Report Abstract

Phthalic Anhydride
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1 CHEMISTRY

Phthalic anhydride may be produced from ortho-xylene or naphthalene by oxidation with air:

\[
\text{ortho-Xylene} + 3\text{O}_2 \rightarrow \text{Phthalic Anhydride} + 3\text{H}_2\text{O} \quad \Delta H_f = -265 \text{ Kcal/g-mole}
\]

Other oxidation products include maleic anhydride, benzoic acid, carbon dioxide, etc. Carbon dioxide is formed when the organic feedstock is completely oxidized.

Historically, naphthalene had been the feedstock for the production of phthalic anhydride (PAN). It remained so until after World War II when Oronite (now Chevron Phillips Chemical Co.) commercialized production of PAN using ortho-xylene.

\[
\text{Naphthalene} + 4.5\text{O}_2 \rightarrow \text{Phthalic Anhydride} + 2\text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H_f = -427 \text{ Kcal/g-mole}
\]

The use of ortho-xylene as a feedstock was confined to the United States, until naphthalene shortages in Europe promoted utilization of ortho-xylene. The switch to ortho-xylene was due to diminishing supplies of naphthalene as a result of lower coke consumption (resulting in low coal tar and naphthalene production) and the increasing availability of ortho-xylene from refinery operations.

In the United States, ortho-xylene became a more prominent feedstock as a result of a major steel strike in 1959 that severely curtailed coal-tar naphthalene supplies. Despite the initially low yields obtained, ortho-xylene became a preferred raw material because of its increasing supply reliability compared to that of naphthalene. This spurred R&D activities to improve the catalysts available.

2 PROCESS CONSIDERATIONS

2.1 Explosion Limits

The lower explosive limit of an ortho-xylene/air mixture is at 46-48 grams of ortho-xylene per normal cubic meter of air. This is equivalent to 3.3 weight percent ortho-xylene at 0°C and atmospheric pressure. Traditional PAN processes are operated at a ratio below the lower explosive limit, at about 42-44 grams per Nm³.
At conventional technology operating conditions, the excess oxygen would allow for an increase in the ortho-xylene concentration. Increasing the ortho-xylene concentration would result in the following:

- less air to be compressed and preheated: energy savings
- higher throughput per unit volume: lower capital cost
- less tail gas per unit PAN product: less off-gas to the environment and savings in capital cost.

Though attractive, operation at higher ratios results in a flammable mixture in the reactor tubes.

In modern phthalic anhydride plant design, ortho-xylene is oxidized by air in a multi-tubular reactor cooled by a eutectic mixture of nitrate and nitrite salts.

2.2 Catalysts

Catalysts for the oxidation of xylenes contain vanadia and titania, usually with other promoters on a refractory support. The active site for selective oxidation is surface vanadia coordinated to the TiO$_2$ support. The surface species are more active and more selective than crystalline V$_2$O$_5$. Supports can be of various shapes, although rings or cylinders are particularly favored since they produce a high external surface and low pressure drop. There have been numerous studies on phthalic anhydride catalysts both from the theoretical and process points of view.

A typical catalyst consists of support beads coated with an active layer 0.02 mm thick. The monolayer of V$_2$O$_5$ on TiO$_2$ anatase is the basis for all current industrial catalysts. A typical catalyst should have a high selectivity (over 75 mole percent), a long life (at least three years), and must be operable with ortho-xylene concentrations of at least 60 grams/Nm$^3$ at high space velocity.

2.3 Reactors

The major challenge with the PAN process is the removal of heat from the reaction zone to prevent overheating and deactivation of catalyst. The most common processes use gas phase reactions that occur while passing through a catalyst contained in multi-tubular fixed bed reactors. Other arrangements have been used in the past, specifically fluidized bed catalyst reactors for conversion of naphthalene and a liquid phase process for conversion of ortho-xylene. However, multi-tubular fixed bed reactors are now the standard for new designs, with up to 25,000 tubes available in a single reactor. The tubes are contained in a shell and cooled by circulating a eutectic mixture of salts (sodium nitrite, sodium nitrate, and potassium nitrate).

The conventional fixed bed reactor tube is about 25 mm in diameter and 3 m in length. ortho-Xylene conversions approaching 100 percent can be obtained at a space velocity of about 2,500 hr$^{-1}$ and ortho-xylene loadings of 60-80 grams/Nm$^3$. Yields are typically 112 weight percent, equivalent to 80 percent of the theoretical.
Fluidized bed systems have not been commercialized for ortho-xylene oxidation in contrast to naphthalene oxidation. There are potential advantages to a fluid bed in reduced reactor cost and reduced hazard in using high concentrations of ortho-xylene in the feed. An analogy could be drawn between fixed and fluid bed processes for oxidation of butane to maleic anhydride. The fluid bed process is a development that has been commercialized for maleic anhydride production.

3 ECONOMICS

Two cases have been considered for the production of phthalic anhydride at different capacities (and processes) under a consistent U.S. Gulf Coast first quarter 2007 price scenario.

Furthermore, production cost estimates have been generated for the production of ortho-xylene and naphthalene since they are the raw materials used in the production of PAN. It is assumed in all cases that raw materials are available over the fence at prices that reflect cost of production plus ten percent return on investment.

The selected cases are:

- Phthalic anhydride from ortho-xylene (USGC, Lurgi-BASF)
- Phthalic anhydride from naphthalene (USGC, Conventional Process)

Observations from economic analysis include:

- Phthalic anhydride from either ortho-xylene or naphthalene has a negative value for utilities as a result of a steam credit.
- In this current high crude oil price environment, PAN produced from naphthalene has a somewhat lower cash cost than when it is produced from ortho-xylene.
- The production of PAN, from the oxidation of ortho-xylene, exhibits a slightly higher full cost of production than from the oxidation of naphthalene.

4 COMMERCIAL ANALYSIS

PAN is a commodity petrochemical, with no product differentiation and widely available technology. The major use for PAN is in plasticizers for PVC, which is strongly tied to the housing market. The basic purpose is to impart flexibility to otherwise rigid PVC. In general, the lower molecular weight dialkyl phthalates with the alkyl groups in the 4 to 7 carbon number range are used for their solvency and rapid fusion. Because of their higher vapor pressure, they have a tendency to volatilize from the compound, which results in a stiffer product. Higher carbon number, especially in the 8 to 10 range are more common in plasticizer applications. The higher molecular weight phthalates, 11 to 13 carbon number alcohols, are especially useful in the high temperature wire and cable industry because of their low volatility, even at elevated temperatures. The highest volume plasticizer is dioctyl phthalate (DOP) (diisooctyl phthalate (DIOP)). Other important plasticizers are diisononyl phthalate, diisodecyl phthalate, dinonyl phthalate, and dibutyl phthalate.
The second largest demand sector for PAN is in unsaturated polyester resins (UPR), used in the manufacture of reinforced laminates, and in specialized applications such as surface coatings. The major market sectors are those using large quantities of reinforced laminates: construction, marine, automotive, sporting goods, and electrical goods. Because the major markets for reinforced fiberglass are in the recreational area, sales volumes are very sensitive to changes in the economy.

The third use for PAN is in alkyd resins, most of which are used in solvent-based paints. The continuing trend toward latex-based paints based on vinyl acetates and acrylics is reducing the alkyd resin's share in protective coatings; alkyd resins are also being replaced in important industrial applications by water-borne systems and powder coatings. Trends toward decorative paints based on vinyl acetate and acrylics, and solvent free systems, indicates that a slow decline in alkyd resin consumption is anticipated. Estimated PAN end use profile for the United States is shown in Figure 1.

**Figure 1 United States PAN Demand by End Use, 2006**

There are many small uses of PAN as a chemical intermediate. Applications include the manufacture of dyes and pigments, herbicides, insecticides, flame retardants, and others.