SECTION VII

INDUSTRIAL PROCESSES

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PETROCHEMICAL INDUSTRY

The petrochemical industry is a large and complex source category that is very difficult to define because its operations are “intertwined functionally or physically with the inorganic sector of the chemical industry, with downstream (manufacturing), fabrication or compounding

activities, or with the petroleum refining industry. (This results in) mixing of vertical operating steps in official statistics". Petrochemical industries are involved in the production of several chemicals which fit into one or more of the following four categories:

1. Basic raw materials
2. Key intermediates
3. Minor intermediates
4. End products

The petrochemical industry also includes the treatment of hydrocarbon streams from the petroleum refining industry and natural gas liquids from the oil and gas production industry. Some of the raw materials used in the petrochemical industry include petroleum, natural gas, ethane, hydrocarbons, naphtha, heavy fractions, kerosene, and gas-oil. Natural gas and petroleum are the main feedstocks for the petrochemical industry. That is why about 65 percent of petrochemical facilities are located at or near refineries.

The petrochemical industry produces solvents and chemicals of various grades or specifications which are used to produce industrial organic chemicals, including benzene, the butylenes, cresols and cresylic acids, ethylene, naphthalene, paraffins, propylene, toluene, and xylenes. Approximately 2500 organic chemical products are produced directly or indirectly from basic petrochemicals. The industrial organic chemicals produced from petrochemicals are employed in downstream industries including plastics and resins, synthetic fibers, elastomers, plasticizers, explosives, surface active agents, dyes, surface coatings, pharmaceuticals, and pesticides.

A. PROCESS DESCRIPTION

A process converts a raw material into products, by-products, intermediate products, or waste streams. The main processes conducted in the basic petrochemicals industry are separation and purification. Some chemical conversion processes such as cracking, hydrogenation, isomerization, and disproportionation are also carried out. Six groups of related processes, termed operations, are employed by the petrochemical industry:

1. Olefins production
2. Butadiene production
3. BTX production
4. Naphthalene production
5. Production of cresols and cresylic acids
6. Separation of normal paraffins

Each operation employs several varied process lines and procedures. The production of 1,3-butadiene will be used as an example of the types of processes used in the petrochemical industry.

1,3-butadiene is a high-volume, intermediate organic chemical used commercially to produce various types of rubber, resin, and plastics. 1,3-butadiene is involved in several different reactions, including addition, oxidation, and substitution reactions; however, its main use is for polymerization.

Producers of 1,3-butadiene typically generate the feedstock at the same location as the 1,3-butadiene production. Most 1,3-butadiene is used in synthetic elastomer production, and some is used in adiponitrile production, the raw material for nylon 6,6 production. The overall demand of 1,3-butadiene is expected to increase due to the growth of specialty uses for 1,3-butadiene.

1,3-butadiene is produced by one of two processes:

(1) Recovery from a mixed hydrocarbon stream, and
(2) Oxidative dehydrogenation of n-butenes.

1,3-butadiene production through recovery is by far the most common approach. In this process, a mixed hydrocarbon stream containing butadiene, coproduced in an olefins plant during cracking of large-molecule hydrocarbons to manufacture ethylene or other alkenes (Exhibit 1), is routed to a recovery unit where the butadiene is separated.

In an olefins plant a steam cracking furnace is used to crack the hydrocarbon feedstock. The heavy hydrocarbons are broken into two or more fragments, forming a stream of mixed hydrocarbons. The concentration of butadiene in this mixed hydrocarbon stream varies with the type of feedstock. The flue gas from the cracking furnace is vented to the atmosphere.

After the cracking step, the mixed hydrocarbon stream is cooled and, if naphtha or gas oils were the initial feedstock, the stream is sent to a gasoline fractionator. The fractionator is used to recover heavy hydrocarbons (C_5 and higher). For some olefins units the quenching step shown occurs after gasoline fractionation. The mixed stream is then compressed prior to removal of acid gas (hydrogen sulfide) and carbon monoxide. Acid removal usually involves a caustic wash
step. The mixed hydrocarbon stream then goes through additional refining steps, where it is separated from olefins (C_3 and lower).

The mixed C_4 stream may be sent directly to butadiene recovery at the same plant. Olefins plants that do not produce finished butadiene use the by-product mixed C_4 streams in the following ways: (1) recover the crude butadiene from the stream and sell it to a butadiene producer, (2) recirculate the stream into the front of the ethylene process, and/or (3) use the stream to fuel the equipment (e.g., furnaces) in the ethylene process.

EXHIBIT 1

The second part of this butadiene production process involves recovering the butadiene from the mixed C_4 stream. The mixed C_4 stream is fed from pressurized storage tanks into a hydrogen reactor along with hydrogen to convert some of the unsaturated hydrocarbons such as acetylene to olefins. The product C_4 stream from the hydrogenator is combined with a solvent (typically furfural) and fed into an extractive distillation operation. In this operation, most of the butanes and butenes are separated from butadiene, which is absorbed in the solvent along with residual impurities. A stripping operation is then used to separate the butadiene from the solvent.

The stream containing butadiene typically has a small amount of residuals. Some of these

residuals are alkynes that were not converted to olefins in the hydrogenation reactor. These residuals are removed from the butadiene stream by distillation and are usually vented to an emission control device. The bottom stream exiting the acetylenes removal operation contains butadiene and residuals such as polymer and 2-butene. The residuals are removed in the butadiene finishing operation and sent to a waste treatment system or recovery unit. The finished butadiene is then stored in pressurized tanks.

In the dehydrogenation process, steam and air are combined with n-butenes and preheated, then passed through a dehydrogenation reactor. Hydrogen is removed from the butenes feed stream. Next, the stream is compressed and sent to a hydrocarbon adsorption and stripping process. The product is then routed to a light-ends column for further separation. Finally, distillation and separation take place, with the finished butadiene sent to storage.

B. SOURCES OF POLLUTION

There are five main sources of pollutant emissions in the production of 1,3-butadiene:

- process vent discharges,
- equipment leaks,
- secondary sources,
- storage, and
- emergency or accidental releases.

Process vent discharges can be from reactor vessels, recovery columns, and other process vessels. Equipment leaks include pump seals, process valves, compressors, safety relief valves, flanges, open-ended lines, and sampling connections. Secondary sources include process and other waste streams. Emissions from storage vessels are assumed negligible since 1,3-butadiene is stored in pressure vessels with no breathing or working losses. There are no data available regarding emission amounts from emergency or accidental releases.

C. POLLUTANTS AND THEIR CONTROL

Exhibits 2 and 3 identify air pollutants and hazardous waste pollutants, respectively. Little information is available regarding amounts of pollutant emissions from the entire petrochemical industry, including 1,3-butadiene production. Many petrochemical processes are located at or near petroleum refining operations; therefore, many of the air pollutants and hazardous wastes generated by the petroleum industry are also present at petrochemical facilities. It is important to note that the Exhibits represent facility-wide pollution.

In general, the waste streams from the petrochemical industry are quite similar to those of the petroleum refining industry. Limited data are available, but almost all assume waste management operations and facilities are probably of the same degree of sophistication as those of the petroleum refining industry.

Wastewater, which is a basic source of emissions, can be categorized in five ways:

(1) Wastes containing a principal raw material or product;

(2) By-products produced during reactions;
(3) Spills, leaks, washdowns, vessel cleanouts, or point overflows;
(4) Cooling tower and boiler blowdown, steam condensate, water treatment wastes, and general washing water; and
(5) Surface runoff.

Disposal of solid wastes is a significant problem for the petrochemical industry. Waste solids include water treatment sludges, ashes, fly ash and incinerator residue, plastics, ferrous and nonferrous metals, catalysts, organic chemicals, inorganic chemicals, filter cakes, and viscous solids. General methods of disposal are depicted in Exhibit 3.

Exhibit 2: Pollutant Profile of the Petrochemical Industry

Pollutants	Control Device	Control Efficiency (%)
Particulates		
VOC		
Hydrocarbons		
SO_x		
NO_x		
CO		
Chemicals used or produced (benzene, 1,3-butadiene, naphthalene)	• (For gases)	
- Gas recovery (boiler)		
- Flare		
- Incinerator		
99.9		
98		
98		

Exhibit 3: Hazardous Waste Generation From the Petrochemical Industry

Pollutant	Amount	Disposal Method
Hazardous solids	Not available	Land disposal Incineration
Hydrocarbons	Not available	Salvage & recycle
Any hazardous chemicals used or produced	Not available	Chemical & biological treatment

D. REFERENCES

1. Federal Energy Administration (Office of Economic Impact). Report to Congress on Petrochemicals. Public Law 93-275, Section 23 (no date: circa 1974).

2. Industrial Process Profiles for Environmental Use. Chapter 5 - Basic Petrochemical Industry, EPA document 600/2-77-023, January, 1977.

3. Locating and Estimating Air Emissions from Sources of 1,3-Butadiene, EPA document

450/2-89-021, December, 1989.