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# Technology for 1,2-Butylene Oxide Production and Market Analysis

Mujing Li*, Ziwei Zhou

Sinopec Shanghai Research Institute of Petrochemical Technology, SINOPEC, Shanghai 201208, PR China
limj.sshy@sinopec.com

1,2-Butylene oxide (BO) is a crucial chemical raw material and intermediate that is extensively utilized in organic synthesis, coatings, adhesives, plastics, and surfactants. The primary industrial production routes for BO are the chlorohydrin process, peroxyacetic acid process, and cumene hydroperoxidation (CHP) process. The chlorohydrin process has the advantages of short process flow and low production cost, but is now facing obsolescence because of environmental pollution. The volume of peroxyacetic acid process is small, mainly concentrated in the field of medicine. The CHP process was first applied in industry last year, with high purity and flexible production process, providing a feasible way to achieve energy saving and low carbon. The ethylbenzene to butylene oxide (EBHP) process, hydrogen peroxide to butylene oxide (HPBO) process, and direct oxidation process have not been industrialized due to technical, economic, and safety concerns. In 2022, the global BO market revenue was approximately $ 70 million. Given the rapid development of global industry and the lack of feasible alternatives, the demand for 1,2-butylene oxide keeps rising, with the Asian region emerging as the primary driver of the market's expansion. The global BO market revenue is expected to reach 100 million dollars in 2027, growing at a CAGR of 7.4 % from 2022 to 2027. By analyzing the advances in BO production technology and changes in market consumption trends, it is proposed that with the need of energy saving and emission reduction, choosing CHP process will promote transformation and upgrading of refining enterprises to achieve sustainable development.

## 1. Introduction

1,2-Butylene oxide (BO) is an important fine chemical, belonging to the same family as ethylene oxide (EO) and propylene oxide (PO). It is mainly used as a polyether polyol monomer and other intermediates in synthetic materials. It can be used in the preparation of medicines, cosmetics, foams, synthetic rubbers, non-ionic surfactants, and can also replace acetone as a diluent for nitro lacquer.

Although there are some reports focusing on BO catalysts, the focus on BO production process has been rarely explored. Especially for the cumene hydroperoxidation (CHP) process that features some unparalleled merits like low power and high efficiency. Unfortunately, little attention was paid to BO market situation.

Studies have shown that polyether polyols synthesized from BO have superior hydrophobicity, hydrolysis resistance and corrosion resistance compared to EO and PO (Wang et al., 2023).

With the development of more application scenarios of polyether polyols, the demand for BO will be further expanded. The top three global producers, Dow Chemical, BASF, and SINOPEC, account for 90% of global nameplate capacity. At present, the limited production capacity of BO is mainly produced by chlorohydrin process, which causes serious environmental pollution and needs to be optimized and iterated urgently. The ethylbenzene to butylene oxide (EBHP) process and hydrogen peroxide to butylene oxide (HPBO) process have made some technological breakthroughs however have not yet been industrialized because of the lack of technical economics and operational stability. The CHP process (Yang et al.,2019) developed by SINOPEC was successfully started at the end of last year, making SINOPEC the largest supplier of BO in China, and it's of great significance to extend C4 industry chain, complement epoxidation industry chain, and enhance phenol acetone industry chain.

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## 2. Production processes and technological advances

BO is mainly produced by chlorohydrin process, peroxyacetic acid process, EBHP process, CHP process, HPBO process, direct oxidation and other developing technologies. All processes use butylene as the primary feedstock. Chlorohydrin routes represent the largest share of the worldwide supply followed by the CHP process, with peroxyacetic acid process accounting for most of the remainder.

### 2.1 Chlorohydrin process

The main sources of butylene oxide are direct chlorohydrin synthesis and by-product recovery from the chlorohydrin production of propylene oxide. The direct synthesis of butylene oxide by the chlorohydrin process includes three processes: chlorohydrinization, saponification, and refining. It is produced by the chlorohydrinization of butene with hypochlorite, followed by epoxidation. The reaction conditions are similar to those of the chlorohydrin process for propylene oxide. In addition, the by-products from the production of propylene oxide by the chlorohydrin process can be used to prepare butylene oxide after distillation and purification. In the process of PO production by chlorohydrinization and saponification with cracking tail gas, the butylene oxide kettle residue is obtained, which contains 74.6 % butylene oxide, 16.7 % PO, 0.7 % EO, 3.1 % water, and a small amount of high-boiling matter. By distilling the kettle residue, collecting the 50-70 ℃ fractions from the middle of the tower, condensing, and removing water, the content of the finished butylene oxide product is about 87 %. If higher purity products are needed, further distillation separation is required. Figure 1 illustrates a simplified process flow diagram of chlorohydrin-based BO plant that is integrated with a chlor-alkali plant. The chlor-alkali plant provides chlorine for the chlorohydrin reaction and cell liquor (sodium hydroxide) for the dehydrochlorination reaction and accepts the brine solution produced in the dehydrochlorination reactor.

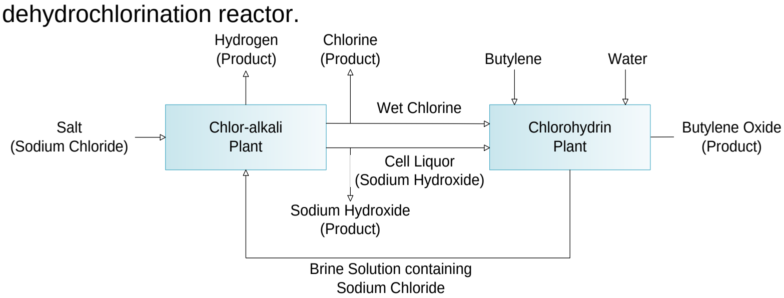


*Figure 1: Simplified flow diagram of integrated chlor-alkali and chlorohydrin plant*

The core of the production technology for the chlorohydrin process is the chlorohydrination reactor. Representative reactor technologies worldwide include the tubular reactor technology of Dow Chemical, the tubular tower reactor technology of AGC in Japan, and the tower reactor technology of Mitsui Chemicals, Inc. and Showa Denko Company.

The chlorohydrin process has the advantages of a mature process, high conversion rate, and low investment costs. However, its shortcomings are also very obvious. In addition to the lower purity of the product, the "three wastes" generated during the production process and the corrosion of hypochlorite on the equipment need improvement and solutions. Due to the severe environmental pollution caused by traditional chlorohydrin production, the United States has phased out the chlorohydrin process and is making efforts to develop a new, non-polluting, and environmentally friendly BO production process. Nevertheless, no industrialization of the new technology has been reported so far. With the implementation of the Guidance Catalog for Industrial Structure Adjustment (2024), no new chlorohydrin plants are expected to be built in the next 10 years, and even currently operating plants in China are at risk of shutdown to meet stricter environmental policies regarding emissions and wastewater.

### 2.2 Peroxyacetic acid process

The peroxyacetic acid process is another industrialized process for the production of BO, using 1-butene and peroxyacetic acid as the main raw materials. Under the action of a catalyst, the active oxygen in peroxyacetic acid is transferred to 1-butene to produce BO. Compared with the chlorohydrin process, the peroxyacetic acid process has low steam consumption and by-product acetic acid can be recycled. However, the reaction system contains a large amount of acid, which is highly corrosive to the chemical equipment, and the operability has been an issue using this technology.

### 2.3 EBHP process

Compared with the chlorohydrin process and peroxyacetic acid process, the EBHP process for producing BO does not generate a large amount of wastewater and waste residue, making it greener and more environmentally friendly. Hongbaoli Group (Shan et al., 2019), introduced a titanium-silicon molecular sieve catalyst preparation process, which can be used for the epoxidation of butene and ethylbenzene peroxide to prepare BO. The conversion rate of ethylbenzene peroxide reaches 99.5 %, and the selectivity of BO also reaches 99.5 %. However, EBHP process relying on coproduct values has been subject to the volatility of the coproduct markets over the years. It has not been industrialized yet due to the lengthy process, large investment in equipment, and low techno-economic feasibility. And In view of the difficulty of recovering BO contained in tail gas in EBHP plant, a novel absorption process for BO recovery with extraction solvent and extractive distillation (Li et al., 2023) was proposed, in that the reaction of both BO non-catalyzed hydrolysis reaction was considered.

## 2.4 CHP process

SINOPEC's CHP process for producing BO uses 1-butene as the raw material and CHP as the oxidizing agent, epoxidizing butene under the action of superhydrophobic titanium-containing mesoporous molecular sieve catalysts. The process includes the following steps: (1) Catalytic epoxidation of butene and CHP to produce BO and DMBA; (2) Separation of the epoxidation reaction products, including separation of butene and refining of BO; (3) Hydrogenolysis of DMBA to produce cumene or thickening of crude DMBA to obtain commercial DMBA; (4) DMBA is hydrogenated to cumene in the presence of Pd-based catalyst, then cumene is oxidized to CHP for recycling, or DMBA is enriched to more than 90% and sold as a product.

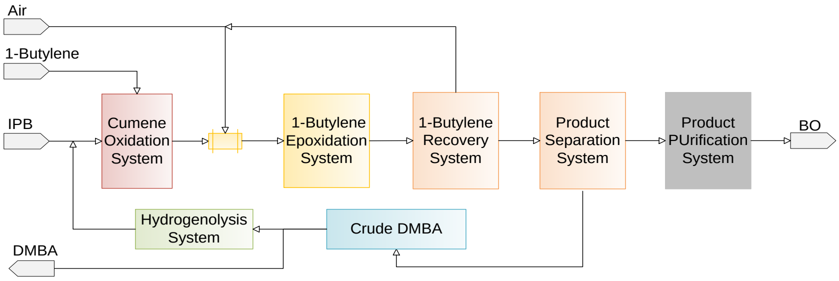


*Figure 2: The technological process of CHP process*

The process adopts multi-stage tandem, inter-stage heat removal and high-efficiency extractive distillation technology, which improves the catalyst life and enables continuous production. The conversion rate of CHP is ≥99 %, the selectivity of BO is ≥99 %, and the product purity is ≥99.8 %, which has been realized industrially. The technological process is shown in Figure 2.

Wang et al. (2018) used a $TiO_2/SiO_2$ molecular sieve catalyst to carried the epoxidation reaction of 1-butene and CHP, with the concentration of CHP feedstock ranging from 30 % to 60 %, and the molar ratio of 1-butene to CHP being 6:1. The reaction system consisted of a columnar fixed-bed reactor and an adiabatic fixed-bed reactor connected in series, with the mass-air velocity of CHP feedstock in the columnar reactor being 0.75 $h^{-1}$. The final CHP conversion is ≥99.4 %, and the molar selectivity of BO is ≥99.0 %.

## 2.5 HPBO process

Li et al. (2007) stated that the selectivity of 1,2-butylene oxide in the epoxidation reaction of 1-butene and hydrogen peroxide can be up to 99 % or more at a reaction temperature of 100 °C, a reaction pressure of 0.5~8.5 MPa, a reaction bed liquid airspeed of 0.11 $h^{-1}$, and a molar ratio of low-carbon alcohol, 1-butene, and water peroxide of 160: (0.5~10):1. When methanol is used as a solvent, it can significantly improve the conversion rate of 1-butene and the selectivity of BO. Due to the close boiling points of methanol and BO, subsequent separation, nonetheless, is difficult. Wang (2020) stated that in the presence of an acid or a base, a raw material mixture containing 1-butene, methanol, and an oxidizing agent is contacted with an oxidation catalyst for a reaction to obtain a second mixture containing methanol and butylene glycol. The second mixture is then separated to obtain butanediol, which is finally contacted with a dehydration catalyst to carry out a dehydration reaction to obtain BO. And the separation is still difficult. The HPBO process, in general, has not yet been industrialized with high energy consumption, low product purity, and complicated operation.

## 2.6 Direct oxidation

Direct oxidation is a process which involves the oxidation of butylene with air or molecular oxygen or ozone in the presence of a catalyst to produce BO. Li et al. (2018) used organic aldehyde and butene as raw materials, oxygen or air as the oxidizing agent, an organic liquid solvent as the medium, and pyrrole synthetic metal salt as the catalyst. The reaction occurs at temperatures of 50~160°C and pressures of 0.05~3.5 Mpa, simultaneously producing organic acid and BO with a product selectivity higher than 95 %. Ji et al. (2021)

used a cyclic organic nitrogen-oxygen radical precursor catalyst, butene as the raw material, isobutyraldehyde as the co-reductant, and oxygen as the oxidizing agent to achieve the preparation of BO at room temperature. This process is still in the small-scale testing stage, and the selectivity of the reaction and the conversion rate need to be further improved. Huang et al. (2019) disclosed a device for the continuous preparation of 1,2-butylene oxide, which includes an ozone feedstock tank, a 1-butene feedstock tank, a fixed-bed reactor, a first gas-liquid separator, and a second gas-liquid separator. The direct oxidation route is a potentially greener process with economic and environmental benefits as it involves fewer reaction steps and does not producee any significant amount of co-products compared to the conventional butylene oxide production technologies.

### 2.7 Other production processes

Perer et al. (1996) employed palladium catalyst to prepare BO via catalytic hydrogenation of ethylene oxide. And Thomas (1995) employed a rhodium-based catalyst for the hydrogenation of 3,4-epoxy-1-butene to 1,2-butylene oxide in high yields, with good selectivity, and at commercially acceptable reaction rates. However, the technology economy and commercial feasibility need to be enhanced due to the use of noble metal catalyst. Zhang et al. (2019) synthesized BO by cheap metalloporphyrin catalysts, and experiments indicated that the conversion rate of butylene reached 96.39 %， the yield of BO reached 95.04 % and the selectivity of BO reached 98.61 % under optimum reaction conditions. But for industrial amplification, the selectivity needs to be further improved. Luo et al. (2019) prepared BO from a mixture of ethylene glycol and 1,2-butanediol, and and the separation challenge was solved.The process flow diagram is shown in Figure 3.

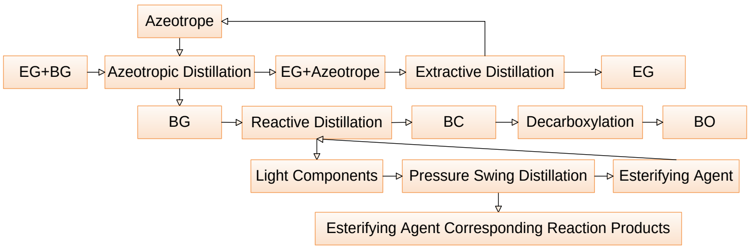


*Figure 3: Process flow of butylene oxide production by continuous decarboxylation*

Wang et al. (2022) disclosed a continuous decarboxylation system for the preparation of BO, which was equipped with a material recycling unit to realize the decarboxylation reaction and the separation process simultaneously. The process flow, as shown in Figure 4, is relatively simplified, and the productivity and safety of the reaction system are improved.

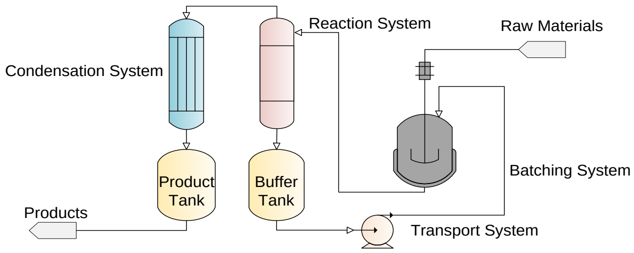


*Figure 4: Device system for the preparation of butylene oxide by continuous decarboxylation*

## 3. Downstream applications and market demand

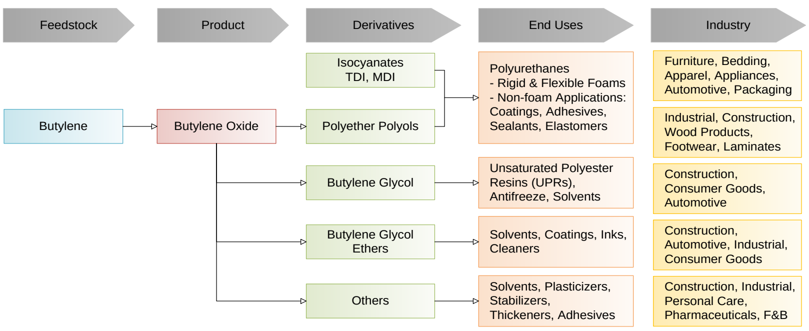


*Figure 5: Overall BO value chain*

BO is a highly reactive chemical intermediate with no direct consumer application. The dominant end use for propylene oxide is to produce polyether polyol, butylene glycol, butylene glycol ether, isobutanol amine, and diethyl carbonate. The overall value chain of BO is illustrated in Figure 5. Due to the unit price of BO for sale exceeds RMB 50,000/ton, its high cost limits large-scale downstream applications. Consequently, most end-users have small dosages with a dispersed distribution.

Since aldehydes cause odor and affect health, water affects the hydroxyl value and foaming properties of polymers, isomers act as the envelope for long chains of polymerization, BO products have strict requirements for the content of aldehydes, water and isomers. The quality and purity requirements for the qualified product of 1,2-butylene oxide in the enterprise standard of BASF are BO ≥99.5 %, isomers of BO ≤0.2 %, total aldehydes ≤0.05 %, water ≤0.03 % (Hu et al., 2019).

BO production capacity is fairly concentrated due to barriers to entry related to proprietary, with core manufacturers including Dow Chemical, BASF, and SINOPEC. Dow Chemical produces BO from 1-butene at a 16,000 ton/year plant at Freeport, Texas. Dow toll converts large amounts of 1-butene to BO for Chevron Phillips, which consumes BO internally as an intermediate in the production of a gasoline additive that is marketed under the trade name of Techron. BASF produces BO for captive and merchant demand used as industrial solvents, stabilizers for automotive coatings, and intermediates for pharmaceuticals, cosmetics, and nonionic surfactants. Sinopec Yanshan Branch's 4,000 t/a BO plant using the CHP process was put into operation in November 2023, with isomer and other impurity content lower than BASF's corporate standards. It is mainly supplied to the Chinese market for the preparation of high-end polymer products. Product indicator comparisons are shown in Table 1.

*Table 1: Comparison of product indicators*

| Item | BASF's standard | SINOPEC's quality |
|---|---|---|
| 1,2-Butylene oxide, wt% | 99.5 | 99.97 |
| Total aldehydes, wt% | ≤0.05 | 0.016 |
| Water, % | ≤0.03 | 0.0086 |
| Acidity, wt% | ≤0.006 | 0.0036 |
| Chromaticity, APHA | ≤5 | <5 |

Globally, Because of the strong industrial base and well-established industrial chain, the demand for BO in Europe and the United States is very large and tends to be stable. Influenced by rapid economic growth, population surge, and other factors, Asia has become the main growth driver for BO market demand.

In 2013 and 2015, the production of BO in the U.S. consumed about 19,000 metric tons of 1-butene, and it is forecast to maintain steady growth. In 2022, the global BO market revenue was approximately 70 million dollars. With the application development and performance optimization of BO downstream products, the development of the BO industry chain ushers in new opportunities. It is estimated that the global market value of BO will increase to 100 million dollars in 2027, an annual compound growth rate of over 7 %.

By introducing crosslinking epoxy butane to prepare carazole cavity transport material, Ye et al. (2022) further introduced it as a cavity transport layer to organic semiconductor devices, especially organic luminescence devices, effectively improving the solvent resistance and cavity transmission capacity.

Leino et al. (2011) first reported that BO was introduced to the reaction system as a dehydrating agent in order to overcome thermodynamic constrains and shift the equilibrium towards diethyl carbonate production. The underlying reason for choosing BO was the acute toxicity of short-chain epoxides. As an olefin epoxide, compared with EO and PO, BO possesses a greater number of -$CH_2$- functional groups. When synthesized as a monomer into a polyether polyol, its products have excellent properties such as strong hydrophobicity, hydrolysis resistance, and corrosion resistance, making it particularly suitable for waterproof coatings on the external surfaces of buildings and equipment with strict requirements. Additionally, the polyurethane material synthesized by copolymerizing BO as a monomer has excellent cold-resistant properties, making it especially suitable for areas with severe cold climates.

At present, the polyether field mainly uses PO and EO as raw materials, and the polyether polyol synthesized from BO as a monomer accounts for a small market share. If BO is used as an alternative raw material, its excellent performance can significantly improve the performance of the polyether, leading to a huge demand and a broad prospect for development. When possible, the price of BO is appropriately adjusted downward while ensuring profit margins, the polyether polyol field will be a huge market. For this reason, current market research and development in butylene oxide polyether enterprises are in the minority. SINOPEC, BASF, Dow Chemical, Covestro, Bayer, and other chemical companies in this area have developed a variety of functional polyether products and special polyurethane as a series of technical reserve.

With the continuous improvement of the global requirements for dual-carbon and environmental protection, BO, as an important epoxy compound, not only has market demand in traditional fields, but also in the pursuit of more integrated and environmentally friendly applications such as oil-soluble polyether, hydrophobic polyols, slow rebound foam, cold-resistant power battery electrolytes, medical surfactants, biodegradable plastics, leading to the gradual transformation and upgrading of production enterprises.

## 4. Conclusions

The analysis compares the cost of production, risks of safety and environmental contamination for the BO production technologies to determine attractiveness of each across the changes faced by the industry over the next decade. There could be closures of chlorohydrin units as environmental concerns regarding the safe disposal of aqueous calcium chloride co-product could become restrictive. The less-competitive plants are expected be rationalized in the long run. In 2023, SINOPEC commercialized the CHP process that avoids the use of chlorine while minimizing byproduct volumes. And it’s an important technological choice for refining enterprises to take their own advantages to achieve economic growth and green growth. With the breakthrough of BO production technology and the expansion of production capacity, the market supply and demand pattern is shifting from tight to loose. As a result, the bargaining power and influence of the downstream demand side are increasing, gradually reflecting the characteristics of the “buyer market”. With price reductions, the market potential will be further released.

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