Technology Aspects of the Hydrogenation of Cyclopentadiene to Cyclopentene

Jiří Krupka*1, Josef Pašek1, Vlastimil Fíla2, Jan Patera1, Zdeněk Severa1

1 Department of Organic Technology, Institute of Chemical Technology, Technická 5, 166 28 Praha 6, Czech Republic, e-mail: Jiri.Krupka@vscht.cz
2 Department of Inorganic Technology, Institute of Chemical Technology, Technická 5, 166 28 Praha 6, Czech Republic

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Abstract. The liquid phase partial hydrogenation of cyclopentadiene over the catalyst Pd/Al₂O₃ was studied. Effects of the type of the hydrogenation reactor, reaction pressure, reaction temperature, and diluting medium on the reaction selectivity to cyclopentene in the area of higher conversion of cyclopentadiene were investigated. Various alternatives of the hydrogenation arrangement were discussed concerning their feasibility to be applied to an industrial process producing highly pure cyclopentene. A short review on the cyclopentene utilisation forms a part of the paper as well.

Key words: cyclopentene, cyclopentadiene hydrogenation, selectivity, mass transfer effect, batch slurry reactor, trickle-bed reactor, Berty-type reactor

Introduction

The current trend is to process crude oil more and more completely and deeply to obtain products having maximum added and utility value. Steam cracking units, which process heavier hydrocarbon feedstocks, provide, besides basic olefins, a significant amount of pyrolysis condensates, which are attractive raw material for the production of valuable products. Diolefines contained in pyrolysis condensates, including cyclopentadiene (CPD), belong to the most important ones. Cyclopentadiene may be relatively easily isolated in the form of its dimer – dicyclopentadiene (DCPD). CPD/DCPD is a desired petrochemical raw material having a broader use in various branches of chemical industry [1]. One of the many opportunities for the further evaluation of cyclopentadiene is to hydrogenate it selectively to cyclopentene – to the commodity with a very prospective future due to its use either in the production of specialty chemicals and either in the production of special polymers.

![Reaction scheme 1. The cyclopentadiene hydrogenation](image)

The cyclopentene (CPEN) production is at the order of kilotonnes. It finds its use in the production of polypentenamers. These polymers are prepared through the ring opening metathesis polymerization (ROMP) of cyclopentene over special catalysts. The products are easily vulcanised elastomers applied in rubber industry mostly as a component of commercial blends [2, 3]. What is very promising is the use of CPEN as a co-monomer in the production of cyclic olefin copolymers (COC) with ethylene or α-olefins over metallocene-based catalysts. These copolymers form a new class of amorphous thermoplastic materials, which glass-transition temperature can be altered within a wide range.
by means of the cycloalkene monomer content in a polymer, or by selecting such a monomer, respectively. They have numerous precious properties as, for example, dimensional stability controlled within a wide range, high barrier effect against water, good resistance to solvents, acids, and other chemicals, and excellent optical and electrical properties. In numerous ways they outperform polycarbonates. As early as nowadays they are utilised for the production of optical discs, optical fibre, special precision lenses, and other optical and medical components [4, 5, 6]. Although in the selection of a cyclic comonomer as a component of commercially manufactured COC it is rather norbornene or tetracyclododecene, which have been preferred so far, it is likely that in future the application of cyclopentene will be more spread. Studies [7] can be found in literature, in which cyclopentene is used for the preparation of linear polyethylene with extremely narrow distribution of molecular weight (polydispersity degree Mw/Mn up to 1.04) through ring opening metathesis polymerization of cyclopentene and subsequent hydrogenation.

Cyclopentene may be the initial compound for the preparation of cyclopentanol, cyclopentanone, or potentially other derivatives of cyclopentane, which are semi-products featuring a wide range of applications. Cyclopentanone, an attractive chemical commodity, is used as the starting raw material for the production of certain pesticides (pencycuron), numerous drug substances (cyclopenthiazid, for instance) yet its largest amount is consumed for the production of perfume components (those of jasmine type). The standard procedure of the cyclopentanone production is the decarboxylative cyclization of adipic acid esters over ZnO at temperature around 400°C [8]. An alternative method of preparation could be the hydration of cyclopentene to cyclopentanol [9] and subsequent oxidation [for example in [10]] or dehydrogenation to cyclopentanone [11]. A procedure analogical to the Wacker production method of acetaldehyde provides other alternative, in which cyclopentanone is formed in the cyclopentene oxidation with oxygen over PdCl2 and CuCl2 [12, 13]. An illustrative example of prospects of the cyclopentene use in the field of specialty chemical production is the fact that the important petrochemical company of Nippon Zeon, which is, inter alia, the world major producer of cyclopentanone with annual capacity of 2 000 tons of cyclopentanone from adipic acid, announced the launch of the construction of its new unit for the cyclopentanone production using cyclopentene as the starting material. As a reason they gave the new process will enable substantially reduced costs compared to the conventional adipic acid process [14].

The present study deals with technology aspects of the liquid phase partial hydrogenation of cyclopentadiene to cyclopentene. The paper objective was to determine the hydrogenation selectivity for various types of the hydrogenation reactor and on the basis of these findings to discuss the potential of their application in a process producing highly pure cyclopentene at high yield. Because of the future the study was concentrated on the process, which would produce CPEN of purity compliant not only with the subsequent synthesis of specialty chemicals yet also with the CO-copolymer production, in which requirements for the CPEN purity are much more severe. The paper objective was also to optimise operating parameters of the hydrogenation to be employed in such process.

The research concept and experimental data evaluation

There are a great number of studies on the CPD hydrogenation in literature. They mention the CPEN preparation both in liquid [15–17, for example] and in gaseous phases [18–21, for instance]. According to literature the liquid phase CPD hydrogenation boasts higher selectivity than that in gaseous phase [22, 23]. Moreover, in the gaseous phase hydrogenation there is a threat of the catalyst deactivation by means of DCPD oligomers. The fast catalyst deactivation in the gaseous phase process and the need for the catalyst regeneration is also confirmed in papers [24, 25]. In the liquid phase hydrogenation the potentially formed DCPD oligomers are not interfering because they are continuously washed out by the reaction mixture. For this reason, this paper is focused on the experimental studies on the liquid phase CPD hydrogenation and summarises outcomes of these studies.

There are highly strict requirements upon purity of cyclopentene to be used for the copolymerization with ethylene and the zeolite-catalyzed hydration to cyclopentanol, namely its diene content (i.e. including CPD) should not exceed several tens ppm. The alkane content is not that critical factor. Incomplete conversion of CPD in the hydrogenation, which gives a better ratio of CPEN/CPAN in the product, has little advantage for a process producing highly pure CPEN. Patent literature
describes processes of the CPD hydrogenation with incomplete CPD conversion, in which majority of unreacted CPD is removed by dimerization \cite{26, 27} and then by binding to certain chemicals \cite{27} or sorbents \cite{21}. Yet the CPD dimerization, as a second-order reaction, may not really reduce the CPD concentration below 1 %. The separation of a larger amount of unreacted CPD (in units or tens of per cent) from CPEN to a concentration lower than 100 ppm by rectification is almost unrealistic (or very complicated) \cite{28}.

Extractive rectification with a polar solvent (analogical to the butadiene isolation) is not very prospective for the inappropriate relation of boiling points and moreover it is complicated by the dimer formation. The aforementioned analysis demonstrates that the suitable method is to carry out the hydrogenation to complete conversion of CPD, or potentially to conversion limiting near to 100% (99.90 – 100%). Then the reduction of the CPD concentration in CPEN from 500 – 1000 ppm to 20 ppm, for example, by means of rectification is feasible \cite{28}. The total CPD hydrogenation is also advantageous from the standpoint of the pentadienes’ removal, which as a rule accompany CPD as crucial impurities. Pentadiene isomers may be contained in CPD at the concentration of 0.1 – 0.5 % and if they are not converted into more easily separable pentenes they cannot be virtually separated from CPEN by rectification. The following product in the CPD hydrogenation to CPEN, i.e. cyclopentane (CPAN), is not waste, it is used mostly as a blowing agent in the production of polyurethane foams. Its price is, however, low compared to the price of CPEN and keeps at the level of the price of the starting raw material - DCPD. CPAN is hard to separate from CPEN through rectification, nevertheless, the concentration reduction to, for instance 0.1%, is realistic \cite{28}. It may be stated that it is appropriate to carry out the hydrogenation at maximum selectivity to CPEN under complete conversion of CPD. Therefore in this research selectivity to cyclopentene $S_{\text{CPEN}}$ at the cyclopentadiene conversion $X_{\text{CPD}}$ nearing 100% was chosen as the main evaluation criterion of the process operating parameters. Selectivity and conversion of CPD were defined as follows:

$$S_{\text{CPEN}} = \frac{c_{\text{CPEN}}}{c_{\text{CPEN}} + c_{\text{CPAN}}} \times 100 \quad [\%]$$

$$X_{\text{CPD}} = \frac{c_{\text{CPD}}}{c_{\text{CPD}}^0} \times 100 \quad [\%]$$

where

According to literature palladium on alumina features the highest selectivity for the CPEN formation out of the common heterogeneous catalysts \cite{15, 23, 27}. Catalysts based on other metals usually provide lower selectivity. Previous paper \cite{29} of our laboratory confirmed these results and furthermore, it followed from the studies that the most selective catalysts for the liquid phase hydrogenation discussed are palladium catalysts on alumina having the Pd content in between 0.2 and 1 %. Hydrogenation activity of the catalysts mentioned was sufficient even at low temperature (25°C) when the extent of the undesirable cyclopentadiene dimerization is low. On the contrary, the tested catalysts based on Pt and Ru demonstrated very low hydrogenation activity at reaction temperature 25°C. Therefore attention in the study was concentrated on the hydrogenation catalysed by Pd/Al$_2$O$_3$.

**Experimental**

CPD for hydrogenation tests was prepared by thermal decomposition of DCPD and prior to its use it was purified by distillation under nitrogen atmosphere. The hydrogenation experiments were implemented in three alternative arrangements as follows:

- **Set A**: isothermally in a laboratory batch slurry-reactor (stirred autoclave 160 ml in volume);
- **Set B**: isothermally in a laboratory batch stirred autoclave fitted with a basket for a pelleted catalyst (gradientless recycle reactor, Berty-type, internal volume of the reactor 250 ml).
- **Set C**: in a continuous pilot plant apparatus with an adiabatic trickle-bed catalytic reactor (catalyst layer height 113 cm, bed inner diameter 10 cm, Testing Laboratories of Chemopetrol Co., Litvínov, Czech Republic).

In the experiments of the Set A the hydrogenation kinetics was affected neither by any external nor internal mass transport (kinetic regime). In the experiments of the Set B in the Berty-type reactor reaction kinetics was limited by the internal mass transport in the catalyst particles yet the reactor design excluded any effects of external mass transport.
The suppression of the undesirable CPD dimerization extent during the liquid phase hydrogenation required the selection of a low reaction temperature and the dilution of CPD with an inert to a low concentration. A commercial catalyst 0.4 wt.% Pd/γ-alumina (ref. code CHEROX 40-00, BET surface area 131 m²/g) produced by Eurosupport Manufacturing Czechia was employed in the study. For the experiments of the Sets B and C the original form of the catalyst was utilised: tablets 5x5 mm and spheres ∅ 3 mm (egg shell type catalyst, palladium impregnated layer thickness of approx. 0.3 mm). For the experiments of the Set A the original pellets were crushed and sieved and the fraction of particles smaller than 56 µm was finally employed.

The laboratory hydrogenation tests were focused on the determination of the reaction mixture composition over time at various reaction temperatures, hydrogen partial pressure, type of diluting medium, and the CPD initial concentration in the diluting medium. Experimental conditions of these tests can be found in Table 1. The hydrogen consumption rate was observed and samples of the liquid reaction mixture were withdrawn at selected time intervals. In the case of the hydrogenation tests in the continuous flow apparatus the reaction mixture from the reactor was cooled down in an exchanger and liquid samples of the reaction mixtures were, once hydrogen was removed from in a separator, taken to analysis. The analysis was carried out by gas chromatography in a 30-metre-long capillary with silicone DB-5 (J. & W. Scientific). The employed chromatographic method enabled to detect cyclopentadiene at the amount starting from 5 ppm in the reaction mixture. Selectivity $S_{CPEN}$ as well as the CPD conversion $X_{CPD}$ were determined analytically according to the reaction mixture composition.

<table>
<thead>
<tr>
<th>Table 1. Experimental conditions of laboratory hydrogenation tests</th>
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<tbody>
<tr>
<td><strong>Parameter</strong></td>
</tr>
<tr>
<td>Reaction temperature range</td>
</tr>
<tr>
<td>Reaction pressure range</td>
</tr>
<tr>
<td>CPD initial concentration</td>
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<tr>
<td>Tested solvents</td>
</tr>
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</table>

Results and Discussion

**CPD hydrogenation on the powdered Pd catalyst in the batch slurry-reactor**

A typical course of the hydrogenation on the selective Pd catalyst in powder form implemented in the arrangement marked as the Set A (kinetic regime) is depicted in Fig. 1. It can be seen that the amount of hydrogen consumed was proportionally increasing with the reaction time up to the amount equimolar to cyclopentadiene. The reaction rate, expressed as the rate of hydrogen consumption divided by the amount of the Pd catalyst, was constant since this state (the hydrogenation is a zero-order reaction to the substrate). Then the reaction rate was stepwise reduced while it was several times lower to the „second“ degree ($r_1/r_2 = 5 – 50$ depending on the reaction conditions), which is important for the control of the process of the hydrogenation CPD to CPEN.

In the left side of Table 2 there are values of selectivity to CPEN depending on the CPD conversion, which were measured in the hydrogenation of 10% CPD solution in cyclohexane at 25°C and 2 MPa. Selectivity is virtually constant (~ 99 %) up to high CPD conversion near 99.9 %. Within the area limited by CPD conversion 99.5 % and the moment when CPD disappears from the reaction mixture there is a selectivity drop by 3 – 4 %. Selectivity values found under other reaction conditions are given in Tables 3 and 4 and graphs plotted in Figs. 5 and 6 (as blank circles). It may be summarised that the hydrogenation on the highly selective Pd catalyst carried out in kinetic regime enables, at 99.9 % cyclopentadiene conversion, to achieve values of selectivity to cyclopentene higher than 98 % even at relatively high hydrogen pressure of 2 MPa.
Figure 1. A typical course of the CPD hydrogenation on the selective Pd catalyst in powder form. 
\( n(H_2) \) – hydrogen consumption; 25°C, 2 MPa, 1.9 g 0.4% Pd/Al_2O_3 (grains < 56 µm), 1 mol CPD as 10 wt.% solution in cyclohexane, batch slurry reactor of Set A.

Table 2. Selectivity to CPEN vs. CPD conversion in the hydrogenation on the Pd catalyst in tablet and powder forms

<table>
<thead>
<tr>
<th>Conditions: 25°C, 1 mol CPD as 10 wt.% solution in cyclohexane, arrangement of Set A&lt;sup&gt;a&lt;/sup&gt; and Set B&lt;sup&gt;b&lt;/sup&gt;</th>
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<tr>
<td>particles &lt; 56 µm&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>( X_{CPD} )</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>90.9</td>
</tr>
<tr>
<td>98.3</td>
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<tr>
<td>99.9</td>
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<td>99.95</td>
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<td>99.98</td>
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<tr>
<td>99.99</td>
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<tr>
<td>100</td>
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<td>100</td>
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</table>

**CPD hydrogenation on the pelleted Pd catalyst in a batch, Berty-type reactor**

The typical course of the hydrogenation on pellets of the highly selective Pd catalyst carried out in the arrangement marked as the Set B is demonstrated in Fig. 2. In contrast to the stepwise change in the reaction rate observed in the hydrogenation on powdered catalyst here the change in reaction rate was gradual. Dividing the initial reaction rate of the CPD hydrogenation on catalyst pellets by the reaction rate of the hydrogenation (to the first degree) carried out under the same conditions in kinetic regime on the powdered catalyst the value of internal diffusion factor \( \eta \) was acquired. \( \eta \) was equal to 0.009 for the hydrogenation with parameters given in the legend to Fig. 2. Depending on the reaction conditions, as described in Table 1, then the \( \eta \) value fell within the range 0.004 and 0.01. Thus the hydrogenation on pellets of the Pd catalyst was carried out in the area of heavy influence of the internal mass transfer in the catalyst particles. This is very surprising finding considering palladium was impregnated in a thin layer over the pellets' surface.

Results of the hydrogenation tests in the batch Berty-type reactor (in the form of values of \( S_{CPEN} \ vs. X_{CPD} \)) are recorded in the right side of Table 2 and graphs drawn in Figs. 3, 5, and 6 (squares). It follows from these values that the hydrogenation on Pd catalysts in the form of pellets may attain selectivity over 95% at the CPD conversion 99.9 – 99.95 %, if the hydrogenation is carried out in isothermal manner at temperature below 30°C and hydrogen pressure below 1 MPa. In the laboratory Berty-type reactor, however, the influence of external mass transport on the hydrogenation kinetics is eliminated and this, as a rule, may not be achieved over catalyst pellets in common industrial continuous flow reactors.
Figure 2. A typical course of the CPD hydrogenation on the high selectivity Pd catalyst in pellet form 

\[ n(\text{H}_2) \text{– hydrogen consumption; } 25^\circ\text{C, } 2 \text{ MPa, } 21.7\text{g } 0.4\% \text{ Pd/Al}_2\text{O}_3 \text{ (tablets } 5\times5 \text{ mm), } 1 \text{ mol CPD as } 10 \text{ wt.\% solution in cyclohexane, batch, fixed-bed Berty-type reactor of the Set B.} \]

**CPD hydrogenation on the pelleted Pd catalyst in an adiabatic trickle-bed reactor**

Besides the laboratory hydrogenation tests in the batch reactors, a pilot plant experiment in an adiabatic trickle-bed reactor in a continuous unit (Set C) was also carried out. Concerning technology aspects, an adiabatic trickle-bed reactor is the simplest alternative for a continuous process. Objective of the pilot plant experiment was to find out if a trickle-bed reactor with catalyst pellets can be utilised for a highly pure CPEN technology having higher capacity. The pilot plant unit was deliberately preferred to a laboratory one because a hydrodynamic regime, which is typical to industrial reactors, cannot be achieved in laboratory reactors (different trickling density, other extent of wall effects, etc.). Conditions of this experiment can be found in the legend to Fig. 3. The value of the CPD conversion in the reactor outlet was altered within the range of 93.7 and 99.8 \% by changing the catalyst trickling density within the range of 0.76 – 1.02 l.h\(^{-1}\).cm\(^{-2}\). Operating pressure in the reactor of 0.25 MPa ensured that the exothermal hydrogenation occurred along the entire length of the catalyst layer in liquid phase. The graph in Fig. 3 shows values of selectivity measured in the hydrogenation of 5\% CPD solution in cyclohexane at inlet temperature 15°C (marked as triangles). For the sake of comparison, the graph also shows values of selectivity of hydrogenation runs carried out isothermally in the laboratory batch Berty-type reactor on the same pelleted catalyst under temperature 25 and 50°C, respectively (marked as squares). It is obvious from the graph that even though operating hydrogen pressure in the trickle-bed reactor was set to more favourable value concerning selectivity to CPEN than in the case of the Berty-type reactor (0.25 against 1 MPa) selectivity values measured in the continuous flow trickle-bed adiabatic reactor were dramatically lower. It may be deduced that the selectivity drop observed is a result of not merely adiabatic temperature rise, which varies, even when the substrate is diluted below 10\%, in tens °C (see Fig. 4.) yet, at non-negligible level, also a result of effects of external mass transport. These effects are eliminated in the hydrogenation in the batch Berty-type reactor.

It is obvious if the hydrogenation were implemented in a fix-bed (trickle- or flooded-bed) reactor with an intensive heat exchange the process selectivity would vary somewhere in the range limited by the values of selectivity measured in the Berty-type reactor and in the adiabatic trickle-bed reactor. Yet such a reactor is substantially complex to be applied in industry. First of all, because it requires uniform distribution of the liquid feed into the respective cooled pipes in the reactor. This type of reactor is especially inappropriate for a process, in which an intermediate is desired from a system of two consecutive reactions, while containing a minimum amount of the initial compound and the consecutive product.
**Fig. 3.** Effects of the reactor type on the hydrogenation selectivity at various conversions of CPD. Pelleted catalyst: 0.4 % Pd/Al₂O₃, spheres 3 mm, egg-shell type, initial material: 5% CPD in cyclohexane; ▲ – Adiabatic trickle-bed reactor (layer height 113 cm, 10 cm, 5.65 kg catalyst, trickling density 0.76-1.02 l/h.cm², feed inlet 60-80 l/h, inlet temperature 15°C, outlet temperature 80°C); ■ and □ – laboratory batch isothermal Berty-type reactor (Set B)

**Fig. 4.** Dependence of the value of adiabatic temperature rise (in the liquid phase CPD hydrogenation) on the substrate concentration in the starting raw material. Initial material: CPD solution in cyclohexane, Values of adiabatic temperature rise in the moment when CPD reacted off for the hydrogenation with selectivity S_CPEN=80%. Calculated from literature tabulated thermo-dynamic data.

**Optimization of reaction conditions for the selected reactor**

Results given in previous chapters have indicated that for a process producing highly pure cyclopentene at a high yield it is advantageous to employ the highly selective Pd catalysts in the powder form. Up to a certain volume of the CPEN production it is possible the industrial process to be implemented in a batch slurry-reactor operated in isothermal regime. Operating parameters
were optimised for such reactor. Curves plotted in Figs. 5 – 6 demonstrate the found dependences of selectivity on reaction pressure and reaction temperature in the hydrogenations carried out either on the catalyst powder in the batch slurry-reactor either on pellets of the same catalyst in the batch Berty-type reactor.

**Fig. 5.:** The influence of reaction pressure on selectivity of the hydrogenation at the CPD conversion 99.90%
The hydrogenation of 10% CPD in cyclohexane on the catalyst 0.4 % Pd/Al₂O₃ under reaction temperature 25°C; ○ – grains < 0.056 mm; □ – tablets 5x5 mm.

**Fig. 6.:** Effects of reaction temperature on selectivity of the hydrogenation at the CPD conversion 99.90%
The hydrogenation of 10% CPD in cyclohexane on the catalyst 0.4 % Pd/Al₂O₃ under reaction pressure 2 MPa; ○ – grains < 0.056 mm; □ – tablets 5x5 mm.

It can be seen from the plots that while in the case of the hydrogenation on the catalyst in pellet form the influence of reaction conditions on selectivity plays an essential role, in the case of the powdered catalyst this influence is barely appreciable within a wide range of the conditions. Concerning selectivity there is a substantial room for the selection of reaction pressure and temperature in the batch slurry-reactor. Reaction rate of the undesirable side reaction – dimerization of CPD grows with increasing temperature and therefore it is, of course, advantageous to choose reaction temperature for the hydrogenation as low as possible, i.e. 25°C, for example. On the
contrary, the value of reaction pressure should be, for technology reasons (reactor performance), rather higher. It was found experimentally that reaction rate of the CPD hydrogenation is, in the same manner as in majority of other hydrogenation reactions, proportional to hydrogen pressure. The pressure influence ceases to act at a relatively high pressure (> 4 MPa). Therefore the hydrogenation reactor performance will be increased with increasing pressure. In a number of literature studies CPD is hydrogenated at atmospheric pressure, which limits reaction temperature to approx. 30°C in the liquid phase hydrogenation (because of vapour pressure of reaction components).

Due to the spontaneous dimerization of CPD the dilution with inert is a must. Therefore it was investigated if the initial CPD concentration in the charge for the hydrogenation affects the process selectivity. The inert chosen was cyclohexane. Results are summarised in Table 3. It can be seen that the CPD concentration within a wide range of values from 5 to 50 wt% has virtually no effect on the reaction selectivity. At the CPD concentration as low as below 5% selectivity SCPEN become to drop significantly in the area of a high CPD conversion. The effect observed can be elucidated the way that in the area of the CPD conversion limiting close to 100% the hydrogenation is not a zero-order reaction to the substrate and relation in between adsorption coefficients of CPD, CPEN, CPAN and the solvent - cyclohexane become to act. This way, in the area of high CPD conversion, by the more is the starting material diluted, adsorption of CPD is less and less pronounced related to the adsorption of cyclohexane and CPEN.

It can be seen in Fig. 7 that under reaction temperature 25°C it may not be operated at the CPD concentration over 10 % without suffering a significant loss of the substrate due to the dimerization. The optimum inlet concentration of CPD into the hydrogenation falls in the range in between 5 and 10 wt%. When designing a suitable inlet CPD concentration for a CPEN production process the fact, that with increasing dilution of the substrate costs for the rectification separation of CPEN from the hydrogenate are growing, shall be taken into account.

Under reaction temperature 25°C and pressure 2 MPa the CPD hydrogenation on the powdered Pd catalyst was carried out in various solvents. Results are shown in Table 4. It was found that in the case the CPD is diluted with non-polar compounds the course of the hydrogenation is virtually independent on the selection of a concrete type of the diluting inert. In the hydrogenation in polar methanol selectivity is somewhat lower and, moreover, due to a higher reaction rate of the hydrogenation into the „second“ degree the ratio of rates \( r_1/r_2 \) is lower compared to those measured in the hydrogenation in non-polar solvents. The lowest hydrogenation selectivity to cyclopentene was determined in the case using CPEN as diluting medium. Selectivity of hydrogenation of 10 % solution of CPD in CPEN carried out to conversion \( X_{CPD}=99.8 \) % was 92.7 % (see Table 4). The ratio of the CPD/CPEN contents in this hydrogenation product was nearly identical with the CPD/CPEN ratio in the product of the hydrogenation of 10 % CPD solution in an inert, which was terminated at conversion \( X_{CPD} = 99.98 \) %. Concerning the difficulty of the rectification separation of CPD – CPEN both the reaction mixtures are thus identical. That means, in the hydrogenation product of 10% CPD solution in CPEN carried out to conversion \( X_{CPD} = 99.8 \) %, the rectification may effectively reduce the CPD content to the concentration limit values required (~20 ppm, see chapter Research Concept). It can, therefore, be stated that the cyclopentadiene diluting by the circulated hydrogenate (containing mostly CPEN) may represent a certain alternative to the use of an inert solvent in the CPEN production process. Price paid for this alternative without a solvent would be a drop in the process selectivity by roughly 10 %.

### Table 3. The cyclopentadiene concentration effect on the selectivity to CPEN in the hydrogenation on the powdered Pd catalyst

*Conditions: 25°C, 2 MPa H₂, 0.2g of the 0.4 % Pd/Al₂O₃ catalyst (grains < 56 µm), 70g of the CPD solution in cyclohexane, batch slurry reactor of Set A.*

<table>
<thead>
<tr>
<th>CPD concentration [wt. %]</th>
<th>( X_{CPD} ) [%]</th>
<th>( S_{CPEN} ) [%]</th>
<th>( X_{CPD} ) [%]</th>
<th>( S_{CPEN} ) [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>81.8</td>
<td>79.3</td>
<td>91.5</td>
<td>89.2</td>
</tr>
<tr>
<td>3</td>
<td>91.5</td>
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<td>99.95</td>
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</tr>
<tr>
<td>10</td>
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<td>98.1</td>
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</tr>
<tr>
<td>20</td>
<td>98.0</td>
<td>97.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. The cyclopentadiene hydrogenation on the powdered Pd catalyst in various solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( r_1 ) [mol.min(^{-1}).g(_{\text{cat}})(^{-1})]</th>
<th>( r_2 ) [mol.min(^{-1}).g(_{\text{cat}})(^{-1})]</th>
<th>( r_1/r_2 )</th>
<th>( X_{\text{CPD}} ) [%]</th>
<th>( S_{\text{CPEN}} ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>0.132</td>
<td>0.0030</td>
<td>44</td>
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<tr>
<td>Cyclopentane</td>
<td>0.166</td>
<td>0.0030</td>
<td>55</td>
<td>97.1</td>
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<tr>
<td>Toluene</td>
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<td>0.0035</td>
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<td>98.9</td>
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<td>Methanol</td>
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<td>23</td>
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<td>92.7</td>
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<td>Methylcyclopentane</td>
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<td>0.0022</td>
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<td>98.6</td>
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<tr>
<td>Cyclopentene</td>
<td>0.123</td>
<td>0.0035</td>
<td>35</td>
<td>99.8</td>
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</tbody>
</table>

**Fig. 7.:** The drop in the CPD concentration in an inert solvent (cyclohexane) due to the spontaneous thermal dimerization of CPD at 25°C depending on the initial CPD concentration. (Calculated on the basis of kinetic data of the laboratory own measurements [30]; there are curves for the initial concentration of 1, 3, 5, 10, and 20 wt% CPD plotted here.)

**Conclusions**

This study results revealed that because of very low process selectivity the adiabatic continuous flow trickle-bed reactor is not suitable for the liquid phase selective hydrogenation of cyclopentadiene to cyclopentene. A certain improvement to selectivity can be made by a change of the reactor operating regime from the adiabatic regime to the isothermal one. Yet a trickle-bed reactor with an intensive heat exchange is rather complex to be applied in industry. Therefore the hydrogenation should be implemented in some other method using highly selective catalysts in powder form. This way, high values of selectivity to cyclopentene (over 96 %) can be achieved at almost total conversion of cyclopentadiene (\( X_{\text{CPD}} \approx 99.95 \% \)). For a smaller production volume of highly pure CPEN a stirred isothermal batch slurry reactor operated at periodic hydrogenation cycles would work.
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References