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1,4-Butanediol/ Tetrahydrofuran (BDO/THF)

PERP 2012-3

Report Abstract
April 2013

Nexant

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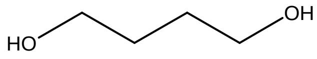
INTRODUCTION

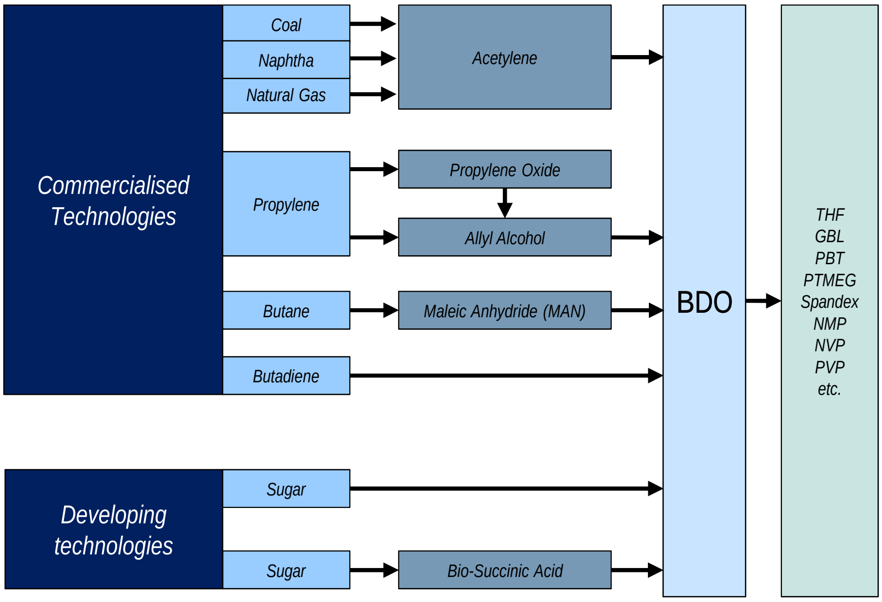
1,4-Butanediol ($HO(CH_2)_4OH$) is a low viscosity glycol used almost exclusively as an intermediate to synthetize other chemicals and polymers.



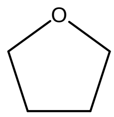
Due to its bi-functional reactivity from the two OH groups, most of its use is in the area of polymers, such as polyurethanes (prepolymers, cast elastomers, thermoplastic elastomers, reaction injection molding and fibers such as spandex), polybutylene terephthalate (PBT), a large family of homopolymers and copolymers, and copolyester-ether thermoplastic elastomers.

The development of butanediol and derivatives technology has spanned over eight decades. The initial invention of BDO synthesis via Reppe technology in the 1930s has evolved to the developments of Davy Process Technology, ARCO (LyondellBasell), and DuPont in the 1990s. And now, the production technology is evolving further, showing signs of transitioning from chemical synthesis routes to optimized bio-based fermentation routes, as global pressures focus on more sustainable processes for deriving core industrial chemicals, such as BDO.

Figure 1 Summary of Major Commercial & Emerging Process Routes to BDO/THF



Tetrahydrofuran ($O(CH_2)_4$) is a heterocyclic ether and powerful organic solvent.



Tetrahydrofuran (THF) is typically derived from BDO by dehydration or it can be formed concurrently during the production of BDO (e.g., using the Davy process).

This report includes:

- An overview of the status of the licensing technology and other proprietary technology holders;
- Strategic considerations for a new entrant to the BDO/THF business;
- A detailed discussion of established process technologies (petroleum-derived routes), i.e., maleic anhydride, propylene (via allyl alcohol), propylene oxide, Reppe (acetylene), and butadiene based routes to BDO/THF
- Comprehensive literature review with respect to fermentation pathways and microorganism engineering employed for the direct and indirect fermentation routes
- Detailed review of emerging indirect (i.e., via succinic acid) and direct bioroutes to BDO and THF employing fermentation of sugar(s)
- Process economics for the technologies offered by Myriant/Davy Process Technology and Genomatica have been developed and compared to the process economics for the petroleum derived (fossil fuel) routes listed above;
- Regional Process economics for established leading capacities and speculative plants to be built in the next five years on a region specific basis (i.e., on the same region basis as where the plant is operating and/or expected to be built);
- Commercial end-use applications, global and regional (supply/demand) market analysis

COMMERCIAL TECHNOLOGIES

A thorough review of BDO and THF technology is provided. The focus is targeted to commercial petroleum-derived (fossil fuel based) technologies that hold significant market relevance.

Acetylene based Process (Reppe Chemistry)

Historically, acetylene-based production is the most embedded into the BDO industry. BDO produced via Reppe chemistry still accounts for about 40 percent of the global BDO capacity. Key producers still using the Reppe chemistry include BASF, Ashland (formerly ISP), and DuPont.

The Reppe process is particularly popular in China, which in recent years, has decided to use its abundant coal resources to make chemicals. Acetylene is reacted with formaldehyde to form butynediol (BYD) which then undergoes high-pressure hydrogenation to form BDO. The efficiency of the technology focuses on acetylene purification (via CaC_2 from coal) in conjunction with proprietary catalyst and reactor technology, followed by BDO refining steps. The produced BDO undergoes ring closing chemistry to form THF.

The Reppe process chemistry, technology and key distinguishing features are discussed.

Butadiene-based Process (Mitsubishi)

The late 1970s marked a new period for BDO technology, and Mitsubishi Chemical Industries became the first company to break the technology barrier with the commercialization of its butadiene acetoxylation process. Ironically, this process uses butadiene as the feedstock for BDO, whereas historically, BDO was initially developed as an intermediate for butadiene production.

The Mitsubishi process employs a multi-step synthesis of BDO based on the acetoxylation of butadiene to 1,4-diacetoxy-2-butene, followed by hydrogenation to produce BDO, followed by hydrolysis of BDO to form THF. Acetic acid, produced as a co-product to BDO, is often recycled throughout the process.

Maleic Anhydride-based Process (Davy Process Technology)

Since its initial development in the 1990s, Davy has continued to simplify its maleic anhydride (MAN) esterification process and subsequent hydrogenation process, reducing complexity, equipment requirement, and overall capital costs.

Notable improvements are its transition into di-esterification of MAN with methanol to form DMM, followed by hydrogenation of DMM into DMS and through to BDO. Additionally, DPT has integrated isolation methods for key derivatives GBL and THF. These options allow for chemical producers to convert n-butane to three key derivative products that are core to the plastic, rubber, and fiber industries.

Such continuous improvements to their technology have allowed Davy Process Technology (DPT) to maintain global market presence, exemplified by recent plants in China and the Middle East.

Process chemistry, technology, and key distinguishing features of DPT's maleic anhydride route to BDO/THF are discussed.

Propylene- based Process via Allyl Alcohol (Dairen)

In 1998, Dairen Chemical Corporation (DCC) became the first local BDO producer to use its own developed technology for BDO production in Taiwan. The original plant had a nameplate capacity of 30 000 tons per year and produced BDO via hydroformylation of allyl alcohol (itself obtained from propylene acetoxylation and hydrolysis) followed by hydrogenation to form BDO.

In 2002 an additional plant was built in Kaohsiung, Taiwan, with a capacity of 100 000 tons per year. Dairen has not licensed its technology to other producers of BDO.

Dairen's process chemistry, technology and key distinguishing features are discussed.

Propylene Oxide based Process (LyondellBasell)

LyondellBasell is one of the leading producers of BDO both in Europe and the U.S.; its facility in the Netherlands is one of the largest BDO production plants in Europe. This plant (which belongs to a LyondellBasell subsidiary, Lyondell Chemie Nederland) was cited to be the largest single-train BDO plant to be built in the early 2000s. It was also the second plant to utilize the original ARCO propylene oxide (PO) to BDO technology. Currently, this technology is only accessible via joint-ventures with LyondellBasell.

LyondellBasell’s process chemistry, technology and key distinguishing features are discussed.

EMERGING TECHNOLOGIES

The emerging technologies evaluated in this study focus on those that Nexant believes have demonstrated potential for commercialization within the next five years and have maintained consistent momentum with regard to development; and considerable promise with respect to scaling up trials.

Esterification followed by hydrogenolysis of succinic acid (Myriant/DPT)

Myriant partnered with Davy Process Technology in March 2011, focusing on engineering a process to produce BDO (as well as THF and GBL derivatives) using biosuccinic acid produced by Myriant as a straight substitute of MAN in DPT’s process. Nexant understands from Myriant that Davy has tested succinic acid that has been produced by Myriant and that the results to date have been positive.

Myriant/DPT’s process (including biochemistry and chemistry), technology and key distinguishing features are discussed.

Fermentation of sugard to BDO and THF (Genomatica)

Since June 2011, Genomatica has been producing BDO at its demonstration-scale facilities in Decatur, Illinois, U.S. – owned and operated by the food ingredients company, Tate & Lyle. The two companies have agreed to explore potential for a commercial-scale plant in North America, using dextrose sugar feedstock supplied by Tate & Lyle. Genomatica’s process uses an engineered microorganism for the direct fermentation of sugars to BDO and potentially THF via cyclization in an acidic fermentation medium.

Genomatica’s process (including biochemistry and chemistry), technology and key distinguishing features are discussed.

Hydrogenation of succinic acid (BioAmber)

BioAmber’s previous work focusing on the production of bio-based succinic acid has led to the development of a process to convert biosuccinic acid to BDO. In 2010, BioAmber licensed DuPont's hydrogenation catalyst technology to make bio-BDO and bio-THF from biosuccinic acid. Since then, efforts have focused on scaling up DuPont’s technology to produce 100 percent bio-based BDO, THF, and GBL.

BioAmber’s process (including biochemistry and chemistry), technology and key distinguishing features are discussed.

PROCESS ECONOMICS

Cost of production estimates are presented for:

- Davy Process Technology's maleic anhydride process (two cases considered 80/20 percent and 50/50 percent BDO /THF output)
- Dairen's allyl alcohol process
- LyondellBasell propylene oxide process
- Reppe process
- Genomatica's direction fermentation of sugars
- Myriant/Davy Process Technology hydrogenolysis of succinic acid
- Mitsubishi's butadiene process

Detailed cost of production estimates are presented on a USGC location and same scale for a process benchmark. Various sensitivity analyses have been carried out (i.e., variation of production cost with feedstock price and plant scale)

In addition, detailed cost of production estimates are also presented on a regional basis giving:

- A forecast on future competitiveness of emerging processes against conventional petroleum-derived technologies.

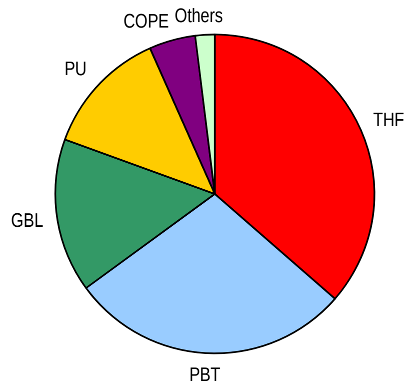
The cost of production tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities consumed (electrical energy, cooling water, fuel etc.), direct and allocated fixed costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a cost estimate. Capital costs are broken down according to inside battery limits (ISBL), outside battery limits (OSBL), other project costs, and working capital.

COMMERCIAL MARKET REVIEW

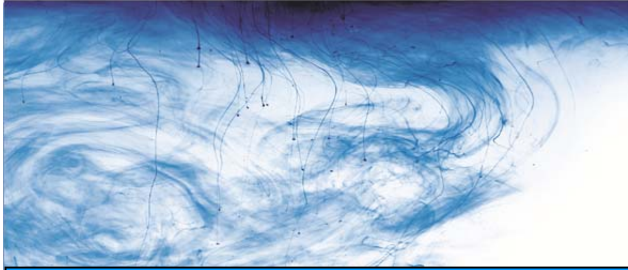
The global BDO market reached and estimated to be about 1.5 million tons in 2012 serving applications such as engineering polymers, performance elastomers and polymers, specialty solvents and fine chemical intermediates. Just over about a third of BDO is expected to be consumed in THF production in 2012.

Figure 2 BDO End-Uses

(2012)



- Commercial end-use analysis for 1,4-butanediol is given (including end-use analysis of THF as a sub-category)
- BDO and THF global supply, demand and trade data is given and discussed
- In addition, BDO and THF supply, demand and trade data is given and discussed according to key regions (i.e., North America, Western Europe, Asia Pacific, and Rest of the World)
- A list of production plants in each of the key regions above is given showing specific plant capacities, owning company, location and annual tonnage produced



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