Trends and Views in the Development of Technologies for Propylene Oxide Production

Sumitomo Chemical Co., Ltd.
Petrochemicals Research Laboratory
Tomonori Kawabata
Jun Yamamoto
Chiba Works
Hirofumi Koike
Shuhei Yoshida

Sumitomo Chemical Co., Ltd. has developed a propylene oxide (PO)-only manufacturing process where cumene acts as the oxygen carrier, which has a high reputation as a production method that offers distinct advantages of a high PO yield and superior stability in plant operation. In this article we outline the trends in PO manufacturing technology, and also introduce the status of licensing activities and features of the Sumitomo Chemical process.

This paper is translated from R&D Report, “SUMITOMO KAGAKU”, vol. 2019.

Introduction

Propylene oxide (PO) is a major industrial product with production of more than 10 million tons per year worldwide. Approximately 70% of it is used for polyether polyols (polyols) in the raw materials for polyurethanes, and approximately 17% of it is used for propylene glycol in the raw material for unsaturated polyesters, food product additives and cosmetics (**Fig. 1**). The demand for polyurethanes is growing remarkably, particularly in Asia, and the world’s major PO producers have announced start-up plans for new plants over recent years (**Fig. 2**). **Fig. 3** shows proportions of PO production by production method worldwide.

Current commercialized methods for PO production can be roughly divided into three methodologies from the viewpoint of their history. The first generation was the chlorine method for manufacturing PO by using chlorine (CL), and the second generation was a co-production method producing PO and co-products such as styrene monomers (SM) or *tert*-butyl alcohol (TBA) using organic hydroperoxide (PO/SM, PO/TBA). These production methods have drawbacks such as problems with processing of by-products or difficulties in balancing the markets for PO and the co-products in terms of economics. A new environmentally friendly PO-only manufacturing process without any co-product has become desirable. As a result, third-generation production methods based on the use of cumene as an oxygen carrier (POC) and hydrogen peroxide to propylene

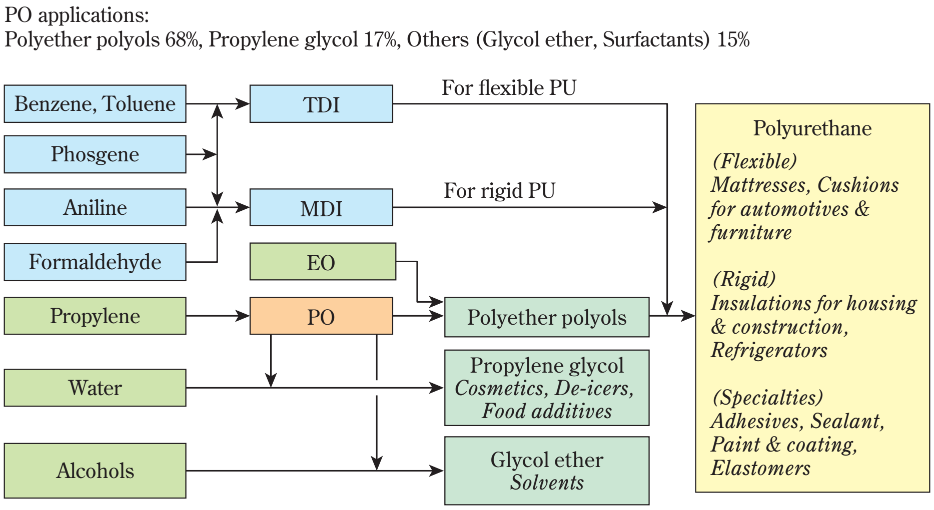


Fig. 1 Main applications of PO and market outlook

Copyright © 2019 Sumitomo Chemical Co., Ltd.

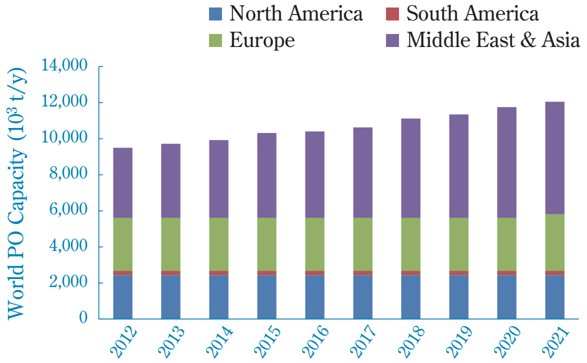


Fig. 2 Forecast world PO production capacity (estimated by Sumitomo Chemical Co., Ltd.)

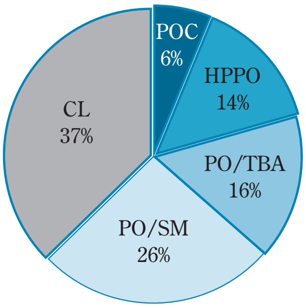


Fig. 3 PO production technologies (2018) (estimated by Sumitomo Chemical Co., Ltd.)

oxide (HPPO) were commercialized. Since 2015, third-generation production methods have accounted for half or more of production capacity among new plants with a production capacity of more than 200,000 tons/year.

Taking the opportunity of our successfully development of a new epoxidation catalyst in 1998, Sumitomo Chemical was successful in establishing POC technology, and started 150,000 tons per year commercial production at the Chiba Works in 2003. Thereafter, we implemented a plant enhancement to 200,000 tons per year in the fall of 2005 based on healthy demand in Asia, and operations have been continuing smoothly with constant working on rationalization for further enhancing competitiveness and for reducing the environmental impact. Through the fusion of the high performance epoxidation catalyst technology developed independently by Sumitomo Chemical and process development technology adopting thermally stable cumene hydroperoxide, we have been successful with an extremely high PO yield and low energy consumption for separation and purification, making for the method superior to existing processes in terms of both yield and energy. Therefore, we have received various awards such as the 2006 Chemical Society of Japan Chemical Technology Award (2006), Minister of Economy, Trade and Industry Award for the 8th Green Sustainable Chemistry (GSC) Award (2008) and the 2008 Japan Petroleum Institute Award (2008), so that this is highly regarded as a technology that contributes to development of a sustainable society.

At the same time, POC is a process with superior stability in plant operation than other production methods, and there have been many requests for technology licenses from overseas. Up to now we have implemented three licenses (**Table 1**). In 2009, Petro Rabigh (joint venture between the Saudi Arabian Oil Co. and Sumitomo Chemical Co., Ltd.) started up the first licensed plant. S-Oil Corp. (South Korea) implemented a license in 2015, and PTT Global Chemical Public Co., Ltd. (Thailand) concluded a license agreement in 2017 and is currently in construction building toward starting operations in 2020.

In this article, we will give an explanation of trends and views on the development of technologies for PO production and will also introduce the features of POC.

Commercialized PO Production Methods

1. Chlorine Method

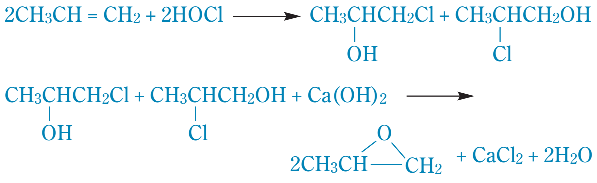
The chlorine method is the oldest PO production method that has been implemented industrially, and PO is manufactured through generating propylene chlorohydrine with propylene, chlorine and water as raw materials followed by dehydrochlorination. The largest producer using this method is The Dow Chemical Co. (currently DowDuPont, Inc.), and there are

Table 1 Licensing history for Sumitomo POC technology

Plant	Location	Capacity (10^3 t/y)	Start-up
Sumitomo Chemical Co., Ltd.	Japan	200	2003
Rabigh Refining and Petrochemical Co. (Petro Rabigh)	Saudi Arabia	200	2009
S-Oil Corp.	South Korea	300	2018
PTT Global Chemical Public Co., Ltd. (PTTGC)	Thailand	200	2020

Copyright © 2019 Sumitomo Chemical Co., Ltd.

two Japanese producers, AGC Inc. and Tokuyama Corp. The impact on the environment of the waste processing is high since approximately 40 tons of waste water containing approximately 1.9 tons of calcium chloride is generated per ton of PO. Even now the chlorine method accounts for approximately 40% of the PO production capacity worldwide, but it is difficult to construct new facilities because of recent trends toward increased restrictions regarding the environment.1)

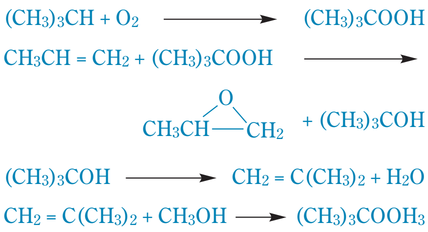


$$2CH_3CH=CH_2 + 2HOCl \longrightarrow CH_3\underset{\underset{\displaystyle OH}{|}}{C}HCH_2Cl + CH_3\underset{\underset{\displaystyle Cl}{|}}{C}HCH_2OH$$

$$CH_3\underset{\underset{\displaystyle OH}{|}}{C}HCH_2Cl + CH_3\underset{\underset{\displaystyle Cl}{|}}{C}HCH_2OH + Ca(OH)_2 \longrightarrow 2CH_3CH\overset{O}{—}CH_2 + CaCl_2 + 2H_2O$$

2. Co-Production Method

The co-production method was first developed by Halcon International Inc. and Atlantic Richfield Co. (later LyondellBasell Industries Holdings B.V.) in the 1970s. Co-production methods include PO/SM and PO/TBA, and they use ethyl benzene hydroperoxide and *tert*-butyl hydroperoxide (TBHP), respectively, as organic peroxides for manufacturing PO by epoxidation of propylene. At the same time, a styrene monomer (SM) or *tert*-butanol (TBA) is produced as the co-product. Typical producers using the PO/SM method are LyondellBasell Industries Holdings B.V. and Royal Dutch Shell plc, and representative producers using the PO/TBA method are LyondellBasell Industries Holdings B.V. and Huntsman International LLC. In a reflection of the trends in demand for the two sets of co-products in the 2000s, new PO plants have mostly employed the PO/SM method, but in recent years the PO/TBA method has mainly been employed. The PO/TBA co-production process will be described in the following.



$$(CH_3)_3CH + O_2 \longrightarrow (CH_3)_3COOH$$

$$CH_3CH=CH_2 + (CH_3)_3COOH \longrightarrow CH_3CH\overset{O}{—}CH_2 + (CH_3)_3COH$$

$$(CH_3)_3COH \longrightarrow CH_2=C(CH_3)_2 + H_2O$$

$$CH_2=C(CH_3)_2 + CH_3OH \longrightarrow (CH_3)_3COOH_3$$

In the PO/TBA method, PO is produced by generating TBHP by air oxidation of isobutane followed by epoxidation of propylene by TBHP. Oxidation of isobutane is carried out in the liquid phase under conditions of 120 - 140 °C and 3 - 4 MPaG, and the isobutane conversion is 35 - 50% and the TBHP selectivity is 50 - 60%. Epoxidation of propylene is normally carried out in the presence of a catalyst including a molybdenum compound in the liquid phase under conditions of 90 - 130 °C and 1.5 - 6 MPaG. The propylene conversion is approximately 10%, the TBHP conversion is 95% or greater and the PO selectivity is approximately 90%. If TBA is dehydrated, it forms isobutylene, and if it is further reacted with methanol, methyl *tert*-butyl ether (MTBE), which is useful as an octane booster for gasoline, can be synthesized. Since this method produces approximately 2.1 tons of MTBE as a by-product for each ton of PO, profitability of the process is severely affected by the MTBE market conditions. Similarly, profitability of the PO/SM method is not independent of the market because the method produces approximately 2.5 tons of SM as a by-product per ton of PO.

3. Third-Generation Production Method 1 (POC)

The POC method and the hydrogen peroxide to propylene oxide (HPPO) method, which substantially only have water as a by-product, have been commercialized one after the other as production methods that are not affected by market conditions for co-products.

The POC method established by Sumitomo Chemical started commercial production in 2003 (**Fig. 4**), and is a three-reaction-step process with a process for generating cumene hydroperoxide (CMHP) by air oxidation of cumene (CUM), an epoxidation process for propylene (C_3') using the CMHP, and a step for recovering cumene by hydrogenation of α-cumyl alcohol (CMA) formed in the epoxidation process.

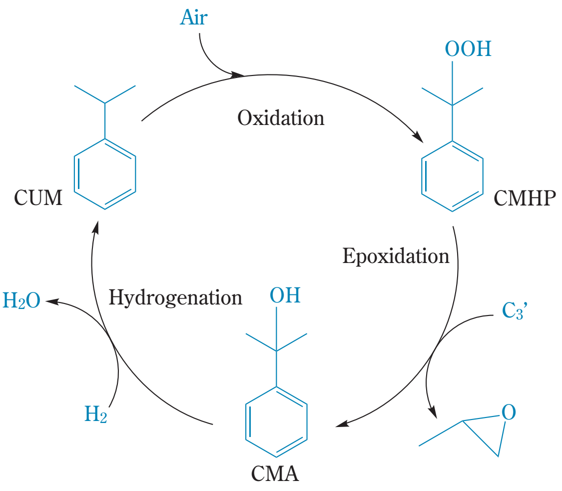


Fig. 4 Sumitomo PO production process (POC)

Copyright © 2019 Sumitomo Chemical Co., Ltd.

(1) POC Using a Ti-silicon Oxide High Performance Epoxidation Catalyst

In the POC method, silicon oxide containing titanium (Ti) (called Sumitomo Ti catalyst in the following) is used as an epoxidation catalyst that is highly active and has high PO selectivity. The Ti silicate catalyst (TS-1) used in HPPO has a zeolite structure classified as an MFI type in which Ti is substituted for Al. It is not suitable for reactions with large molecules since it only has micropores of 5 - 6 Å. The Sumitomo Ti catalyst is characterized by having nanoscale mesopores and was designed to have high activity for reactions with large molecules such as cumene hydroperoxide.

The reason for the high performance of the Sumitomo Ti catalyst can be ascribed to the following three elements; the mesopores described above, and the tetrahedral titanium in the silica matrix in a highly dispersed state, which is highly active in epoxidation reactions, and high hydrophobicity superior to other Ti silicates. **Fig. 5** shows an atomic resolution electron microscope image of the Sumitomo Ti catalyst, and the tetrahedral Ti species, which has high epoxidation activity, was confirmed in the silica matrix in atomic form. The presence of this local structure has also been confirmed from the results of analysis such as Ti K-edge EXAFS.[2)]

Next, the hydrophobicity of the Sumitomo Ti catalyst was evaluated, and the results of a comparison with TS-1 and silica gel are shown in **Fig. 6**. When the catalyst was immersed in an α-cumyl alcohol/cumene solution containing water and the amount of H_2O adsorption on the catalyst was measured, it was found that the amount of H_2O adsorption was less than TS-1 which is known to have high hydrophobicity. For the Sumitomo Ti catalyst, this high hydrophobicity increases the affinity with propylene and can be assumed to make for expression of high epoxidation activity.

(2) Overview of POC Process

The characteristics of POC are an extremely high PO yield by means of a high performance epoxidation catalyst and much lower energy consumption for separation and purification than other PO production methods. In the following, we will explain each process.

(i) Oxidation Process

In the oxidation process, cumene is oxidized by air and cumene hydroperoxide (CMHP) is obtained. Since the oxidation process is carried out by automatic oxidation, no catalyst is required.[3)] It is known that the reaction rate of cumene oxidation is greater than that of ethylbenzene oxidation, and the reaction normally progresses under comparatively mild conditions of 90 - 130 °C at 0 - 1.0 MPa-G (**Fig. 7**).[4)] The yield for CMHP is high, and the valuable component selectivity reaches 95% or greater. In addition, CMHP can be used with

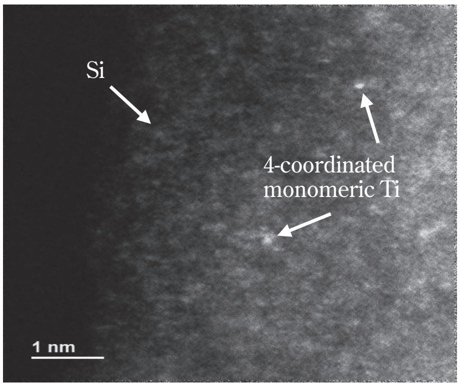


Fig. 5 Atomic resolution TEM image of Sumitomo Ti catalyst

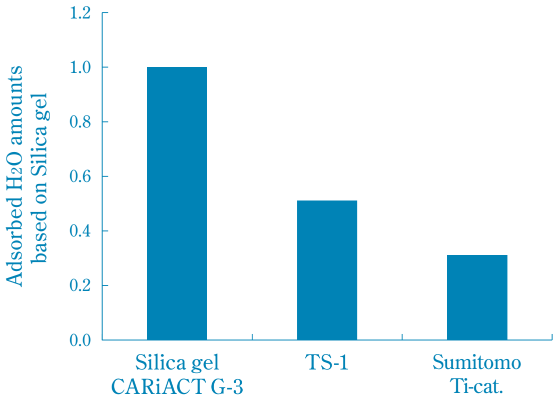


Fig. 6 Comparison of hydrophobicity in the view of H_2O adsorption between TS-1, silica gel, and Sumitomo Ti catalyst

$$\mathrm{ROOH} \xrightarrow{k_i} \mathrm{R}\cdot$$

$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{RO_2}\cdot$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_p} \mathrm{ROOH} + \mathrm{R}\cdot$$

$$2\mathrm{RO_2}\cdot \xrightarrow{k_t} \mathrm{inert}$$

Comp.	k_p	$2k_t$	$k_p/(2k_t)^{0.5}$	yield (%)
Cumene	0.72	0.04	35.6	84.8
Ethylbenzene	2.4	20	5.30	low

Rate constant at 60 °C (L/mol · sec),
yield at $d[O_2]/dt = 10^{-4}$ (L/mol · sec)

Fig. 7 Comparison of hydroperoxide yield between cumene and ethylbenzene

Copyright © 2019 Sumitomo Chemical Co., Ltd.

greater concentration due to its higher stability than ethylbenzene oxidation and isobutane oxidation. Thus, large reduction in energy consumption can be achieved by reducing the amount of cumene circulating in the whole production process.

(ii) Epoxidation Process

Epoxidation is a process for reacting CMHP and propylene to obtain PO and α-cumyl alcohol. With the use of the high performance epoxidation catalyst developed by Sumitomo Chemical and a non-aqueous system, the hydrolysis reaction from PO to propylene glycol is suppressed, and an extremely high PO selectivity of 95% or greater is achieved. In addition, use of cumene, which is substantially inert for PO, as a solvent contributes to the high PO selectivity because there is no PO loss by sequential reactions with the solvent. As will be discussed later, in the hydrogen peroxide to propylene oxide (HPPO) method, the PO selectivity seems to be lower than that for POC because the HPPO method is carried out in an aqueous, methanol-containing solvent, which is highly reactive with PO. In addition, CMHP is much more thermally stable than hydrogen peroxide and the reaction in the case of POC takes place at a higher temperature than that for HPPO.

(iii) Hydrogenation Process

Hydrogenation is a process for obtaining cumene from α-cumyl alcohol (CMA) and hydrogen.

The reaction is a normal fixed bed process where the bed is packed with a hydrogenation catalyst, and it is carried out by supplying the CMA/cumene solution and hydrogen. Unlike the α-phenylethanol and *tert*-butanol produced in the PO/SM and PO/TBA methods, respectively, CMA is converted almost quantitatively to cumene. Cumene is recovered through purification such as by separating out the water produced in the hydrogenation reaction and recycled to the oxidation process.

4. Third-Generation Production Method 2 (Hydrogen Peroxide to Propylene Oxide (HPPO))

In 2009, BASF SE-The Dow Chemical Co. and Evonik Degussa GmbH-thyssenkrupp AG started commercial operations with HPPO independently, in which PO is produced from propylene and hydrogen peroxide (H_2O_2) using the TS-1 catalyst.

HPPO itself has a one-step reaction process for propylene epoxidation using hydrogen peroxide (H_2O_2), but it is essentially a three step process in the case that the production of H_2O_2 through the alkylanthraquinone oxidation/reduction cycle (called the anthraquinone process) is included (**Fig. 8**). It can be said that there are only a few differences fundamentally from POC. As an example, **Fig. 9** gives an overview of the process

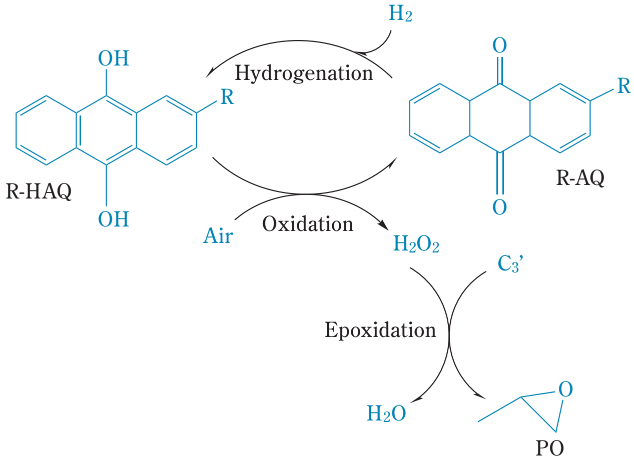


Fig. 8 HPPO process (including anthraquinone H_2O_2 production)

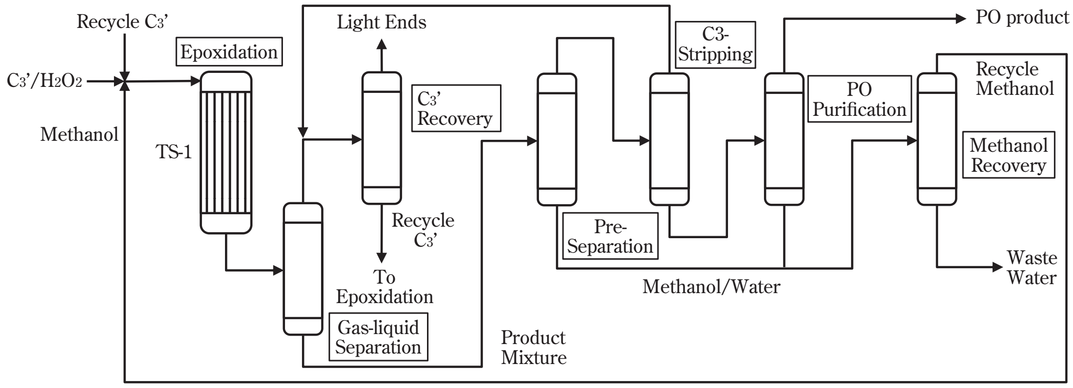


Fig. 9 Evonik/thyssenkrupp HPPO process

Copyright © 2019 Sumitomo Chemical Co., Ltd.

developed by Evonik Degussa GmbH-thyssenkrupp AG.[5] The main process other than epoxidation is the recovery and recycling process for the methanol solvent, and this process consumes a large amount of energy for separation and purification of the solvent.

(i) Epoxidation Process

Epoxidation is a process for obtaining PO by reacting H_2O_2 and propylene.

The reaction is carried out by flowing propylene and H_2O_2 with a methanol (MeOH) solvent into a reactor filled with the TS-1 catalyst. A shell-and-tube type reactor is used, and the catalyst is repeatedly regenerated by baking or MeOH washing. The reaction temperature is held to around 50 °C, and the upper limit of the PO concentration in the reaction solution is around 10 wt%[6] because the thermal stability of H_2O_2 is low, and PO reacts easily with water and MeOH. It is predicted that reaction heat recovery at this low reaction temperature would be difficult and that there would be limits to utilizing the reaction heat for other processes.

(ii) MeOH Recovery Process

MeOH recovery is a process for separation and recovery of MeOH from the epoxidation reaction solution.

Gas components and crude PO are separated sequentially from the reaction solution obtained in the epoxidation process and then a MeOH/water mixture containing sequential reaction products such as propylene glycol and other high-boiling-point impurities is obtained. MeOH is recovered by distillation and is recycled to the epoxidation reaction. As was described previously, the PO concentration in the epoxidation reaction solution is kept low; therefore, a large excess in the amount of MeOH as a solvent to the PO is necessary. The evaporative latent heat of MeOH is as large as 1,100 kJ/kg; therefore, it can be presumed that energy consumption per amount of PO produced will be comparatively high in the case of HPPO.

Comparison of Energy Consumption for POC and Hydrogen Peroxide to Propylene Oxide

Fig. 10 compares POC and HPPO[7] in terms of energy used by the production process as a whole. Since POC includes the oxidation process for producing the hydroperoxide, the energy required for producing the raw material H_2O_2[8] is also taken into account in the case of HPPO.

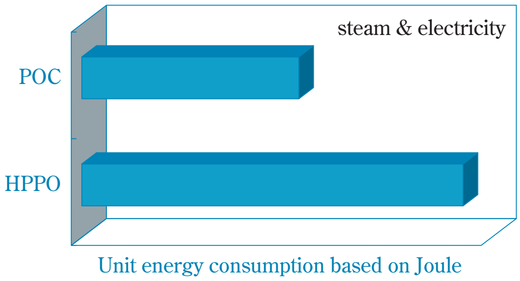


Fig. 10 Comparison of unit energy consumption between POC and HPPO

As **Fig. 10** shows, POC is superior to HPPO in terms of the total energy consumption and can be said to be an economical and eco-friendly process. One of the reasons for the superiority is efficiency of oxygen carriers. In all HPPO cases, H_2O_2 is produced by using anthraquinone (AQ) as an oxygen carrier, and the efficiency of alkylanthraquinone (oxygen/AQ = 32/264) is much worse than cumene (oxygen/cumene = 32/120). Additionally, the solubility of AQ in hydrocarbon media is low; therefore, there is a problem with the energy required for liquid circulation being high. In addition, in HPPO, the epoxidation reaction is carried out in MeOH, and the evaporative latent heat of MeOH is 1,100 kJ/kg, which is three times higher than that of cumene at 330 kJ/kg; therefore, it is estimated that the recovery energy is much greater than that for POC.

With the increasing international consciousness of environmental problems such as global warming in recent years, countermeasures for climate change such as reduction of carbon dioxide and greenhouse gases will surely be required. The value of POC, which has achieved greater reduction of resources and energy than other PO production methods, will increase even further.

Other PO Production Methods Under Development

1. Improved Hydrogen Peroxide to Propylene Oxide (Improved HPPO)

As described previously, there are issues with PO yield improvement and reducing the amount of energy used in the case of HPPO at present and various companies are thought to be carrying out investigations into improvements independently. As an example, we will give a descriptive outline of technology being investigated based on patent information disclosed publicly starting in 2015.

Copyright © 2019 Sumitomo Chemical Co., Ltd.

Evonik Degussa GmbH constructed a reaction process with a water/propylene two-phase system using a homogenous Mn complex catalyst that dissolved in water.[9] An epoxidation reaction of olefins by H_2O_2 using a water-soluble Mn complex had been known previously, but there have been problems with low yields of epoxidation products based on H_2O_2 consumed because the H_2O_2 decomposition activity for Mn complexes is high.[10] The process envisioned by Evonik Degussa GmbH as described in the publicly disclosed patent is shown in **Fig. 11**. A loop type reactor is adopted, and epoxidation is carried out using a two phase system of a water phase and an oil phase (propylene (C3')). The purposes of this improvement are reducing the separation energy by not using a solvent such as methanol, and improving PO yield by controlling H_2O_2 decomposition and sequential reaction of PO by shortening the contact time. However, even though it is a low temperature reaction at around 15 °C, the PO yield does not exceed around 75%, and the problem of suppressing H_2O_2 decomposition appears to remain.

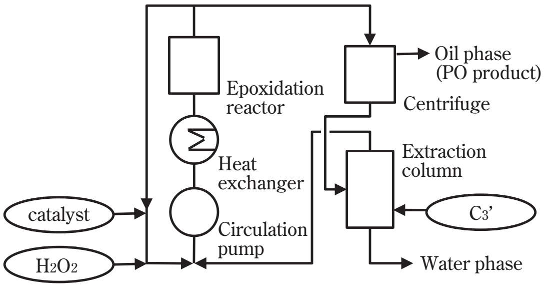


Fig. 11 Evonik modified process

BASF Corporation and Dow Chemical Company are jointly developing a method for reducing the energy consumption by changing the solvent.[11] Ti-MWW, which has a zeolite structure that is a modification of zinc oxide, is presumed to be used as the epoxidation catalyst.[12] The MWW has a unique crystal structure that includes a 12 member ring side pocket, two types of 10 member ring pores that are independent of each other and a 12 oxygen member ring supercage,[13] which offers larger spaces that can be utilized for reaction than TS-1, which only has one 10 member ring pore.

2. Direct Oxidation

Direct oxidation is a production method for air oxidation of propylene in the gas phase, which is the same system used in the production of industrial ethylene oxide (EO). From the standpoint of energy consumption, it is the ideal PO production method, but it is difficult to control combustion reactions accompanied by dehydrogenation of allylic methyl groups of propylene, and it has yet to be established industrially. **Table 2** shows representative examples of reports extracted from publicly disclosed patent applications and academic papers since 2014. The catalyst systems being investigated are roughly divided into Ag catalyst systems used in the EO process and radical reaction catalyst systems.

3. Other Production Methods

LyondellBasell Industries Holdings B.V. and China Petroleum & Chemical Corp. (Sinopec Corp.) have disclosed a method (called in-situ HPPO) for generating hydrogen peroxide (H_2O_2) in the liquid phase from hydrogen/oxygen by means of a noble metal such as Pd and carrying out epoxidation of propylene using this H_2O_2 in the same reactor. For the most part, noble metal supported Ti silicates are used as catalysts.

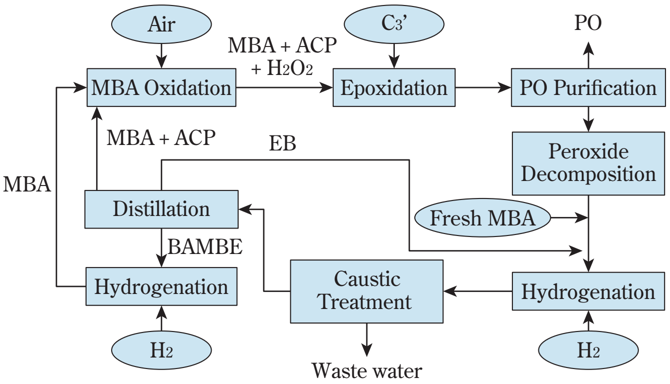
For example, LyondellBasell Industries Holdings B.V. has found that quinone-derived additives are effective for suppressing propane produced as a by-product from the reaction of propylene with hydrogen,[20] but it can be presumed that practical application is difficult because of low PO productivity and low PO selectivity (< 50%) based on the hydrogen consumed.

Table 2 Example of published research of PO production by direct propylene epoxidation (2014 ~)

Company or research institution	Catalyst	Typical results	Reference
LyondellBasell Industries Holdings B. V.	Ag-Mo/$CaCO_3$	PO sel. 40~50%	14)
China Petroleum & Chemical Corp.	Nano hollow $Fe_2(MoO_4)_3$	PO sel. <15%	15)
LOTTE Chemical Corp.	Ag-(Mo-W)/ZrO_2	propylene conv. 12%, PO sel. 58%	16)
University of Oxford	$NiAg_{0.4}$/SBA-15	propylene conv. 0.04%, PO sel. 71%	17)
East China University of Science and Technology	Ag-Cu-Cl/$BaCO_3$	propylene conv. 1%, PO sel. 84%	18)
Fuzhou University	Fe_2O_3-MoO_3-Bi_2SiO_5/SiO_2	propylene conv. 12%, PO sel. 60%	19)

Copyright © 2019 Sumitomo Chemical Co., Ltd.

As another method, LyondellBasell Industries Holdings B.V. has disclosed a PO production method using Ti-MWW as the epoxidation catalyst with α-methylbenzyl alcohol (MBA) both as the H_2O_2 carrier and the solvent (**Fig. 12**).[21] This same company found the principles for producing H_2O_2 by using MBA as an oxygen carrier in the 1990s,[22] and it can be assumed that this process was considered by combining discovering the Ti-MWW catalyst described previously. To separate and remove bis-α-methylbenzyl ether (BAMBE) produced as a by-product, all of the unreacted MBA is distilled and recycled to the oxidation process. The evaporative latent heat of MBA is 400 kJ/kg, and the energy consumption is lower than the methanol used in HPPO, but it can be presumed that the energy consumption will be larger than that for the POC method (evaporative latent heat of cumene being 330 kJ/kg).



EB; Ethylbenzene, ACP; Acetophenone,
BAMBE; bis-α-methylbenzylether

Fig. 12 LyondellBasell Industries modified process

Conclusion

Currently, the first generation to third generation production methods have roughly equal proportions among the PO production technologies, but the third-generation production methods are taking over the main role. The POC method, which was introduced in this article, is a process with a low environmental impact and is compatible with the Sumitomo Chemical Group concept regarding the furthering of sustainability. We hope that we can contribute to the continued development of society by improving POC even further and developing new technology in the future.

References

1) Chuugoku ni okeru Kankyou Kisei to Shijou Kibo no Saishin Doukou Chousa 2018-nen 1-gatsu [Survey on Latest Trends in Environmental Regulations and Market Scale in China, January 2018], Japan External Trade Organization, https://www5.jetro.go.jp/newsletter/shanghai/2018/180126/doukou.pdf (Ref. 2019/3/4).
2) J. Tsuji *et.al.*, SUMITOMO KAGAKU, **2006-I**, 4 (2006).
3) K. Weissermel and H.-J. Arpe, Industrial Organic Chemistry: Fifth Edition, Translated by T. Mukaiyama, Tokyo Kagaku Dozin (2004), p.289.
4) Y. Kamiya, *Journal of the Fuel Society of Japan*, **49**, 603 (1970).
5) F. Schmidt *et al.*, *Chimica Oggi-Chemistry Today*, **32**, 31 (2014).
6) Degussa AG and Uhde GmbH, WO 2005/000827 A1, etc.
7) ThyssenKrupp Uhde, "Propylene Oxide, The Evonik-Uhde HPPO technology, Innovative · Profitable · Clean", https://www.digitalrefining.com/data/literature/file/1994182549.pdf (Ref.2019/4/23).
8) "Process Economics Program Report 68B", IHS Markit (1992).
9) Evonik Degussa GmbH, JP 2018-508505 A, etc.
10) D. E. De Vos *et al.*, *Tetrahedron Lett.*, **39**, 3221 (1998).
11) T. Tatsumi, *PETROTECH*, **36**(7), 521 (2013).
12) BASF SE, WO 2018/115117 A1, etc.
13) Y. Kubota and T. Tatsumi, *J. Vac. Soc. Jpn.*, **49**(4), 205 (2006).
14) Lyondell Chemical Technology, L. P., US 2017/0056860 A1.
15) China Petroleum & Chemical Corporation, CN 103664832 A (2014).
16) Lotte Chemical Corporation, WO 2018038505 A1.
17) B. Yu *et al.*, *Appl. Catal.*, *B*, **243**, 304 (2019).
18) Q. Zhang *et al.*, *Chin. J. Catal.*, **38**, 65 (2017).
19) Fuzhou University, CN 108816243 A (2018).
20) Lyondell Chemical Technology, L. P., US 2012/0083612 A1, etc.
21) Lyondell Chemical Technology, L. P., WO 2016/164585 A1, etc.
22) Arco Chemical Technology L. P., US 5268160 A (1993).

Copyright © 2019 Sumitomo Chemical Co., Ltd.

PROFILE

Tomonori KAWABATA

Sumitomo Chemical Co., Ltd.
Petrochemicals Research Laboratory
Senior Research Associate, Ph.D.

Hirofumi KOIKE

Sumitomo Chemical Co., Ltd.
Chiba Works
General Manager, No.1 Manufacturing Dept.
(Currently: Senior Technical Advisor)

Jun YAMAMOTO

Sumitomo Chemical Co., Ltd.
Petrochemicals Research Laboratory
Senior Research Associate

Shuhei YOSHIDA

Sumitomo Chemical Co., Ltd.
Chiba Works
Chief Engineer

Copyright © 2019 Sumitomo Chemical Co., Ltd.