Petrochemical Industry

DEFINTIONS OF PETROCHEMICALS

Petrochemicals are chemicals derived from petroleum products. Examples of petrochemicals are plastics, rubbers, fibres, paints, solvents, and detergents.

In fact, petroleum products are mixtures of hydrocarbons, whereas the raw materials for petrochemicals are pure hydrocarbons separated and converted to desirable products, such as polymers, solvents, and surfactants, usually in several stages and may be grouped as:

(1) Feedstocks (first-generation petrochemicals).

(2) Intermediates (second-generation petrochemicals).

(3) Finished products (third-generation petrochemicals).

Products similar to petrochemicals derived from non-petroleum sources are not strictly petrochemicals. For example, cellulose, natural rubber, natural resins, nylon 11, and ethanol of plant origin are strictly non-petrochemicals.

Coal distillation is also a source of varieties of coal chemicals, e.g., benzene, toluene, xylene, and naphthalene. In fact, before petroleum sources were known, coal chemicals were used to produce a variety of products. Many of the chemicals from non-petroleum sources are co-processed with petrochemicals to the finished product.

Non-hydrocarbons obtained from petroleum, e.g., hydrogen, carbon monoxide, carbon dioxide, sulfur, and carbon, are also loosely called petrochemicals. Hydrogen, nitrogen and oxides of carbon manufactured from steam reforming and partial oxidation of naphtha are also petrochemicals. These are used for production of ammonia, urea, melamine, fertilizer, etc.

FEEDSTOCKS

Feedstocks are the raw hydrocarbons obtained from crude oil refining by distillation and thermal and catalytic processes. For instance, hydrocarbon gases and naphtha are available from atmospheric distillation of crude oil; similarly, benzene, toluene, and xylene, obtained by catalytic reforming and catalytic cracking processes, are the major raw materials for the manufacture of second-generation petrochemicals.

Benzene, toluene, xylene, and heavier aromatics are also generated as by-products from petrochemical plants. Thus, the feedstocks for petrochemical plants are either directly obtained from refineries or are further processed to generate them in the petrochemical plant itself.

Natural gas and refinery products are the major source of feedstocks for petrochemicals.

INTERMEDIATES

Thermal cracking of ethane, propane, butane, and naphtha produces cracked gases or olefins (ethylene, propylene, butylenes, acetylene, etc.) and liquids (benzene, toluene, xylene, etc.). Olefins are the starting material (monomers) for polyolefin plants. Olefins are also reacted with other hydrocarbons or non-hydrocarbon chemicals to generate vinyl chloride, ethylene glycol, neoprene, ethylene oxide, etc., and these are used as the starting materials (monomers) for the manufacture of a variety of polymers.

FINISHED PRODUCTS

Using the above intermediates, a variety of plastics, rubber, fibre, solvent, paint, etc.,are manufactured. Polymerisation reactions are carried out for these monomers or intermediates to various polymers, resinous and liquid products. Plastics are available in the form of extrudates, granules, powders, beads, etc., from the manufacturing units as the finished products. These are converted into plastic commodities, such as bags, films, furniture, and products of various shapes and sizes by casting, moulding, or blowing machines, as the marketable products. Plastics are classified into two types, namely, thermoplastic (or thermoplast) and thermosetting plastics (or thermoset).

A variety of chemical reactions are involved in the petrochemical manufacturing processes. Most of these reactions are catalytic with heat effects. Examples are dissociation, dehydrogenation, hydrogenation, addition, polymerisation, and condensation.

Dissociation reactions occur during the thermal and catalytic cracking process. Dehydrogenation also occurs catalytically or thermally during cracking. Additional reactions, such as oxidation, chlorination, fluorination, and sulfonation of the parent olefin or aromatic hydrocarbons, are required to make intermediates or monomers. Polymerisation occurs mostly in the presence of initiators or catalysts with heat evolution.Two types of polymerisation reactions occur, i.e., addition polymerisation and condensation polymerisation.

Addition polymerisation involves a chain reaction in which monomer molecules join in a chain. For example, olefins or diolefins are polymerised in the presence of initiators, such as free radicals, ionic compounds, or complexes.

Condensation polymerisation involves two monomers, same or different, which combine to form a polymer with the elimination of small molecular weight by-products like water.

A large number of unit operations and processes are involved in a petrochemical plant. Since catalysts play a major role in the synthesis of petrochemicals, research and development of new catalysts is a continuous endeavour by the manufacturers. It is also to be noted that in a polymerisation plant, catalysts may not be recovered rather this is entrained in and become a part of the polymer. The presence of catalyst ingredients in the polymer per unit mass may pose a problem as far as quality is concerned. Hence, a catalyst is selected that requires minimum consumption. The reactors used are tubular, stirred tank or kettle type. These may be packed bed or fluidized bed types, Both single and multiple numbers of reactors are used. The selection of a suitable reactor is a challenging decision in a petrochemical manufacturing unit.

Primary Raw Materials for Petrochemicals

In general, primary raw materials are naturally occurring substances that have not been subjected to chemical changes after being recovered. Natural gas and crude oils are the basic raw materials for the manufacture of petrochemicals.

Secondary raw materials, or intermediates, are obtained from natural gas and crude oils through different processing schemes. The intermediates may be light hydrocarbon compounds such as methane and ethane, or heavier hydrocarbon mixtures such as naphtha or gas oil. Both naphtha and gas oil are crude oil fractions with different boiling ranges.

Coal, oil shale, and tar sand are complex carbonaceous raw materials and possible future energy and chemical sources. However, they must undergo lengthy and extensive processing before they yield fuels and chemicals similar to those produced from crude oils (substitute natural gas (SNG) and synthetic crudes from coal, tar sand and oil shale).

NATURAL GAS (Non-associated and Associated Natural Gases)

Natural gas is a naturally occurring mixture of light hydrocarbons accompanied by some non-hydrocarbon compounds. Non-associated natural gas is found in reservoirs containing no oil (dry wells).

Associated gas, on the other hand, is present in contact with and/or dissolved in crude oil and is coproduced with it. The principal component of most natural gases is methane. Higher molecular weight paraffinic hydrocarbons (C2-C7) are usually present in smaller amounts with the natural gas mixture, and their ratios vary considerably from one gas field to another.

Non-associated gas normally contains a higher methane ratio than associated gas, while the latter contains a higher ratio of heavier hydrocarbons.

The non-hydrocarbon constituents in natural gas vary appreciably from one gas field to another. Some of these compounds are weak acids, such as hydrogen sulfide and carbon dioxide. Others are inert, such as nitrogen, helium and argon. Some natural gas reservoirs contain enough helium for commercial production.

Higher molecular weight hydrocarbons present in natural gases are important fuels as well as chemical feedstocks and are normally recovered as natural gas liquids. For example, ethane may be separated for use as a feedstock for steam cracking for the production of ethylene. Propane and butane are recovered from natural gas and sold as liquefied petroleum gas (LPG).

NATURALGAS TREATMENT PROCESSES

Raw natural gases contain variable amounts of carbon dioxide, hydrogen sulfide, and water vapor. The presence of hydrogen sulfide in natural gas for domestic consumption cannot be tolerated because it is poisonous. It also corrodes metallic equipment.

Carbon dioxide is undesirable, because it reduces the heating value of the gas and solidifies under the high pressure and low temperatures used for transporting natural gas. For obtaining a sweet, dry natural gas, acid gases must be removed and water vapor reduced. In addition, natural gas with appreciable amounts of heavy hydrocarbons should be treated for their recovery as natural gas liquids.

Acid Gas Treatment

Acid gases can be reduced or removed by one or more of the following methods:

1. Physical absorption using a selective absorption solvent.

2. Physical adsorption using a solid adsorbent.

3. Chemical absorption where a solvent (a chemical) capable of reacting reversibly with the acid gases is used.

Physical Absorption

Important processes commercially used are the Selexol, the Sulfinol, and the Rectisol processes. In these processes, no chemical reaction occurs between the acid gas and the solvent. The solvent, or absorbent, is a liquid that selectively absorbs the acid gases and leaves out the hydrocarbons. In the Selexol process for example, the solvent is dimethyl ether of polyethylene glycol. Raw natural gas passes counter currently to the descending solvent. When the solvent becomes saturated with the acid gases, the pressure is reduced, and hydrogen sulfide and carbon dioxide are desorbed. The solvent is then recycled to the absorption tower. Figure 1 shows the Selexol process.

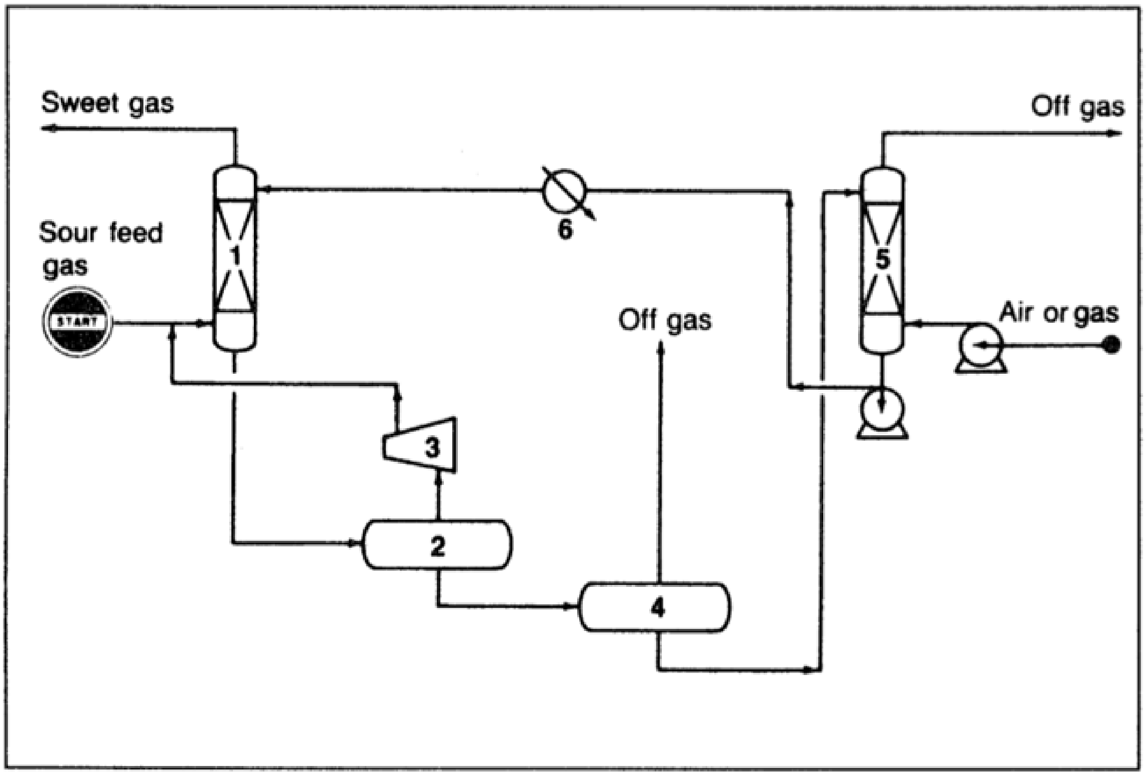

Figure 1The Selexol process for acid gas removal:2 (1) absorber, (2) flash drum, (3) compressor, (4) low-pressure drum, (5) stripper, (6) cooler.

Regeneration is accomplished by passing hot dry fuel gas through the bed. Molecular sieves are competitive only when the quantities of hydrogen sulfide and carbon disulfide are low. Molecular sieves are also capable of adsorbing water in addition to the acid gases.

Physical Adsorption

In these processes, a solid with a high surface area is used. Molecular sieves (zeolites) are widely used and are capable of adsorbing large amounts of gases.

In practice, more than one adsorption bed is used for continuous operation. One bed is in use while the other is being regenerated. Regeneration is accomplished by passing hot dry fuel gas through the bed. Molecular sieves are competitive only when the quantities of hydrogen sulfide and carbon disulfide are low. Molecular sieves are also capable of adsorbing water in addition to the acid gases.

Chemical Absorption (Chemisorption)

These processes are characterized by a high capability of absorbing large amounts of acid gases. They use a solution of a relatively weak base, such as monoethanolamine. The acid gas forms a weak bond with the base which can be regenerated easily. Mono- and diethanolamines are frequently used for this purpose. The amine concentration normally ranges between 15 and 30%. Natural gas is passed through the amine solution where sulfides, carbonates, and bicarbonates are formed. Diethanolamine is a favored absorbent due to its lower corrosion rate, smaller amine loss potential, fewer utility requirements, and minimal reclaiming needs. Diethanolamine also reacts reversibly with 75% of carbonyl sulfides (COS), while the mono- reacts irreversibly with 95% of the COS and forms a degradation product that must be disposed of.

Diglycolamine (DGA), is another amine solvent used in the Econamine process (Fig 2). Absorption of acid gases occurs in an absorber containing an aqueous solution of DGA, and the heated richsolution (saturated with acid gases) is pumped to the regenerator. Diglycolamine solutions are characterized by low freezing points, which make them suitable for use in cold climates. Strong basic solutions are effective solvents for acid gases. However, these solutions are not normally used for treating large volumes of natural gas because the acid gases form stable salts, which are not easily regenerated.

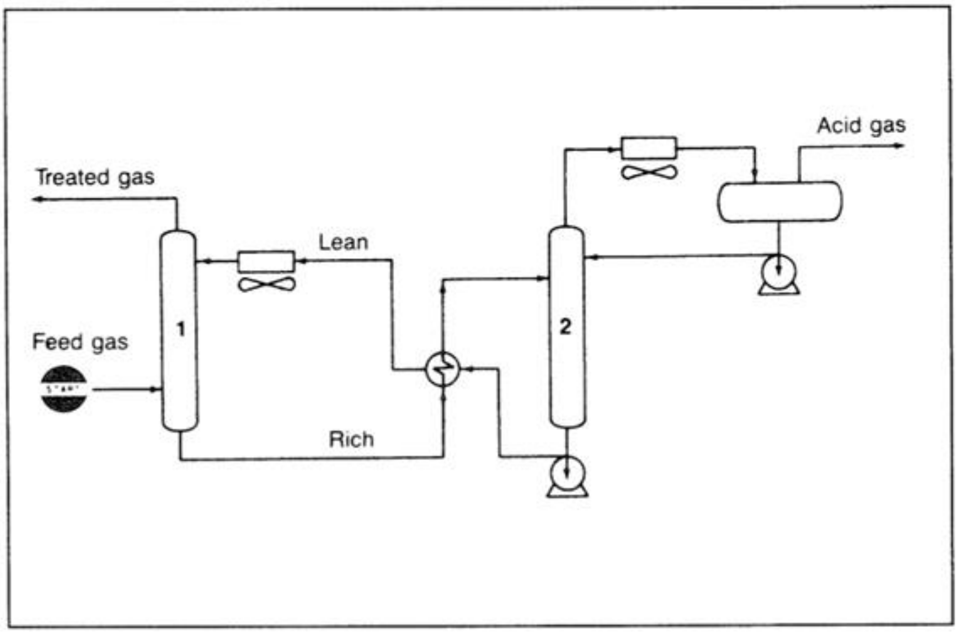

Figure 2 The Econamine process:4 (1) absorption tower, (2) regeneration tower

For example, carbon dioxide and hydrogen sulfide react with aqueous sodium hydroxide to yield sodium carbonate and sodium sulfide, respectively.

$$CO_2 + 2NaOH_{(aq)} \rightarrow Na_2\,CO_3 + H_2O$$

$$H_2S + 2\,NaOH_{(aq)} \rightarrow Na_2S + 2\,H_2O$$

However, a strong caustic solution is used to remove mercaptans from gas and liquid streams. In the Merox Process, for example, a caustic solvent containing a catalyst such as cobalt, which is capable of converting mercaptans (RSH) to caustic insoluble disulfides (RSSR), is used for streams rich in mercaptans after removal of H_2S. Air is used to oxidize the mercaptans to disulfides. The caustic solution is then recycled for regeneration. The Merox process (Fig. 3) is mainly used for treatment of refinery gas streams.

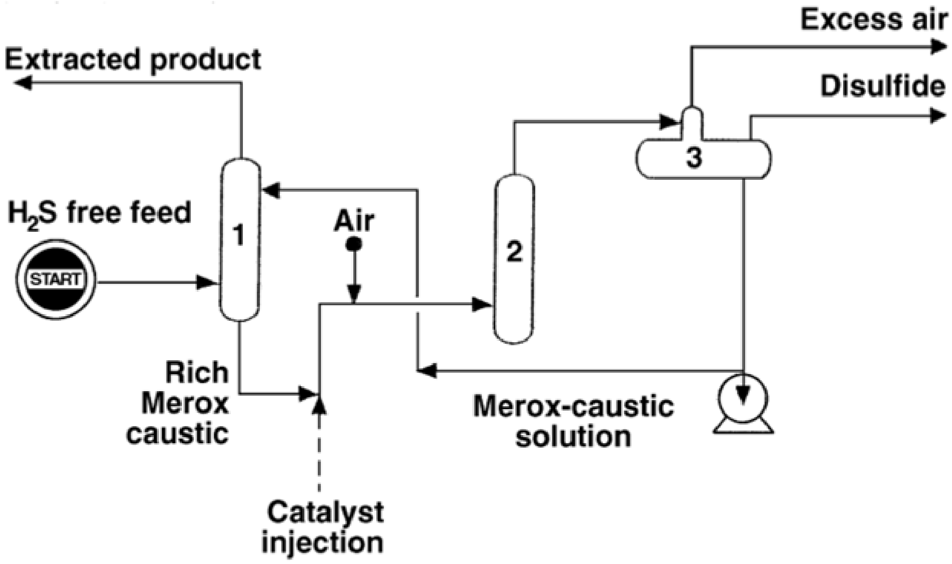

Figure 3 The Merox process: (1) extractor, (2) oxidation reactor

Water Removal

Moisture must be removed from natural gas to reduce corrosion problems and to prevent hydrate formation. Hydrates are solid white compounds formed from a physical-chemical reaction between hydrocarbons and water under the high pressures and low temperatures used to transport natural gas via pipeline. Hydrates reduce pipeline efficiency. To prevent hydrate formation, natural gas may be treated with glycols, which dissolve water efficiently. Ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) are typical solvents for water removal. Triethylene glycol is preferable in vapor phase processes because of its low vapor pressure, which results in less glycol loss. The TEG absorber normally contains 6 to 12 bubble-cap trays to accomplish the water absorption. However, more contact stages may be required to reach dew points below –40°F. Calculations to determine the number of trays or feet of packing, the required glycol concentration, or the glycol circulation rate require vapor-liquid equilibrium data. Predicting the interaction between TEG and water vapor in natural gas over a broad range allows the designs for ultra-low dew point applications to be made.6 Acomputer program was developed by Grandhidsan et al., to estimate the number of trays and the circulation rate of lean TEG needed to dry natual gas. It was found that more accurate predictions of the rate could be achieved using this program than using hand calculation. (Figure 4) shows the Dehydrate process where EG, DEG, or TEG could be used as an absorbent. One alternative to using bubble-cap trays is structural packing, which improves control of mass transfer. Flow passages direct the gas and liquid flows countercurrent to each other. The use of structural packing in TEG operations has been reviewed by Kean et al. Another way to dehydrate natural gas is by injecting methanol into gas lines to lower the hydrate-formation temperature below ambient. Water can also be reduced or removed from natural gas by using solid adsorbents such as molecular sieves or silica gel.

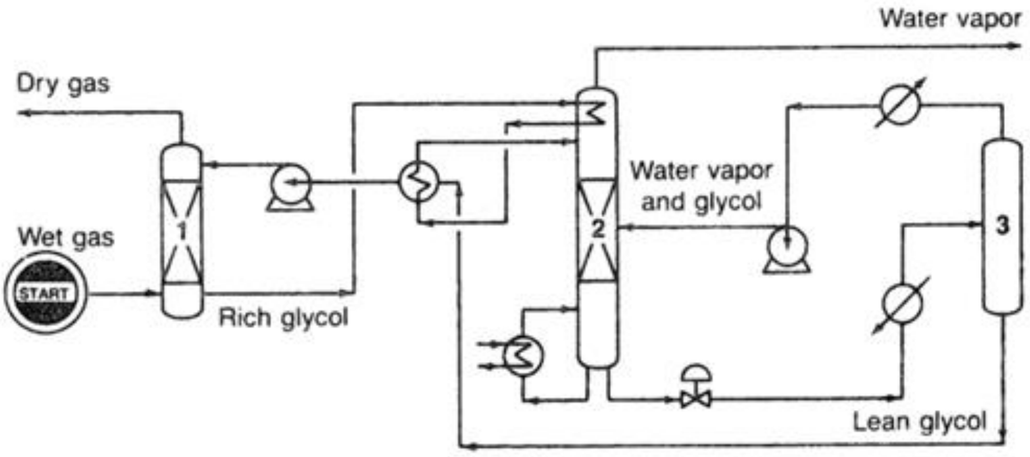

Figure 4 Flow diagram of the Dehydrate process: (1) absorption column, (2) glycol sill, (3) vacuum drum

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References

1. **Uttam Ray Chaudhuri “Fundamentals of Petroleum and Petrochemical Engineering.” University of Calcutta Calcutta, India, 2011.**

2. **Matar S., Hatch L.F, "Chemistry of PETROCHEMICAL PROCESSES ", 2nd Edition, Gulf Publishing Company, (1994).**