Development of Process for Production of Highly Valuable Chemicals Derived from Dicyclopentadiene for Comprehensive Utilization of C5 Chemicals

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C5 chemicals (isoprene, dicyclopentadiene, piperylene) are co-produced by an extractive distillation process using C5 fraction, by-product of ethylene from naphtha cracker, as a raw material. The authors have developed a new process for producing cyclopentanone and a commercial process for manufacturing cyclopentyl methyl ether using dicyclopentadiene as a starting material for the comprehensive utilization of the C5 chemicals. In this report, we introduce the technical knowledge, especially about catalyst deactivation, obtained in the technical studies for the process development. In addition, we will review recent topics on the development of manufacturing technology for C5 chemicals itself, which is essential to the growth of the C5 chemicals business.

Keywords
C5 fraction, Dicyclopentadiene, Cyclopentanone, Cyclopentene, Catalyst deactivation, Cyclopentyl methyl ether

1. Introduction

The C5 chemicals is a generic name for compounds having 5 carbon atoms, and generally refers to three compounds of isoprene (hereinafter IPM), dicyclopentadiene (hereinafter DCPD) and piperylene (hereinafter Pips). DCPD is classified as a C5 chemicals because it is produced by the dimerization of cyclopentadiene (hereinafter CPD). The first driver of C5 chemicals was the development of isoprene rubber (IR). IR has a 1,4-cis structure similar to that of natural rubber, and is mainly used as a tire rubber. 67 % (586,000 t/yr) of the global demand for isoprene in fiscal 2015 is the raw material for isoprene rubber. Global IPM demand is expected to steadily increase going forward, and IPM demand is said to reach 1,600,000 t/yr in fiscal 2030.

As an industrial production method of IPM, extractive distillation of C5 fraction (hereinafter C5F) obtained from ethylene cracker, dehydrogenation of isopentane and/or t-amylene, reaction of isobutylene with formaldehyde (Prins reaction) are known. Among these, the main industrial production process is extractive distillation of C5 fraction, which accounts for 53 % of the total production volume (478,000 t/yr in 2015) of IPM. The block flow diagram of typical extractive distillation process for IPM production, known as GPI (Geon Process of Isoprene), is shown in Fig. 1.

Production of IPM by extractive distillation is overwhelmingly cost competitive in terms of production cost compared to other production processes. But the concentration of IPM in the raw material (C5F) is relatively low, and the remaining components has been returned to ethylene center and has been treated as alternative naphtha and/or fuel. Table 1 shows the typical composition of C5F, and the boiling points of major components are shown in Table 2.

In order to solve this problem, derivatives of Pips and DCPD contained in C5F have been developed. With the increase of demand for the derivatives developed, the extractive distillation process for IPM production has been improved, and now Pips and DCPD are industrially co-produced from the same extractive distillation process.

The purity of Pips produced by the extractive distillation process is approximately 55-65 wt%. In order to improve the purity of Pips, impurities such as amylenes and C5 cyclic compounds such as cyclopentanone (hereinafter CPA) and cyclopentene (hereinafter CPE) must be removed. However, due to the closeness in the boiling point of these impurities and Pips, distillation purification requires a huge distillation column and enormous energy. So it is not economically feasible to purify the Pips by distillation. Therefore, the majority of Pips applications (90 % of the total application) are raw materials for petroleum resin. The fact that amylenes and cyclopentene, which are impurities, function as molecular weight modifiers at the time of petroleum...
resin production is also one of the factors that greatly expanded the application of Pips to petroleum resins.

On the other hand, DCPD is distributed in four grades: low purity (75 wt%), normal (85 wt%), high purity (92 to 95 wt%), and ultrahigh purity (99 wt%). The applications vary greatly depending on the grade. Low-purity products and normal products are used as raw materials for unsaturated polyesters and petroleum resins (including hydrogenated petroleum resins), and account for 69% of DCPD applications (437,000 t/yr in FY 2015). High-purity products are used as raw materials for ethylidene norborne, as vulcanization accelerators for ethylene and propylene rubber (EPDM) and as raw materials for special chemicals. These applications account for 22% of the overall applications (139,000 t/yr in FY 2015).

On the other hand, the use of high purity products is only 9% of the whole, and is used as a raw material of cycloolefin polymer (COP), cycloolefin copolymer (COC), poly-DCPD and reaction injection molding (RIM).

Looking at the applications of C5 chemicals, they are overwhelmingly used as polymer raw materials. It seems that there is a history of preferential development of applications in which a certain amount of usage can be expected, since the production of IPM by extractive distillation results in co-production of DCPD and Pips at the same time in the amounts similar to IPM respectively. The exceptional ones are the fine chemical products from IPM developed by Kuraray Co., Ltd. They developed a wide range of fine chemical products, including synthetic flavors linalool, ionone, citral, etc. Kuraray Co., Ltd. produces IPM by modifying the production method by Prins reaction, which was originally a two-step method, to a one-step method. Since this
production method is a process of producing only IPM, it is possible to adjust production according to the balance of supply and demand. That seems to be the reason that the fine chemical business using IPM as a starting material could be commercially realized.

Raw materials of fine chemicals are generally required to have extremely high purity. When Pips is used as a raw material for fine chemicals, as described above, it is very difficult to improve the purity by distillation. Also, no practical application case of technology for producing Pips by a synthetic method has been found so far, and there is currently no method for economically obtaining high purity Pips.

On the other hand, DCPD can produce a product with a purity of 90% or more by distillation. DCPD can be easily cracked by heat to generate CPD. CPE is a very useful compound in introducing a cyclic C5 unit in organic synthesis and can be easily converted to an alcohol or ketone such as cyclopentanol (hereinafter CPL) or cyclopentanone (hereinafter CPN). Also, the ether can be easily synthesized by addition of alcohol.

CPN is produced worldwide at 26,000 Mt/yr (FY 2015) and is widely used as a raw material for methyl dihydro jasmonate, which is the main component of jasmine note, and as a solvent for electronic materials [14].

On the other hand, cyclopentyl methyl ether (hereinafter CPME) is an entirely new type of ether developed mainly as a solvent for fine organic synthesis [15,16]. The production route of CPN and CPME starting from DCPD is shown in Fig. 2.

This is a production route for high value-added chemicals, which is completely different from conventional DCPD applications. Here, we will introduce mainly the topics related to the catalyst obtained by the technical study for establishing this manufacturing route, and outline the future issues of the entire C5 chemicals.

2. Development of the New Process for Manufacturing CPN from DCPD

CPN is usually produced by a reaction of adipic acid as shown in Scheme 1 [17-19].

In this production method, equimolar amounts of carbon dioxide gas and water are generated. Since CPN has an azetotropic composition with water, the unit energy consumption for purification is relatively large, and loss of CPN itself cannot be ignored. Particularly in the case of electronic material applications, the specification of moisture is very strict, and the loss at the time of purification significantly increases. Moreover, this reaction is generally operated by a batch method. So in order to perform mass production, installation of a large-scale batch reactor is required, and there are many additional facilities which concern on processes other than reaction. Furthermore, if the demand exceeds the production capacity, it may be difficult to enhance the capacity. This is due to the need to install a large number of equipment including ancillary equipment other than the reactor which is the main body. Furthermore, due to the problem of corrosion by adipic acid, corrosion resistant materials must be used for the reactor body, which leads to increased investment in equipment.

In the view of these circumstances, the authors focused on the fact that CPN has a 5-membered ring...
structure, and devised a unique manufacturing route composed of 4 step reactions (Schemes 2 to 5)\(^20\).

As for the production method of CPE by selective hydrogenation of CPD shown in Scheme 3, various methods such as liquid phase batch method and gas phase continuous method have been studied\(^21\)–\(^51\), but only the process by the liquid phase batch method has been applied to commercial production. This process involves holding a large amount of liquid CPD. Liquid CPD is easy to start oligomerization (Diels-Alder reaction) accompanied by heat, and is rapidly progressed when it reaches a certain temperature, which may lead to a runaway reaction. Therefore, in order to ensure safety, a very complex interlock system has been introduced in production facilities. In addition, a Ni-based catalyst is used to maintain a high raw material conversion rate. When the reaction is simply carried out with only the catalyst, hydrogenation proceeds more than necessary and a large amount of CPA is produced. Therefore, in order to achieve high selectivity to CPE, special additives are used in the liquid phase batch process.

On the other hand, in the gas phase continuous method, CPD obtained by the thermal clacking is introduced as it is in the form of gaseous into the selective hydrogenation step without cooling and liquefying. This means that the process of holding a large amount of CPD in liquid can be fundamentally excluded from the process. Therefore, the commercialization of the gas phase continuous method leads to avoid the Diels-Alder reaction above-mentioned, and has very important meaning also from the viewpoint of process safety. A large number of patents have been reported for metal catalysts such as Ni-based and Pd-based hydrogenation catalysts for use in the gas phase continuous process, but they have not been put to commercial use. This is due to the fact that a catalyst life is not enough to withstand commercial operation. The authors investigated catalyst deactivation in gas phase selective hydrogenation to solve this problem\(^52\),\(^53\). A bench scale reactor was used to perform selective hydrogenation of CPD using 0.5 wt% Pd/Al\(_2\)O\(_3\) as a catalyst. When the operation time reached 100 h, a decrease in catalyst activity and an increase in CPE selectivity were observed at the same time as the point of maximum temperature in reaction tube (Hot Spot) disappeared in the temperature distribution in the reaction tube (Figs. 3 and 4)\(^52\).

From the characterization of the spent and virgin catalysts, model experiments with the spent catalyst after regeneration treatment, and the results of continuous operation using feedstocks of different purities, it is revealed that the sulfur-containing impurities in the feedstock are the main cause of the catalyst deactivation. A conceptual diagram of the catalyst deactivation mechanism is shown in Fig. 5\(^53\).

By the way, in the production of CPN by the dehydrogenation reaction of CPL shown in Scheme 5, a fixed bed continuous reaction is adopted and a Cu/ZnO catalyst is used. When a Cu/ZnO catalyst is used for the dehydrogenation reaction, activation treatment by hydrogen reduction is generally performed before the start of the operation, but in the case of CPL dehydrogenation reaction, the hydrogen reduction significantly reduces the selectivity. If CPL dehydrogenation is performed without hydrogen reduction, although some initial induction period exists, it has been confirmed that stable operation can be performed for 300 h with high selectivity after the induction period\(^20\).

Figure 6 shows the time course of catalyst activity and selectivity in continuous operation for 300 h.
The results of catalyst characterization have revealed that the active components present in the form of CuO just after catalyst preparation are reduced to Cu by the CPL dehydrogenation reaction itself. In addition, it is also clear that the reduction of the specific surface area is suppressed when the reaction is performed without the hydrogen reduction, while the specific surface area of the catalyst is significantly reduced when the hydrogen reduction is performed. Furthermore, as a result of examination by model experiments etc., it is clear that the gradual decrease in activity at the initial stage of the operation is caused by the decrease in aldol condensation activity of CPN which is the main side reaction.

3. Development of the Process for Manufacturing CPME

CPME is an entirely new type of ether, developed primarily as a solvent for fine organic synthesis. Unlike tetrahydrofuran, CPME has excellent energy-saving and safety characteristics; facile separation and recovery from water, easy, a small latent heat of vaporization, and negligible generation of peroxide. Therefore, it is an environmentally friendly solvent and

![Fig. 3](image1.png)

**Fig. 3** Change of Temperature Profiles of Reactor in the Selective Hydrogenation of CPD Using DCPD with 95% Purity as Feedstock

![Fig. 4](image2.png)

**Fig. 4** Change of Relative Catalytic Activity (solid line) and Relative Selectivity (broken line) in the Selective Hydrogenation of CPD Using DCPD with 95% Purity as Feedstock

![Fig. 5](image3.png)

**Fig. 5** Schematic Image of Deactivation and Regeneration Mechanisms of Pd/γ-Al₂O₃ Catalyst Based on the Examinations
its safety is suitable for university or college experimental curriculum from the viewpoint of ensuring student safety. The difference in physical properties between CPME and other common ethers is shown in Table 3(54).

Being ethers having these properties, they are widely used as reaction solvents for alkylation, silylation, organometallic reactions, Grignard reactions, optically selective reactions, reduction reactions, polymerizations, etc.(55)–(61). CPME was conventionally produced by a synthesis method using CPL as a starting material (Scheme 6).

Since this reaction is carried out in a batch process, it is necessary to introduce a large-scale reaction kettle for mass production. In addition, the reaction mixture after reaction termination must be washed with water to remove by-produced NaI, but since it is an equimolar reaction, CPME generated and equimolar amount of NaI must be treated as waste. Also, additional equipment for this operation is required. Furthermore, since the raw material CPL is produced by hydrogenating CPN, the raw material is expensive. For these reasons, production of CPME by the reaction of Scheme 6 has not been economically feasible.

Therefore, in order to develop a production method that can withstand mass production, the authors devised a production method by addition reaction of methanol (hereinafter MeOH) shown in Scheme 7 using CPE as a starting material(62).

The authors examined the application of strongly acidic ion exchange resin to gas phase continuous reaction. As a result, it has been found that strongly acidic ion exchange resins exhibit good catalytic performance and are sufficiently applicable to gas phase continuous reactions(62). However, in order to develop a process that can withstand commercial operation, it is necessary to confirm whether the catalyst life is economically sufficient. Therefore, the authors examined the catalyst stability and deactivation factors in the CPME synthesis reaction by fixed bed gas phase continuous reaction catalyzed by ion exchange resin(63). From the results of experiments using an apparatus visualizing the inside of the reaction tube and the results of continuous operation using raw materials with different purities, it becomes clear that C5 diolefins contained in CPE as the raw material are causal substances of the catalyst deactivation.

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**Table 3** Comparison of Physical Properties of CPME and Other Ethers

| Ethers          | Cyclopentyl methyl ether (CPME) | Tetrahydrofuran (THF) | Diethyl ether |
|-----------------|---------------------------------|-----------------------|--------------|
| Chemical structure | ![Chemical Structure](image) | ![Chemical Structure](image) | ![Chemical Structure](image) |
| Density (20 °C) [g cm⁻³] | 0.86 | 0.89 | 0.71 |
| Vapor specific gravity (air = 1) [-] | 3.45 | 2.49 | 2.56 |
| Boiling point [°C] | 106 | 65 | 34.6 |
| Heat of vaporization (at boiling point) [kJ kg⁻¹] | 289.7 | 410.7 | 360.5 |
| Solubility in water (23 °C) [g 100 g⁻¹] | 1.1 | ∞ | 6.5 |
| Water solubility in ether (23 °C) [g 100 g⁻¹] | 0.3 | ∞ | 1.2 |
| Flash point [°C] | -1 | -14.5 | -45 |

![Fig. 6](image) Change of Relative Catalytic Activity (solid circle) and Relative Selectivity (open circle) in the Life Test of Cu₁₂Zn Catalyst without Reduction
with time of the specific yield of CPME and the C5 diolefins leakage are shown in Fig. 9. The length of the colored area of the catalyst bed increased linearly with time on stream (Fig. 8). On the other hand, the relative yield slowly decreased with time on stream, whereas the diolefin leakage increased (Fig. 9), until the operation time reached 21 h, when 86% of the catalyst bed was colored. These observations suggest that polymerization of C5 diolefins proceeded rapidly on the ion exchange resin because of its strong acid cites.

Furthermore, from the fact that the tar deposited on the catalyst is soluble in CPA and the results obtained by pyrolysis gas chromatography, it is concluded that the tar covering the catalyst surface is formed by the polymerization of C5 diolefins. Figure 10 shows a schematic of the assumed catalyst deactivation mechanism.

Based on the findings obtained through these studies, we established a process for removing impurities in the raw material and conducted a final demonstration test of the catalyst life. As a result, the target 1000 h of stable operation was achieved.

4. Future Challenges for the Development of the C5 Chemicals Business

The authors commercialized the CPN manufacturing process, using DCPD as a starting material, in 2003, and the CPME manufacturing process in 2005 respectively. The two processes are still running well and product demand is also showing strong growth.

On the other hand, DCPD, which is a raw material, is produced by the extractive distillation process described in Chap. 1, and the production amount is determined in consideration of the supply and demand balance including IPM and Pips. This is because the production amounts of the three types of C5 chemicals are limited by the concentration in C5F, the raw material, and can be said to be the fate of the distillation process. Therefore, the current situation is that the production volume of C5 chemicals does not always match the demand volume.

Recently, some efforts are under way to overcome this situation. For example, a process of actively controlling the balance between supply and demand of three types of C5 chemicals by utilizing the C5 raffinates which has not been utilized conventionally, and utilizing by-produced hydrogen has been studied. Also, studies on individual unit operations of the process are being conducted. On the other hand, studies are also underway to convert linear and/or
branched C5 hydrocarbons into DCPD\(^{(69)}\). Petrochemical complexes in Japan are mainly composed of ethylene cracker, and use ethylene and other by-products (propylene, aromatic compounds, etc.) to produce various petrochemical products. In ethylene crackers in Japan, almost all the raw materials for producing ethylene are naphtha (some of them are designed to use ethane, propane and butane), and their cost competitiveness largely depends on naphtha price. On the other hand, in the West, there are many crackers that use raw materials other than naphtha. Figure 11 shows the composition of the petrified material in Japan, the US and Europe\(^{(70)}\).

The product distribution of the ethylene crackers is highly dependent on the source. The relationship between raw materials for ethylene production and product distribution is shown in Table 4\(^{(71)}\).

When ethylene is produced using ethane as a raw material, the amount of C5F generated is reduced to about 1/10 as compared to the case where ethylene is produced using naphtha as a raw material. On the other hand, when ethylene is produced using ethane as the raw material, its breakeven point is said to be overwhelmingly better than when ethylene is produced using naphtha as the raw material\(^{(72)}\). In the future, as ethane cracker becomes mainstream, production of C5 chemical by the present extractive distillation may become difficult in terms of securing raw materials. As mentioned in Chap. 1, C5 chemicals produce a wide variety of unique products. Future technological innovation is also expected for the C5 chemicals manufacturing process that supports the basis of variable and attracting C5 derivatives.

5. Conclusion

As part of the comprehensive utilization of C5 chemicals, the authors have been working on the development of methods for producing high value-added products, using DCPD as a starting material. As a result, we commercialized a new production method of CPN and a production method of CPME. As we proceeded with technological development, we were able to obtain various findings on catalyst life in particular. Progress in developing unique products and their manufacturing methods is expected in the future. On the other hand, since DCPD, which is a raw material, is co-produced by IPM and Pips in an extractive distillation process, it is difficult to perfectly match supply and demand. In addition to downstream development of DCPD, there is also a need to strengthen competitiveness through technological innovation in the C5 chemical manufacturing

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Fig. 11 Comparison of Feedstocks for Ethylene among Japan, United States and Europe in 2011

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As the upstream. Through these efforts, I would like to greatly expect further development of the more attractive C5 chemical business.

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要旨

CSケミカルの総合利用を指向したジクロペンタジエンを出発原料とする高付加価値製品の生産技術開発

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CSケミカル（イソプレン、ジクロペンタジエン、ビペリレン）は、ナフサクラッカーで副生するCS留分を原料として、抽出蒸留プロセスにより同時生産される。著者らは、これらCSケミカルの総合利用を目的として、ジクロペンタジエンを出発原料とするジクロベンタンノールの新製造法とジクロペンチルエーテルの製造法を開発した。本報では、技術開発の中で得られた触媒劣化に関する技術的な知見を紹介する。具体的には、ジクロペンタジエンを出発原料とした気相水素化法によるジクロペンテンの製造用触媒の活性低下要因に関する研究、ジクロペンテンを出発原料としたジクロペンチルエーテル合成用触媒の劣化要因に関する研究、ジクロペンタノールを出発原料としたジクロペンタンノール合成用触媒の活性変動要因に関する研究について述べる。また、CSケミカル事業の発展に不可欠なCSケミカル自体の製造技術開発について、最近のトピックスを概観する。

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