

A comparative unit production cost prediction on isomerization by AlCl_3 in comparison with HY(30) zeolite for the synthesis of tetrahydro tricyclopentadiene through a two-step process

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Abstract—In our previous study, we verified that a two-step process was superior to the one-pot process for the manufacture of THTCPD, assuming the pilot-scale production aspect of a comparative economic analysis by using an engineering estimation method to predict the unit manufacturing cost. Among the processes of the two-step process, our study was intended to focus on the isomerization to produce the final THTCPD products with outstanding physical properties including a specific gravity, a heat of combustion, a viscosity and a freezing point. Although HY(30) was used as an isomerization catalyst in the previous study, the catalytic activity of HY(30) did not surpass that of AlCl_3 in terms of isomerization conversion, possibly due to lower *exo*-THTCPD selectivity by Brönsted acid sites of HY(30) than that by Lewis acid sites of AlCl_3 . However, AlCl_3 has some drawbacks of the impossibility for the catalyst regeneration during the manufacturing process due to the difficulty of the catalyst separation and recovery after isomerization, which causes environmental problems and biological toxicity issues due to its corrosivity. Therefore, our study concentrated on catalyst regeneration assuming the real production process in a pilot scale using AlCl_3 in comparison with HY(30). Then, we investigated whether the isomerization catalyst AlCl_3 or HY(30) was more commercially favorable through a comparative unit production cost prediction applying an engineering estimation in this study. In conclusion, the unit production cost for AlCl_3 was lower than that for HY(30) with the fresh catalyst. Conversely, unit production costs for HY(30) with increase in catalysts regeneration number (N) were lower than those for AlCl_3 due to the drastic decrease in the unit material cost of HY(30) unlikely with that of AlCl_3 due to its non-reusability.

Keywords: High-energy-density Fuel, Isomerization, Cycloaddition, Tetrahydrodicyclopentadiene, Lewis Acid Catalyst, Engineering Estimation

INTRODUCTION

High-energy-density fuel (HEDF) with high density and volumetric energy enables us to use more propulsive energy than typical aviation fuels from a petroleum refinery [1-5]. Study of the synthesis of HEDF has become a field of increasing interest, since it can considerably improve the flight distance and loading of aircrafts. Synthesized HEDF is typically hydrocarbon with 3-5 rings, such as THDCPD, THTCPD, and dihydrogenated norboradiene dimer (NBDD). Among them, tetrahydro tricyclopentadiene (THTCPD) has been considered a potential candidate of HEDF since it has high density and energy [1-5]. THTCPD is manufactured in several stages. First, tricyclopentadiene (TCPD) is obtained through a Diels-Alder cycloaddition with dicyclopentadiene (DCPD) and cyclopentadiene (CPD). Then, it is hydrogenated to THTCPD [6-8]. The generated THTCPD after hydrogenation usually exists as an *endo*-

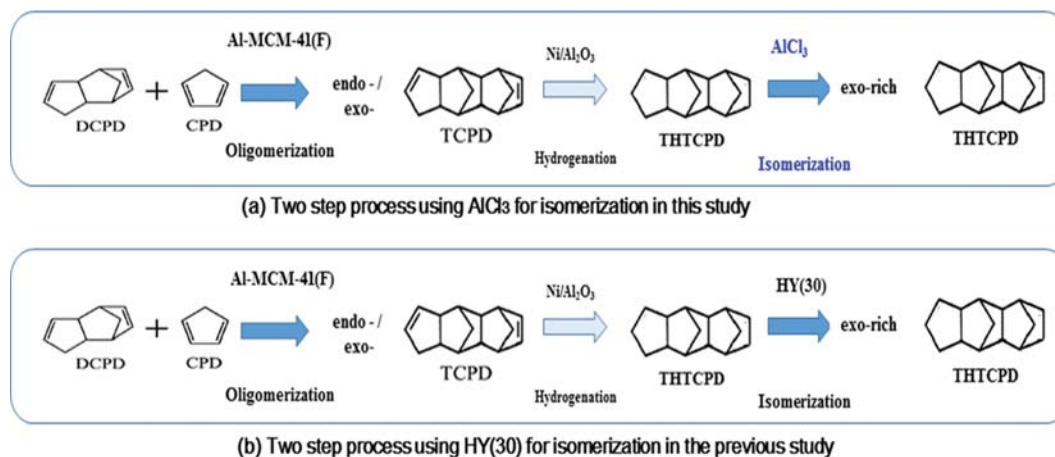
dominant THTCPD, which cannot satisfy the requirements of the liquid fuel, since it is in a wax state at ambient temperature [9]. Thus, *endo*-major THTCPD might go through isomerization to become *exo*-major THTCPD (*exo*-THTCPD) with a liquid form. Aluminum chloride (AlCl_3) is the most commonly used Lewis acid and also one of the most powerful. It finds application in the chemical industry as a catalyst for Friedel-Crafts reactions, both acylations and alkylations. Anhydrous aluminium chloride is a powerful Lewis acid, capable of forming Lewis acid-base adducts with even weak Lewis bases such as benzophenone and mesitylene [13]. AlCl_3 can be also used as an efficient Lewis acid catalyst for isomerization of HEDF such as a THTCPD [10-12]. Several studies have been conducted to isomerize *endo*- to *exo*-THTCPD via an acid-catalyzed reaction using Lewis acid catalysts such as AlCl_3 and AlCl_3 -based ionic liquid (IL) catalysts [10-12]. AlCl_3 generally shows higher isomerization conversion than the zeolite-typed catalysts, since AlCl_3 acts as a Lewis acid in the homogeneous catalytic isomerization in the presence of a halohydrocarbon such as 1,2-dichloroethane (1,2-dichloroethane), which may enable *endo*-THTCPD molecules to contact far more isomerization catalyst molecules than those in heterogeneous catalytic isomerization using a

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Scheme 1. The reaction step of two-step process using AlCl₃ (a) and HY(30) (b) for isomerization.

zeolite such as HY(30) in our previous study [19]. Wang et al. investigated the isomerization route from *endo*- to *exo*-THTCPD for the first time at a relatively low temperature range (0–50 °C) over AlCl₃ catalysts at various concentrations. The isomerization conversion rate of that study was 87% at the reaction temperature condition of 5 °C [12]. Kim et al. reported that the *endo*- to *exo*-THTCPD isomerization was performed in a homogeneous catalytic system over an ionic liquid catalyst using three types of cation precursors with AlCl₃ as the base. The relatively high isomerization conversion of approximately 99.3% was achieved at the reaction temperature of 80 °C using a PHC-based IL catalyst for only ten minutes [11]. These isomerization conversions (87% [12] and 99.3% [11]) were higher than that at 275 °C of our previous study (75.6%) [19]. In our previous study [19], we verified that the two-step process represented a better result than the one-pot process for the manufacture of THTCPD, assuming the pilot-scale production of a comparative economic analysis through an engineering estimation. In the two-step process, our study focused on the isomerization to obtain the final THTCPD products with desirable physical properties, including a specific gravity, a heat of combustion, a viscosity and a freezing point. Although HY(30) was used as an isomerization catalyst for the previous study [19], HY(30) does not have superior catalytic activity to AlCl₃ in terms of isomerization conversion.

The AlCl₃ catalyst has relatively higher catalytic performance of isomerization than the zeolite catalyst due to its homogeneous catalytic reaction, as mentioned in other studies [11,12]. However, it has critical drawbacks, including the inability of catalyst regeneration after isomerization and requirement of post-treatment processes such as incineration to remove AlCl₃ waste and co-solvent recovery due to its corrosive nature, which causes environmental problems and biological toxicity issues such as investigated by several studies [14–17]. To overcome these shortcomings of the AlCl₃-catalyzed isomerization, we tried *endo*- to *exo*-THTCPD isomerization in our previous studies [18,19] using HY(30) as an isomerization catalyst, but the level of isomerization conversion of HY(30) did not surpass that of AlCl₃. Thus, we focused on the catalyst regeneration instead of the catalytic activity in the comparison of AlCl₃ with HY(30). We intended to perform a comparative economic analysis between AlCl₃ and HY(30) applying an engineering estimation

to calculate the unit production (manufacturing) cost in this study.

Comprehensively, the isomerization of *endo*- to *exo*-THTCPD is the key process to determine important physical properties of the finished THTCPD according to ASTM (American Society for Testing and Materials) standards, which include a specific gravity, heat of combustion, viscosity and freezing point [20–23]. Therefore, it was valuable for us to focus the isomerization using AlCl₃ in comparison with HY(30) in our previous study [19] as shown in Scheme 1, since HY(30) shows crucial handicaps: lower isomerization conversion (75.6%) than AlCl₃ (more than 80%) and higher reaction temperature (275 °C) than AlCl₃ (0–50 °C) in the manufacture of THTCPD. However, it was very important for us to consider the catalyst regeneration and requirement of additional processes to remove AlCl₃ waste and recover the co-solvent as critical factors of the real catalytic process and economic feasibility of a pilot-scale production. From the viewpoint of catalyst reusability, we investigated whether the isomerization catalyst AlCl₃ or HY(30) was more favorable and economically efficient using an engineering estimation by calculating the unit production cost in this study.

EXPERIMENTAL

1. Materials

Aluminum chloride (AlCl₃) as a Lewis acid catalyst was obtained from Nippon Light Metal Company Ltd. Commercial dicyclopentadiene (*endo*-DCPD) with 96% purity as a raw material was obtained from Kolon Chemical Co. Ltd; 1,2-dichloroethane as a co-solvent for the THTCPD isomerization on the AlCl₃ catalyst was purchased from DEAJUNG Chemicals & Metals Co. Clay particles for the clay filtration after isomerization with Grade F25X were obtained from BASF Corporation.

2. Catalytic Reactions and Treatment Process

All catalytic reactions were carried out in a Parr autoclave 1 L batch reactor (see Fig. 1). The reaction conditions of cycloaddition (oligomerization) on Al-MCM-41(F) [19] and isomerization using AlCl₃ in this study are described in Table 1. Hydrogenation was performed in the same 1 L batch-type reactor to prepare the test samples to analyze important physical properties with reaction conditions in the same manner of the previous study (temperature 130 °C, reac-



Fig. 1. Parr autoclave 1-L batch reactor and baskets for catalysts inside a batch reactor.



Fig. 2. Apparatus for the clay filtration as an aspirator.

tion time 20 hrs, stirring rate 300 rpm under hydrogen gas, pressure 15 bar, and 28-wt% $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst) [19]. Clay filtration after the completion of THTCPD isomerization was performed using clay particles (Grade F25X) to remove the remaining acidity from the AlCl_3 catalyst and AlCl_3 particle residues for 6-7 hrs through aspiration. The amount of clay particles was 18-20 wt% of the isomeri-

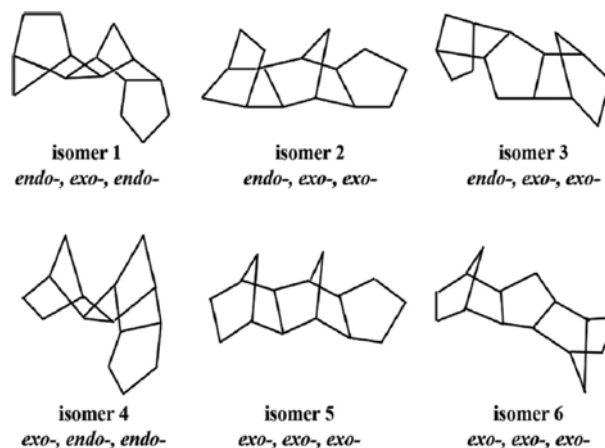


Fig. 3. Possible THTCPD isomers.

zation product (*exo*-THTCPD). The apparatus for clay filtration is described in Fig. 2. Then, vacuum distillation was carried out after the hydrogenation to get the *exo*-major THTCPD samples to check four important physical properties: specific gravity, heat of combustion, viscosity and freezing point as the same vacuum distillation conditions as the previous study (temperature 110-140 °C, stirring rate 500 rpm, and vacuum condition 6.6 mbar) [19]. Four important physical properties of each final sample above mentioned were analyzed based on ASTM D1298, D240, D445, and D2386, respectively [20-23].

3. Product Analysis

The product sample was analyzed by a GC (Agilent 6890) with a flame ionization detector and a capillary column (HP-1, 50 m×0.33 μm). The reactant conversions (*endo*-DCPD and *endo*-THTCPD), and TCPD selectivity can be estimated according to Eqs. (1) and (3) as shown in our previous study [19].

$$\begin{aligned} \text{endo-DCPD conversion (\%)} \\ = \left(1 - \frac{\text{concentration of residual endo-DCPD}}{\text{concentration of initial-DCPD}} \right) \times 100 \end{aligned} \quad (1)$$

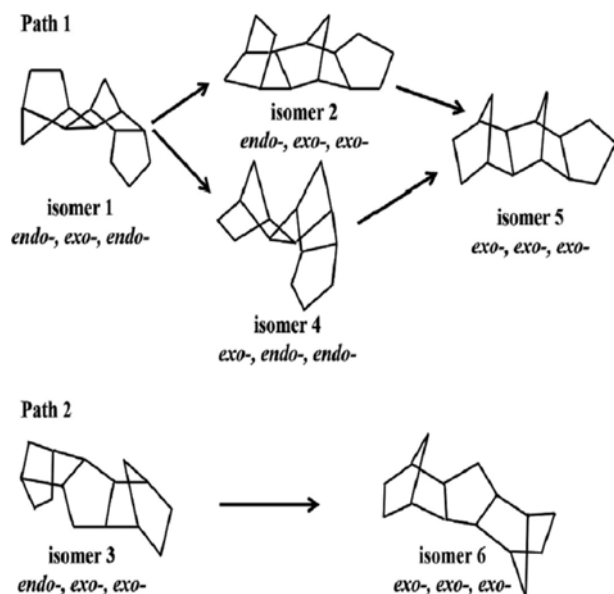
$$\begin{aligned} \text{TCPD selectivity (\%)} \\ = \left(1 - \frac{\text{concentration of endo-TCPD isomer}}{\text{concentration of the total TCPD}} \right) \times 100 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{endo-THTCPD conversion (\%)} \\ = \left(1 - \frac{\text{concentration of final endo-THTCPD isomer}}{\text{concentration of initial endo-THTCPD isomer}} \right) \times 100 \end{aligned} \quad (3)$$

The possible THTCPD isomers and isomerization routes of *endo*-

Table 1. The reaction conditions of cycloaddition on Al-MCM-41(F) and isomerization using AlCl_3

		Reaction condition			Reference	
Process		Catalyst	Temperature (°C)	Time (hrs)	Co-solvent	
Two-step process	Cycloaddition (Oligomerization)	Al-MCM-41 (F) (5 wt%)	175	6	None	[19]
	Isomerization	AlCl ₃ (10 wt%)	30	5	1,2-dichloroethane (200 wt%)	-



Scheme 2. Reaction routes of *endo*- to *exo*-THTCPD.

to *exo*-THTCPD are shown in Fig. 3 and Scheme 2. Isomers 1 and 3 are *endo*-forms prior to isomerization, and isomers 2, 4, 5, and 6 are *exo*-forms after isomerization [18,19].

In this study, reactant conversions (*endo*-DCPD and *endo*-THTCPD), TCPD yield and selectivity could be calculated according to the variations in area ratio of the GC peak for the reactant reduced and GC peak groups for the products newly generated after the cycloaddition and isomerization. We did not apply Eqs. (1) and (3) to the industrial application as done in the previous study [19].

RESULTS AND DISCUSSION

1. Cycloaddition of *endo*-DCPD and CPD on Al-MCM-41(F)

In this study, the experimental results of the cycloaddition of *endo*-DCPD and CPD on Al-MCM-41(F) are cited from those of our previous study [19].

2. Isomerization of THTCPD over AlCl_3 in Comparison with HY(30)

As mentioned in the introduction, we commented on the importance of the isomerization of *endo*- to *exo*-THTCPD and the reason to use AlCl_3 as an isomerization catalyst in this study. Although AlCl_3 has excellent catalytic performance compared to HY(30) in terms of isomerization conversion, it cannot regenerate after isom-

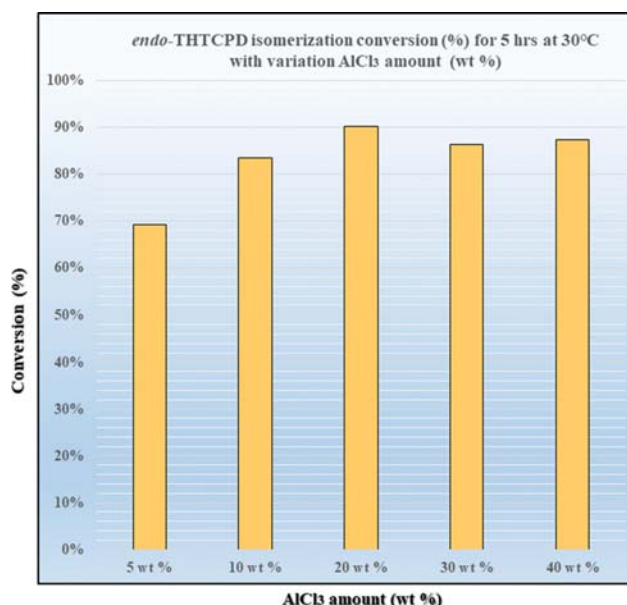


Fig. 4. *endo*-THTCPD isomerization conversion (%) for 5 hrs at 30°C with variation AlCl_3 amount (wt%) with 200 wt% co-solvent.

erization and requires post-treatment processes such as clay filtration to eliminate the residual acidity from AlCl_3 and incineration to remove the AlCl_3 waste and used co-solvent. Thus, we investigated the catalytic performance of various zeolites to study the feasibility as a catalyst for *endo*- to *exo*-THTCPD. Then, we revealed that HY(30) was the best alternative in our previous studies [18,19]. To compare the catalytic activity of AlCl_3 and HY(30) with the same amount of catalyst per *endo*-THTCPD, the isomerization conversion over AlCl_3 on the presence of 200 wt% of the co-solvent was examined at 30°C for 5 hrs with varying AlCl_3 amounts: 5 wt% (69.2%), 10 wt% (83.4%), 20 wt% (90.3%), 30 wt% (86.3%), and 40 wt% (87.4%), as shown in Fig. 4 (see Table 1S in Supporting material). The isomerization conversion of *endo*-THTCPD was the highest (90.3%) at 20 wt% of AlCl_3 . The lower isomerization conversion of THTCPD at 30 wt% (86.3%) and 40 wt% (87.4%) of AlCl_3 appears to be due to the disturbance of the stirring during the isomerization. If HY(30) is used as an isomerization catalyst of *endo*-THTCPD, the best result of *endo*-THTCPD isomerization occurred at 20 wt% of HY(30) in the previous study (87.5%) [18], so it was comparable with that using AlCl_3 in this study. The isomerization conversion of *endo*-THTCPD at 10 wt% of AlCl_3 (86.3%) was also comparable with that with 10 wt% of HY(30) in our previous re-

Table 2. Comparison of *endo*-THTCPD isomerization conversion over AlCl_3 with that over HY(30) in our previous studies at the same weight percent (10 wt% and 20 wt%) of the catalyst, respectively

Catalyst	Isomerization conversion (%)		Reaction condition		
	Amount of the catalyst per <i>endo</i> -THTCPD		Temperature (°C)	Time (hrs)	Co-solvent
	10 wt%	20 wt%			
AlCl_3	83.4	90.3	30	5	1,2-dichloroethane (200 wt%)
HY(30)	75.6 [19]	87.5 [18]	275	6	None

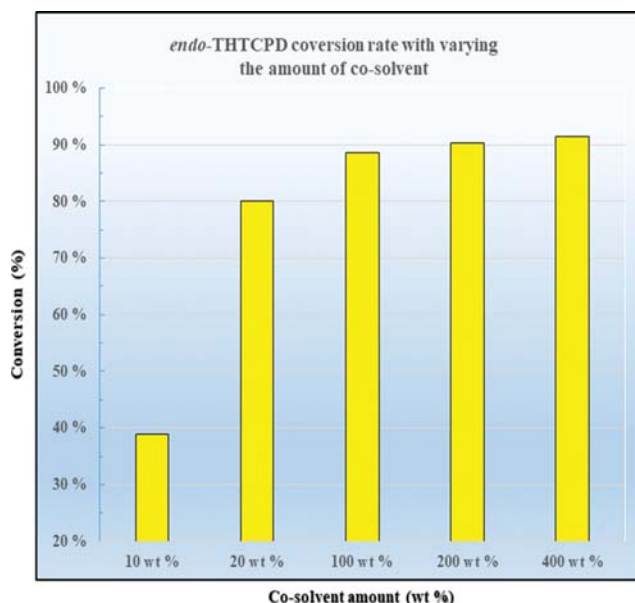


Fig. 5. The effect of a co-solvent amount on isomerization conversion of *endo*-THTCPD over AlCl_3 (20 wt%) for 5 hrs at 30 °C.

search (75.6%) [19]. Table 2 shows the comparison of *endo*-THTCPD isomerization conversion over AlCl_3 and $\text{HY}(30)$ in our previous studies [18,19] at the same weight percent of catalyst (10 wt% and 20 wt%). The *endo*-THTCPD isomerization conversion with AlCl_3 was better than those with $\text{HY}(30)$ in our previous studies [18,19].

Apart from the *endo*-THTCPD isomerization conversion, we must consider whether the AlCl_3 catalyst and co-solvent can be regenerated and recovered by separation from the mixtures of final THTCPD products after the isomerization is finished for a pilot-scale production. Thus, we investigated the *endo*-THTCPD isomerization over AlCl_3 with and without the co-solvent. With the co-solvent, the *endo*-THTCPD isomerization conversion was increased with the increase in co-solvent amount at relatively low temperature condition (30 °C) as shown in Fig. 5 (see Table 2S in Supporting material). The isomerization conversion increased from 38.9% to 80.1%, 88.6%, 90.3%, and 91.5% with proportion to the increase in co-solvent amount from 10 wt% to 20 wt%, 100 wt%, 200 wt%, and 400 wt%, respectively. The increase in isomerization conversion with the increase in co-solvent amount was probably due to the solubility increase of AlCl_3 against the co-solvent.

Without co-solvent, the isomerization temperature must be increased, since the *endo*-THTCPD isomers usually exist in the wax state at 30 °C. Thus, the *endo*-THTCPD isomerization at 30 °C with 20 wt% of AlCl_3 hardly proceeded, since an extremely low fluidity of *endo*-THTCPD isomers probably had a poor contact with AlCl_3 without the co-solvent at 30 °C. For the isomerization going forward, we raised the temperature to 70 °C and examined the isomerization conversion with increasing isomerization times (21 hrs, 43 hrs, and 140 hrs) as shown in Fig. 6 (see Table 3S in Supporting material). It took a considerable amount of time to approach the levels of *endo*-THTCPD isomerization conversion for each reaction time: 21 hrs (54.9%), 43 hrs (64.5%), and 140 hrs (73.8%). For the *endo*-THTCPD isomerization over AlCl_3 , a co-solvent such as an

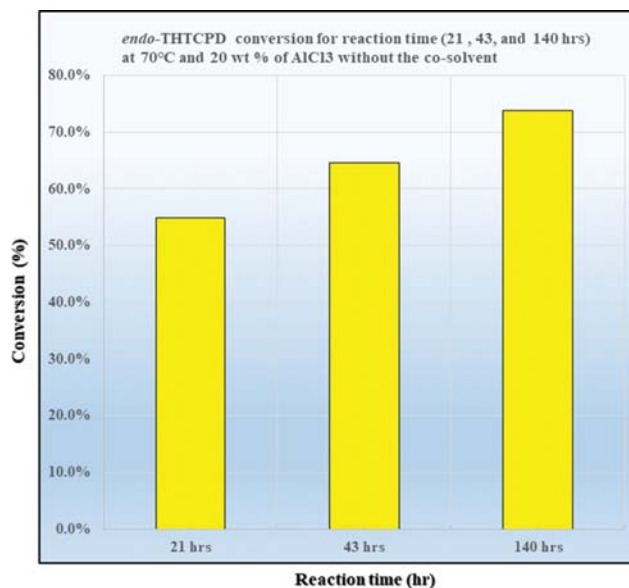


Fig. 6. *endo*-THTCPD isomerization conversion (20 wt% of AlCl_3) with a variation of reaction time (21 hrs, 43 hrs, and 140 hrs) at 70 °C in the absence of the co-solvent.

1,2-dichloroethane should be applied to make the isomerization more efficient in pilot-scale production to drastically reduce the isomerization time, although additional processes after isomerization are required, such as clay filtration to eliminate the residual acidity from AlCl_3 and incineration to remove the AlCl_3 waste and used co-solvent.

In case of *endo*-THTCPD isomerization over $\text{HY}(30)$, we did not have to perform additional processes after isomerization, such as clay filtration and incineration to remove the waste catalysts and used co-solvent, since zeolite catalysts like $\text{HY}(30)$ do not demand a co-solvent during the catalytic isomerization like AlCl_3 . However, the *endo*-THTCPD isomerization temperature over $\text{HY}(30)$ (approximately at or above 275 °C) [18,19] was much higher than that over AlCl_3 (relatively low temperature range of 30–70 °C in this study). To approach the higher *endo*-THTCPD isomerization conversion level on $\text{HY}(30)$ with 20 wt% of the reactant (more than 90%), a considerable time for isomerization is required: approximately 20 hrs at 275 °C or 6 hrs at a relatively higher temperature (300 °C) [18]. As mentioned, it was impossible for us to perform the comparative isomerization conversion between $\text{HY}(30)$ in the previous studies [18,19] and AlCl_3 with or without the co-solvent at the same isomerization temperature condition, since the catalysts have totally different possible isomerization temperature ranges, and the boiling points of AlCl_3 (180 °C) and 1,2-dichloroethane (84 °C) are much lower than the isomerization temperature level for $\text{HY}(30)$ (275–300 °C) [18].

Thus, we compared the isomerization over AlCl_3 with the co-solvent with the isomerization over $\text{HY}(30)$ in our previous study [19]. Then, we selected the isomerization reaction conditions using AlCl_3 to calculate the unit production cost through an engineering estimation assuming a pilot-scale production in this study.

3. Selection of Isomerization Reaction Conditions and Comprehensive Analysis for *endo*-THTCPD Isomerization over AlCl_3

The *endo*-THTCPD isomerization conversion over AlCl_3 with

the co-solvent and HY(30) was the highest when the catalyst was at 20 wt% of the reactant (more than 90%). However, the economic feasibility in case of a practical pilot-scale production, such as how to save the process time, reduce the process, and minimize

harmful damage to workers and the environment. In particular, using AlCl_3 as an *endo*-THTCPD isomerization catalyst, it is crucially important to consider the removal of waste AlCl_3 and use the co-solvent mixture to minimize the harmful damages to the

Table 3. The selected reaction condition on the isomerization of THTCPD over AlCl_3 for a pilot scale production

Reactant	Temperature (°C)	AlCl_3 amount per reactant (wt%)	Reaction time (hr)	Pressure (atm)	Co-solvent amount per reactant (wt%)	Isomerization conversion (%)
<i>endo</i> -THTCPD	30	10	5	atm	1,2-dichloroethane : 200 wt% of the reactant	83.4

Table 4. The measurement results of four major physical properties of the final isomerized THTCPD for the selected reaction condition compared with the previous study

Properties	Measurement results		Remarks
	Isomerization over AlCl_3 in this study	Isomerization over HY(30) in the previous study [19]	
Specific gravity (15.6/15.6 °C)	1.015	1.010	ASTM D4052
Heat of Combustion (MJ/L)	44.66	44.59	ASTM D240
Viscosity (cst, 20 °C)	25.4	21.0	ASTM D445
Freezing point (°C)	−38.0	−27.0	ASTM D2386

	This study	Previous study
Oligomerization	<ul style="list-style-type: none"> ▪ Catalyst : Al-MCM-41(F) (5 wt %) ▪ Reaction temp. : 175 °C ▪ Reaction time : 6 hrs ▪ Pressure : 1 ~ 9 bar ▪ TPCD yield : <u>43.93%</u> 	<ul style="list-style-type: none"> ▪ Catalyst : Al-MCM-41(F) (5 wt %) ▪ Reaction temp. : 175 °C ▪ Reaction time : 6 hrs ▪ Pressure : 1 ~ 9 bar ▪ TPCD yield : <u>43.93%</u>
Hydrogenation	<ul style="list-style-type: none"> ▪ Catalyst : Ni/Al₂O₃ (28 wt %) ▪ Reaction temp. : 130 °C ▪ Reaction time : 20 hrs ▪ Pressure : 15 bar ▪ Conversion rate : 100% 	<ul style="list-style-type: none"> ▪ Catalyst : Ni/Al₂O₃ (28 wt %) ▪ Reaction temp. : 130 °C ▪ Reaction time : 20 hrs ▪ Pressure : 15 bar ▪ Conversion rate : 100%
Isomerization	<ul style="list-style-type: none"> ▪ Catalyst : <u>AlCl_3</u> (10 wt %) ▪ Reaction temp. : 30 °C ▪ Reaction time : 5 hrs ▪ Pressure : <u>ATM</u> ▪ Conversion rate : <u>83.40 %</u> ▪ Co-solvent : 200 wt % of <i>endo</i>-THTCPD 	<ul style="list-style-type: none"> ▪ Catalyst : HY(30) (10 wt %) ▪ Reaction temp. : 275 °C ▪ Reaction time : 6 hrs ▪ Pressure : ATM ▪ Conversion rate : 75.6 % ▪ Co-solvent : Not required
Clay filtration	<ul style="list-style-type: none"> ▪ Clay : 18~20 wt % of THTCPD ▪ Filtration time : 6 ~ 7 hrs 	<ul style="list-style-type: none"> ▪ Clay filtration : Not required
Vacuum distillation	<ul style="list-style-type: none"> ▪ Distillation temp. : 110 ~ 140 °C ▪ Degree of vacuum : 6.6 mbar 	<ul style="list-style-type: none"> ▪ Distillation temp. : 110 ~ 140 °C ▪ Degree of vacuum : 6.6 mbar
Filtration	<ul style="list-style-type: none"> ▪ Filtration prior to inspection and package of the final product 	<ul style="list-style-type: none"> ▪ Filtration prior to inspection and package of the final product
Incineration of waste AlCl_3 mixture	<ul style="list-style-type: none"> ▪ Neutralization of waste AlCl_3 mixture prior to feeding to the incinerator (4 ~ 5 hrs) ▪ Incineration with off gas treatment : temp. > 1,000 °C, 20 ~ 30 kg/hr 	<ul style="list-style-type: none"> ▪ Incineration : Not required

Scheme 3. Comparison of the main process of the two-step process using isomerization over AlCl_3 in this study and previous study using isomerization over HY(30).

workers and environment besides the *endo*-THTCPD isomerization conversion, saving process time, *etc.* Therefore, we selected the reaction conditions for *endo*-THTCPD isomerization over AlCl_3 with the co-solvent of this study and HY(30) of the previous study [19] at the catalyst amount for 10 wt% (instead of 20 wt%), respectively. The selected reaction conditions on *endo*-THTCPD isomerization over AlCl_3 in comparison with those over HY(30) of our recent previous study [19] are represented in Table 3.

The final THTCPD for the selected reaction condition was analyzed through ASTM methods in the same way as we did in the previous study (see Table 4) [19]. As shown in Table 3, the specific gravity and heat of combustion value of this study were similar level

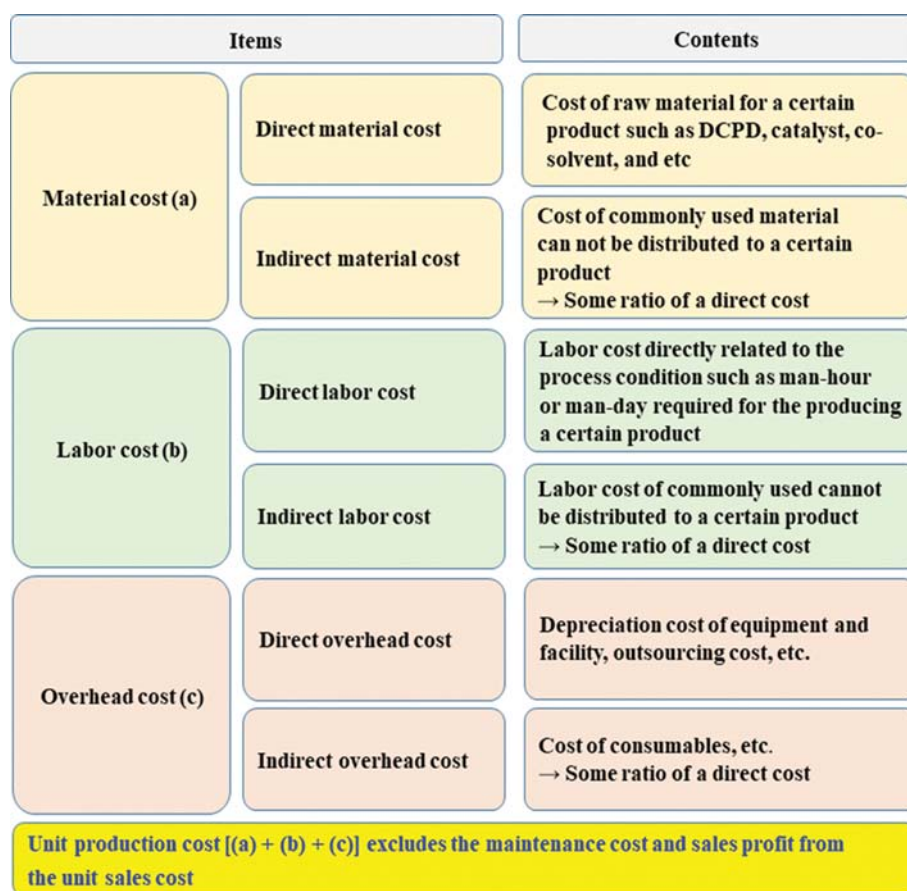
or slightly better than those of the previous study. A freezing point value of this study is more desirable (lower) than that of the previous study [19].

4. The Comparative Unit Production Cost Prediction on Isomerization over AlCl_3 in Comparison with HY(30)

To investigate the realistic possibility for the pilot production of THTCPD, including the two-step process of cycloaddition on Al-MCM-41(F) and isomerization over AlCl_3 with 200 wt% co-solvent of the feedstock, the unit production cost prediction was carried out through an engineering estimation. In our previous study, another two-step process comprised of cycloaddition on Al-MCM-41(F) and isomerization on HY(30) already investigated aspects of the

Table 5. Several advantages and disadvantages for two-step process using isomerization on AlCl_3 in this study compared with two-step process using isomerization over HY(30) of the previous study

Advantage	Disadvantage
<ul style="list-style-type: none"> Milder reaction conditions of oligomerization and isomerization Higher isomerization conversion rate: 83.4% > 75.6% The cost of isomerization catalyst(AlCl_3) is much cheaper than HY(30) of the previous study: 12.27 USD/kg < 292.72 USD/kg 	<ul style="list-style-type: none"> Co-solvent for isomerization is required Additional clay filtration required to removal of the corrosive acidity from AlCl_3 Non-reusable catalyst for isomerization different from a zeolite such as HY(30) Probable environmental issue due to AlCl_3 Additional incinerator required to removal of the used AlCl_3/co-solvent mixtures for resolving environmental issues



Scheme 4. The constitution of the unit production (manufacturing) cost.

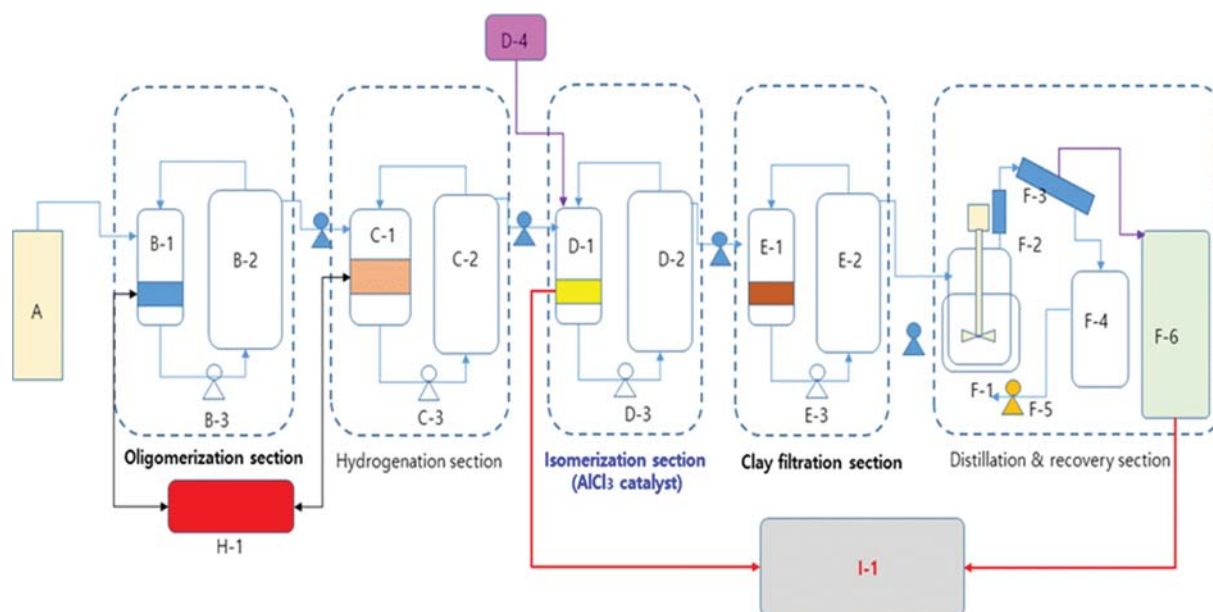
unit production cost prediction using an engineering estimation [19]. The comparison between the main process of the two-step process using AlCl_3 in this study and previous study using HY(30) is given in Scheme 3.

As given in Scheme 3, a two-step process which consists of cyc-

load addition on Al-MCM-41(F) and isomerization on AlCl_3 relatively seems to have several advantages of milder reaction conditions on cycloaddition and isomerization, higher *endo*-THTCPD isomerization conversion in comparison with a two-step process of the previous study [19], while some disadvantages in having to use the

Table 6. The relationship between major raw material cost and the number of catalysts regeneration (N) for two-step process of this study and previous study in the assumptions for the unit production cost estimation for a pilot scale

Process	Raw material	Raw material cost (USD/kg)	Raw material cost variation with N (N=0, 1, 4)	Assumption of TCPD yield (%)
Two-step process of this study	DCPD (feedstock)	5.23	Independent of N	43.93
	Al-MCM-41(F)	327.27	$327.27 \div [N+1]$	
	$\text{Ni/Al}_2\text{O}_3$	136.36	$136.36 \div [N+1]$	
	AlCl_3	12.27	Independent of N	
	1,2-Dichloroethane	8.55	Independent of N	
	Clay	3.32	Independent of N	
Two-step process of previous study [19]	DCPD (feedstock)	5.23	Independent of N	43.93
	Al-MCM-41(F)	327.27	$327.27 \div [N+1]$	
	$\text{Ni/Al}_2\text{O}_3$	136.36	$136.36 \div [N+1]$	
	HY(30)	292.72	$292.72 \div [N+1]$	



A : Feedstock (DCPD)

B-1 : PBR for oligomerization (100L) ; **B-2** : Buffer storage tank for oligomerization (400L) ; **B-3** : Circulation pump for oligomerization

C-1 : PBR for hydrogenation (200L) ; **C-2** : Buffer storage tank for hydrogenation (400L) ; **C-3** : Circulation pump for hydrogenation

D-1 : PBR for isomerization (100L) ; **D-2** : Buffer storage tank for isomerization (800L) ; **D-3** : Circulation pump for isomerization ;

D-4 : Co-solvent (1,2 dichloroethane) feed line

E-1 : PBR for clay filtration (100L) ; **E-2** : Buffer storage tank for clay filtration (800L) ; **E-3** : Circulation pump for clay filtration

F-1 : Vessel for simple distillation with an agitator (200L) ; **F-2** : Distillation column ; **F-3** : Condenser

F-4 : Reservoir for product (THDCPD) (200L) ; **F-5** : Vacuum pump, **F-6** : Reservoir for used co-solvent recovery (800L)

H-1 : Furnace or oven for catalysts regeneration

I-1 : Incinerator and off gas treatment system for used AlCl_3 catalyst and co-solvent

Scheme 5. The conceptual process diagrams for a pilot plant of two-step process using the isomerization over AlCl_3 .

co-solvent for isomerization such as an 1,2-dichloroethane, an additional clay filtration process required due to removal of the corrosive acidity from AlCl_3 after isomerization is completed. Table 5 represents several advantages and disadvantages for the two-step process using isomerization on AlCl_3 in comparison with a two-step process using isomerization on HY(30) in the previous study [19].

It was desirable to do the unit production cost prediction applying an engineering estimation since the two-step process consists of cycloaddition on Al-MCM-41(F) and isomerization over AlCl_3 has several merits and drawbacks in comparison with the two-step process in our previous study as described in Table 5. To undertake the unit production cost estimation, some basic information should be essentially given to predict the unit production cost, applying an engineering estimation in the same way that we had already done in our previous study [19] (see Scheme 4). For the unit production cost prediction, a regeneration of the catalysts is crucial and should be considered for the unit production cost estimation in view of availability for cutting down the production cost. In this study, the unit production cost calculation was carried out with three cases in the same manner as the previous study [19] compared with that of our previous study [19].

Table 6 shows the correlation between major raw material cost and the reuse number of catalyst for this study and previous study. Definite explanation of basic premises in the unit production cost prediction for this study is specified in supporting material of tables (see Table 4S).

Scheme 5 shows the conceptual process diagrams for a pilot plant of the two-step process using the isomerization on AlCl_3 . Designs of the feeding tank for feedstock (DCPD), the packed bed reactors (PBRs) for cycloaddition, isomerization and hydrogenation were applied the same as in our previous study [19]. However, different from the case for the previous study [19], additional equipment such as a clay filtration, a reservoir for the co-solvent recovery, incinerator for used AlCl_3 and co-solvent mixture was required with the larger buffer tanks capacity (800 L) for handling the sufficient amount of co-solvent during the process in comparison with the two-step process of our previous study. AlCl_3 catalysts cannot be reused through calcination in an oven after isomerization, since the reactant (*endo*-THTCPD)/ AlCl_3 mixture becomes a sludge-like state with the co-solvent, which is different from the case of an isomerization HY(30) of the previous study.

The estimated unit production costs for the two-step process using isomerization over AlCl_3 in this study and isomerization over HY(30) of the previous study [19] are shown in Table 7 based upon basic premises (Supporting material (see Table 4S)). As represented in

Table 7, for the fresh catalysts, the unit production cost using AlCl_3 for isomerization (384.72 USD/kg) was approximately 1.88% lower than that of using HY(30) (391.95 USD/kg, [19]). However, the unit production costs estimated to use HY(30) for isomerization became lower (284.33 USD/kg and 202.76 USD/kg) than the corresponding values (320.92 USD/kg and 269.89 USD/kg) to use AlCl_3 in the 1st and 4th regenerations of the catalysts, respectively. This reversion of unit production costs between two-step processes with increasing catalyst regeneration causes a restriction of AlCl_3 regeneration, while HY(30) can be reused several times after calcination, which drastically reduces the processing cost. Additional required equipment to incinerate the used catalyst and the co-solvent and clay filtration become obstacles to decreasing the unit production cost.

In conclusion, the isomerization of *endo*-THTCPD over AlCl_3 has better processing cost using fresh catalysts than the isomerization over HY(30). However, the isomerization of *endo*-THTCPD over HY(30) shows more desirable results of the decrease in processing cost as the catalyst regeneration increases due to the sharper decrease in the unit material cost of HY(30), unlikely with that of AlCl_3 due to its non-reusability for recovery.

CONCLUSION

Bench scale reactions for *endo*-THTCPD isomerization over AlCl_3 were performed to compare the catalytic activity (isomerization conversion) and economic feasibility assuming a pilot-scale production with isomerization over HY(30) in our previous study [19]. Using AlCl_3 as a catalyst for the *endo*-THTCPD isomerization has meaningful merit of a milder reaction temperature (30 °C) and decreases the unit price of the isomerization catalyst (12.27 USD/kg) compared to the corresponding values in our previous study with HY(30) (reaction temperature (275 °C) and unit price of the catalyst (292.72 USD/kg)). It also has some drawbacks of the non-reusable catalyst: the possible environmental damage due to the toxicity of AlCl_3 and additional requirements of the co-solvent, such as 1,2-dichloroethane and processes such as a clay, and filtration to remove the remained acidity from AlCl_3 .

As a result of the bench scale reaction and comparative unit production cost prediction using the engineering estimation, the *endo*-THTCPD isomerization over AlCl_3 had relatively better results of *endo*-THTCPD conversion (83.4%) probably due to better *exo*-THTCPD selectivity by Lewis acid sites of AlCl_3 than that by Brönsted acid sites of HY(30) and unit production cost with the fresh catalysts (384.72 USD/kg) than the corresponding values (*endo*-THTCPD conversion (75.6%) and unit production cost with the fresh catalysts (391.95 USD/kg)) in the previous study [19]. Regard-

Table 7. The unit production costs estimated for two-step processes using isomerization on AlCl_3 and using isomerization on HY(30) for the fresh, 1st regeneration, and 4th regenerated catalysts

Items	Product yield (%)	Unit production cost (USD/kg)*		
		Fresh	1 st Regenerated	4 th Regenerated
Two-step process with AlCl_3	43.93	384.72	320.92	269.89
Two-step process with HY(30) [19]	43.93	391.95	284.33	202.76

*Note: The unit manufacturing cost excludes the maintenance cost and sales profit from the unit sales cost.

ing important physical properties including a specific gravity, heat of combustion, viscosity, and freezing point, the two-step processes in this study showed similar levels in comparison with those of our previous study, except the freezing point. The freezing point of this study (-38°C) was more favorable than that in the previous study (-27°C).

However, unit production costs in this study were higher than those in the previous study when the catalyst regeneration number (N) increased ($320.92\text{ USD/kg} > 284.33\text{ USD/kg}$ ($N=1$), and $269.89\text{ USD/kg} > 202.76\text{ USD/kg}$ ($N=4$)) since the isomerization over AlCl_3 has some limitation in a direct material cost down due to its non-reusable characteristics of the catalyst and additional processes required, such as clay filtration and an incinerator for the used catalyst and co-solvent mixtures. In the event, HY(30) was the better catalyst for *endo*-THTCPD isomerization than AlCl_3 considering not only its activity (conversion) but also the unit production cost as the catalyst regeneration number (N) increased.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

A comparative unit production cost prediction on isomerization by AlCl_3 in comparison with HY(30) zeolite for the synthesis of tetrahydro tricyclopentadiene through a two-step process

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Table 1S. *endo*-THTCPD isomerization conversion (%) for 5 hrs at 30 °C with variation AlCl_3 amount (wt%) with 200 wt% of the co-solvent

Reactant	Temperature (°C)	Co-solvent amount per reactant (wt%)	Catalyst amount per reactant (wt%)	Isomerization conversion (%)
<i>endo</i> -THTCPD	30	200	5	69.2
			10	83.4
			20	90.3
			30	86.3
			40	87.4

Table 2S. The effect of a co-solvent amount on the isomerization conversion of *endo*-THTCPD over AlCl_3 for 5 hrs at 30 °C

Reactant	Catalyst amount per reactant (wt%)	Temperature (°C)	Co-solvent amount per reactant (wt%)	Isomerization conversion (%)
<i>endo</i> -THTCPD	20	30	10	38.9
			20	80.1
			100	88.6
			200	90.3
			400	91.5

Table 3S. *endo*-THTCPD isomerization conversion (20 wt% of AlCl_3) with a variation of reaction time (21 hrs, 43 hrs, and 140 hrs) at 70 °C in the absence of the co-solvent

Reactant	Temperature (°C)	Catalyst amount per reactant (wt%)	Reaction time (hrs)	Isomerization conversion (%)
<i>endo</i> -THTCPD	70	20	21	54.9
			43	64.5
			140	73.8

Table 4S. The basic premises for calculating the unit production cost estimation of the two step process comprised of cycloaddition on Al-MCM-41(F) and isomerization on AlCl_3 with the fresh and regeneration of the catalysts

Items		Premises for the estimation of unit manufacturing cost of the two step process in a pilot scale			
Yield & conversion	Product yield (THTCPD)	Equivalent to the yield of the cycloaddition (TCPD) over the Al-MCM-41(F) of the scale-up test result with 43.93%.			
	Isomerization conversion	Equivalent to the conversion of the isomerization (THTCPD) over an AlCl_3 test result in bench scale (1 L) with 83.40%.			
Regeneration of the catalysts		Regeneration number (N) of catalysts was assumed to be one and four for each catalyst. TCPD yield and THTCPD conversion for regeneration were equivalent to those of the fresh catalysts.			
Unit cost of raw material & catalysts estimated	DCPD (feedstock)	5.23 USD/kg			
	Al-MCM-41(F)	327.27 USD/kg/[N+1] (5 wt% of the feedstock applied)			
	$\text{Ni}/\text{Al}_2\text{O}_3$	136.36 USD/kg/[N+1] (28-30 wt% of the feedstock applied)			
	AlCl_3	12.27 USD/kg (10 wt% of the feedstock applied)			
	1,2-Dichloroethane	8.55 USD/kg (200 wt% of the feedstock applied)			
	Clay	3.32 USD/kg (10 wt% of the feedstock applied)			
Process condition	Cycloaddition (Oligomerization) in PBR	Temperature	Pressure	Time	Space velocity
		175 °C	1-9 bar	~6 h	0.6-0.7 h ⁻¹
	Hydrogenation in PBR	Temperature	Pressure	Time	Space velocity
		125-130 °C	15-20 bar	20-40 hrs	0.7-0.9 hr ⁻¹
	Isomerization in PBR	Temperature	Pressure	Time	Space velocity
		~30 °C	atm	~5 hrs	0.6-0.7 hr ⁻¹
	Clay filtration in PBR	Temperature	Pressure	Time	Space velocity
		~30 °C	atm	~7 hrs	0.6-0.7 hr ⁻¹
	Distillation	Temperature	Vacuum	Time	Stirring rate
		50-250 °C	50-80 mbar	TBD	150 RPM
	Regeneration of the catalysts	Temperature	Pressure	Time	Regeneration No. (N)
		500-550 °C	1 bar	10-12 hrs	N=0, 1, 4
Equipment specification for a pilot production	PBR for cycloaddition	100-L capacity equipped with the 400-L buffer storage tank			
	PBR for hydrogenation	200 L capacity equipped with the 400 L buffer storage tank			
	PBR for isomerization	100 L capacity equipped with the 800 L buffer storage tank			
	PBR for clay filtration	100 L capacity equipped with the 800 L buffer storage tank			
	Simple distillation vessel	200 L capacity equipped with the agitator and vacuum pump			
	Distillation column	Diameter (150 mm)×L (1,000 mm) packing with glass			
	Distillation Condenser	Diameter (220 mm)×L (1,400 mm) with heat transfer area 3 m ²			
	Vacuum pump	Rotary screw type, Flow rate 2,500 LPM			
	Furnace or oven	High temperature furnace for the catalysts regeneration			
	Incinerator for used AlCl_3 and co-solvent	20-30 kg/hr incineration capacity equipped with the off-gas treatment system			
	Reservoir for used co-solvent	800 L capacity connected to the incinerator for AlCl_3 and co-solvent			