



Report Abstract

Butanediol THF PERP06/07-4

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CHEMSYSTEMS PERP PROGRAM

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For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: http://www.chemsystems.com.

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INTRODUCTION

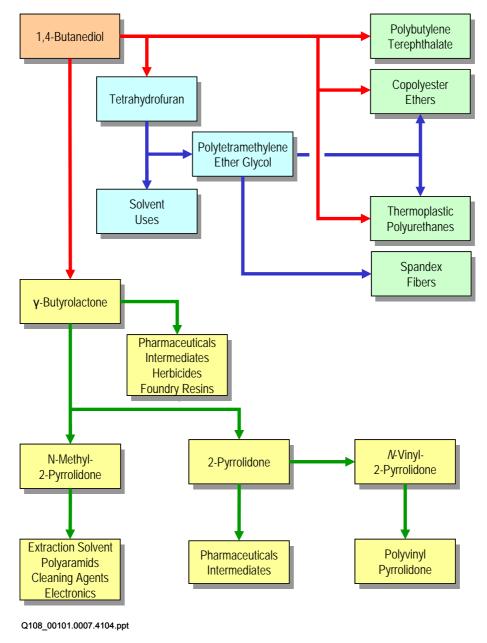
The history of the development of 1,4-butanediol (BDO) and derivative technology since the first processes based on acetylene in the 1930s is summarised below:

- 1930s Dr Reppe of I G Farben developed a process to manufacture BDO from acetylene.
- Post-1945 Tetrahydrofuran (THF via dehydration), γ-butyrolactone (GBL via dehydrogenation) became commercial products as well.
- Early 1970s Development of thermoplastic polyurethanes (TPU) and in particular spandex fibers, provided a real stimulus to the industry with a very large requirement for THF for polytetramethylene ether glycol (PTMEG) production.
- Late 1970s Mitsubishi Chemical Industries breaks the technology entry barrier into the butanediol industry through commercialization of its butadiene acetoxylation process.
- 1980s New BDO production technology via propylene oxide commercialized by ARCO.
- Early 1990s Davy develop a technology based on the esterification of maleic anhydride with ethanol, followed by hydrogenation of the ethyl ester to diethyl succinate then GBL and finally BDO, typically with a THF co-product. The Davy process can utilize maleic anhydride made from either *n*-butane or benzene. The process has the ability to make the output relatively flexible and to make a given proportion of BDO, THF, and GBL to fit downstream business portfolios.
- Mid 1990s BP, together with Lurgi, develop process whereby maleic acid is made in a fluid bed process with subsequent conversion of maleic acid to butanediol.
- 1997 DuPont developed and commercialize a THF process combining maleic acid production in a so called "transport bed" where the oxidation chemistry was carried out with a special catalyst that "picked up" oxygen in one reactor to carry out the oxidation of *n*-butane in another.
- 1998 SISAS enter market with new large-scale integrated BDO/THF/GBL technology, based on maleic anhydride.
- 2000s Trend in industry development likely to continue to support East Asian demand growth: latest development is to commercialize a glucose to succinic acid process, with subsequent purification and hydrogenation to GBL/BDO.

The figure below illustrates the 1,4-butanediol (BDO) - tetrahydrofuran (THF) - γ -butyrolactone (GBL) value chains. The value chain is really sub-divided into three based on BDO uses itself, the THF value chain and the GBL value chain. Historically, pricing of BDO, THF, GBL and derivatives reflected production cost plus value in use. Lower-cost routes based on *n*-butane have compressed industry pricing structures. The situation is further compounded by the commercialization of technology to make GBL and THF directly, without recourse to BDO production.

Even so, GBL represents the specialty segment of the business serving as an intermediate in NMP production as well as 2-pyrrolidone for pharmaceuticals and the monomer N-vinyl-2-pyrrolidone (NVP) for polyvinyl pyrrolidone (PVP) homopolymers and copolymers.

On the THF side, PTMEG is the most important derivative, as this supplies the growing spandex fiber industry. The spandex industry has been commoditized, with major investments in East Asia.



The BDO/THF/GBL Value Chain



This study represents a thorough review of butanediol and tetrahydrofuran technology:

- The technology section covers commercial processes, providing details of process chemistry and process design.
- The emerging technology section focuses on developing BDO/THF technologies.
- The patents analysis section provides a brief review of recently issued BDO/THF patents.
- Process economics are covered in the penultimate section for commercial and developmental technology.
- The final section provides a tri-regional market review.

COMMERCIAL TECHNOLOGY PROCESSES FOR 1,4-BUTANEDIOL

Current production of 1,4-butanediol is based on the now classical two step Reppe chemistry, which has been significantly updated to reflect recent improvements. The first step involves the reaction of acetylene and formaldehyde to produce primarily 1,4-butynediol and propargyl alcohol:

 $HC = CH + HCHO \longrightarrow HC = CCH_2OH$ $HC = CCH_2OH + HCHO \longrightarrow HOCH_2C = CCH_2OH$ $C407_{00101,0007,4104}$

The second step is the hydrogenation of 1,4-butynediol to 1,4-butanediol:

 $\mathsf{HOCH}_2\mathsf{C} \underbrace{=}_{\mathsf{CCH}_2\mathsf{OH}} \mathsf{CH}_2\mathsf{H} + \mathsf{2H}_2 \xrightarrow{} \mathsf{HOCH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{OH}$

Catalyst developments have enabled the 1,4-butynediol synthesis system to operate at lower and safer acetylene partial pressures and have minimized the formation of cupreine polymers.

The production of 1,4-butanediol via low pressure acetylene based technology has two main plant sections: the butynediol synthesis section and the hydrogenation section.

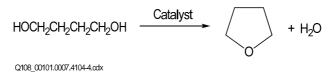
In addition to the Reppe chemistry based on acetylene and formaldehyde, process chemistry and process design technology for the **production of BDO using the following technologies are included in the report**:

- Mitsubishi Chemical Butadiene Acetoxylation
- Lyondell Basell Propylene Oxide Route
- Darien Propylene Acetoxylation/Hydroformylation (Allyl alcohol hydroformylation)
- Davy Process Technology 1,4-Butanediol Process using Maleic Anhydride
- BP/Lurgi GEMINOX[®] from *n*-Butane via Maleic Acid

Process chemistry and a brief description of the Eurodiol (Now BASF) concept based on maleic anhydride is also included.

COMMERCIAL TECHNOLOGY PROCESSES FOR TETRAHYDROFURAN

The conventional Reppe process for tetrahydrofuran involves dehydration and cyclization of 1,4 butanediol:



Thus, for users of the Reppe process 1,4-butanediol is a necessary first step in the manufacture of tetrahydrofuran. The same can be said of the Lyondell propylene oxide process. Processes for 1,4-butanediol production based on *n*-butane invariably produce tetrahydrofuran somewhere in the process.

In addition to the production of THF using the Reppe process, process chemistry and process design technology for **production of THF using the following technologies are included in the report**:

- Mitsubishi Chemical Butadiene Acetoxylation
- **DuPont Transport Bed Concept** (A distinguishing feature of this technology from conventional *n*-butane oxidation are that the catalyst is both the oxidation "catalyst" and the source of the oxygen.)
- **Pentose/Furfural Approach** (Although a former commercial route no longer practiced in the United States, this technology is included in the report because by its nature it could be used in developing economies with access to low cost renewable resources. Any pentosan-containing substance, such as renewable agricultural waste materials, e.g. oat hulls, corn cobs, and sugar cane bagasse, can form a source of commercial furfural.)

EMERGING TECHNOLOGY

The following technologies are detailed in the report:

- **Butadiene Epoxidation**: Eastman has developed proprietary technology for epoxidizing butadiene with oxygen over a silver catalyst.
- Linde/Yukong Acetylene-Based Process: The availability of this process for license may be of interest in countries such as China. There, about one-half of the vinyl chloride manufactured is via calcium carbide-based acetylene. Coal supplies power and coke for preparing the calcium carbide. Cost effective acetylene could also be used for making butanediol.



Also included in the report is a discussion on the **Bio-BDO/THF process**:

• The premise of this approach is to take a renewable substrate such as glucose and develop microorganisms that can efficiently convert the glucose to succinic acid. The succinic acid is then converted to BDO/THF using conventional means such as hydrogenolysis of the acid directly, similar to the BP/Lurgi technology mentioned earlier for taking maleic acid directly to BDO, or the Davy approach where the succinic acid would first be converted to the dimethyl ester and then undergo hydrogenolysis to BDO/THF mixtures. Currently, there are several groups around the world working on this approach or very similar approaches

PATENT ANALYSIS

The following are detailed in the patent analysis section of the report:

- A patent granted to INEOS surveys various catalysts for use in hydrogenation aqueous maleic acid feedstock to give primarily 1,4-butanediol.
- A patent application by BP describes a two-stage hydrogenation of crude aqueous maleic acid solution.
- Two DuPont applications pertaining to hydrogenation of aqueous solutions of precursors to butanediol and tetrahydrofuran.
- A patent application by BASF describes experiments for the hydrogenation of SAN.
- A patent application by BASF dealing with a two-stage gas-phase hydrogenation of MAC to BDO.
- A patent granted to Davy Process Technology describes the hydrogenation of maleic acid esters, in a 3-stage operation with a different catalyst used in each stage.
- A patent granted to the Council of Scientific and Industrial Research in India covering a particular composition of hydrogenation catalyst for the conversion of DEM to THF.

ECONOMIC ANALYSIS

1,4-Butanediol (BDO) Economics

Reppe process economics are presented on both non-integrated and integrated bases. The non-integrated cases charge in acetylene and formaldehyde at their cost plus ROCE values from standalone facilities. The integrated cases attempt to capture the economic advantages of including upstream operations, so as to utilize more basic (and lower cost) feedstocks and to take advantage of co-produced energy and materials. Specifically, costs of production estimate for the following have been carried out:

- BDO via the Non-Integrated Reppe process using acetylene sourced from Partial Oxidation of natural gas
- BDO via the Non-Integrated Reppe process using acetylene sourced from Calcium Carbide
- BDO via the Integrated Reppe process using acetylene sourced from Partial Oxidation of natural gas
- BDO via the **Integrated Reppe** process using acetylene sourced from **Calcium Carbide**

In addition, costs of production estimate for the following have been carried out:

- BDO via the Mitsubishi Acetoxylation process
- BDO via the Lyondell Propylene Oxide Hydroformylation process
- BDO via the **Darien Allyl Alcohol Hydroformylation** process
- BDO via the **Davy Maleic Anhydride Esterification & Hydrogenation** process

Sensitivity to changes in feed prices are evaluated for the Davy, Reppe, Mitsubishi and Lyondell processes.

Tetrahydrofuran (THF) Economics

Some processes, such as the Reppe, Lyondell, and Darien processes, produce only BDO and thus downstream dehydration units are needed to produce THF. Newer versions of the Davy process combine BDO production and dehydration to THF in a single reactor. The Mitsubishi, DuPont, furfural and developing Eastman processes make THF directly.

The developing Eastman process for THF by butadiene epoxidation may hold particular interest in developing economies such as China and India where naphtha cracking for ethylene predominates over lighter feedstocks and, thus, large quantities of butadiene are available for extraction from co-product streams. In contrast, *n*-butane is not readily available in China and India.

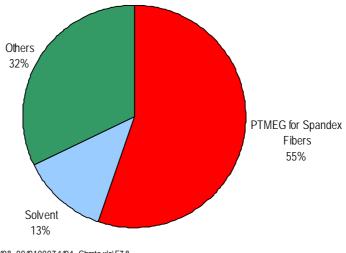
Costs of Production Estimate for the following have been carried out:

- THF via Dehydration of Butanediol process.
- THF via the Mitsubishi Butadiene Acetoxylation process.
- THF via the DuPont Ex Butane (Transport Bed) process.
- THF via the Bagasse Pentosan Hydrolysis process.
- THF via the Eastman Butadiene Epoxidation process.

Sensitivity to changes in feed prices for the Dupont, Mitsubishi and Eastman processes have been evaluated.

COMMERCIAL STATUS

THF finds some use in solvent applications, its major use is as a feedstock for polytetramethylene ether glycol (PTMEG) – as exemplified by the Figure below showing THF demand for the Asia Pacific region.



Asia Pacific THF Demand by End Use, 2007

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PTMEG is combined with BDO in the production of specialty polyester ethers (COPE) and polyurethanes (TPU). However, PTMEG's main use is for the production of spandex fibers, e.g., LYCRA[®] that is produced by DuPont. This is the fastest growing end-use for PTMEG/THF.

As well as providing a feedstock for the production of intermediates, BDO is mainly used as a comonomer for polybutylene terephthalate (PBT) production. PBT is a medium performance engineering thermoplastic made by companies such as DuPont and SABIC.

The following major derivatives of butanediol are also reviewed in this section:

- Thermoplastic polyurethanes (TPU)
- Polybutylene terephthalate (PBT)
- Copolyester ethers (COPE)
- Tetrahydrofuran for solvent use
- Polytetramethylene ether glycol (PTMEG or poly-THF)



BDO is also used to make GBL by dehydrogenation. GBL, as well as being a feedstock for N-methyl-2-pyrrolidone (NMP), has its own applications in agrochemicals, pharmaceuticals, and foundry resins.

- Supply, demand, and trade data for BDO for the regions of North America, Western Europe, and Asia Pacific are given and discussed.
- Supply, demand, and trade data for THF for the regions of North America, Western Europe, and Asia Pacific are given and discussed.





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