Development of New Dipropylene Glycol / Tripropylene Glycol Process

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Both dipropylene glycol (DPG) and tripropylene glycol (TPG) are manufactured by non-catalytic propylene oxide hydration reactions as byproducts of propylene glycol. Owing to the successful development of a new high performance niobium catalyst for DPG/TPG-only production, we have established industrial technology which is a simple and energy-saving process. From now, we are planning on starting promotion activities for licensing this technology.

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Introduction

Dipropylene glycol (DPG) is an industrial product used as a glycol component in unsaturated polyester resins and benzoate ester plasticizers and as a raw material for cosmetics and other products, and tripropylene glycol (TPG) is used for the glycol component in UV and EB cured resins as well as in other applications.

The demand for unsaturated polyester resins is undergoing a remarkable expansion in Asia, particularly in China. It is expected that DPG will form a commensurate market as a denaturing glycol component that gives toughness to unsaturated polyester resins for FRP. In addition, in cosmetics, DPG has the characteristics of preserving skin moisture and maintaining youthfulness; therefore, it is mainly used in texture modifiers and moisturizing agents.1)

UV and EB cured resins are mainly used in fields such as coatings, ink and adhesives. There is an outlook for increased growth in the use of UV and EB cured resin in the future because they can be used as starting materials for solvent-free curing resins, and global demand is increasing because of the need for compliance with the suppression of the generation of volatile organic compounds, and contributions to the improvement of energy consumption and productivity. TPG is derivatized into tripropylene glycol diacrylate by an esterification reaction of acrylic acid, which is mainly used in paint and coating agents as a reaction dilution agent as one of the starting materials for UV and EB cured resins.2)

Industrially, DPG and TPG are byproducts of propylene glycol (PG) production by hydration reaction of propylene oxide (PO), and thus the amount of production is limited. On the other hand, non-PO hydration methods for PG production have increased in recent years, and since these manufacturing methods do not produce DPG and TPG as byproducts, tight demand is forecasted in the mid- and long-term.

Now, Sumitomo Chemical has succeeded in developing a catalyst affording DPG and TPG with high yields using PO and water as the starting materials, and industrialized production technology has also been established. The main features of the Sumitomo Chemical technology are the catalyst keeping high activity and selectivity for a long time, a simple reaction by adopting a fixed bed system and the low-energy consumption process in which the reaction heat is recovered as steam, for example.

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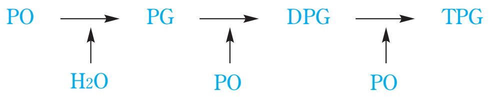
In this article we will give a simple review of the manufacturing method for propylene glycols (PG, DPG and TPG) and also introduce the characteristics of the catalyst and process for the new DPG and TPG manufacturing method (on-purpose DPG and TPG technology) developed by Sumitomo Chemical.

Current Manufacturing Technology for Propylene Glycols

In the following we will introduce the manufacturing technology for propylene glycols currently being carried out industrially.

1. PO hydration method

This is the typical commercial technology for manufacturing PG applying a non-catalytic hydration reaction with PO and water as the starting materials. Part of the PG successively reacts with PO and gives rise to the byproducts DPG and TPG (**Scheme 1**). Further PO addition causes heavy polyol formation, leading to yield decrease. Since DPG and TPG are obtained industrially from the distillation of such a byproduct mixture after the hydration reaction, the amount of DPG and TPG are influenced by the PG production amount.



Scheme 1 PO hydration method

The reaction is carried out at roughly 160–200°C in the liquid phase under high pressure conditions. The proportions of PG, DPG and TPG produced vary according to the mole ratio of PO and water. For example, **Table 1** gives instances of the relationship between the mole ratio and the proportions of each of the propylene glycols produced.$^{3)}$

Table 1 Correlation between water/PO ratio and PG/DPG/TPG production ratio$^{3)}$

H_2O/PO molar ratio	Product distribution (wt%)		
	PG	DPG	TPG
5	63.5	24.0	12.5
9	76.0	19.0	5.0
12	81.0	16.5	2.5
20	88.5	10.5	1.0
25	91.0	8.0	1.0

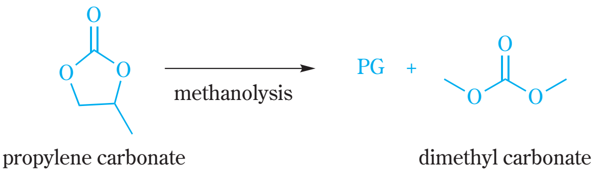
The large amount of heat generated by the PO hydration reaction is able to be absorbed by excess water as sensible heat. The excess amount of water in the reaction mixture should be removed by distillation. Unfortunately, a large amount of energy consumption is required for the evaporation of the water due to its large evaporative latent heat. The operation conditions are optimized from the view of easy management of reaction control, the yield for DPG and TPG, and economy in the energy required for evaporating the water that is used in excess, and so on.

In this sense, the proportions of DPG and TPG with respect to PG are about 1/10 and 1/100, respectively, and it can be presumed that drastically changing the proportion of DPG and TPG would be difficult.

2. PG manufacturing methods other than PO hydration

In recent years, PG manufacturing methods other than PO hydration have increased.

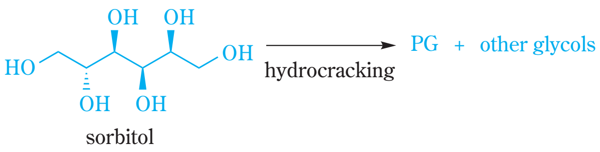
For example, in China, the amount of PG produced as a byproduct of dimethyl carbonate production is roughly 2/3 in regard to entire PG production (**Scheme 2**).$^{4)}$



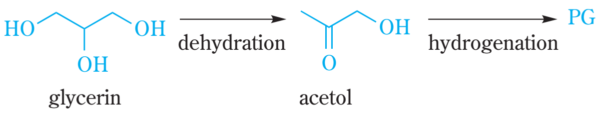
Scheme 2 Dimethyl carbonate method

Other industrial implementations that have been announced recently include a method for manufacturing PG with other glycols from sorbitol made from corn as the starting material (**Scheme 3**)$^{5)}$ and a method for manufacturing PG from glycerin produced as a byproduct during the production of biodiesel fuel (**Scheme 4**).$^{6)}$

With PG manufacturing methods other than the PO hydration, DPG and TPG are not produced as



Scheme 3 Sorbitol method



Scheme 4 Glycerin method

byproducts, so increasing the PG production by these methods results in a tightening of the demand for DPG and TPG.

Development of New Manufacturing Method for DPG and TPG (On-Purpose DPG/TPG Technology)

1. Development of catalysts

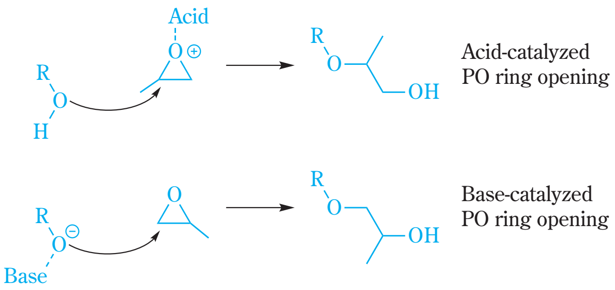
While various investigations have been carried out on catalytic hydration reactions for PO up to now, the purpose of most is to increase the yield of PG,7)–9) and almost no reports of catalysts having high selectivity for DPG and TPG synthesis are found.

In recent years, however, catalysts targeting DPG and TPG have been reported. For example, technology for synthesizing DPG and TPG using a zirconia-supported sodium catalyst with PO and water as the starting materials10) and methods for synthesizing DPG and TPG in the presence of PPh_3 or organic amine catalyst with PO and PG as the starting materials11), 12) have been reported. However, these methodologies show low activity and selectivity.

The niobium catalyst developed by Sumitomo Chemical has both high activity and selectivity for manufacturing DPG and TPG with PO and water as the starting materials and also achieves a long catalyst life, which is important for industrial catalysts. We will introduce this catalyst in detail in the following.

(1) Search for catalysts

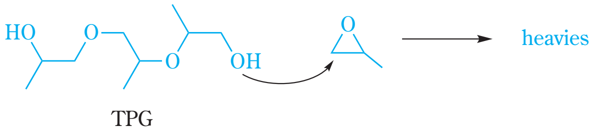
Both acids and bases are known to accelerate ring-opening reactions of oxirane rings by hydroxyl groups,13) and are usable from the standpoint of improving reaction rates.



On the other hand, in the case of manufacturing polyester polyols by polymerization of PO with glycerin or a similar compound as an initiator, base catalysts are used, which seems that base catalysts are not suitable for monomer synthesis like DPG and TPG. Considering this situation, we focused on acid catalysts as the target for developing original DPG/TPG production technology.

Compared to homogenous systems, heterogeneous systems using solid acid catalyst have advantages not only from the standpoint of environmental impact, but also economically because of the ease of separation of products and recovery and reuse of the catalysts. However, the acid center of normal heterogeneous solid acids is poisoned by water and does not function under aqueous conditions. So, catalysts that synthesize DPG and TPG from PO and water must be able to function in water, that is, they must be water-tolerant solid acids.

On the other hand, it can be envisioned that TPG also has reactive hydroxyl groups, so heavy products are generated because of further sequential reactions between the TPG and PO which lead to DPG and TPG yield loss. So, we thought that it is the key to developing water-tolerant acid catalysts that promote reactions between hydrophilic compounds such as water and PG with PO while preventing hydrophobic compounds such as TPG reacting with PO.



As a catalyst having these characteristics, we focused on niobic acid, which shows a strong acidity similar to sulfuric acid in water, among the water-tolerant acids reported14). It has been reported that niobic acid has a distorted polyhedron structure and the Nb-O bonds are highly polarized15). Because of this specific structure of niobic acid, we expected that hydrophilic compounds (water and PG in this case) would approach the active sites of the catalyst and easily react with PO. On the other hand, reactions between PO and hydrophobic compounds (TPG in this case) hardly proceed by keeping a distance from the active site.

The experimental results comparing the catalytic performance of solid acids for PO and water reactions are

Table 2 Catalytic activity for the reaction of PO and H_2O

cat.	PO Conv.	Selectivity (%)				
	(%)	PG	DPG	TPG	tetra-PG*	PA
niobic acid	67	34	56	8	0.5	< 0.1
tantalum oxide	28	23	68	2	0.1	< 0.1
H-ZSM-5	29	39	26	12	3	1
SO_3 type ion exchange resin	33	46	26	12	3	0.5

Reaction condition
PO/H_2O=2/1 (molar ratio)
reaction temperature 373K, reaction time 2h
* tetrapropylene glycol

given in **Table 2**. In the reaction of PO and water, not only are PG, DPG, TPG and heavier compounds produced, but also propionaldehyde (PA) formation by isomerization was expected[13)], so we carefully analyzed and checked the reaction mixture. As a result, niobic acid had a higher activity than zeolite and other typical solid acids while keeping byproduct (tetrapropylene glycol (tetra-PG)) formation low, and moreover, it was found that isomerization of PO to PA did not occur easily which suggests that a high yield of DPG and TPG could be expected from a niobic acid-catalyzed reaction. In addition, tantalum oxide also showed high selectivity, tantalum being in the same fifth group in the periodic table as niobium.

(2) Characterization of catalyst

To analyze the correlation between the reaction results and the physical properties of the catalyst, we prepared separately two types of niobium catalyst A and B, having the same specific surface area but different crystal structures, and compared them. XRD patterns and SEM images of the two catalysts are shown in **Fig. 1** and **Fig. 2**.

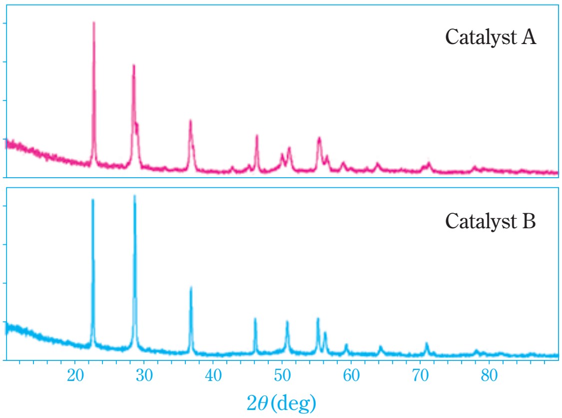


Fig. 1 XRD pattern of catalyst A,B

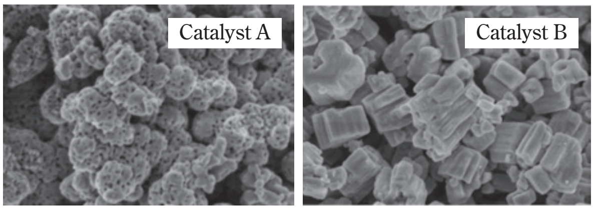


Fig. 2 SEM image of catalyst A,B

The selectivity to DPG and TPG from PO and water as the starting materials was substantially the same in the case of the niobium catalysts A and B, but catalyst B exhibited approximately three times higher activity. Considering this difference in catalytic performance, we carried out an evaluation of the hydrophilicity and an analysis of the amount of acid, including zeolite with its low selectivity, in the search for a catalyst previously described.

In terms of the hydrophilicity of the catalyst, we carried out comparisons using the ratio of H_2O adsorption and N_2 adsorption by the BET method, and both niobium catalysts A and B were found to be more hydrophilic than a typical inorganic oxide such as zeolite (**Fig. 3**). In addition, as a result of analyzing the total amount of acid by NH_3-TPD, we found that the amount of acid for catalyst B was greater than for catalyst A (**Fig. 4**).

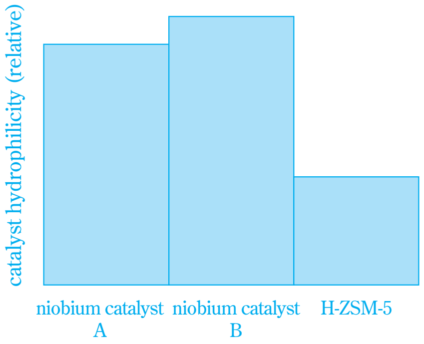


Fig. 3 Relative catalyst hydrophilicity

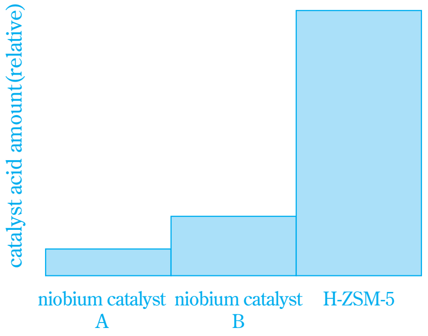


Fig. 4 Relative catalyst acid amount

In other words, it was confirmed that the generation of heavier compounds would be suppressed, which lead to high DPG/TPG selectivities, by using a hydrophilic catalyst and that even greater catalytic activity would be possible with an increase in the amount of acid.

(3) Reaction characteristics of niobium catalyst

Based on our finding that niobium catalysts have superior activity and selectivity for the synthesis of DPG and TPG from PO and water, we started to comprehend the catalyst characteristics for the reaction to develop a reaction process and to proceed with the development of an industrial catalyst.

1) Reaction temperature

The results of comparing selectivity at the various temperatures of 120, 180 and 200°C for the reaction of PO and water using the niobium catalyst are shown in **Fig. 5**. Each experiment was carried out by a batch heterogeneous catalytic reaction method, adjusting the reaction time so that PO conversion of each experiment was greater than 90%.

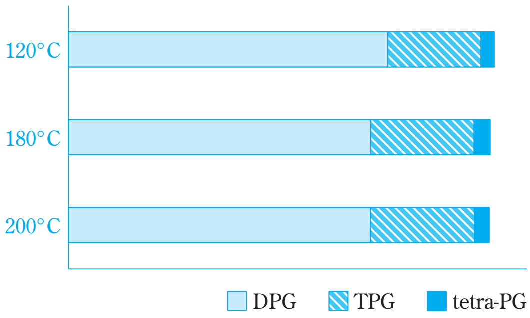


Fig. 5 Temperature dependence of DPG/TPG/tetra-PG selectivity

In a typical catalytic reaction, undesired reactions often increase and the selectivity for the target product is reduced when the reaction temperature is increased greatly. Surprisingly, in the case of the reaction of PO and water with the niobium catalyst, there is a characteristic that the reaction could proceed at 100°C or less and, moreover, no increase in heavy compound production even at 200°C and high DPG/TPG selectivities were obtained.

2) Proportions of PO and water

The effects of molar ratios of PO and water using the niobium catalyst are shown in **Fig. 6**.

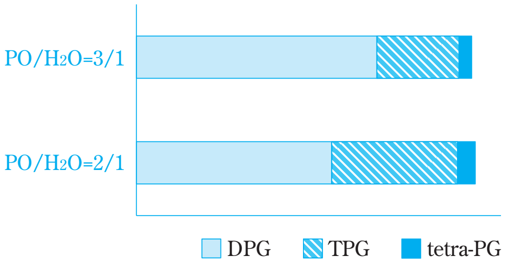


Fig. 6 Molar ratio dependence of DPG/TPG/tetra-PG selectivity

While the proportion of PO and water affects the selectivity for DPG and TPG, the niobium catalyst hardly increased the heavier products at all. It was suggested that the production proportions for DPG and TPG, which are the target products, could be controlled discretionally to some extent by changing the compositional ratio of PO and water as the starting materials.

2. Development of reaction process

The reaction heat for producing DPG and TPG from PO and water is very large at 188 kJ/mol and 268 kJ/mol, respectively (calculated from the standard enthalpy of formation), and when an adiabatic reaction is carried out, a temperature increase of several hundred degrees occurs.

$$2PO + H_2O \rightarrow DPG \quad \Delta Q = -188\ kJ/mol$$
$$3PO + H_2O \rightarrow TPG \quad \Delta Q = -268\ kJ/mol$$

Typically, multi-tube heat exchanging reactors are used in liquid phase reactions generating large amounts of heat. But it has some disadvantages like requiring a large amount of time for catalyst filling, complexity in the introduction of the starting materials uniformly into a large number of reaction tubes, and the large cost of construction of the reaction equipment. Besides this reactor type, there is the method of connecting multiple reactors in series and forming many catalytic layers and cooling of the reaction mixture in between, but the construction costs are large because multiple reactors and heat exchangers are indispensable.

In the case of this reaction, a temperature increase of several hundred degrees occurs within the catalytic layer in a fixed bed reactor with a simple adiabatic system. In the meanwhile, the niobium catalyst has the characteristic of promoting the reaction of the hydrophilic compounds of water and PG with PO while preventing hydrophobic compounds such as TPG with PO from reacting. So even if the raw materials formed from PO and water are diluted by a reaction mixture containing DPG and TPG, little reduction in yield would be predicted because of increasing heavier products. So we designed the reaction process of an adiabatic fixed bed reactor that circulates some of the reaction mixture after cooling it with an external heat exchanger while supplying the starting materials to the catalyst.

In addition, making use of the characteristic that sequential reactions leading to heavier products did not occur easily even if the reaction temperature increased with the niobium catalyst, the reaction temperature was optimized by considering the energy levels such that the reaction heat recovered from the external heat exchanger could be used as a heat source for subsequent distillation towers.

The reaction pressure was set to conditions that maintain a liquid phase state.

A reaction rate equation of Langmuir-Hinshelwood-type adsorption model was created from data obtained by using a laboratory-scale isothermal reactor, and it was verified by actual tests and other results from bench testing described in the following to brush up this equation.

As for the linear velocity, substrate diffusion controlling region, reaction controlling region and fluidization of the catalyst were confirmed in laboratory tests, and suitable conditions were determined within the possible operation range in which changes in load, etc., could be handled from within steady operation. Evaluations of catalyst life and bench testing were carried out under these conditions.

The space velocity (amount of catalyst) was decided not to have an excessive margin because we determined that long life could be expected from our finding from laboratory testing of no changes in performance and physical properties of the catalyst in short life evaluations of roughly 100 hours.

In molding of the industrial catalyst, not only suitable sizes and shapes for the particles from the balance of activity and pressure loss in the catalyst layer were investigated, but also the mechanical strength of catalyst particles was taken into consideration. In other words, consideration was given to not having the catalyst layer obstructed and the reaction mixture drifting because of phenomena such as abrasion during the filling of the catalyst, crushing by its own weight after filling and collapsing during the reaction.

With the accumulation of these investigations, a reaction process for an adiabatic fixed bed reaction system using the industrial catalyst molded into a suitable size was constructed making use of the superiority of the high level of activity of the niobium catalyst for this reaction.

3. Development of total process

(1) Overview of process

The merits of the process with the Sumitomo Chemical technology are to obtain DPG and TPG with a high yield using a compact fixed bed reactor filled by the long life catalyst with its high activity and high selectivity, and the lower energy consumption with the recovery of reaction heat as steam.

The process is simple, composed of a combination of each step shown in **Fig. 7**. In the following, we will give an overview of each step of the process.

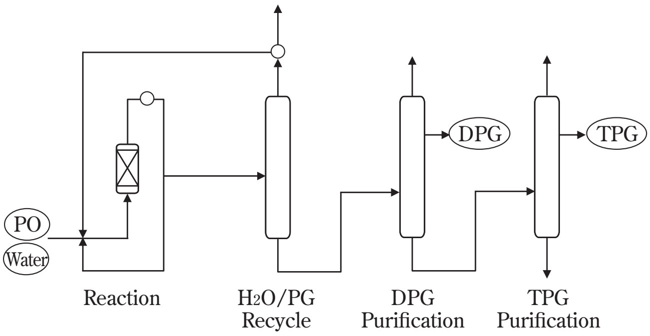


Fig. 7 On-Purpose DPG/TPG process flowsheet

1) Reaction step

PO and water are supplied to a fixed bed reactor that has been filled with the niobium catalyst, and DPG and TPG are produced by the liquid phase reaction. The reaction is carried out in an adiabatic system, so some of the reaction liquid that has been cooled is recycled to suppress excessive temperature increase in the catalyst layer. In addition, the reaction heat is recovered as steam by an external heat exchanger and used effectively.

Another important feature is being able to control the proportion of DPG and TPG products produced discretionally to some extent by changing the compositional ratio of the PO and water as starting materials.

2) H_2O and PG recycling step

Light distillates consisting of unreacted water and the intermediate product PG in the reaction mixture are separated out by distillation and recycled into the reaction process. The light distillates contain trace amounts of several impurities, so portions of distillates are removed to the outside of the system to prevent accumulation. An Aspen Plus® simulation was carried out on the separation behavior of the trace impurities. For not-entry components in the standard Aspen Plus® properties, gas-liquid equilibrium data was acquired from laboratory tests and the physical property parameters were determined. The distillation behaviors of these trace impurities in the recycle process were verified from the bench testing discussed in the following and the technology was completed.

Optimal conditions for the temperature and pressure were determined from consideration of effective use of the reaction heat generated in the reaction process, heat recovery in the condenser and temperature conditions for cooling water.

3) Purification step for DPG and TPG

DPG and TPG are recovered as products by purification using two distillation columns from the bottom stream of the H_2O and PG recycling step. Typically, glycols such as DPG and TPG are known to have a tendency to decompose when heated to high temperatures, so the products are recovered as side cut distillates in each of the distillation columns.

4. Establishment of industrial technology by bench testing

In view of increasing the scale to industrial facilities of ten thousands of tons, a bench facility was designed based on the laboratory tests, and the technology was improved while carrying out verification with continuous operation.

No problems were observed in the start-up operation conducted in the same way as planning for an industrial facility, and stable operation was easily achieved in a short period of time for each step. During continuous operation, reaction tests were carried out while changing the compositional ratio for the raw materials of PO and water. It was confirmed that the proportions of DPG and TPG were controlled as speculated from the reaction rate equation and that the samples of DPG and TPG obtained as products were of a purity equal to current industrial products.

In addition, not only normal operation stop methods but also tests envisioning emergency stops because of severe trouble such as earthquakes were carried out, and technology related to assuring the safety of the plant was established. It was confirmed that catalytic performance equal to that prior to the stop was expressed when restarting after stopping, and highly robust process technology was established.

Evaluations of test pieces in the operating environments for the reactor and each of the distillation columns were carried out, and suitable materials were selected, as the selection of suitable industrial materials is an important point for process industrialization and long-term stable operation.

Regarding catalyst life, which is important in industrial catalysts, a PO conversion rate of substantially 100% was maintained in operations for approximately one year (**Fig. 8**), and excellent results with a yield exceeding 90% as per the design were constantly obtained. In addition, as a result of recovering and analyzing the catalyst after use for one year, almost no deposition of carbon material or sintering of the catalyst was found, and the catalyst performance was comparable to the fresh catalyst. From all of this, it can be assumed that even longer-term use of the niobium catalyst can be expected.

In the bench testing that lasted approximately one

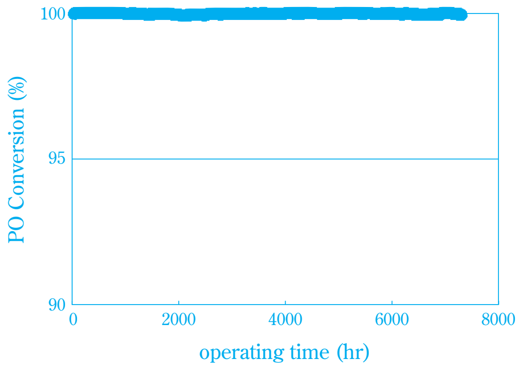


Fig. 8 Plot of operation time vs PO conversion

year, industrial technology was established by engineering data acquisition, the confirmation of effects of catalyst life and reaction liquid recycling and the DPG and TPG product acquisition.

Conclusion

Sumitomo Chemical Co., Ltd. has developed new technology for on-purpose production of DPG and TPG using PO and water as the starting materials and using a niobium catalyst developed by Sumitomo Chemical. Industrial technology has been established by verification and improvements made using bench testing.16), 17)

The catalyst has high activity, high selectivity and long life, and since the reaction is a simple fixed bed system, inexpensive construction costs can be expected; furthermore, a process with little energy consumption was constructed by means such as recovering the reaction heat as steam. In addition, an important feature of this technology is being able to control the proportion of DPG and TPG produced discretionally to a certain extent by means of the compositional ratio of the starting materials of PO and water.

Moving forward, we plan to start promotional activities for this process technology as a new manufacturing method for DPG and TPG (on-purpose DPG and TPG technology).

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