Research on optimization of the synthesis *endo*-tetrahydrodicyclopentadiene from dicyclopentadiene

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ABSTRACT

Endo-tetrahydrodicyclopentadiene (endo-THDCPD) serves as a crucial precursor in the synthesis of exo-tetrahydrodicyclopentadiene (exo-THDCPD), the primary component of JP-10, a single-component hydrocarbon fuel utilized for high-performance cruise missiles, rockets, and supersonic aircraft propulsion. Endo-THDCPD was synthesized through the hydrogenation reaction of dicyclopentadiene (DCPD) using a Pd/C catalyst. In this study, optimal conditions for the hydrogenation process have been thoroughly investigated. Specifically, the reaction is carried out in n-hexane solvent at a reaction temperature of 90 °C, a total H_2 *pressure of 0.5 MPa, a reaction time of 4 hours, and a catalyst/DCPD mass ratio of 10%.*

Keywords: *Endo*-tetrahydrodicyclopentadiene; Dicyclopentadiene; Hydrogenation; *Endo*-THDCPD; DCPD.

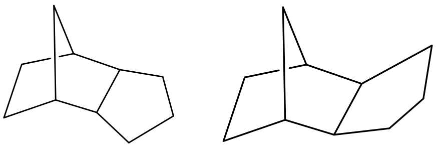
1. INTRODUCTION

In recent decades, scientists have consistently endeavored to increase the flight range of vehicles such as airplanes, missiles, and spacecraft. A straightforward and effective approach to achieving this goal is to improve the volumetric energy density of fuels. Fuels with high energy density can provide more thrust energy than conventional refined fuels, thereby enhancing range, payload capacity, and flight speed, which is particularly beneficial for rockets and missiles with limited mass capacity [1]. Many high-energy liquid fuels are single compounds synthesized through chemical methods. One of the fuels that has recently been researched and gained attention is JP-10.

JP-10 (*exo*-tetrahydrodicyclopentadiene) is a crucial fuel in military applications, particularly in Ramjet engines [2]. The main advantages of JP-10 are its high volumetric energy density, low freezing point, and high flash point. JP-10 is a single-component fuel because it primarily consists of *exo*-THDCPD [3]. JP-10 has been widely used in ground-launched, sea-launched, and air-launched missiles. This fuel has been used to extend the range of cruise missiles [4, 5].

JP-10 is synthesized using *endo*-dicyclopentadiene (*endo*-DCPD) as the raw material [6]. The synthesis process involves hydrogenating DCPD to tetrahydrodicyclopentadiene (THDCPD) and then isomerizing the *endo* configuration to the *exo* configuration. In this process, the hydrogenation reaction is crucial because unsaturated compounds can lead to coke deposition and catalyst deactivation in the downstream isomerization reaction [7-10]. Additionally, the synthesis of *endo*-THDCPD directly influences the yield of *exo*-THDCPD. Moreover, the hydrogenation process requires stringent conditions regarding both the reaction environment and the catalyst used [11].

Furthermore, *endo*-THDCPD, a saturated bicyclic hydrocarbon, is characterized by its high thermal stability, low reactivity, and compact molecular structure (figure 1). These properties make it a valuable compound in various high-performance applications [12]. Especially in material science research, its incorporation into polymer matrices and composite materials enhances their mechanical properties and thermal stability, making it suitable for advanced materials used in aerospace, automotive, and defense industries [13]. Additionally, the compound serves as an important intermediate in synthetic organic chemistry, providing a stable framework for constructing complex molecules and facilitating the development of new synthetic methodologies [14].



***endo*-THDCDP** ***exo*-THDCPD**

Figure 1. *Structural formula of endo-THDCPD and exo-THDCPD.*

Therefore, research on the synthesis of *endo*-THDCDP has garnered attention from scientists worldwide [15]. One of the recent focal points in the synthesis of *endo*-THDCPD is the hydrogenation process of DCPD.

In this paper, we studied the modulation of *endo*-THDCPD through the hydrogenation reaction of DCPD using a Pd/C catalyst. Specifically, our research focuses on optimizing conditions for the hydrogenation process, such as reaction temperature, reaction time, starting material concentration, and catalyst ratio, and analyses the fundamental properties, as well as the ^{1}H-NMR, ^{13}C-NMR, GC spectrum of the synthesized *endo*-THDCPD product.

2. EXPERIMENTAL SECTION

2.1. Materials

The chemicals used include palladium on carbon (Pd/C, 10% Pd), dicyclopentadiene, cyclohexane, *n*-hexane, dichloromethane, ethanol, and *n*-heptane of AR grade from Sigma Aldrich. The H_2 gas with a purity of 99.999% was supplied by Novigas Company.

2.2. Characterization techniques

All reactions were performed in a high-pressure reactor (PARR) with controlled temperature and stirring rate. Reaction progress was monitored by thin-layer chromatography (TLC) on 0.25 mm Merck silica gel plates (60 F254). The eluents were mixtures of *n*-hexane and ethyl acetate (EtOAc), and detection was achieved using UV light or $KMnO_4$ staining solution. Infrared spectra were recorded on Spectrum Two, Perkin Elmer, at the Le Quy Don Technical University. The nuclear magnetic resonance (NMR) spectra have been recorded with Brucker Avance 500 MHz spectrometers at the Institute of Chemistry, Vietnam Academy of Science and Technology. ^{1}H-NMR spectra: δ (H) are given in ppm relative to tetramethylsilane (TMS), using δ ($CDCl_3$) = 7.26 ppm as an internal reference. ^{13}C- NMR spectra: δ (C) are given in ppm relative to TMS, using δ ($CDCl_3$) = 77.0 ppm as an internal reference. Gas chromatography-mass spectrometry (GC-MS) analysis was performed on a GC-456 instrument at the University of Science. The conversion and yield of the reaction were calculated as follows:

Conversion (%): [1 – (amount of remaining DCPD/ initial amount DCPD) x 100%.

Yield (%): [amount of formed *endo*-THDCPD/ amount of theoretical *endo*-THDCPD] x 100%.

2.3. Synthesis *endo*-THDCPD

100 g of DCPD, 300 g of *n*-hexane, and 10 g of Pd/C were added to the PARR reactor. The lid of the reaction vessel was then closed, and N_2 gas was introduced for 3 minutes to purge all the air from the vessel. Subsequently, the H_2 gas valve was opened, the gas release valve was closed, and the lid of the reaction vessel was secured tightly. The mixture was stirred at 500 rpm and heated to 90 °C. The H_2 gas was continually released until the pressure reached 5 atm, and the reaction was maintained for 4 hours. After the reaction, the H_2 gas supply was turned off, and the heating was stopped, allowing the vessel to cool to room temperature. The air release valve was opened to return the pressure to atmospheric level. The mixture was then filtered to recover the Pd/C catalyst,

and the solvent was removed by vacuum evaporation to obtain a white solid (*endo*-THDCPD). The solid was recrystallized from dichloromethane. The reaction process was controlled and monitored by TLC, and the composition of substances after the reaction was determined by GC-MS.

3. RESULTS AND DISCUSSION

3.1. Effect of hydrogenation time on the conversion of dicyclopentadiene (DCPD)

The hydrogenation reaction of DCPD to form *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD) using a Pd/C catalyst is significantly influenced by the reaction time. To evaluate the conversion of DCPD, the research group conducted the hydrogenation reaction over periods ranging from 1 to 5 hours. Samples were taken at 1-hour, 2-hour, 3-hour, 4-hour, and 5-hour intervals and analyzed using TLC with a solvent system of *n*-hexane and ethyl acetate (1:1 volume ratio). The TLC results are shown in figure 2.

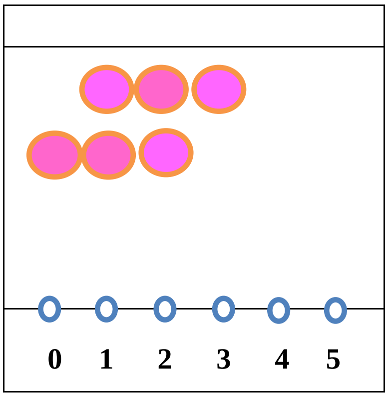
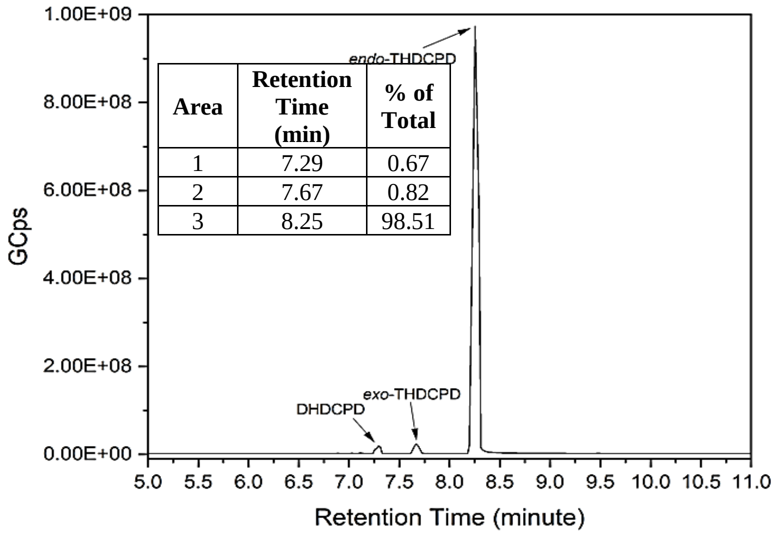


Figure 2. *TLC of starting materials and products according to reaction time.*

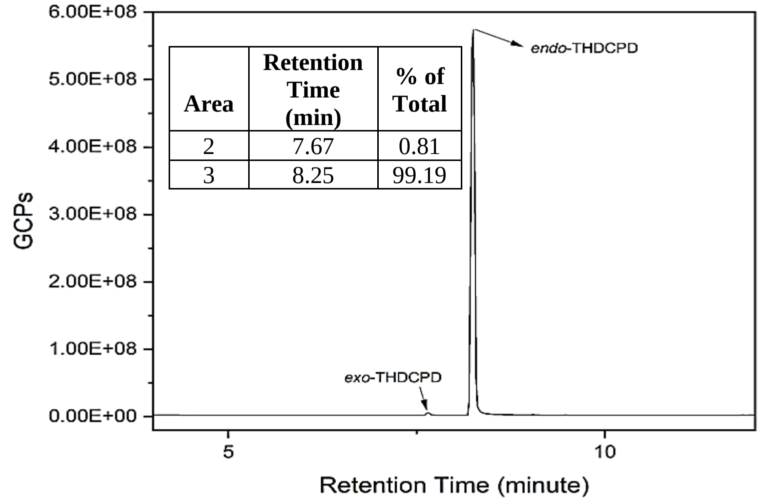
Based on the TLC results, the spot at $R_f = 0.72$ corresponds to the initial DCPD, while the spot at $R_f = 0.81$ indicates the presence of dihydrodicyclopentadiene (DHDCPD), a partially hydrogenated product. Neither *endo*-THDCPD nor *exo*-THDCPD spots were observed on the TLC plate. This suggests that after approximately 3 hours, DCPD was almost completely converted, with residual DHDCPD remaining. By the 4-hour mark, no spots were visible on the TLC plate, indicating a complete conversion of DCPD to *endo*-THDCPD.



Area	Retention Time (min)	% of Total
1	7.29	0.67
2	7.67	0.82
3	8.25	98.51

Figure 3. *GC spectrum of the products after 4 hours of hydrogenation reaction.*

To validate these observations, a sample taken at the 4-hour mark was subjected to gas chromatography analysis. The chromatogram revealed three distinct peaks at retention times of 7.29, 7.67, and 8.25 minutes, corresponding to DHDCPD, *exo*-THDCPD, and *endo*-THDCPD, respectively (figure 3). Importantly, *endo*-THDCPD constituted 98.5% of the total product mixture.



Area	Retention Time (min)	% of Total
2	7.67	0.81
3	8.25	99.19

Figure 4. *GC spectrum of endo-THDCPD after recrystallization.*

After hydrogenation and catalytic removal, the product was recrystallized using dichloromethane as the solvent, followed by subsequent gas chromatography analysis. The results are depicted in figure 4.

From the results shown in figure 4, it is evident that the recrystallized product consists of two compounds: *endo*-THDCPD, which exhibits a purity of 99.2%, and *exo*-THDCPD, present at a concentration of 0.8%. Based on TLC and GC monitoring, it is concluded that the optimal reaction time for the hydrogenation process is 4 hours.

3.2. Effect of hydrogenation reaction temperature on *endo*-THDCPD synthesis yield

Hydrogenation reactions are generally exothermic, and consequently, temperature plays a crucial role in determining the yield of *endo*-THDCPD synthesis. To assess the temperature's influence, the research group conducted the hydrogenation reaction at various temperatures over a period of 4 hours. Detailed findings are presented in figure 5.

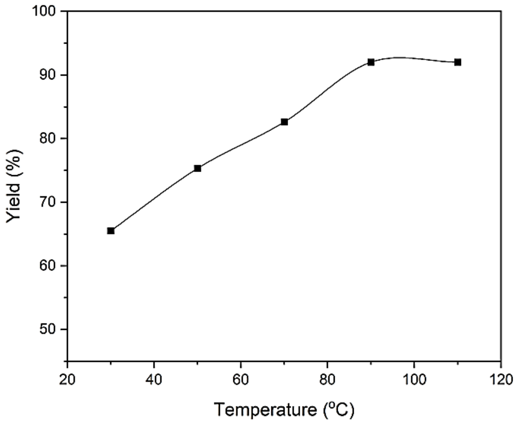


Figure 5. *Effect of temperature on endo-THDCPD synthesis efficiency.*

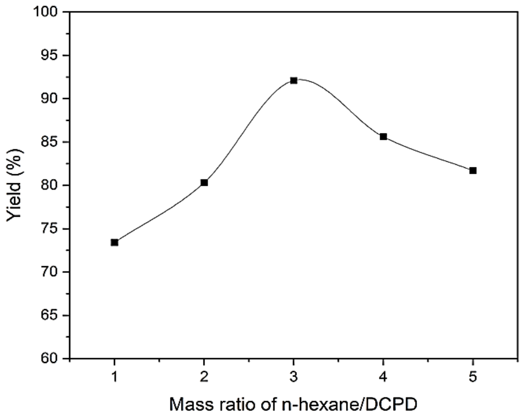


Figure 6. *Effect of the amount of n-hexane solvent on the synthesis efficiency of endo-THDCPD.*

The increase in reaction temperature from 30 °C to 90 °C enhances the synthesis yield due to higher DCPD conversion rates (figure 5). However, further temperature elevation shows a plateau and a slight decline in yield, attributed to the partial conversion of *endo*-THDCPD to *exo*-THDCPD. Therefore, the optimal temperature for the hydrogenation reaction is determined to be 90 °C.

3.3. Effect of solvents on *endo*-THDCPD *endo*-THDCPD synthesis yield

The hydrogenation of DCPD is a heterogeneous reaction involving solid DCPD, gaseous H_2, and solid Pd/C catalyst. Therefore, the use of a reaction solvent is essential for efficient reaction kinetics. To optimize the choice of solvent, the researchers conducted hydrogenation at 90 °C for 4 hours using various solvents: cyclohexane, dichloromethane, ethanol, *n*-hexane, and *n*-heptane. The results, illustrating the impact of different solvents on the yield of *endo*-THDCPD, are summarized in table 1.

Table 1. *The influence of solvents on the synthesis efficiency of endo-THDCPD.*

No.	Solvents	Yield (%)
1	Cyclohexane	81.5
2	*n*-heptane	91.5
3	Dichloromethane	85.6
4	*n*-hexane	92.1
5	Ethanol	79.3

From the data in table 1, it is evident that all solvents used facilitate the conversion of DCPD to *endo*-THDCPD, with *n*-hexane and *n*-heptane yielding higher synthesis efficiencies than other solvents. Due to the low polarity of both DCPD and *endo*-THDCPD, they exhibit good solubility in low polar solvents such as *n*-hexane, and *n*-heptane. However, due to the higher boiling point of n-heptane (98 °C), its use complicates vacuum evaporation, making it more energy-intensive. Therefore, opting for *n*-hexane as the solvent for the hydrogenation reaction is deemed optimal.

To assess the impact of varying amounts of *n*-hexane on synthesis efficiency, the research team conducted the hydrogenation reaction for 4 hours at 90 °C, adjusting the quantity of *n*-hexane. Specific findings and details are illustrated in figure 6.

From figure 6, it is observed that increasing the ratio of solvent to DCPD from 1 to 3 results in a yield enhancement of more than 20%. However, further increases in the ratio, to 4 and 5, lead to decreased yields. This phenomenon can be attributed to the following reasons: at lower solvent ratios, the limited solubility of the solvent with DCPD hinders the reaction kinetics. On the other hand, with higher solvent ratios, the reduced interaction between DCPD and H_2 results in slower reaction rates. Based on these observations, the optimal ratio of *n*-hexane to DCPD is determined to be 3:1.

3.4. Study on the effect of catalyst ratio on *endo*-THDCPD yield

Pd/C catalyst is widely employed in hydrogenation reactions for its effectiveness. The quantity of catalyst applied typically hinges on the nature of the reactant precursor. In this investigation, we explored the influence of catalyst loading on the yield of endo-THDCPD synthesis. The hydrogenation reaction was carried out for 4 hours at 90 °C in *n*-hexane as the solvent, with variations in catalyst loading ranging from 1% to 20% relative to DCPD. The outcomes illustrating the effect of the catalyst loading ratio are depicted in figure 7.

It has been noted that the highest yield is attained with a catalyst loading of 10%. Further increasing the catalyst loading beyond this point does not lead to additional improvement in the synthesis yield. Hence, it can be inferred that the reaction reaches equilibrium with a catalyst loading of 10%.

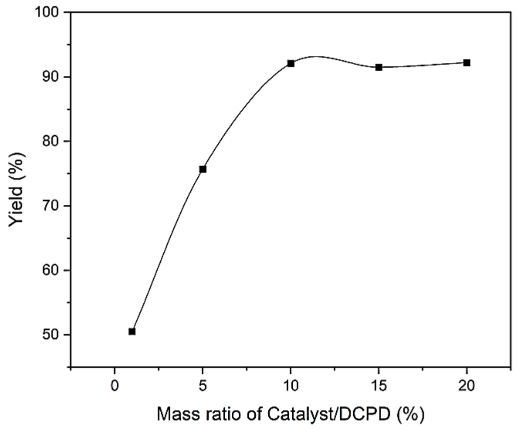


Figure 7. *The influence of Pd/C amount on endo-THDCPD synthesis efficiency.*

3.5. Basic properties and spectroscopic data of *endo*-THDCPD

The synthesized *endo*-THDCPD is a white solid with a melting point of 75 °C, soluble in non-polar organic solvents such as cyclohexane and *n*-hexane. The product was characterized and evaluated using FTIR, NMR, and GC spectroscopy.

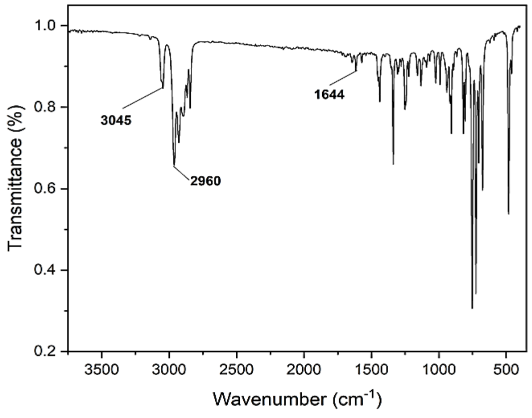


Figure 8. *FTIR spectrum of DCPD.*

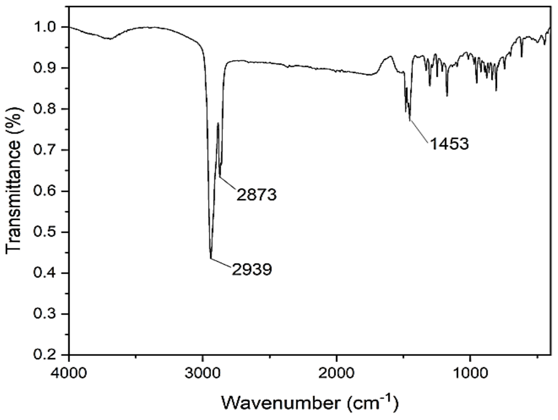


Figure 9. *FTIR spectrum of endo-THDCPD.*

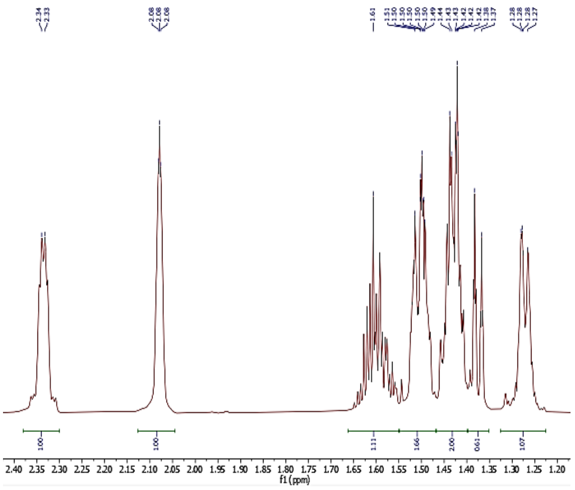


Figure 10. *^{1}H-NMR spectrum of endo-THDCPD.*

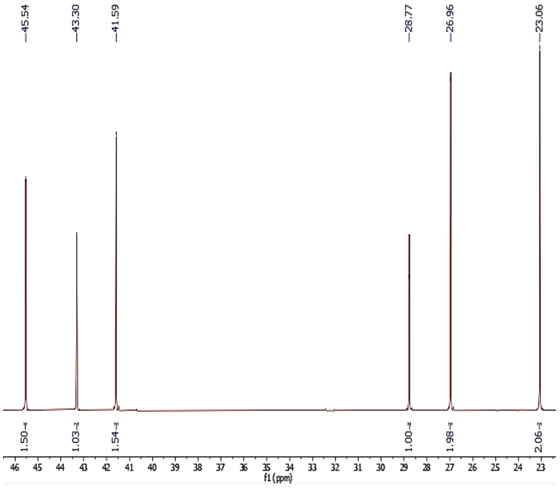


Figure 11. *^{13}C-NMR spectrum of endo-THDCPD.*

Based on the FTIR data of *endo*-THDCPD (figure 9), characteristic peaks corresponding to the $–CH_2$ functional group were identified. Specifically, the stretching vibrations (2939-2873 cm^{-1}) and deformation vibrations (1484-550 cm^{-1}) of the $–CH_2$ group were observed. A comparison of the FTIR spectra between the starting material DCPD (figure 8) and *endo*-THDCPD (figure 9) revealed significant differences. Specifically, the absence of the peak at 1644 cm^{-1} in the *endo*-THDCPD spectrum, which corresponds to the stretching vibration of the C=C bond in DCPD, confirms the complete conversion of DCPD to *endo*-THDCPD. The stretching vibration of the =C-H group in DCPD (3045-2960 cm^{-1}) appears at higher wave numbers compared to the $–CH_2$ group in *endo*-THDCPD (2939-2873 cm^{-1}). Additionally, the vibration range of 100-650 cm^{-1}, characteristic of the deformation vibrations of the =C-H group in DCPD, is weak or absent in the spectrum of *endo*-THDCPD. These observations collectively confirm the successful conversion of DCPD to *endo*-THDCPD, as indicated by the changes in the FTIR spectra.

Furthermore, the ^{1}H and ^{13}C-NMR spectroscopy data (figures 10, 11) provided a comprehensive analysis of all protons and carbon atoms within the *endo*-THDCPD molecule, as detailed in table 2.

Table 2. *Analysis of ^{1}H and ^{13}C-NMR spectral data of endo-THDCPD.*

No.	**δ_H (ppm)**	**δ_C (ppm)**	**Groups**
1	1.42; 1.28	23.06	CH_2
2	2.08	41.57	CH
3	1.42; 1.28	23.07	CH_2
4	2.08	41.59	CH
5	2.34	45.54	CH
6	2.34	45.54	CH
7	1.49; 1.43	26.96	CH_2
8	1.49; 1.43	26.96	CH_2
9	1.60	28.77	CH_2
10	1.50; 1.37	43.30	CH_2

The GC spectrum (figure 4) shows distinct peaks corresponding to *endo*-THDCPD with retention times of 8.255 minutes and a purity of 99.2%.

4. CONCLUSIONS

Endo-THDCPD was successfully synthesized through the hydrogenation of DCPD, achieving a conversion rate of 98.5% and a synthesis efficiency of 92.3%. The optimal reaction conditions were rigorously determined such as the hydrogenation was conducted in *n*-hexane solvent at 90 °C for 4 hours, with a mass ratio of Pd/C to DCPD to *n*-hexane set at 0.1:1:3. Furthermore, comprehensive analysis using FTIR, NMR, and GC spectra confirmed the high purity of the synthesized *endo*-THDCPD product. These spectroscopic techniques provided detailed insights into the chemical structure and composition of the final product, validating the success of the synthesis process under the optimized reaction conditions.

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TÓM TẮT

Nghiên cứu tối ưu hóa tổng hợp endo-tetrahydrodicyclopentadiene từ dicyclopentadiene

Endo-tetrahydrodicyclopentadiene (endo-THDCPD) đóng vai trò là tiền chất quan trọng trong quá trình tổng hợp exo-tetrahydrodicyclopentadiene, là thành phần chính của nhiên liệu JP-10, một loại nhiên liệu hydrocarbon một thành phần được sử dụng cho tên lửa hành trình, tên lửa và động cơ đẩy máy bay siêu thanh hiệu suất cao. Endo-THDCPD được tổng hợp thông qua phản ứng hydro hóa dicyclopentadiene (DCPD) sử dụng chất xúc tác Pd/C. Trong nghiên cứu này, các điều kiện tối ưu cho quá trình hydro hóa đã được nghiên cứu kỹ lưỡng. Cụ thể, phản ứng được thực hiện trong dung môi n-hexane ở nhiệt độ phản ứng 90 °C, áp suất H_2 là 0,5 MPa, thời gian phản ứng là 4 giờ và tỷ lệ khối lượng chất xúc tác/DCPD là 10%.

Từ khóa: *Endo*-tetrahydrodicyclopentadiene; Dicyclopentadiene; Hydro hóa; *Endo*-THDCPD; DCPD.