CHEMSYSTEMS
PERP PROGRAM

Maleic Anhydride (MAN)

Process Technology (including Comparison of Fixed, Fluid, and Transport Bed Reactors, and Solvent and Aqueous Recovery Techniques), Production Costs, and Regional Supply/Demand Forecasts.

PERP07/08-8

Report Abstract

April 2009

Nexant

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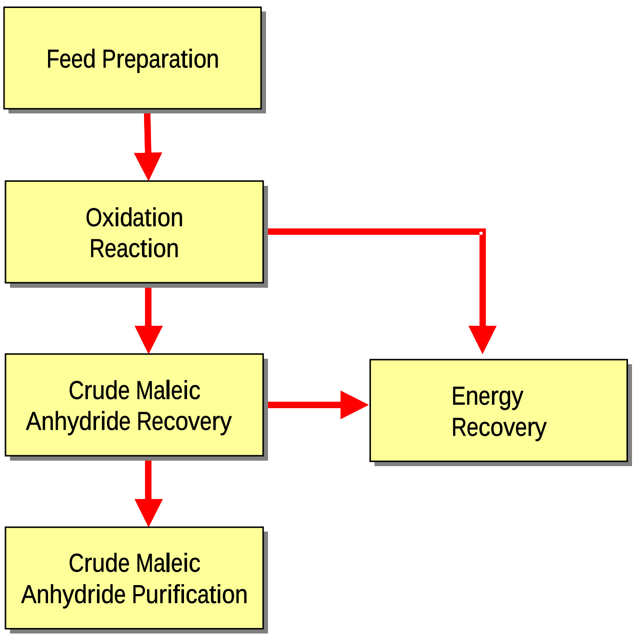
INTRODUCTION

Maleic anhydride is a very versatile molecule that lends itself to many applications requiring a number of properties and functionalities. With three active sites (two carboxyl groups and one double bond), it is an excellent joining and cross linking agent. Its major end use, representing well over half of global demand, is in the manufacture of unsaturated polyester resins, where its cross-linking abilities are important. Maleic anhydride is an important intermediate in the fine chemical industry, particularly in the manufacture of agricultural chemicals and lubricating oil additives. It is also a component of several copolymers in the engineering polymers sector.

Maleic anhydride is the classic Diels-Alder reagent. It was for work in 1928 on the reaction between maleic anhydride and 1,4-butadiene that Diels and Alder were awarded the Nobel prize in 1950. It is through this reaction that maleic anhydride is used in many pesticides and pharmaceuticals. It is also an environmentally acceptable molecule, an important added bonus in those applications. Some examples of the specialty chemicals that can be prepared from maleic anhydride, include tartaric acid, diethyl and dimethyl succinate, glyoxylic acid, malic acid, diisobutylhexahydrophthalate (DIBE), dodecene succinic anhydride, and methyl tetrahydrophthalic anhydride esters.

Two main types of feedstock have been used for commercial maleic anhydride production: benzene and *n*-butane. Irrespective of raw material, the oxidation technology and the separation technology of a maleic anhydride plant resembles the fundamental process scheme shown in the figure below.

Basic Maleic Anhydride Plant Configuration



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Feed Preparation covers the delivery of reactant to the reactor. In all cases, vaporized hydrocarbon and compressed air are intermixed in a controlled manner using static in-line mixers. A catalyst promoter such as trimethyl phosphate is added to either one of the components or the combined stream.

The **Oxidation Reaction** takes place in a specialized reactor irrespective of whether it is a fixed bed multi-tubular or fluid bed. The tremendous heat of reaction must be removed either by internal coils as in a fluid bed or via circulating molten salt. Careful control is needed to prevent hydrocarbon oxygen compositions breaching combustion limits.

In the **Product Separation** section, more heat is removed from the reaction off-gas and then an aqueous or solvent based recovery system is employed to obtain a crude maleic anhydride stream.

Product Purification is a typical two-step distillation approach involving light ends removal and the separation of a heart cut, usually vacuum assisted.

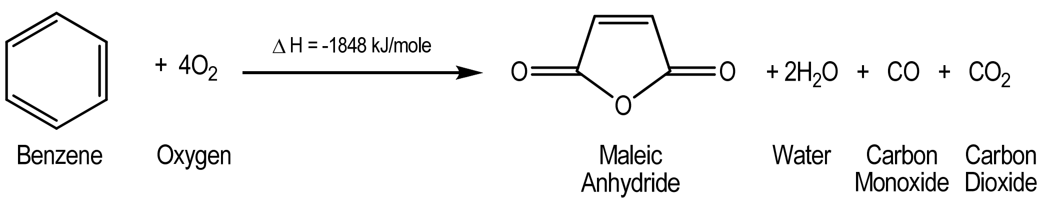
Energy Recovery is a key factor in the economic production of maleic anhydride. Reactor off-gases, post maleic anhydride recovery, non-condensibles from vacuum systems, tank vent gases, and waste hydrocarbon rich liquids, are all incinerated to recover energy as super-heated steam. This steam can be used to supply energy to integrated units.

Chemistry (Oxidation Processes)

Benzene Oxidation

For 50 years, the main process route to maleic anhydride was the oxidation of benzene in the vapor phase, and it remains a commercial route outside the United States accounting for around 15-20 percent of global capacity. Relatively high benzene costs are making the process obsolescent, but it will continue to be used by companies with no alternative feedstock. The technology, in many respects, is very similar to fixed bed processes using *n*-butane. Thus, many fixed bed benzene plants have been retrofitted to use *n*-butane.

The principal reaction in the process can be represented by the chemical equation below, although it should be appreciated that the ratio of CO to CO_2 is not fixed.



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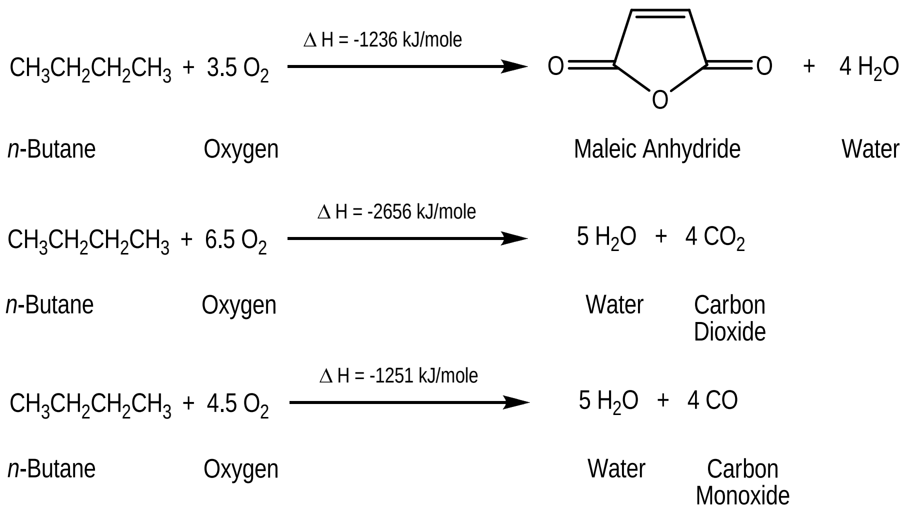
n-Butane Oxidation

The partial oxidation of *n*-butane like benzene is very exothermic. As the following chemical equations show the energy released from *n*-butane oxidation exceeds that of benzene and this is reflected in the steam co-product.



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There are a number of side reactions other than those highlighted. There are mechanisms that result in small amounts of acetic acid and acrylic acid being formed in addition to carbon oxides.

- **A review on catalysts is given in the report for n-butane based systems** (including catalyst preparation, the role of promoters, catalysts for fluid bed operation) **and benzene based systems.**

COMMERCIAL MALEIC ANHYDRIDE TECHNOLOGIES

This section begins with an interesting review of the development of commercial maleic anhydride processes. Following this is a discussion of various commercial technologies that are available - outlined below:

Fixed Bed Technology

- In recent years, Huntsman has been very successful at licensing large-scale maleic anhydride plants supplying integrated butanediol production. Huntsman has the advantage of being able to prove it can operate a large-scale process given that its own plant at Pensacola, FL is of world-scale. Process flow diagram and description are included.
- Scientific Design (owned by Sabic and Sud Chemie) has a very long history of licensing maleic anhydride plants, but mostly smaller scale units. The Scientific Design process produces maleic anhydride from *n*-butane at very high yields using a patented "Series Reactor" design and a continuous recovery system for the production of excellent quality product. Process flow diagram and description are included.
- Technobell Limited has developed technology for the conversion of *n*-butane to maleic anhydride. Process flow diagram and description are included.

Fluid Bed Technology

A fluid bed system has a number of potential advantages over the widely used *n*-butane-based fixed bed technology. The most notable of these advantages is an energy balance that provides export of high-pressure steam as a result of operating with less than half the air rate of the fixed bed technology. In addition, its reactor system has enhanced economy of scale.

- Lummus/POLYNT in recent years has developed a fluid bed technology for maleic anhydride (ALMA®). Process flow diagram and description are included.

  Revitalization of ALMA® process via Cyclone Improvements: In 1989 and 1991, the first two commercial ALMA maleic anhydride plants were started up and performed well; however, the performance of plants subsequent to the first two (the "second round") ALMA plants was seriously impaired by their inability to maintain the necessary particle size distribution in the reactor while utilizing a reasonable (economical) amount of catalyst makeup. This, in turn, was a consequence of two shortcomings of the cyclone system. Improvements, features of the new cyclone system and commercial benefits from the new cyclone systems are discussed.

- The current INEOS maleic anhydride catalyst and technology business has its roots from both Amoco and BP. Both companies established research and development activities for the oxidation of butane in the 1970s, with Amoco focused on fixed bed reaction systems and BP (then SOHIO) focused on fluid bed reaction technology. Both companies successfully advanced these programs, leading to the first commercial applications in the 1970s for Amoco and the 1980s for BP. Upon merging in 1999, BP and Amoco combined their research and development efforts in maleic anhydride. This combination has since produced three new generations of catalyst. Process features and catalysts are discussed.

Transport Bed Technology

DuPont has developed a technology for the production of maleic anhydride from oxidation of butane, using a transport bed reactor (also referred to as a circulating-fluidized-bed reactor, CFBR). The process was commercialized in 1996 in Gijon, Spain. However, due to various operational problems, the plant was closed in 2004 and later dismantled.

DuPont's MAN technology includes a two step process that first oxidizes normal butane to maleic anhydride in a transport bed reactor using a proprietary abrasion-resistant catalyst. Maleic anhydride is then recovered in an aqueous system where the resulting maleic acid is converted to tetrahydrofuran in a hydrogenation reactor. The oxygen depleted catalyst is then re-oxidized in a separate reactor. Process flow diagram and description are given.

Maleic Anhydride from Phthalic Anhydride Recovery Process

A simplified process flow diagram for PA Consulting Group's maleic anhydride recovery technology process is given, as well as a brief description of the recovery process.

Recovery Systems

Most units in current commercial operation employ either a solvent (non-aqueous) recovery or an aqueous recovery approach. Brief descriptions of both types of recovery systems are given in the report.

Revamp Of Fluid Bed Maleic Anhydride Reactors

The decision to revamp a plant and the extent of such revamping is dependent on many factors, eventually determined by cost savings and capital investment payout. This is briefly discussed in the report.

TECHNOLOGY DEVELOPMENTS

The technology of producing maleic anhydride has been used for over 60 years and must today be considered quite mature. However every one of the many steps used in maleic anhydride production has been the subject of numerous improvements over the years and important developments are constantly being made with respect to process and equipment design. Technology development work has centered on catalysts and an increased in yield.

The summary given in the report is intended to give a brief overview of the type of research being performed to improve the maleic anhydride production process.

ECONOMICS

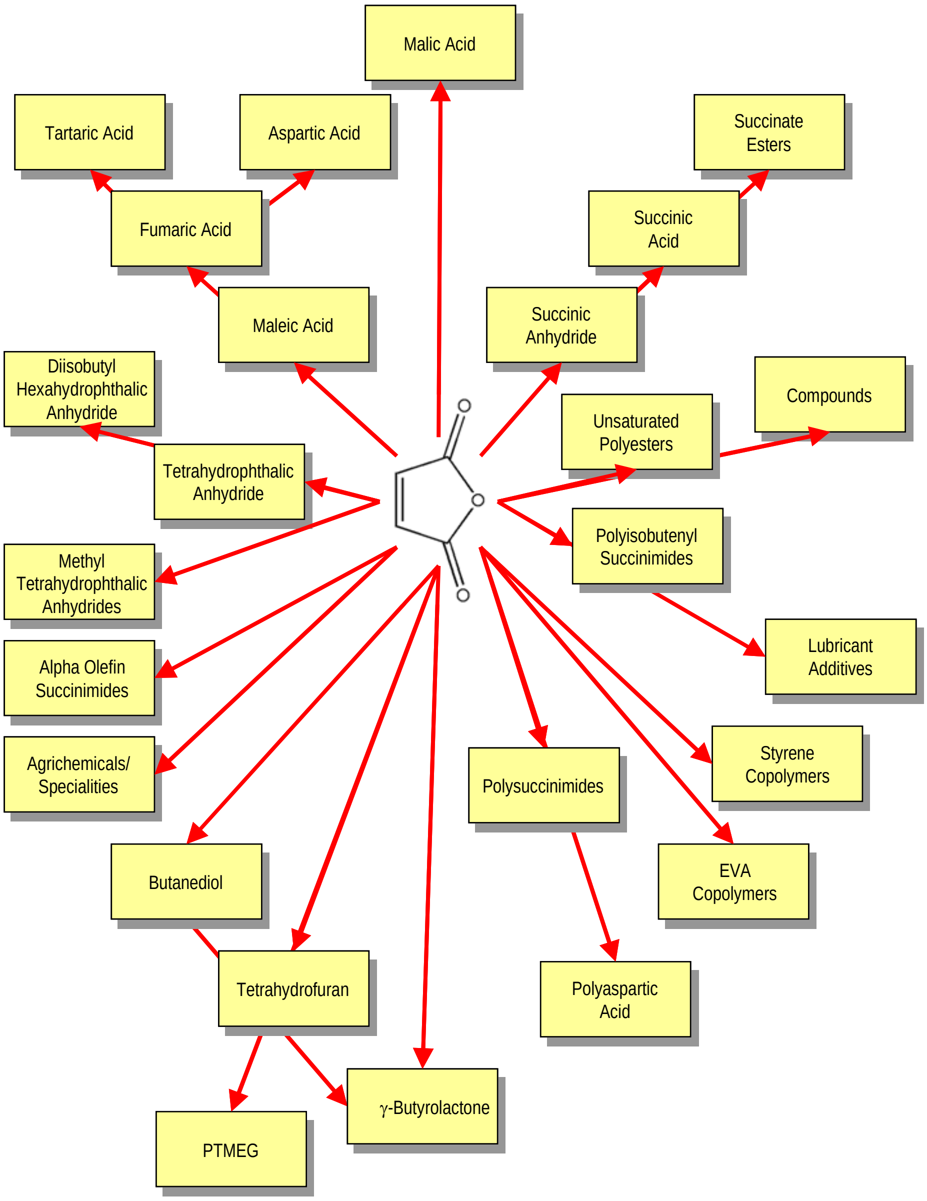
Cost of production estimates that have been considered in this section are:

- Maleic Anhydride production by ***n*-Butane Feed, Fixed Bed technology, with Solvent Recovery**
- Maleic Anhydride production by ***n*-Butane Feed, Fixed Bed technology, with Aqueous Recovery**
- Maleic Anhydride production by ***n*-Butane Feed, Fluid Bed technology, with Solvent Recovery**

COMMERCIAL ANALYSIS

The figure below shows the broad range of maleic anhydride derivatives.

Maleic Anhydride Derivatives
(Illustrative)



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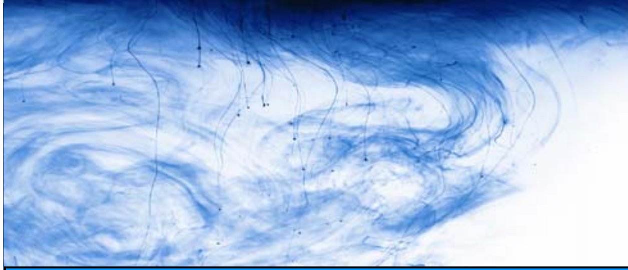
- The application(s) of many of these derivatives are discussed in the report.
- Supply, demand and trade data are given and discussed for the United States, Western Europe and Japan.

Individual production plant capacities by company, location and process type are given for each region.



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