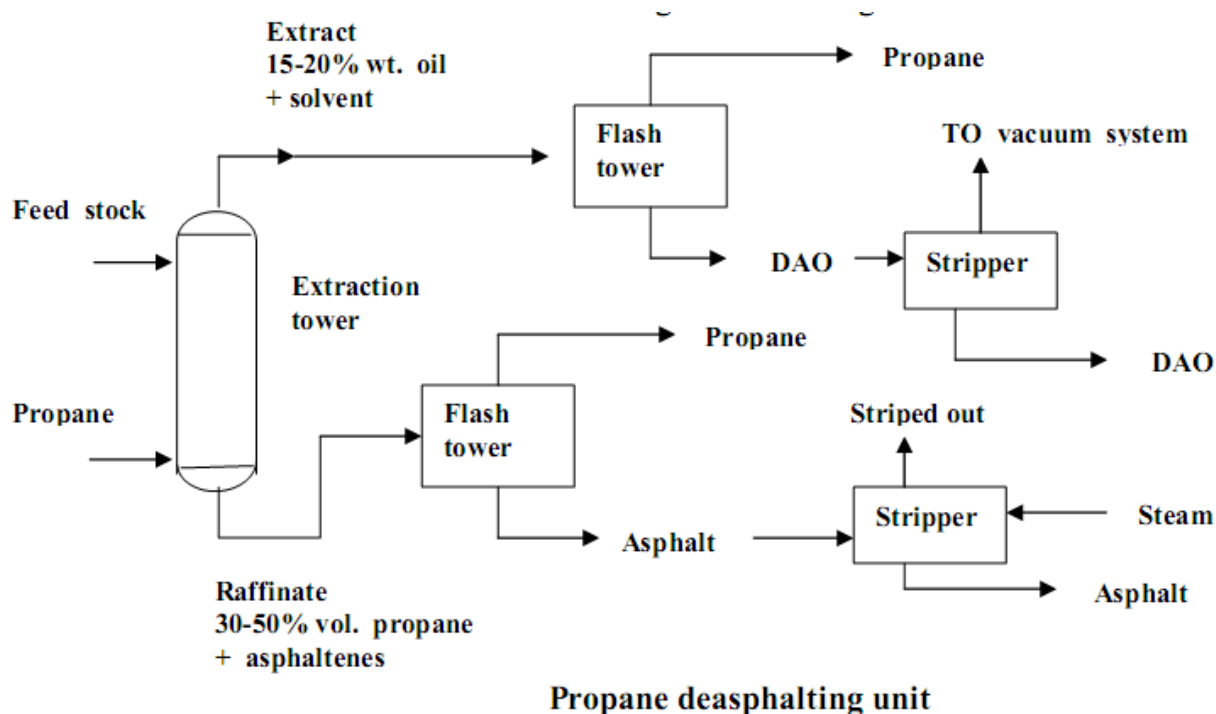
e) Lower organic acidity (Hydrotreating)

Although the main effects of the processes are as discussed, there are also secondary effects which are not shown . For example, although the main result of solvent dewaxing is the lowering of the cloud and pour points of the oil, solvent dewaxing also slightly reduces the viscosity index of the oil. For economic reasons as well as process ones, the process sequence is usually in the order of :1) deasphalting, 2) solvent extraction, 3) dewaxing, and 4)finishing.

Propane Deasphalting

The lighter feed stocks for producing lubricating oil stocks can be sent directly to the solvent extraction units. The atmospheric and vacuum still residues require deasphalting to remove the asphaltenes and resins before undergoing solvent extraction. In come cases highest boiling distillates also contain sufficient asphaltenes and resins and need deasphalting. Propane : is usually used as the solvent in seasphalting but it may be used with ethane and butane in order to obtain the desired solvent properties. (40- 60 °C) paraffins are very soluble in propane, the solubility decreases with increasing temperature, until the critical temperature (96.8 °C) all HC becomes insoluble. (40 – 96.8 °C) the high molecular weight asphaltens and resins are largelyinsoluble in propane. The feed stock is contacted with 4-8 volumes of liquid propane in a

cylindrical tower, usually RDC (rotating disc contactor). The asphalt recovered from the raffinate can be blended with other asphalts , into heavy fuels, or used as a feed to the coking unit. The heavy oil product from vacuum residuum is called bright stock.



Solvent Extraction

There are three solvents used for the extraction of aromatics from lubricating oil feed stocks and the solvent recovery portions of the system are different for each.

The solvents are : 1)Furfural, 2) phenol, 3) N- methyl 2- pyrrolidone (NMP).

The purpose of solvent extraction is :

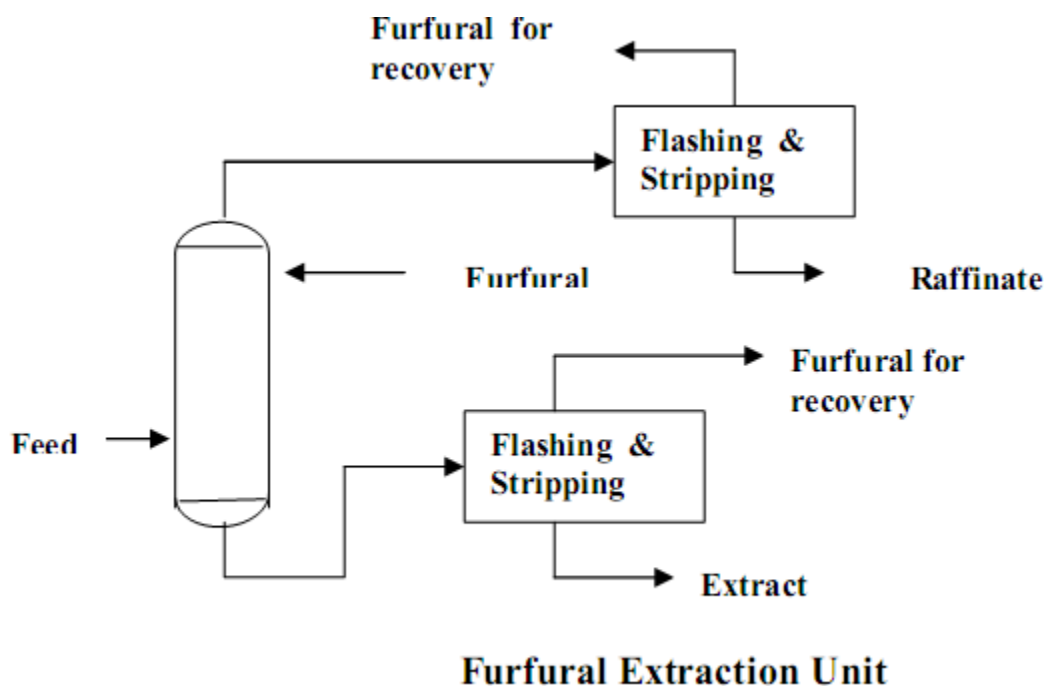
- 1) Improve VI.
- 2) Improve oxidation resistance and color.

3) Reduce carbon and sludge forming tendencies of the lubricants by separating the aromatic portion from the naphthenic and paraffinic portion of the feed stock. Furfural Extraction The most important operating variables are :

1) Furfural / oil ratio (F / O ratio) :It has the greatest effect on the quality and yield of the raffinate. Range 2:1 for light stocks to 4.5 : 1 for heavy stocks.

2) Extraction temperature : Is selected as a function of the viscosity of the oil and the miscibility temperature.

3) Extracted recycle ratio : Determines to some extent the rejection point for the oil and the sharpness of separation between the aromatics and naphthenes and paraffins.



Dewaxing

All the lubricating oil except those from a relatively naphthenic crude oils, must be dewaxed or they will not flow properly at ambient temperature. Dewaxing is one of the most important and most difficult processes in lubricating oil manufacturing.

There are two types of processes in use today :

- 1) Uses refrigeration to crystallize the wax and solvent to dilute the oil portion sufficiently to permit rapid filtration to separate the wax from the oil.
- 2) Uses selective hydrocracking process to crack the wax molecules to light HC. Solvent dewaxing : The solvent used are

a) Propane

- 1) Readily available, less expensive and easier to recover
- 2) Direct chilling can be accomplished by vaporization of the solvent thus reducing the capital and maintenance costs of scraped- surface chiller.
- 3) High filtration rate can be obtained because of its low viscosity at very low temperature.
- 4) Requires use of a dewaxing aid.
- 5) Large difference between filtration temperature and pour point of finished oils (15 to 25 oC)

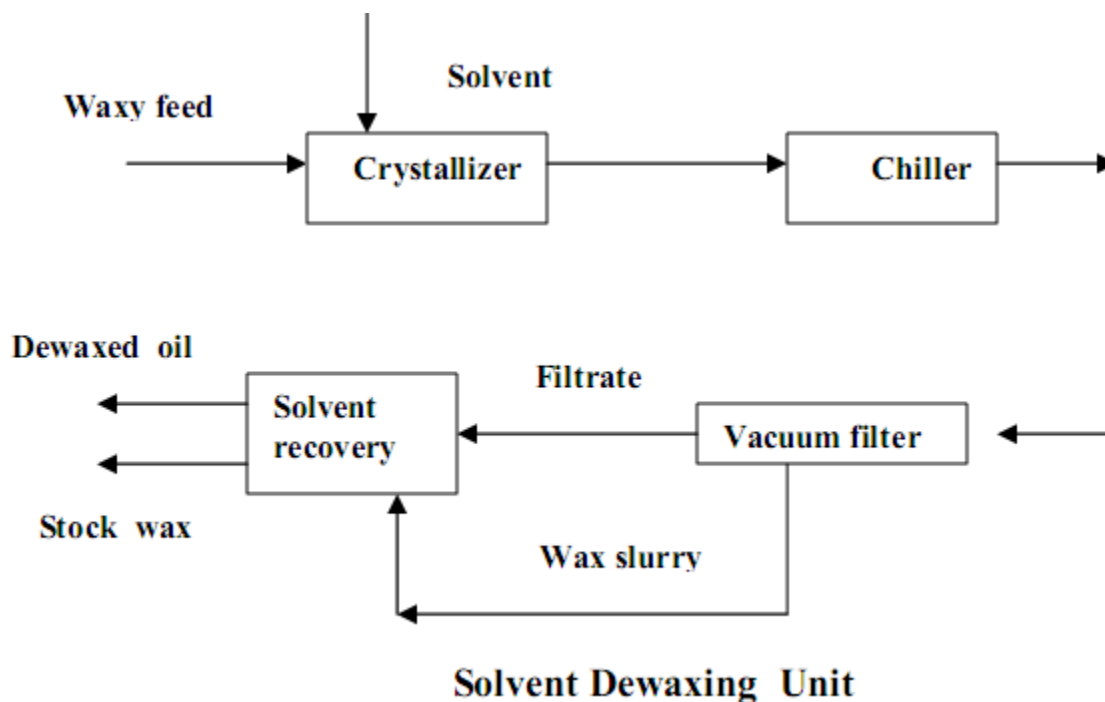
b) Ketone

- 1) Small differences between filtration temperature and pour point of dewaxing oil (5 to 10 oC).
- 2) Fast chilling rate.
- 3) Good filtration rate but lower than propane.

Lower pour point capability : Greater recovery of heat by heat exchanger lower refrigeration requirements.

The dewaxed oil next must go through a finishing step to improve its color and color stability.

The stock wax is used either for catalytic cracker feed or undergoes a de-oiling operation before sold as industrial wax.



Selective hydrocracking :

The feed to selective hydrocracking unit is solvent extracted oil from aromatic extraction units.

The advantages over conventional solvent dewaxing unit

- 1) Production of very low pour and cloud oils from paraffinic stocks.
- 2) Lower capital investment.
- 3) Improved lubrication oils base stock yields.
- 4) A separate hydrofinishing operation is not necessary.

Hydrofinishing

This process is needed to remove chemically active compounds that affect the color stability of lubrication oils. Most hydrotreating operation use cobalt- molybdate catalysts. The removal of nitrogen compounds is a major requirement of the operation because it affect color, usually finished oil yields are approximately 98% of dewaxed oil feed.

Hydrotreating

Hydrotreating: It is a relatively mild operation whose primary purpose is to saturate olefins and/ or reduce the sulfur and/ or nitrogen content (and not to change the boiling range) of the feed.

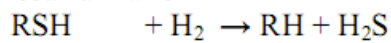
Hydrocracking : Processes whose primary purpose is to reduce the boiling range in which 100% of the feed is converted to product with boiling ranges lower than that of the feed. Hydrotreating and hydrocracking set the two ends of the spectrum and those processes with a substantial amount of sulfur and/ or nitrogen removal and a significant change in boiling range of the products versus the feed are called hydro- processing.

Hydrotreating is a process to catalytically stabilize petroleum products and/ or to remove objectionable from products or feeds stocks by reacting them with hydrogen. Stabilization : Involves converting unsaturated hydrocarbons such as olefins and gum- forming unstable diolefines to paraffins, objectionable elements removed by hydrotreating include sulfur, nitrogen, oxygen , halides, and trace metals. Hydrotreating is applied to wide range of feeds stocks from naphtha to reduce crude . When the process is applied specifically for sulfur removal it is usually called hydrodesulfurization

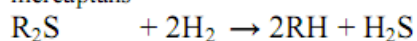
- 1) The oil feed is mixed with hydrogen- rich gas either before or after it is preheated to the proper reactor inlet temperature, below 800 oF to minimize cracking in the presence of metal oxide catalyst.

Reaction

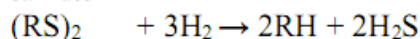
1) Desulfurization



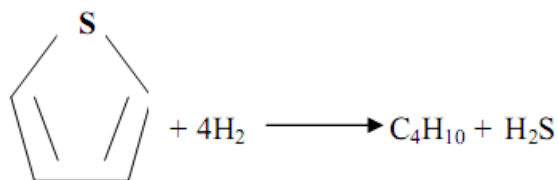
mercaptans



sulfides

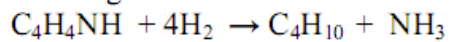


disulfides

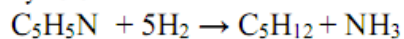


Thiophens

2) Denitrogenation

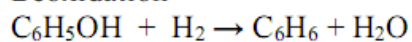


Pyrrole

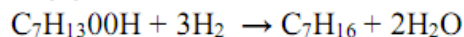


Pyridine

3) Deoxidation

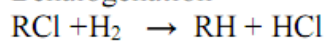


Phenol

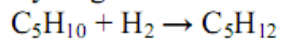


Peroxides

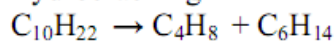
4) Dehalogenation



5) Hydrogenation



6) Hydrocracking

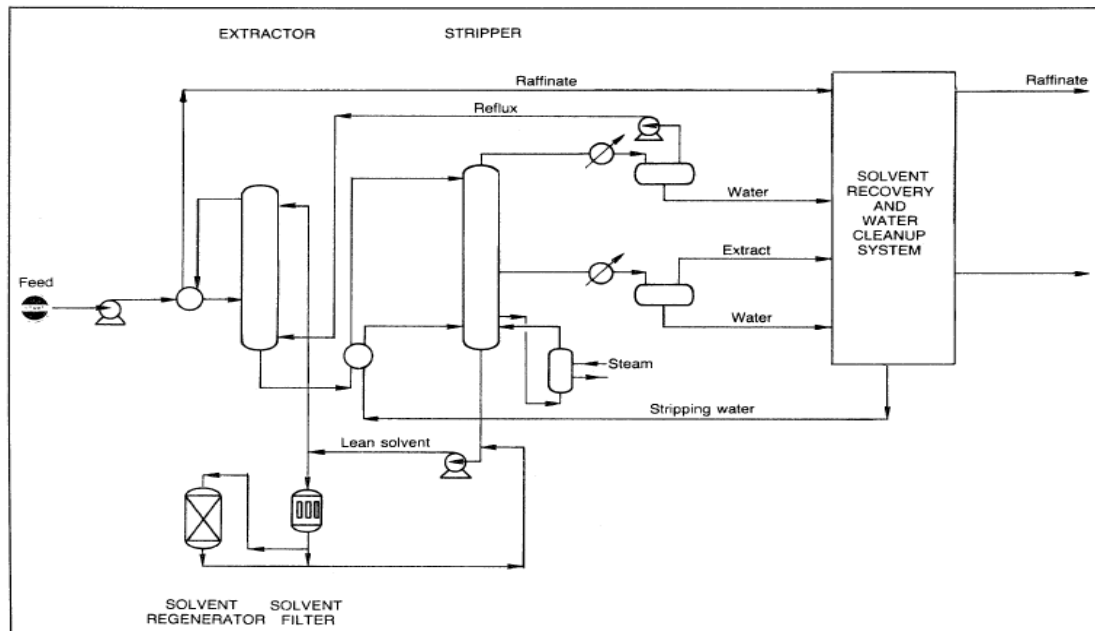


nitrogen removal requires more severe operating conditions than does desulfurization. The ease of desulfurization is dependent upon the type of compound. Lower boiling compounds are desulfurized more easily than higher boiling ones.

3.5 Extraction of Aromatics

EXTRACTION OF AROMATICS

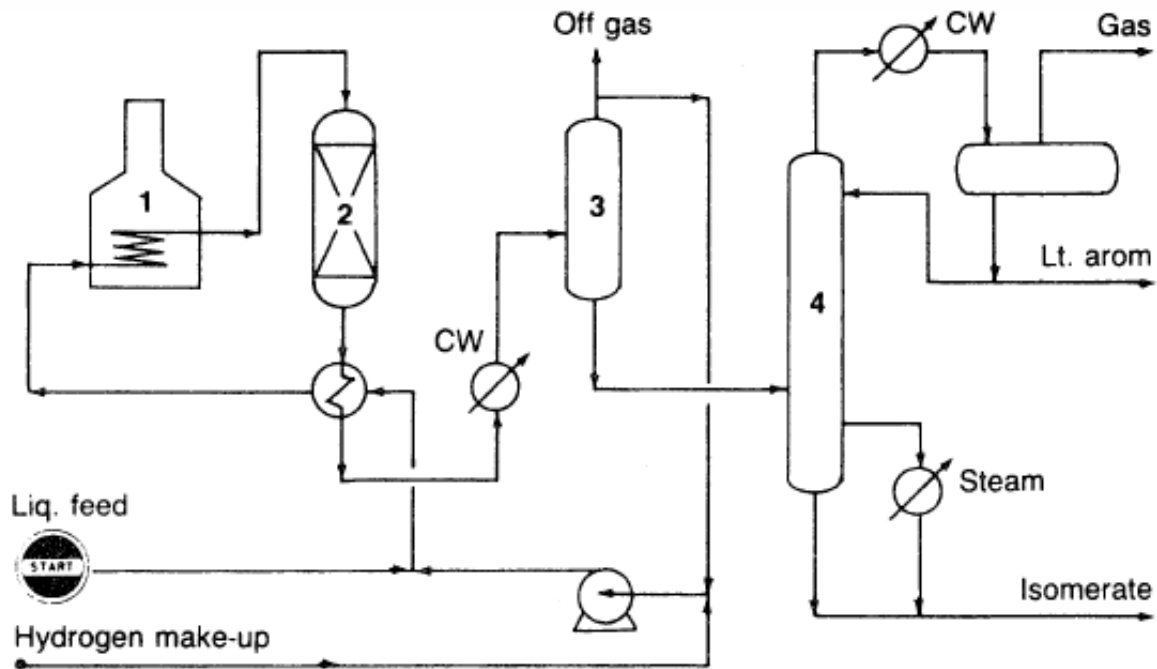
- Benzene, toluene, xylenes (BTX), and ethylbenzene are obtained from the catalytic reforming of heavy naphtha.
- The product is rich in C6, C7, and C8 aromatics, which is extracted by sulfolane or ethylene glycol.
- These solvents are characterized by a high affinity for aromatics, good thermal stability, and rapid phase separation. The process is [Tetra extraction process](#) uses tetraethylene glycol as a solvent.
- The feed (reformate), contains a mixture of aromatics, paraffins, and naphthenes → heat exchange with hot raffinate, is countercurrently contacted with an aqueous tetraethylene glycol solution in the extraction column.
- The hot, rich solvent containing BTX aromatics is cooled and introduced into the top of a stripper column.
- The aromatics extract is then purified by extractive distillation and recovered from the solvent by steam stripping.



The Union Carbide aromatics extraction process using tetraethylene glycol.

- The raffinate (constituted mainly of paraffins, isoparaffins and cycloparaffins) is washed with water to recover traces of solvent and then sent to storage. The solvent is recycled to the extraction tower.
- The extract, which is composed of BTX and ethylbenzene, is then fractionated. Benzene and toluene are recovered separately, and ethylbenzene and xylenes are obtained as a mixture (C8 aromatics).
- Due to the narrow range of the boiling points: C8 aromatics are separation by fractional distillation is difficult. A super-fractionation technique is used to segregate ethylbenzene from the xylene mixture.
- p-xylene is recovered from the xylene mixture by fractional crystallization.

- The overall yield of p-xylene is increased by incorporating an isomerization unit to isomerize o- and m-xylenes to p-xylene.
- An overall yield of 90% p-xylene could be achieved.

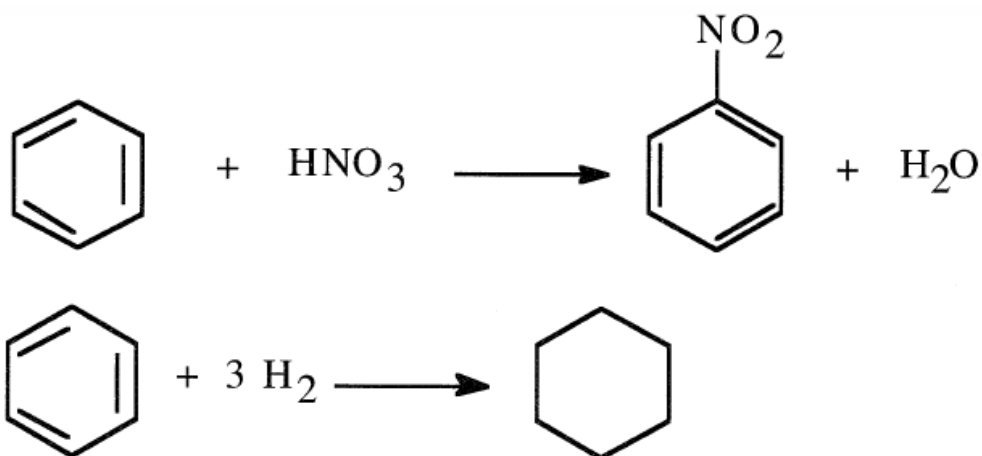


Flow diagram of the Mobil xylene isomerization process

- In this process, partial conversion of ethylbenzene to benzene also occurs. The catalyst used is shape selective and contains ZSM-5 zeolite.

Benzene

- Benzene (C_6H_6) is mainly obtained from catalytic reforming. Other sources are pyrolysis gasolines and coal liquids.
- Benzene is an important chemical intermediate and is the precursor for
- many commercial chemicals and polymers such as phenol, styrene for poly-styrenics, and caprolactom for nylon 6.



Ethylbenzene

- Ethylbenzene ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$) is one of the C8 aromatic constituents in reformates and pyrolysis gasolines. It can be obtained by intensive fractionation of the aromatic extract.
- ethylbenzene is obtained by the alkylation of benzene with ethylene.

Methylbenzenes (Toluene and Xylenes)

- Methylbenzenes occur in small quantities in naphtha and higher boiling fractions of petroleum.
- The primary sources of toluene and xylenes are reformates from catalytic reforming units, gasoline from cat-cracking, and pyrolysis gasoline from steam reforming of naphtha and gas oils

REFERENCE BOOKS:

1. Nelson, W.L., Petroleum Refinery Engineering, 4th Edition., McGraw Hill, New York, 1985
2. Bhaskara Rao B. K., Modern Petroleum Refining Processes, 2nd Edition., Oxford and IBH Publishing Company, New Delhi, 1989.
3. Hobson G. D and Pohl. W., Modern Petroleum Technology, 2nd Edition, Gulf Publishers, 1986.

- Solvent extraction is used to separate these aromatics from the reformat mixture.
- Toluene and xylenes have chemical characteristics similar to benzene, but these characteristics are modified by the presence of the methyl substituents.
- Currently, the largest single use of toluene is to convert it to benzene. para-Xylene is mainly used to produce terephthalic acid for polyesters.
- o-Xylene is mainly used to produce phthalic anhydride for plasticizers.



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 4- CHEMICALS FROM METHANE AND ETHANE

SCHA3002

UNIT IV CHEMICALS FROM METHANE AND ETHANE

1.0 Petrochemicals: Overview

1.1 Introduction

In this lecture, we present a brief overview of petrochemical technologies and discuss upon the general topology of the petrochemical process technologies.

Petrochemicals refers to all those compounds that can be derived from the petroleum refinery products

Typical feedstocks to petrochemical processes include

C1 Compounds: Methane & Synthesis gas

C2 Compounds: Ethylene and Acetylene

C3 Compounds: Propylene

C4 Compounds: Butanes and Butenes

Aromatic Compounds: Benzene

It can be seen that petrochemicals are produced from simple compounds such as methane, ethylene and acetylene but not multicomponent products such as naphtha, gas oil etc.

Definition : These are the chemicals that are made from petroleum and natural gas. Petroleum and natural gas are made up of hydrocarbon molecules, which comprises of one or more carbon atoms, to which hydrogen atoms are attached.

About 5 % of the oil and gas consumed each year is needed to make all the petrochemical products. Petrochemicals play an important role on our food, clothing, shelter and leisure. Because of low cost and easy availability, oil and natural gas are considered to be the main sources of raw materials for most petrochemicals.

Classification: Petrochemicals can be broadly classified into three categories-

a. Light Petrochemicals: These are mainly used as bottled fuel and raw materials for other organic chemicals. The lightest of these -- methane, ethane and ethylene -- are gaseous at room temperature. The next lightest fractions comprise petroleum ether and light naphtha with boiling points between 80 and 190 degrees Fahrenheit.

b. Medium Petrochemicals: Hydrocarbons with 6 – 12 carbon atoms are called "gasoline", which are mainly used as automobile fuels. Octane, with eight carbons, is a particularly good automobile fuel, and is considered to be of high quality. Kerosene contains 12 to 15 carbons and is used in aviation fuels, and also as solvents for heating and lighting.

c. Heavy Petrochemicals: These can be generally categorized as diesel oil, heating oil and lubricating oil for engines and machinery. They contain around 15 and 18 carbon atoms with boiling points between 570 and 750 degrees Fahrenheit. The heaviest fractions of all are called "bitumens" and are used to surface roads or for waterproofing.

Bitumens can also be broken down into lighter hydrocarbons using a process

called "cracking."

1.2 Process Topology

Reactors: Reactors are the most important units in petrochemical processes. Petrochemicals are manufactured by following simple reactions using relatively purer feedstocks. Therefore, reaction chemistry for petrochemicals manufacture is very well established from significant amount of research in this field. Essentially all petrochemical processes need to heavily depend upon chemical transformation to first product the purification.

Separation: With distillation being the most important unit operation to separate the unreacted feed and generated petrochemical product, the separation processes also play a major role in the process flow sheet. Where multiple series parallel reactions are involved, the separation process assumes a distillation sequence to separate all products from the feed. A characteristic feed recycle will be also existent in the process topology. Apart from this, other separation technologies used in petrochemical processing units include phase separators, gravity settling units and absorption columns. Therefore, the underlying physical principle behind all these separation technologies is well exploited to achieve the desired separation.

Dependence on Reaction pathway: A petrochemical can be produced in several ways from the same feedstock. This is based on the research conducted in the process chemistry. For instance, phenol can be produced using the following pathways

- o Peroxidation of Cumene followed by hydrolysis of the peroxide
- o Two stage oxidation of Toluene
- o Chlorination of Benzene and hydrolysis of chloro-benzene
- o Direct oxidation of Benzene

We can observe that in the above reaction schemes, there are two reaction pathways for phenol from benzene i.e., either chlorination of benzene or oxidation of benzene. Therefore, choosing the most appropriate technology for production is a trivial task.

Complexity in pathway: In the above Cumene example case, it is interesting to note that toluene hydrodealkylation produces benzene which can be used to produce phenol. Therefore, fundamentally toluene is required for the generation of various petrochemicals such as benzene and phenol. In other words, there is no hard and fast rule to say that a petrochemical is manufactured using a suggested route or a suggested intermediate petrochemical. Intermediate petrochemicals play a greater role in consolidating the manufacture of other downstream petrochemicals.

1.3 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: $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$

Side reactions: $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$

$2\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{CO}_2$

All above reactions are exothermic

Undesired reaction: $z\text{CO} + a\text{H}_2 \rightleftharpoons \text{alcohols} + \text{hydrocarbons}$

Catalyst: Mixed catalyst made of oxides of Zn, Cr, Mn, Al.

Process Technology

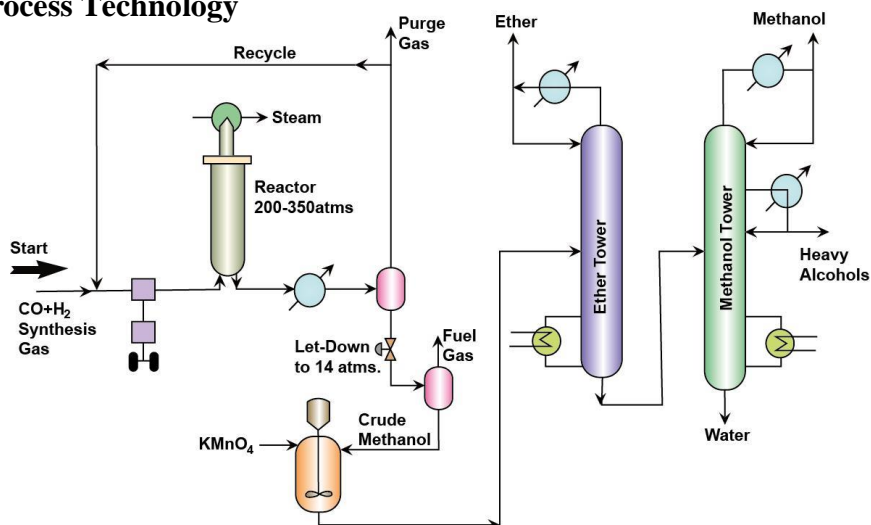


Figure: Flow sheet of manufacture of Methanol from Synthesis Gas

H_2 and CO adjusted to molar ratio of 2.25

The mixture is compressed to 200 – 350 atm

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 atm 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.

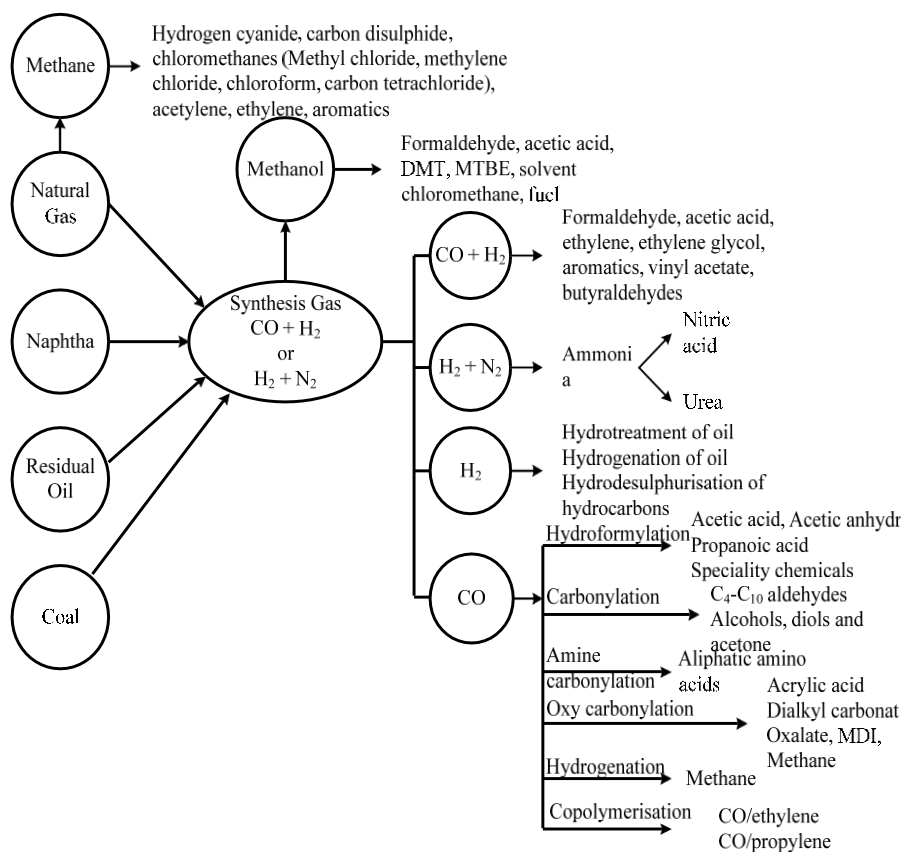
The liquid stream then enters a mixer fed with KMnO_4 so as to remove traces of impurities such as ketones, aldehydes etc.

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.

Methane and synthesis gas are important petrochemical feedstock for manufacture of a large number of chemicals, which are used directly or as intermediates, many of these products are number of which are finding use in plastic, synthetic fiber, rubber, pharmaceutical and other industries. 'Synthesis gas' is commonly used to describe two basic gas mixtures - synthesis gas containing CO, hydrogen and synthesis gas containing hydrogen and nitrogen for the production of ammonia. Major requirements of synthesis gas in world scale petrochemical are given.

Some of the emerging technologies in utilization of synthesis gas and methane for the production of petrochemicals, are Fischer-Tropsch synthesis, oxidative coupling of methane with chlorine to yield ethane and ethylene, methanol to olefin technology (MTO). Fischer-Tropsch synthesis is being studied in great detail world over and it is promising to be a future technology for manufacture of olefins from synthesis gas. CO that can be separated from synthesis gas either by cryogenic or by pressure swing adsorption is a promising feedstock for production of a variety of products. Product profile of methane, synthesis gas and CO based building blocks are given in [Figure BELOW](#)



1.4 SYNTHESIS GAS

Methane and synthesis gas are important petrochemical feedstock for the manufacture of a large number of chemicals, which are used directly or as intermediates, a number of which are finding use in plastic, synthetic fiber, rubber, pharmaceutical and other industries. 'Synthesis gas' is commonly used to describe two basic gas mixtures - synthesis gas containing CO, hydrogen and synthesis gas containing hydrogen and nitrogen for the production of ammonia.

Petrochemical derivatives based on synthesis gas and carbon monoxide have experienced steady growth due to large scale utilization of methanol and development of a carbonylation process for acetic acid and Oxo synthesis process for detergents, plasticizers, and alcohols. Recent market studies show that there will be a dramatic increase in demand of CO and syngas derivatives .

Methanol is the largest consumer of synthesis gas. The reformed gas is to meet certain requirements with regard to its composition. It is characterized by the stoichiometric conversion factor, which differs from case to case

1.5 RAW MATERIALS FOR SYNTHESIS GAS

Various raw materials for synthesis gas production are natural gas, refinery gases, naphtha, fuel oil/residual heavy hydrocarbons and coal. Although coal was earlier used for production of synthesis gas, it has now been replaced by petroleum fractions and natural gas. Petrocoke is the emerging source for Synthesis gas. Coal is again getting importance alone are with combination of petroleum coke. Various Routes for Synthesis gas and Ammonia and Methanol manufacture is shown in [Figure](#). Reactions in the manufacture of synthesis gas by Steam reforming and Partial oxidation in Table

Process Technology

Various synthesis gas production technologies are steam methane reforming, naphtha reforming, auto-thermal reforming, oxygen secondary reforming, and partial oxidation of heavy hydrocarbons, petroleum coke and coal.

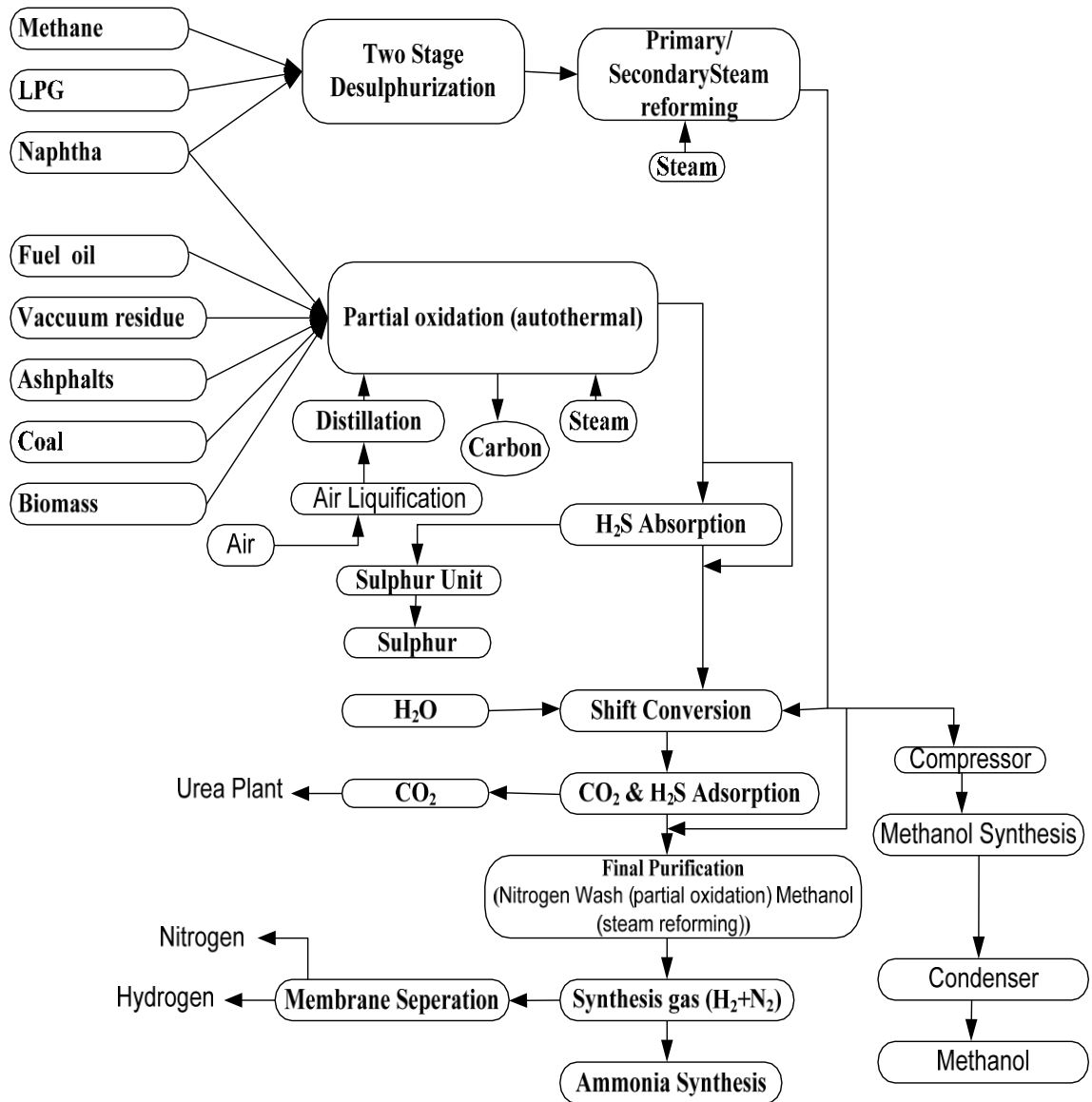
Various steps involved in synthesis gas production through steam reforming are:

- Desulphurization of gas
- Steam reforming and compression

- Separation of CO₂

Various available synthesis gas generation schemes are:

- Conventional steam reforming
- Partial oxidation
- Combined reforming
- Parallel reforming
- Gas heated reforming



Various Routes for Synthesis gas and Ammonia and Methanol manufacture

Reactions in the manufacture of synthesis gas by Steam reforming and Partial oxidation

Process steps	Reaction	Process Condition
Desulphurisation: 1st Stage First Stage	$C_2H_5SH + H_2 \rightleftharpoons H_2S + C_2H_6$ $C_6H_5SH + H_2 \rightleftharpoons H_2S + C_6H_6$ $C_4H_4SH + 3H_2 \rightleftharpoons H_2S + C_4H_9$ $CS_2 + 4H_2 \rightleftharpoons 2H_2S + CH_4$	Al-Co-Mo Al-Ni-Mo Catalyst 350-400 °C
2 nd Stage Second Stage	$COS + H_2 \rightleftharpoons H_2S + CO$ $CH_3SC_2H_5 + H_2 \rightleftharpoons H_2S + CH_4 + C_2H_4$ $H_2S + ZnO \rightleftharpoons ZnS + H_2O$	Zinc oxide absorbent 200-500 °C
Steam reforming two stages	$C_nH_m + \frac{1}{4}(4n-m)H_2O \rightleftharpoons \frac{1}{8}(4n+m)CH_4 + \frac{1}{8}(4n-m)CO_2$ $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ $CO + H_2O \rightleftharpoons CO_2 + H_2$	Nickel catalyst 800 °C Endothermic reaction
Partial Oxidation	$C_nH_m + \frac{(2n+m)}{4} O_2 \rightleftharpoons nCO + \frac{m}{2} H_2O$ $C_nH_m + nH_2O \rightleftharpoons nCO + (n+m/2) H_2$ $2CO \rightleftharpoons C + CO_2$ $CO + H_2 \rightleftharpoons C + H_2O$	Exothermic reaction

1.6 METHANOL

Methanol was first obtained by Robert Boylein in the year 1661 through rectification of crude wood vinegar over milk of lime and was named adiaphorous spiritusliglorum. The term methyl was introduced in chemistry in 1835. Methanol is one of the largest volume chemicals produced in the world. Methanol consumption can be separated into three end use categories – chemical feedstock, methyl fuels, and miscellaneous uses. About 71% of the current global consumption of methanol is in the production of formaldehyde, acetic acid, methyl methacrylate, and dimethyl terephthalate. The global methanol industry has experienced very fundamental and structural changes and has settled down considerably.

1.7 METHANOL PROCESS TECHNOLOGY

From the early 1800s until 1920s, the distillation of wood to make wood alcohol was the source of Methanol. The most common industrially favored method for the production of methanol was first developed by BASF in 1923 in Germany from synthesis gas utilising high pressure process using zinc-chromic oxide catalyst. However, due to high capital and compression energy costs compounded by poor catalyst activity, high-pressure process was rendered obsolete when ICI in the year 1966 introduced a low-pressure version of the process at 5-10 MPa and 210-270 °C, with a new copper-zinc oxide based catalyst of high selectivity and stability.

Process steps involved in the production of methanol are:

- Production of synthesis gas using steam reforming or partial oxidation
- Synthesis of methanol
- High-pressure process (25 – 30 MPa)
- Medium pressure (10-25 MPa) process
- Low-pressure process (5-10 MPa)

Figure BELOW illustrate the production of methanol from steam reforming of natural gas and naphtha.

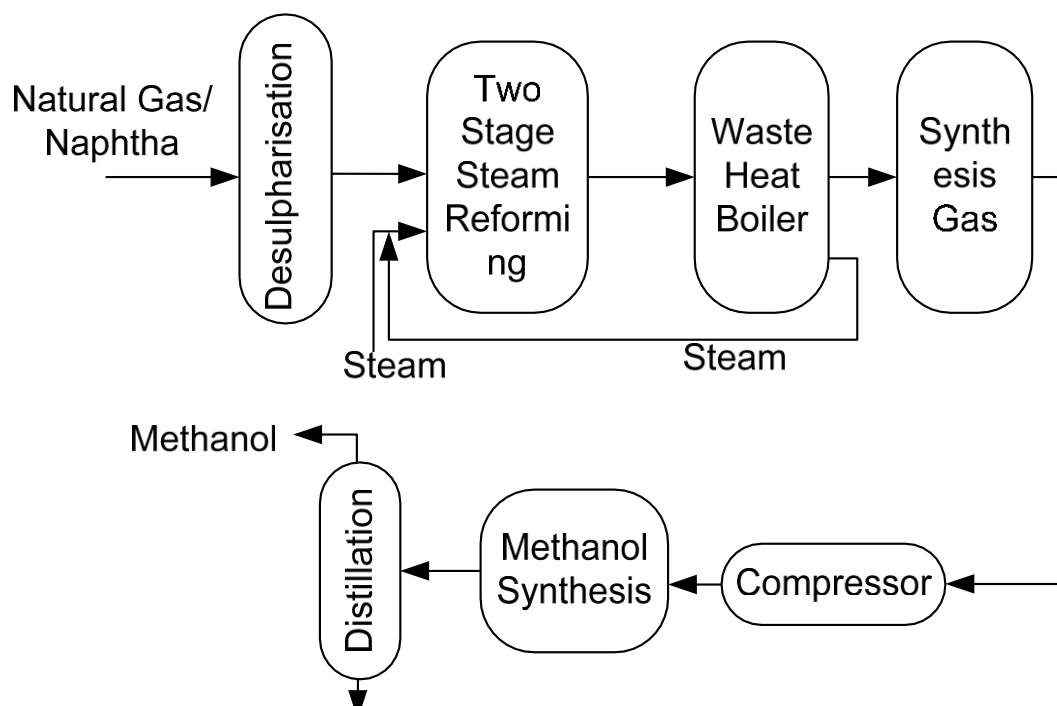
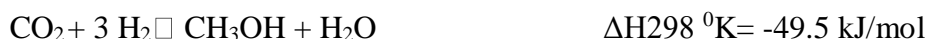


Figure : Methanol from steam reforming of Natural gas and Naphtha

The major reactions take place during methanol synthesis converter can be described by following equilibrium reactions:



The first two reactions are exothermic and proceed with reduction in volume. In order to achieve a maximum yield of methanol and a maximum conversion of synthesis gas, the process must be effected at low temperature and high pressure.

After cooling to ambient temperature, the synthesis gas is compressed to 5.0-10.0 MPa and is added to the synthesis loop which comprises of following items – circulator, converters, heat exchanger, heat recovery exchanger, cooler, and separator. The catalyst used in methanol synthesis must be very selective towards the methanol reaction, i.e. give a reaction rate for methanol production which is faster than that of competing

2.0 Formaldehyde

Introduction

In this lecture, we present the production technology for formaldehyde .
Formaldehyde is produced from methanol

Formaldehyde production

Reactions

Oxidation: $\text{CH}_3\text{OH} + 0.5 \text{O}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}$

Pyrolysis: $\text{CH}_3\text{OH} \rightarrow \text{HCHO} + \text{H}_2$

Undesired reaction: $\text{CH}_3\text{OH} + 1.5 \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$

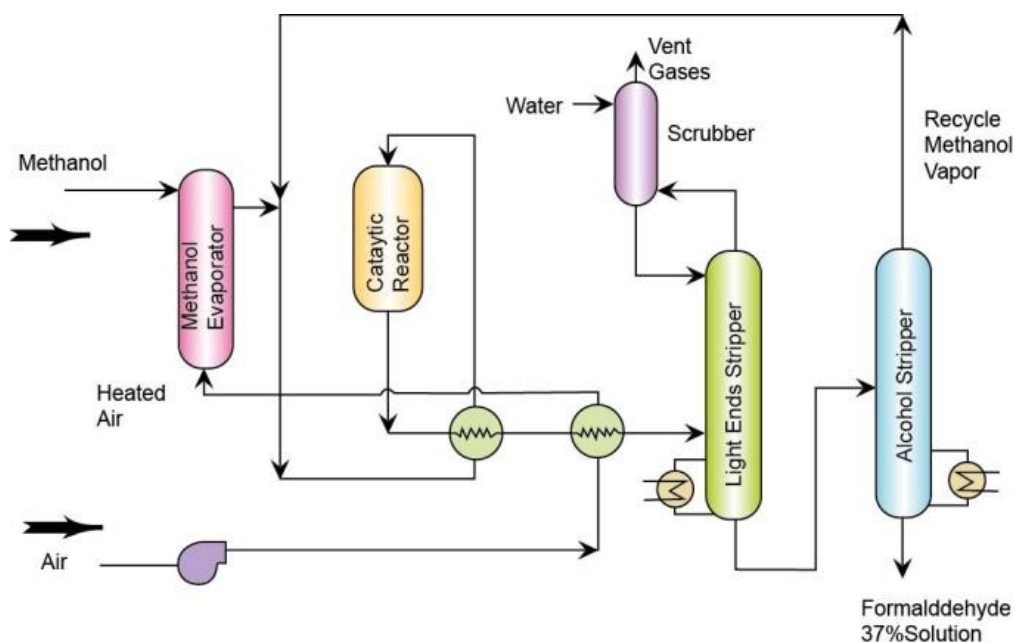
In the above reactions, the first and third are exothermic reactions but the second reaction is endothermic. The reactions are carried out in vapour phase.

Catalyst: Silver or zinc oxide catalysts on wire gauge are used.

Operating temperature and pressure: Near about atmospheric pressure and 500 – 600 °C

Process Technology :

Air is sent for pre-heating using reactor outlet product and heat integration concept.



Flow sheet of Formaldehyde production

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 °C.

The feed ratio is about 30 – 50 % for $\text{CH}_3\text{OH} : \text{O}_2$

After reaction, the product is a vapour mixture with temperature 450 – 900 °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).

3.0 Hydrocarbon Steam Cracking for Petrochemicals

Introduction

In industrial processes, hydrocarbons are contacted with H₂O, depending upon the desired effect. When hydrocarbon vapors at very high pressures are contacted with water, water which has a very high latent heat of vaporization quenches the hydrocarbon vapors and transforms into steam. In such an operation, chemical transformations would not be dominant and energy lost from the hydrocarbons would be gained by water to generate steam. The quenching process refers to direct contact heat transfer operations and therefore has maximum energy transfer efficiency. This is due to the fact that no heat transfer medium is used that would accompany heat losses. The steam cracking of hydrocarbons is an anti-quenching operation, and will involve the participation of water molecule in reactions in addition to the cracking of the hydrocarbons on their own. Since steam and the hydrocarbons react in the vapour phase the reaction products can be formed very fast. Therefore cracking of the hydrocarbons on their own as well as by steam in principle is very effective.

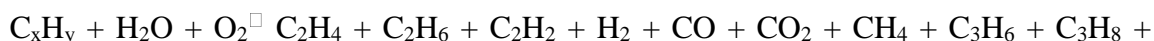
When steam cracking is carried out, in addition to the energy supplied by the direct contact of steam with the hydrocarbons, steam also takes part in the reaction to produce wider choices of hydrocarbon distribution along with the generation of H₂ and CO.

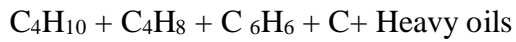
Hydrocarbons such as Naphtha and LPG have lighter compounds.

When they are subjected to steam pyrolysis, then good number of petrochemicals can be produced. These include primarily ethylene and acetylene along with other compounds such as propylene, butadiene, aromatics (benzene, toluene and xylene) and heavy oil residues.

The reaction is of paramount importance to India as India petrochemical market is dominated by this single process.

Reaction





The reaction is pretty complex as we produce about 10 to 12 compounds in one go

The flowsheet will be reaction-separation-recycle system only in its topology. But the separation system will be pretty complex.

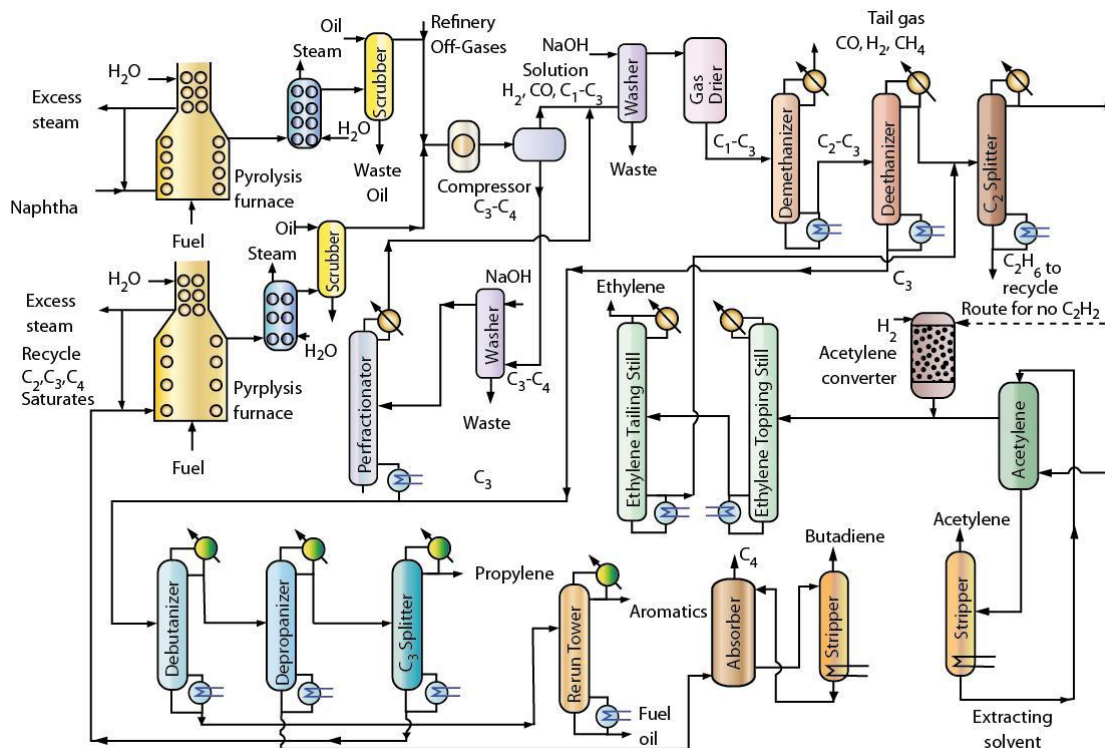
Almost all basic principles of separation appears to be accommodated from a preliminary look. Important separation tasks: Elimination of CO and CO₂, Purification of all products such as ethylene, acetylene etc.

The process can be easily understood if we follow the basic fundamental principles of process technology

Typical feed stocks are Naphtha & LPG

Reaction temperature is about 700 – 800 °C (Vapor phase reaction).

Process technology



Flow sheet of Hydrocarbon Steam Cracking for Petrochemicals

Naphtha/LPG saturates is mixed with superheated steam and fed to a furnace fuel gas + fuel oil as fuels to generate heat. The superheated steam is generated from the furnace itself using heat recovery boiler concept.

The C₂-C₄ saturates are fed to a separate furnace fed with fuel gas + fuel oil as fuels to generate heat.

In the furnace, apart from the steam cracking, steam is also generated. This is by using waste heat recovery concept where the combustion gases in the furnace.

After pyrolysis reaction, the products from the furnace are sent to another heat recovery steam boiler to cool the product streams (from about 700 – 800 °C) and generate steam from water.

After this operation, the product vapours enter a scrubber that is fed with gas oil as absorbent. The gas oil removes solids and heavy hydrocarbons.

Separate set of waste heat recovery boiler and scrubbers are used for the LPG furnace and Naphtha steam cracking furnaces

After scrubbing, both product gases from the scrubbers are mixed and fed to a compressor. The compressor increases the system pressure to 35 atms.

The compressed vapour is fed to a phase separation that separates the feed into two stream namely the vapour phase stream and liquid phase stream. The vapour phase stream consists of H_2 , CO, CO_2 C_1 - C_3 + components in excess. The liquid phase stream consists of C_3 and C_4 compounds in excess.

Subsequently, the vapour phase and liquid phase streams are subjected to separate processing.

Gas stream processing: CO_2 in the vapour phase stream is removed using NaOH scrubber. Subsequently gas is dried to consist of only H_2 , CO, C_1 - C_3 components only. This stream is then sent to a demethanizer which separates tail gas ($CO + H_2 + CH_4$) from a mixture of C_1 - C_3 components. The C_2 - C_3 + components enter a deethanizer which separates C_2 from C_3 components. Here C_2 components refer to all kinds of C_2 s namely ethylene, acetylene etc. Similarly, C_3 the excess of propylene, and propane.

The C_2 components then enter a C_2 splitter which separates ethane from ethylene and acetylene.

The ethylene and acetylene gas mixture is fed to absorption unit which is fed with an extracting solvent (such as N-methylpyrrolidinone) to extract Acetylene from a mixture of acetylene and ethylene.

The extractant then goes to a stripper that generates acetylene by stripping. The regenerated solvent is fed back to the absorber.

The ethylene stream is fed to a topping and tailing still to obtain high purity ethylene and a mixture of ethylene and acetylene as the top and bottom products. The mixture of ethylene and acetylene is sent back to the C_2 splitter unit as its composition matches to that of the C_2 splitter feed.

Liquid stream processing

The liquid stream consists of C_3 , C_4 , aromatics and other heavy oil components is fed to a NaOH scrubber to remove CO_2 .

Eventually it is fed to a pre-fractionator. The pre-fractionator separates

lighter components from the heavy components. The lighter components are mixed with the vapour phase stream and sent to the NaOH vapour phase scrubber unit.

The pre-fractionator bottom product is mixed with the deethanizer bottom product.

Eventually the liquid mixture enters a debutanizer that separates C_3 , C_4 components from aromatics and fuel oil mixture. The bottom product eventually enters a distillation tower that separates aromatics and fuel oil as top and bottom products respectively.

The top product then enters a depropanizer that separates C3s from C4 components.

The C4 components then enter an extractive distillation unit that separates butane + butylenes from butadiene. The extractive distillation unit consists of a distillation column coupled to a solvent stripper. The solvent stripper produces butadiene and pure solvent which is sent to the distillation column.

The C3 components enter a C3 splitter that separates propylene from propane + butane mixture. The saturates mixture is recycled to the saturates cracking furnace as a feed stream.

Why two separate furnaces are used for C2-C4 saturates and Naphtha feed stocks?

Ans: The purpose of steam cracking is to maximize ethylene and acetylene production. For this purpose if we mix C2-C4 saturates and naphtha and feed them to the same furnace, then we cannot maximize ethylene and acetylene production. The naphtha steam cracker has its own operating conditions for maximizing ethylene and acetylene and so is the case for C2-C4 saturates.

Why the product gases from naphtha and C2-C4 saturates steam cracker processed separately before mixing them and sending them to the compressor?

Ans: Both crackers produce products with diverse compositions. Both cannot be fed to a single scrubber and remove the heavy hydrocarbons and oil components. While the scrubber associated to naphtha steam cracking needs to remove significantly the oil and heavy hydrocarbons, this is not the case for steam cracker product vapour processing.

An alternate way of designing a single scrubber is to design a complex scrubber that has multiple feed entry points correspond to both product gases entering from various units. This refers to process intensification and would be encouraging.

Why a tailing and topping still is required for ethylene production?

Ans: The distillation column for separating ethylene from ethylene from C2 components needs to carry out a difficult separation. This is also due to the fact that the boiling points of C2 components is very close. Therefore, there needs to be two columns (indicating good number of trays).

Explain how extractive distillation enables the separation of butadiene?

Ans: Dimethyl formamide (solvent) is fed to the distillation column fed with butadiene, butane and butylenes. The solvent interacts differently with the components and therefore adjusts the relative volatility of the mixture which was close to 1 previously. Thereby, the solvent forms a high boiling mixture at the bottom with butadiene and thereby enables the difficult separation of butadiene from the C4 compounds. Thereby, the solvent + butadiene is fed to a stripper which removes butadiene from the DMF. One important issue here is that the solvent does not form an azeotrope with the butadiene and is therefore, easy to separate.

When acetylene is not required, what process modifications will exist to the technology?

Ans: When acetylene is not required, then the top product from C2 splitter (which is a mixture of acetylene and ethylene) is fed to a packed bed column and H_2 to convert the acetylene to ethylene. Eventually, one does not require the absorber-stripper technology for acetylene purification.

4.0 Vinyl Chloride from Ethylene

Introduction

In this lecture we study the process technology involved in the production of Vinyl Chloride from Ethylene

Vinyl chloride is produced in a two step process from ethylene

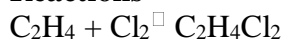
Ethylene first reacts with Chlorine to produce Ethylene dichloride

The purified Ethylene dichloride undergoes selective cracking to form vinyl chloride.

We first present the process technology associated to Ethylene Chloride

Ethylene dichloride

Reactions

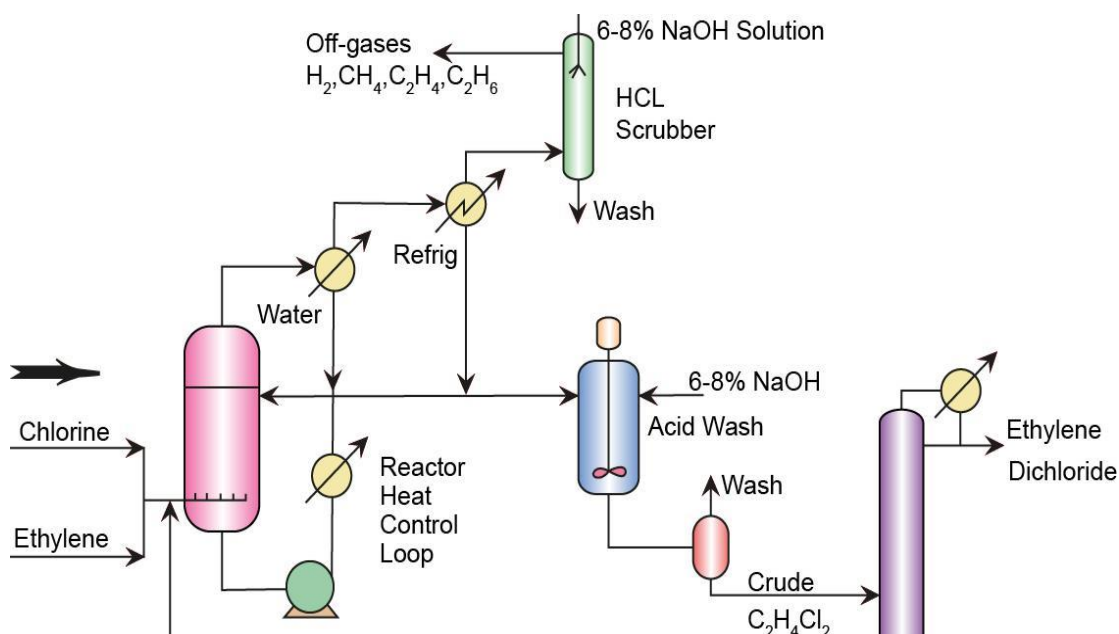


Undesired products: Propylene dichloride and Polychloroethanes

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

Process Technology



Flow sheet of production of ethylene dichloride

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 $50^\circ C$ 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

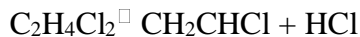
dichloride. A settling tank is allowed to separate the spent $NaOH$ solution and crude $C_2H_4Cl_2$ (as well liquid).

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 .

4.1 Vinyl chloride production

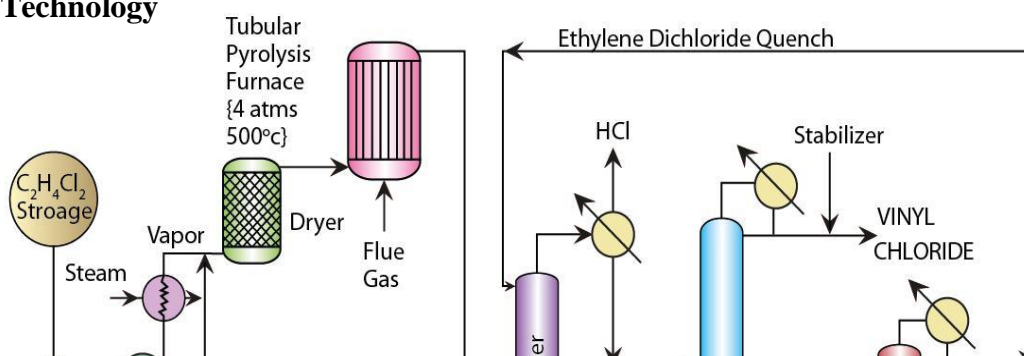
Reaction



Charcoal is used as the catalyst

The reaction is a reversible gas phase reaction

Process Technology



Flow sheet of production of vinyl chloride

Ethylene dichloride is initially vaporized using a heat exchanger fed with process steam

Ethylene vapors then enter a dryer that removes traces of water molecules

After drying, the vapors enter a pyrolysis furnace operated at 4 atm and 500 °C. The furnace is similar to a shell and tube arrangement with the gases entering the tube side and hot flue gas goes past the tubes in the shell side.

The product vapors eventually enter a quenching tower in which cold ethylene dichloride is used to quench the product gases and cool them.

The gases from the quench tower then enter a partial condenser which produces HCl as a gas and the liquid stream consisting of vinyl chloride, unreacted ethylene dichloride and polychlorides.

The liquid stream from the quench tower as well as the condenser is fed to the vinyl still which produces the vinyl chloride product. The product is stabilized using a stabilizer as vinyl chloride is highly reactive without stabilizer.

The bottom product from the vinyl still is fed to a distillation column which separates the ethylene dichloride from the polychlorides. The ethylene dichloride vapors are recycled back to the cracking furnace and the ethylene dichloride liquid is sent to the quenching tower to serve as the quenching liquid.

5.0 FORMALDEHYDE

Some major intermediates derived from formaldehyde are chelating agents, acetal resins, 1,4-butanediol, polyols, methylene diisocyanate. It is also used for the manufacture of wide variety of chemicals, including sealant, herbicides, fertilisers, coating, and pharmaceutical.

Formaldehyde is commercially available as aqueous solution with concentration ranging from 30-56 wt.% HCHO. It is also sold in solid form as paraformaldehyde or trioxane. The production of

formaldehyde in India has been growing at a fairly constant rate during last ten years. There are presently about 17 units in India. Installed capacity and production of formaldehyde during 2003-04 was 2.72 lakh tonnes and 1.89 lakh tonnes respectively.

Various industrial processes for manufacture of formaldehyde using silver and iron- molybdenum catalyst are given below:

<u>Catalyst</u>	<u>Process licensor</u>
Silver catalyst processes	Bayer, Chemical construction, Ciba, DuPont, IG Farben, CdF Chemie process, BASF process, ICI process,
Iron-molybdenum catalyst processes	Degussa process, Formox process, Fischer-Adler, Hiag-Lurgi, IFP-CdF Chimle Lumus, Motedisous, Nikka Topsoe, Prolex

Product Profile of Formaldehyde

Product	Uses
Formaldehyde	Thermosetting resin: Phenol, Urea Melamine, Formaldehyde resins Hexamethylenetetramine, Plastic & pharmaceuticals 1,4-Butadiol Methylene diisocyanate Fertiliser, Disinfectant, Biocide Preservative, Reducing agent, Corrosion inhibitor Polyaceta resin p-formaldehyde Pentaerythritol (Explosive-PETN), Alkyl resins

Process diagram for manufacture of formaldehyde using silver and iron-molybdenum catalyst is shown in [Figure](#)

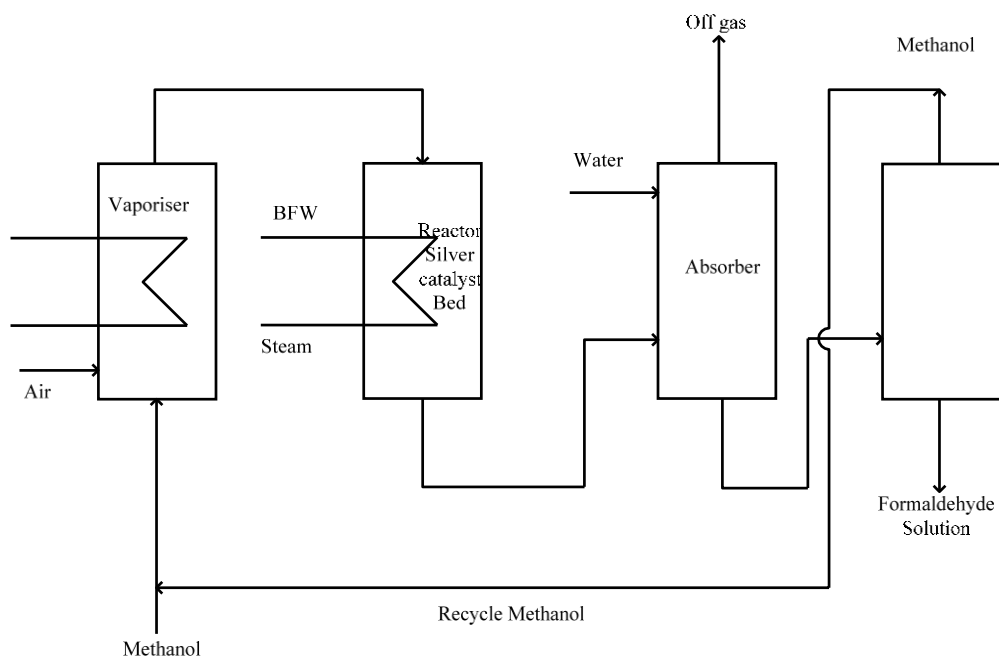


Figure : Formaldehyde Using Silver Catalyst

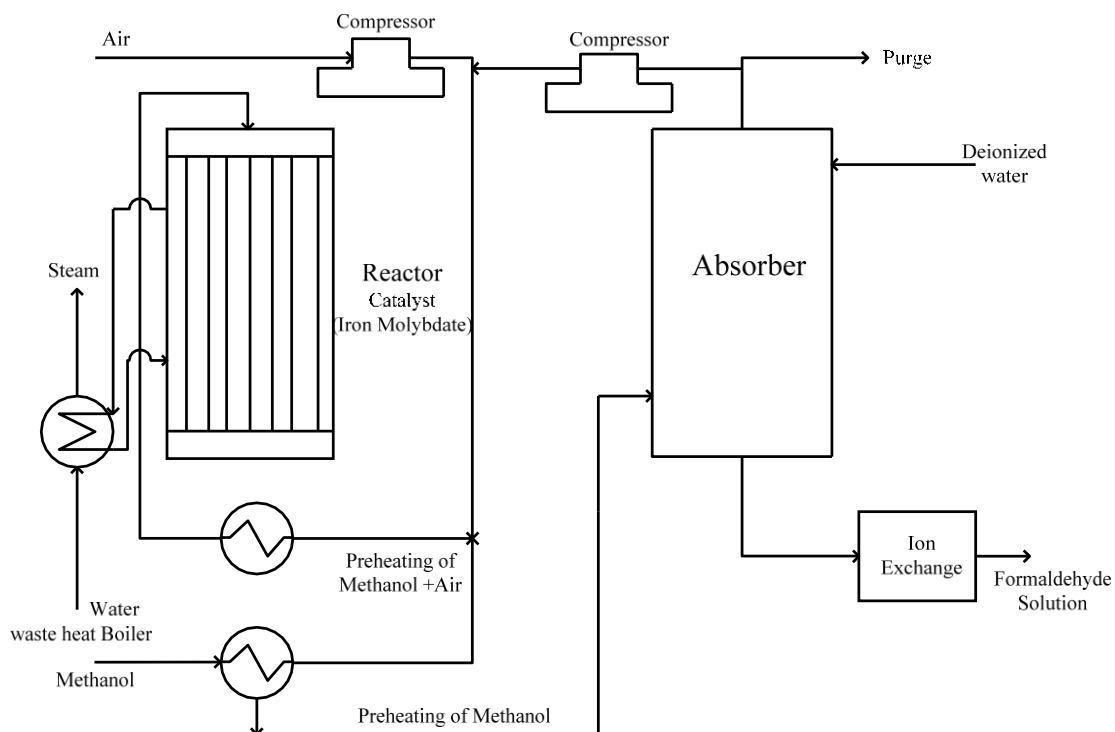


Figure : Formaldehyde from Iron Molybdenum Catalyst

6.0 ACETYLENE

Various Routes for Acetylene:

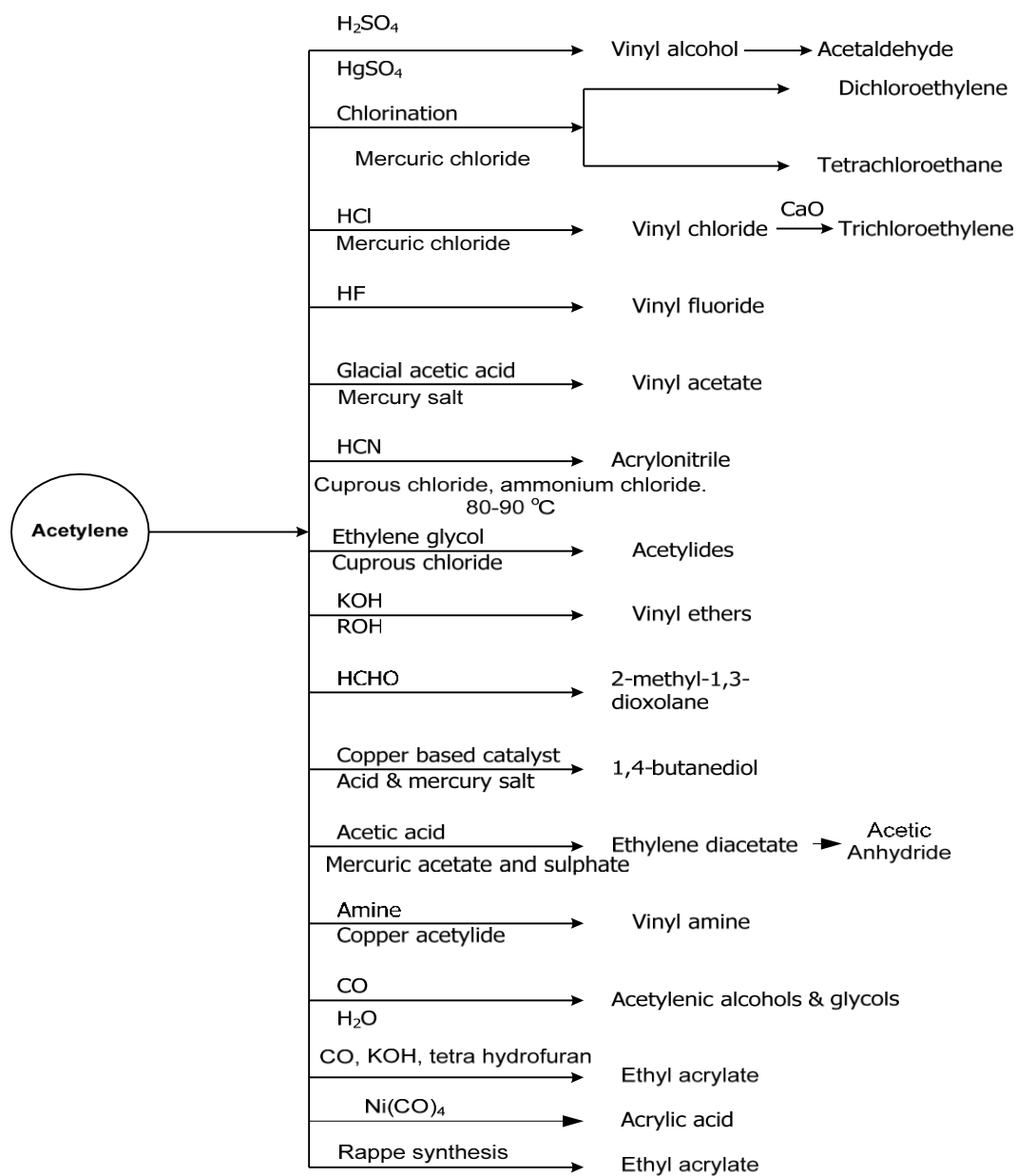
Calcium Carbide Route: This is the oldest method for production of acetylene and still acetylene is produced by this process in small scale as well large scale. Calcium carbide is produced by reacting lime with coke at temperature 2,000-2,100 °C in an electric furnace. Two processes produce acetylene from calcium carbide process: Wet process and Dry process. Dry process is preferred as in case of calcium hydroxide, which is produced during the process (is produced in the form of dry calcium hydrate).



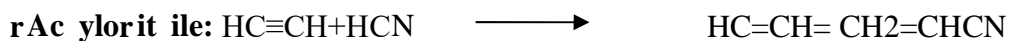
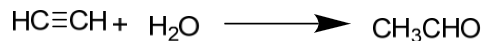
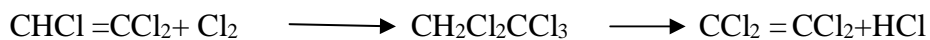
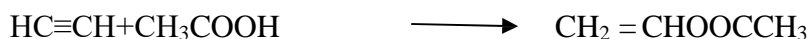
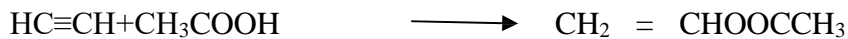
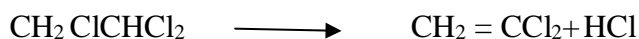
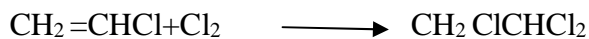
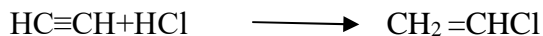
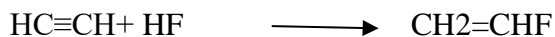
Acetylene from Cracking of Hydrocarbons: Cracking of hydrocarbons such as methane, ethane, propane, butane, ethylene, and natural gas can make acetylene.



Product Derived from Acetylene: Acetylene is extremely reactive hydrocarbon and was initially used for the manufacture of large number of chemicals which are now being derived from acetylene route.



PRODUCT PROFILE OF ACETYLENE

Acetaldehyde:**Chlorinated solvents:****Vinyl acetate:****Chloroprene****Vinyl Chloride and Vinylidene Chloride****Vinyl fluoride:****Reactions in Acetylene derived Chemicals**

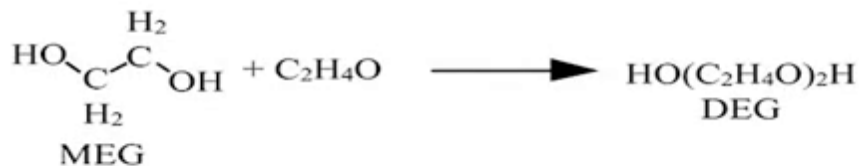
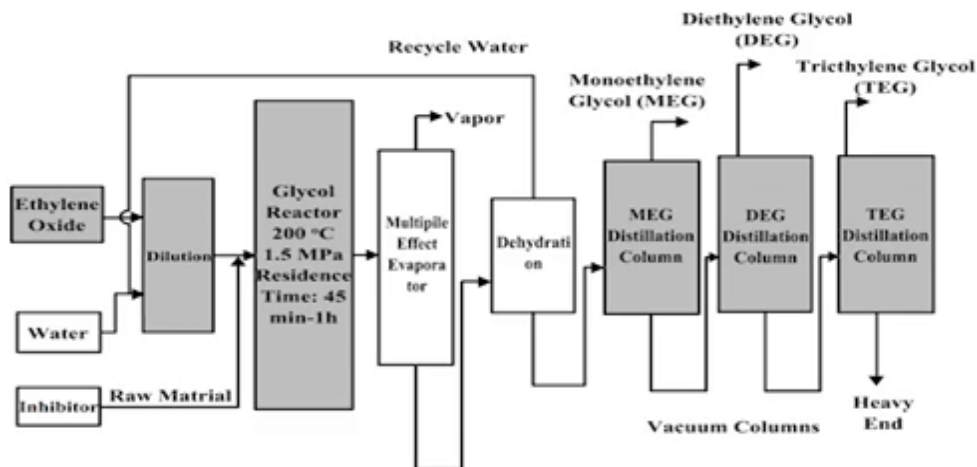
7.0 ETHYLENE GLYCOLS

Mono-, Di-, Tri- Ethylene Glycols (MEG, DEG, TEG)

A major petrochemicals and find application in manufacture of polyester and as antifreeze accounts for 70% of Ethylene oxide production. Ethylene oxide preheated to 195°C

EO: H₂O ratio 10:1 to maximise MEG production.

By Products DEG, TEG



8.0 VINYL CHLORIDE

Vinyl Chloride From Acetylene Route



Vinyl Chloride from Ethylene

Direct chlorination :



Oxychlorination :



Ethylene dichloride pyrolysis :



Overall reaction :



Vinyl Chloride From Oxychlorination Process

```
graph LR
    Ethylene1[Ethylene] --> Chlorination[Chlorination]
    Chlorine[Chlorine] --> Chlorination
    Chlorination --> Oxidation[Oxidation]
    Ethylene2[Ethylene] --> Oxidation
    HCl[HCl] --> Oxidation
    Air[Air / O2] --> Oxidation
    Oxidation --> Crude[Crude Ethylene Dichloride]
    Chlorination --> Crude
    Crude --> Distillation1[Distillation]
    Distillation1 --> LightEnd[Light End]
    Distillation1 --> Distillation2[Distillation]
    Distillation2 --> EthyleneDichloride[Ethylene dichloride]
    Distillation2 --> HeavyEnd1[Heavy End]
    EthyleneDichloride --> EthyleneDichlorideC[Ethylene dichloride Cracking]
    EthyleneDichlorideC --> Quench[Quench]
    Quench --> Residue[Residue]
    Quench --> HClRecycle[HCl Recycle]
    HClRecycle --> HCl[HCl]
    HCl --> Oxidation
    HClRecycle --> VinylChloride[Vinyl chloride]
    Quench --> VinylChloride
    VinylChloride --> VinylChlorideColumn[Vinyl chloride column]
    VinylChlorideColumn --> VinylChloride
    VinylChlorideColumn --> HeavyEnd2[Heavy End]
```

The diagram illustrates the process flow for producing Vinyl Chloride from Ethylene and Chlorine via the oxychlorination process. The process involves several stages: Chlorination, Oxidation, Distillation, and Vinyl Chloride Separation. Key inputs include Ethylene, Chlorine, HCl, and Air/O₂. Key outputs include Vinyl Chloride, Ethylene dichloride, and Heavy End. A recycle stream for HCl is also shown.

9.0 VINYL ACETATE

Vinyl Acetate: Process Technology

The ethylene route has replaced the traditional process of manufacture of vinyl acetate.

The production of vinyl acetate through acetylene route, which was developed by Wacker in 1930, involves reaction of acetylene and acetic acid in liquid phase at 60-80 °C and 1-2 atm pressure in presence of mercury salt catalyst.

Vinyl acetate from Ethylene route

Vinyl acetate is made by reaction of ethylene with acetic acid by liquid phase process or by vapor phase process in presence of palladium and cupric chloride catalyst.

Vinyl Acetate

Vinyl acetate is one of the important derivatives of ethylene which is used as intermediate for manufacture of polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, etc.

Vinyl Acetate From Ethylene Route



Use of Vinyl Acetate

Vinyl Acetate	Ethylene Vinyl Acetate Copolymers	Textile and Paper Coating
	Vinyl chloride comonomers	VC-VAC, LP Records, VC-VAC Coating
	Polyvinyl Butyraldehyde	Safety Glass

Ethanol

Ethanol apart from its major use as a beverage is one of the most versatile chemicals and is one of the basic building blocks of the organic chemical industry. Ethanol is generally produced by fermentation of molasses, due to the development of petrochemical industry and availability of ethylene, now ethylene provides another major route of formation of ethanol.

10.0 MANUFACTURE OF ETHANOL

Ethanol

Various routes for manufacture of ethanol

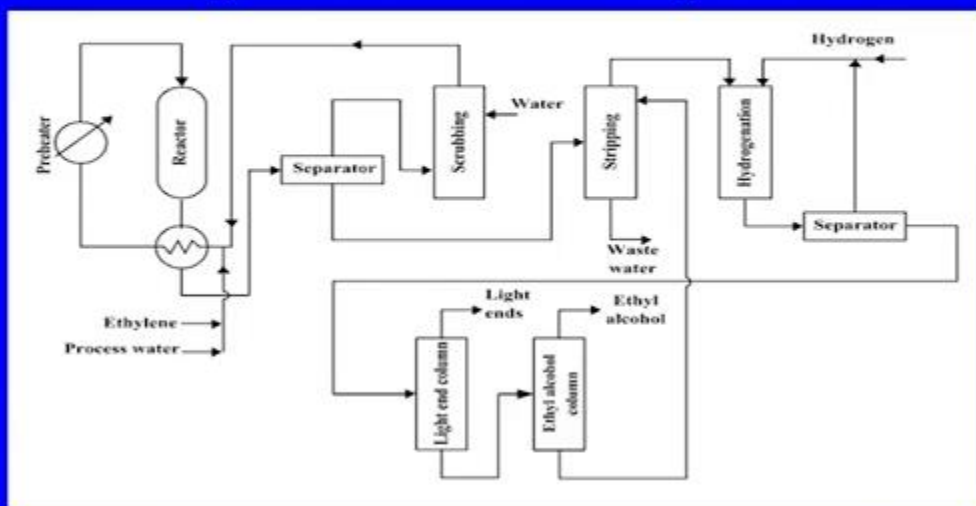
- Fermentation of molasses
- Catalytic hydration of ethylene.
- Ethylene esterification and hydrolysis.

Ethanol by Vapor Phase Hydration of Ethylene

An ethylene rich gas is mixed with water and heated to about 300 °C and passed on to fixed bed catalytic reactor where catalytic hydration of ethylene takes place



Ethanol From Catalytic Recycle Hydration of Ethylene



REFERENCE

1. www.indiainfoline.com/sect/chor/ch05.html
2. Gunardson, H.H, Abrardo, J.M., "Produce CO rich synthesis gas", *Hydrocarbon Processing*, Volume 66, No. 4, 1998, p. 87.

3. Mall, I.D. "Petrochemical process technology", first edi., New Delhi, Macmillan India ,2007
4. Huang, Sun-Yi, Lipp, D.W., Farinto, R.S. "Acetylene derived chemicals" in Kirm Othomer encyclopedia of Chemical technology, Fifth edition volume 1 wiley-Interscience, p.227
5. Chemistry Industry News, March 2004 SRI consulting, World Petrochemicals Program
6. Chemical Industry Digest, July 2012,p.29
7. Chemical Weekly, November 15, P-199, 2011.
8. Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008
9. Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – 5- CHEMICALS FROM HIGHER ALKANES SCH3002

UNIT V CHEMICALS FROM HIGHER ALKANES

Cracking of naphtha and gas for the production of ethylene, propylene
Isobutylene
Butadiene
Synthetic fibers.

1.0 Cracking of naphtha and gas for the production of ethylene, propylene

Olefins are major building blocks for petrochemicals. Because of their reactivity and versatility, olefins especially the light olefins like ethylene, propylene, butenes, butadiene, etc., there has been tremendous growth in the demand of the olefins. Olefins are finding wide application in the manufacture of polymers, chemical intermediates, and synthetic rubber. Ethylene itself is basic building block for large number of petrochemicals and is quoted as king of chemicals.

The steam cracker remains the fundamental unit and is the heart of any petrochemical complex and mother plant and produces large number of products and byproducts such as olefins - ethylene, propylene, butadiene, butane and butenes, isoprene, etc., and pyrolysis gasoline. The choice of the feedstock for olefin production depends on the availability of raw materials and the range of downstream products. Naphtha has made up about 50-55 percent of ethylene feedstock sources since 1992.

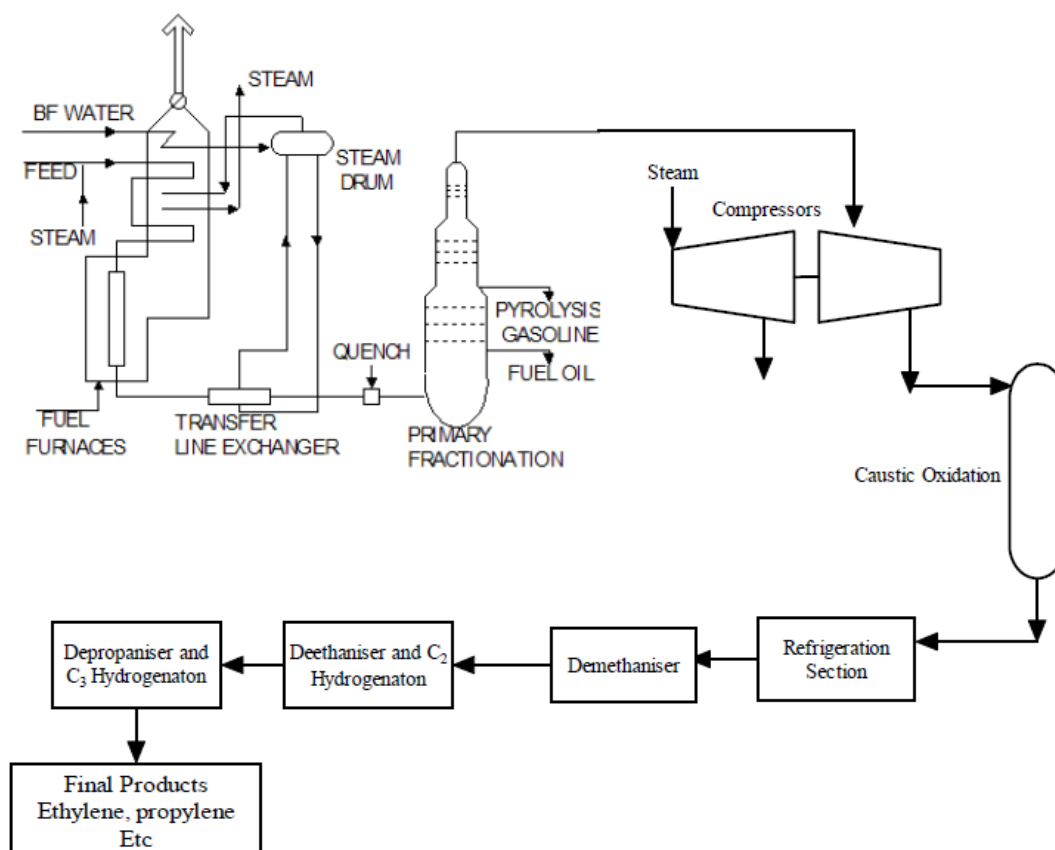
Modern ethylene plants incorporate following major process steps : cracking compression and separation of the cracked gas by low temperature fractionation. The nature of the feed stock and the level of pyrolysis severity largely determine the operating conditions in the cracking and quenching section. Various steps involved in the pyrolysis of naphtha and separation of the products are discussed below. In case of gas cracking separation of ethane and propane from natural gas is involved. Flow diagram for pyrolysis of naphtha is given in
FIGURE B.E.O.W

Hot Section

It consists of convection zone and radiant zone. In the convection zone, hydrocarbon feed stock is preheated and mixed with steam and heated to high temperature. In the convection zone the rapid rise in temperature takes place and pyrolysis reaction takes place. The addition of dilution steam enhances ethylene yield and reduces the coking tendency in the furnace coils. The production of the pyrolysis reaction consists of a wide range of saturated and unsaturated hydrocarbons.

Quench Section

To avoid subsequent reaction the effluent are fixed in their kinetic development by sudden quench first by indirect quench by water to 400 – 450 °C in transfer line exchanger or quench boiler. This is a large heat exchanger that is a bundle of metal tubes through which the gases pass and around which is circulated water under pressure. The hot water produced is used to generate steam for use in the plant. In the next step the quench is done by heavy product of pyrolysis.



Typical Naphtha Cracker Plant

HOT SECTION

Convection Zone

Feed stock is pyrolysed and the effluent conditioned

Radiation Zone

Quench

The product formed are separated and purified
To avoid subsequent reaction the effluents are fixed in their kinetics development by sudden quench.

I Indirect

Indirect quench by water to 400-500°C generation of high pressure steam

II Direct

Primary Fractionation Column

Direct quench by heavy residue by-product of pyrolysis
Separation of light products of pyrolysis as top and bottom as pyrolysis product

Compression	Compression of light products
Caustic Scrubbing and Drying	Scrubbing with caustic followed by molecular sieve adsorption to remove sulphur compounds, mercaptan, etc.

Cold Section

After compression, caustic scrubbing and drying the light effluents enter the cold section of the unit which performs the separation of (i) hydrogen to various concentration (ii) ethylene containing 99.4 percent (iii) 95 percent propylene (iv) A C₄ cut containing 25-50 percent butadiene (v) pyrolysis gasoline which is rich in aromatic hydrocarbons.

The complexity of the separation section of a cracker increases markedly as the feed changes from ethane.

COLD SECTION · Hydrogen separation

- Ethylene separation 99.9 percent
- Propylene separation
- A C₄ cut containing 25-50 percent butadiene
- Complementary fraction of pyrolysis gasoline rich in aromatic hydrocarbons

Demethaniser	Methane condensed at top around – 100°C pressure 32 Pa
Deethaniser	Separation of C ₂ cut; (Ethane and ethylene) Acetylene eliminated by selective hydrogenation Catalyst : Palladium or Nickel 40-80°C, 3 kPa
Separation of Ethylene	Ethylene is fractionated and unreacted ethane recycled
Depropaniser	C ₃ ⁺ cut from bottom of deethaniser is fractionated. C ₃ cut from top of depropaniser is selectively hydrogenated to remove methyl acetylene and propadiene. Propylene content 95 percent. Separation in supplementary column for more pure propylene.
Removal of propane from propylene	Separation in supplementary column for more pure propylene
Debutaniser	Separation of C ₄ stream from C ₅ ⁺ stream

REACTIONS IN STEAM CRACKING

The reactions involved in thermal cracking of hydrocarbons are quite complex and involve many radical steps. The thermal cracking reaction proceeds via a free radical mechanism. Two types of reactions are involved in the thermal cracking (i) primary cracking where the initial formation of paraffin and olefin takes place (ii) secondary cracking reaction where light products rich in olefins are formed. The total cracking reactions can be grouped as follows:

- Initiation reaction.
- Propagation reaction.

- Addition reaction.
- Isomerization reaction.
- Termination reaction.
- Molecular cyclization reaction

OPERATING VARIABLES OF STEAM CRACKING

The main operating variables in the pyrolysis of hydrocarbon are composition of feed stock, reaction temperature, residence time, hydrocarbon partial pressure and severity.

Composition of Feed Stock

Naphtha are mixture of alkane, cycloalkanes, and aromatic hydrocarbons depending on the type of oil from which the naphtha was derived. The group properties of these components greatly influence the yield pattern of the pyrolysis products. A full range naphtha boiling range approximately 20 to 200°C would contain compound, with from 4-12 carbon atoms. Short naphtha boiling point range from 100-140°C and long chain naphtha boiling point lies around 200-220°C. The steam cracking of the naphtha yields wide variety of products, ranging from hydrogen to highly aromatic heavy liquid fractions. The thermal stability of hydrocarbons increases in the following order: paraffins, naphthenes, aromatics. Yield of ethylene as well as that of propylene is higher if the naphtha feed stock is rich in paraffins. It may be seen that relative production of ethylene decreases as the feed stock becomes heavier. The percentage of pyrolysis gasoline C5-200°C cut increases. Simultaneously butadiene yield varies slightly with feed stock in the treatment of liquid petroleum fractions.

With the rising demand of ethylene and propylene, there has been a tremendous growth in the steam cracking of hydrocarbons during the last four decades. Similarly, FCC (Fluid Catalytic Cracking) has developed into a major upgrading process in the petroleum refinery industry for the conversion of heavy fuel oil into more valuable products ranging from light olefins to naphtha and middle distillate. Large amounts of C₄ and C₅ compounds are produced along with the production of ethylene in steam cracking and gasoline in FCC. C₄ & C₅ streams are an important source of feedstock for synthetic rubber and many chemicals.

With increasing demand of C₅ hydrocarbons and oxygenates, upgrading of C₄ and C₅ streams from steam crackers and catalytic cracker is important to the economic performance of the above processes. It also provides a rich resource of reactive molecules, which forms the backbone of the synthetic rubber industry. The quantity and composition of the C₄ and C₅ stream depends on

the severity of the steam cracker operation and feedstock processed.

FLUID CATALYTIC CRACKING

Fluid catalytic cracking (FCC) converts low value crude oil into a variety of higher value products which include gasoline, diesel, heating oil and valuable gases containing LPG, propylene and C4 and C5 gases. Various products from fluid catalytic cracking and their uses are given in Table FCC units are versatile and can be operated in three main modes which are aimed at maximizing middle distillate, gasoline, or olefins respectively by means of the adequate combination of various parameters such as catalyst type, catalyst to oil ratio, rise of outlet temperature and recycle of fractionators bottom. FCC is the second largest source of propylene supplied for petrochemical application.

Conventional FCC 4-7% propylene and 1-2 % Ethylene

High Severity FCC:10% propylene

Petro FCCTM (UOP): Ethylene 6%, Propylene 20-22%, Higher aromatics (18%) in Naphtha

Higher C₄₋₈ olefins yield which can be cracked to yield lower olefins by Total

Petrochemicals ATOFINA/UOP Olefin cracking Process

Although FCC is an important petroleum refining process, however, FCC gases have now become important petrochemical feedstock for production of LPG that can be converted to aromatics and C₃, C₄, & C₅ hydrocarbons, i.e. propylene, butene, isobutene, pentene, etc.

Product distribution from FCC depends

- Reactor temp
- Feed preheat temperature
- Catalyst activity
- Catalyst circulation rate
- Catalyst activity
- Recycle rate

Various Petroleum Products from FCC and their uses

Product	Composition and Uses
Light gases	Primarily H ₂ , C ₁ and C ₂ s, ethylene can be recovered
LPG	C ₃ s and C ₄ s containing light olefins suitable for alkylations

Gasoline	C ₅ + high octane component for gasoline pool or light fuel
Light cycle oil (LCO)	Blend component for diesel or light fuel
Heavy cycle oil (HCO)	Fuel oil or cutter oil
Clarified oil	Carbon black feedstock
Coke	Used in regenerator to provide the reactor heat demand

Propylene Recovery from FCC: FCC gases has important source of propylene from refinery and now FCC units are being operated both in gasoline mode and propylene mode. Details of propylene from FCC are given in Lecture 5 Module 6. Propylene from FCC may be as high as 25% with new FCC based propylene technologies. increased production of olefins from FCC units has been achieved through changes in operations, base cracking catalyst and additive catalysts and in hardware designs [Teng and Xie, 2006]

UPGRADING OF C₄ and C₅ Streams

C₄ and C₅ Streams from Steam Cracker and FCC contains C₄ and C₅ hydrocarbons recovery of which has become important steps for improving the overall economy of these processes. Some of the important C₄ streams from Cracker and FCC butadiene (from cracker plant only), butene-1, 2-butane, isobutylene, mixed n-butene, isobutene..C₄ stream of steam cracker contains appreciable amount of butadiene which is being recovered from naphtha cracker plants. Typical composition of C₄ stream of naphtha cracker and FCC is given Table M-VII 3.3. The distribution product will depend on the feed stock, cracking severity and catalyst in case of FCC

1.1 ISOBUTYLENE

Isobutylene is present in the C₄ stream naphtha cracker and FCC. Major application of isobutene is in the manufacture of gasoline blending component such as MTBE, ETBE, alkylation, polymer gasoline. Polymer grade isobutylene can be made by cracking MTBE or for manufacture of polyisobutylene. Isobutylene is used in manufacture butyl rubber which is made by copolymerization of isobutylene with small amount of isoprene.

Various Routes for Isobutylene

Extraction of C4 cuts from steam cracking / FCC: Isobutylene is separated from C4 cuts from naphtha cracker after extraction of butadiene and from FCC gases after propylene recovery. First isobutylenes is converted to MTBE by etherification and the recovered by cracking of MTBE to get polymer grade isobutylene it is also obtained by hydration of isobutylene containing stream and then cracking.

Isomerisation of Butene: isobutylene can be also produced from butane by isomerisation using zeolite ferrierite (zeolite of medium pore size) [Maulijanet al.2001]

Dehydrogenation of Isobutene:

BUTENE -1

Butene-1 is co-monomer in the production of low density polyethylene and high density polyethylene. Butene-1 can be separated from C4 stream of cracker after extraction of butadiene SHB-CB process: This process selectively hydrogenate the butadiene in the C4 cut by converting it to butane-1 and butane-2. Acetylenes and dienes are likewise hydrogenated. If the process is optimized to produce butane-1, about 60% of butadiene is converted to butane-1. The process is operated in the liquid phase mild temperatures and moderate pressures.

UPGRADING OF C₅ CUTS

The steam cracker C₅ stream is a rich resource of olefins and diolefins which can be upgraded to produce elastomers, resins and fine chemical intermediates. In steam crackers during cracking process along with ethylene, propylene, C₄ stream, aromatics and pyrolysis gasoline bare also formed. Apart from aromatics, Pyrolysis gasoline stream also contains C₅ stream [Morgan,1996]. The quantity and composition of the stream depend on the nature of the cracked product and severity of cracker operation C₅ stream.

1.2 Butadiene and Benzene Manufacture

Introduction

In this lecture, we present the process technologies associated to Butadiene and Toluene.

Butadiene manufacture is considered using n-Butane as the feed stock.

Benzene process technology refers to the famous hydrodealkylation process that uses toluene as the feed stock.

We first present the process technology associated to Butadiene.

Butadiene

Reactions

Main reaction: $\text{n-Butane} \rightarrow \text{Butadiene} + \text{Hydrogen}$.

Side reaction: $\text{n-Butane} \rightarrow \text{n-Butylene} + \text{Hydrogen}$.

Catalyst: Chromium oxide on alumina.

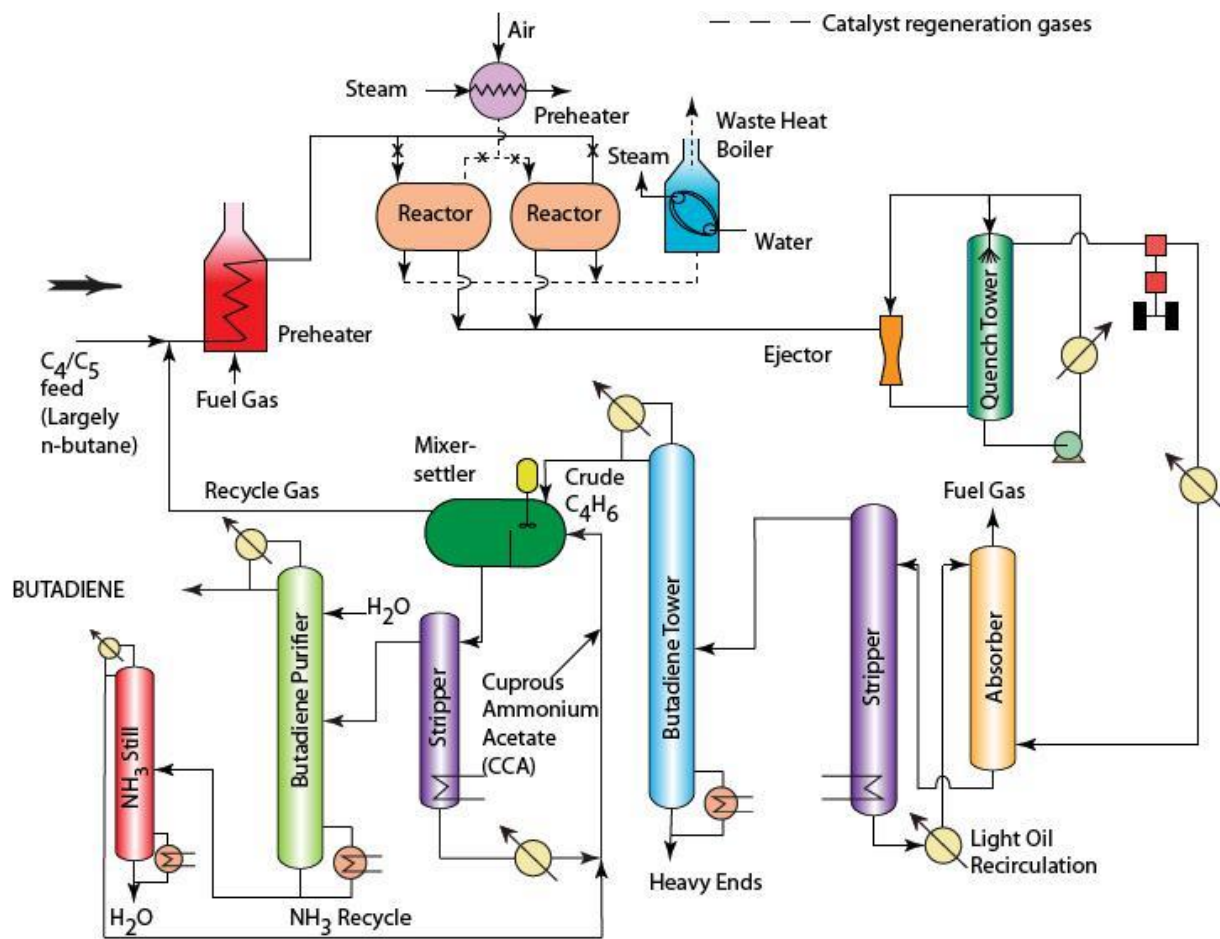
Coke deposition is a very important issue. Therefore, catalyst regeneration needs to be carried out very frequently.

Reaction is exothermic .

Operating conditions: 650°C and 120-150 mm Hg (low pressure).

Feed stock: n-Butane with some isopentane from refinery processes.

Process Technology



Flow sheet of Butadiene manufacture

- The process technology for Butadiene manufacture consists of a reactor-separator-recycle system.

The separation network is extremely complex and involves quenching, absorption, distillation and extractive distillation process.

First, the feed stock is pre-heated in a furnace along with unreacted gases that have been recovered in the process using the separator network.

After pre-heating in a furnace to desired temperature, the gases enter the catalytic packed bed reactors loaded with the catalyst.

After the specified residence time, the product is withdrawn and the feed to the unit is stopped. The product withdraw and stoppage of the feed flow to the reactor unit is carried out using valves.

The coked catalyst is subjected to combustion using pre-heated air. Air pre-heating is done using steam in an extended area heat exchanger equipment. Therefore during regeneration, another set of valves operate to allow the pre-heated air in and enable the product withdrawal after the combustion.

The pre-heated air not only removes the coke as CO_2 but increases the reactor temperature to 650°C .

The flue gases are sent to a waste heat recovery boiler so as to generate steam from water.

The entire operation of a feed entry, product withdrawal, pre-heated air entry and combustion gases withdrawal from the packed bed reactor corresponds to one single cycle.

Since the above operation is a batch operation, to make the operation continuous in accordance to the separation network, two reactors are used and these reactors are operated in cyclic fashion i.e., when the first reactor is subjected to reaction, the second reactor is subjected to catalyst regeneration and vice-versa.

The hot reactor outlet gases are sent to a quenching operation where light gas oil is used to quench the gases using a recirculating quenching tower.

After product gases from the quenching tower are compressed and cooled to enter an absorber

In this absorber, naphtha is used as an absorbent to absorb all hydrocarbons except fuel gas.

The absorbent + hydrocarbons enter a stripper that produces fresh naphtha and hydrocarbon mixture. The hydrocarbon mixture consists of unreacted feed stock and butadiene and some heavy ends.

This mixture now enters a fractionator to separate the crude butadiene and heavy ends.

The crude butadiene consists of butadiene and unreacted feed stock i.e., n-butane and isopentane. The separation of n-butane, other hydrocarbons with butadiene is one of the difficult separations and they cannot be separated using ordinary distillation. Therefore, a complicated route of separation is followed next that involves azeotropic distillation using ammonia.

The crude butadiene is mixed with ammoniated cuprous ammonium acetate solution in a mixer settler. This solution is generated by absorbing ammonia into fresh cuprous ammonium acetate solution.

The ammoniated cuprous ammonium acetate is sent to a mixer settler unit where the butadiene dissolves in the ammoniated solution. The gas from the mixer settler unit is recycled to mix with the feed stock and enter the pre-heater.

The ammoniated cuprous ammonium acetate solution is thereby stripped to separate butadiene + ammonia from the ammonium acetate solution. The regenerated fresh solvent is allowed to absorb NH_3 and thereby enter the mixer-settler unit.

The ammonia + butadiene mixture enters a fractionator fed with water. Here, water interacts with ammonia and generates the ammonium hydroxide product as the bottom product and butadiene is obtained as the top product.

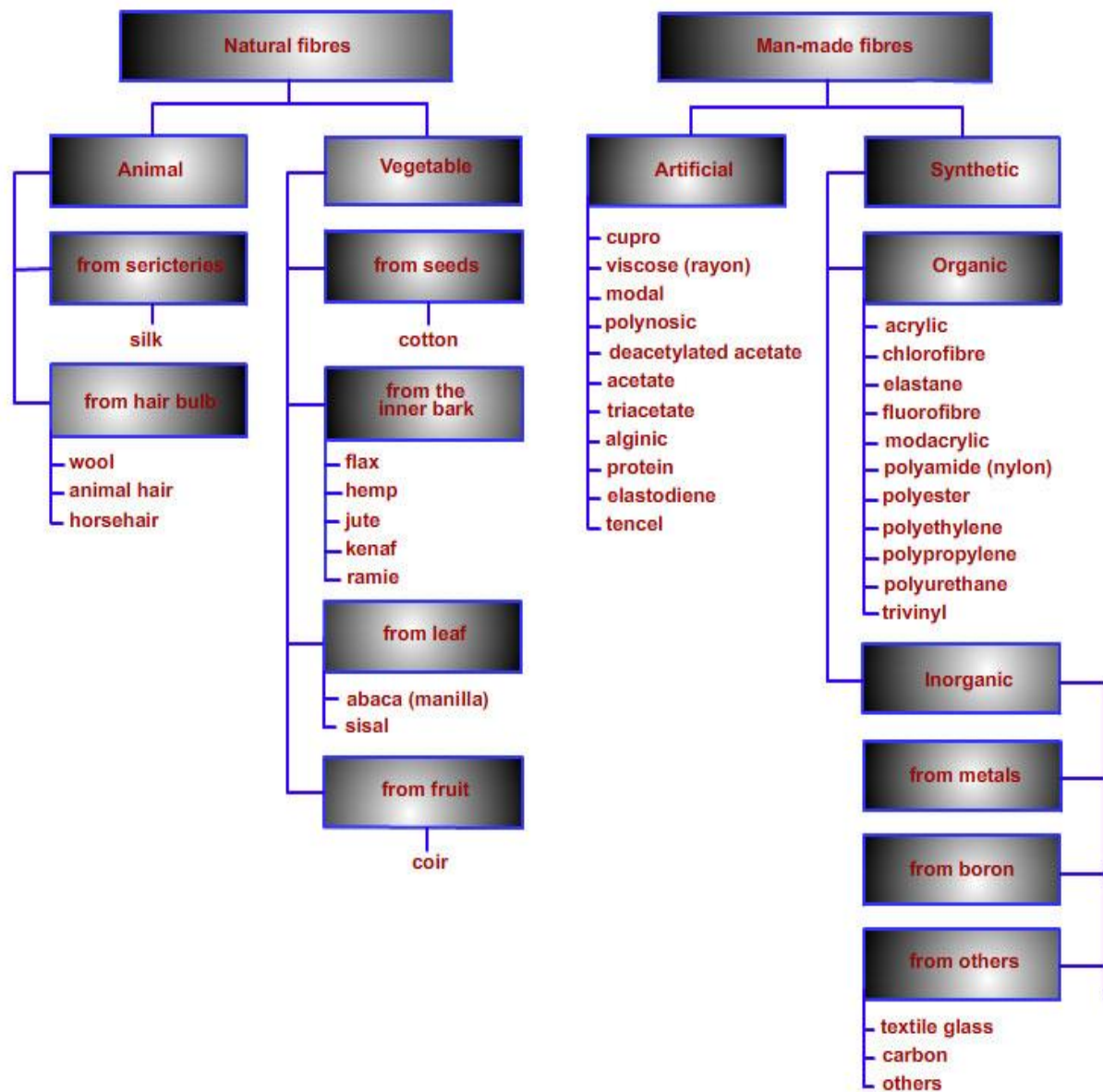
The ammonia solution is subjected to stripping to separate water and ammonia. The water is recycled back to the butadiene purifier and ammonia is allowed to get absorbed into the fresh cuprous ammonium acetate solution.

This process is not followed in India. In India, it is manufactured from ethanol by catalytic cracking at 400-450 °C over metal oxide catalyst.

1.3 Synthetic fibers

Synthetic fibers and synthetic fabrics consist of bulk fibers, yarns, woven cloth or other textile products manufactured from **polymer**-based materials such as polyamide (**nylon**), polyester, aramid, or other spun thermoplastics. The end-product is the form of the fiber/fabric when manufacturing is complete.

Classification of fibres



REFERENCES

1. Briggs, B.A., Simpson S.O., Lemerck C.A., Ward D.J., "Fluid catalytic cracker as a source of petrochemical olefins", Chemical Age of India, Volume 38, No. 1, 1987, p. 21.
2. Chauvel, A., Lefebvre G., "Treatment of olefinic C₄ and C₅ cuts", in Petrochemical Processes, Synthesis-Gas derivatives and major hydrocarbons, Editions Technip Paris 1985, p. 195.
3. Chemical Weekly, December, 27, P-198, 2011.
4. Convers, A., "Make chemicals from C₄olefinic fractions", Chemical Age of India,
5. Morgan, M., "C₅ hydrocarbons and derivatives new opportunity", Chemistry and industry 2 September, 1996, p.646.
6. Moulijian, J.A., Makkee, M., Diepen, A.V., "Chemica Process technology", John Wiley & Sons, 2001
7. Teng, J., Xie, Z., "OCC process for propylene production", Hydrocarbon Asia May/June 2006,p.26
8. Vermilion, W.L., Niclaes H.J., "Petrochemicals from the FCC unit", Hydrocarbon Processing, September 1977, p. 193.

