

# Reactive Distillation for the Production of Cyclohexanol: Experiments and Simulations



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Cyclohexanol is an organic chemical intermediate product widely used in chemical industry and commonly produced by cyclohexene hydration. Because of the low mutual solubility of cyclohexene and water, the reaction is limited by chemical equilibrium, which has the disadvantage of low conversion of cyclohexene. In this paper, the hydration reaction of cyclohexene catalysed by A-36 cation exchange resin catalyst was analysed by Aspen Plus V8.6 simulation software in the presence of isophorone as cosolvent. The process model of synthesising cyclohexanol by catalytic distillation was verified by process experiments. The simulation experiments were carried out using the process model, and suitable operating conditions of the catalytic distillation column were obtained. These are: ketene feed ratio 1.5, alkene/water ratio 0.5, distillation stage trays 5, reaction stage trays 12, stripping stage trays 6, cyclohexene feed at the 18th tray, water and isophorone feed at the 5th tray, reflux ratio 3, feed ratio (D/F) 0.25. Under these operating conditions, the conversion of cyclohexene can reach 40.63 %.

## Keywords

cyclohexanol, catalytic distillation, hydration, simulation, cosolvent, cyclohexene

## Introduction

Cyclohexanol is a commonly used chemical intermediate that exhibits excellent dissolving properties in addition to other good physical properties, and is widely used in fuels, solvents for paint, etc.<sup>1,2</sup> The production of cyclohexanol mainly includes benzene method and phenol method. The oldest production method is the phenol method, which uses phenol as a raw material for hydrogenation to generate cyclohexanol.<sup>3</sup> The benzene method is mainly divided into two types, one is the cyclohexane oxidation method in which benzene is completely hydrogenated to cyclohexane, and then the cyclohexane is partially oxidised to cyclohexanol. The other is the cyclohexene hydration method in which benzene is partially hydrogenated to cyclohexene, and then cyclohexene is hydrated to form cyclohexanol.<sup>4,5</sup> Due to its low cost and high safety record, the cyclohexene hydration method has attracted great attention from both academia and industry.

The cyclohexene hydration process, first developed by Asahi Kasei Corporation of Japan, has the disadvantages of slow reaction rate and low equilibrium

conversion, because the reaction is limited by a chemical equilibrium, and the mutual solubility of cyclohexene and water is extremely low. Qiu *et al.* used 1,4-dioxane as a cosolvent to increase the miscibility between the two phases.<sup>6</sup> They adopted a catalytic distillation process to break the chemical reaction equilibrium limitation of the cyclohexene hydration. Although 1,4-dioxane is easy to separate from cyclohexanol, it is miscible with water and has a similar boiling point, making it difficult to separate, and cannot be used as a suitable cosolvent for cyclohexene hydration reaction.

Panneman and Beenackers found that adding isophorone to the reaction system and using high silica zeolite ZSM-5 as a catalyst can improve the yield of cyclohexanol.<sup>7,8</sup> Under the same reaction conditions, the final yield of the reaction without cosolvent was 12.0 %, and the final yield of the reaction with isophorone as cosolvent was 24.3 %.<sup>9</sup> Isophorone as a cosolvent can improve the solubility of cyclohexene in water. It hardly participates in the reaction during the reaction, and has a large boiling point difference, and is therefore easy to separate and recover in the post-treatment process. It can be used as a suitable cosolvent for cyclohexene hydration reaction.

Although the catalytic distillation was employed in chemical production early in the last century, its industrial applications have been limited.<sup>10,11</sup> Indeed, the catalytic distillation process is particu-

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larly complex, and it is impossible to explore in detail the effects of all operating conditions on the reaction. However, with the development of computer simulation software, and improvements in the physical property methods and the physical property database, it is possible to simulate the actual chemical production process accurately and reliably, although some controversy remains regarding the accuracy and practicability of computer simulation results.<sup>12,13</sup> Allan *et al.* modelled the phase equilibrium of interest in biodiesel production by reactive distillation. Databanks of vapour-liquid equilibrium, liquid-liquid equilibrium and vapour-liquid-liquid equilibrium experimental data were created for the mixtures in the biodiesel production process. The experimental data evaluated were then used to develop rigorous thermodynamic modelling using the Non-Random Two-Liquid (NRTL) model. The proposed phase equilibrium modelling was then validated against experimental results reported for biodiesel production by reactive distillation.<sup>14</sup> The reliability of the simulation model can be verified by experiments, and the process operating conditions can be optimised by simulations.<sup>15</sup>

In this study, isophorone was used as a cosolvent to increase the mutual solubility between the two phases, and catalytic distillation was used to break the chemical equilibrium limit; thus, a new cyclohexene hydration process is formed. Based on previously conducted experiments, reported by Zeng *et al.* the following experimental conditions were selected: fixed water and cyclohexene molar ratio of 3, space velocity of  $0.213 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$ , feed temperature of  $25 \text{ }^\circ\text{C}$ , and reflux ratio of 1. The temperature and concentration distribution profiles of the column were studied.<sup>16</sup> The maximum relative error of temperature was 2.44 %, and the concentration distribution profile was within the allowable range of error, which verified the reliability of the catalytic distillation column model. Thus, the best distillation operating parameters, number of trays in the reaction and stripping section, as well as the feed ratio and feed position were obtained through simulation by Aspen Plus V8.6 process simulation software, which provided data support for operating the catalytic distillation column.

## Experimental

### Materials

The raw materials employed herein were cyclohexene (analytically pure, Shanghai McLean Biochemical Co., Ltd.), cyclohexanol (analytically pure, Shanghai McLean Biochemical Co., Ltd.), isophorone (chemically pure, Shanghai Maclin Biochemical Co., Ltd.), toluene (analytically pure,

Tianjin Guang cheng Chemical Reagent Co., Ltd.), A-36 Cation exchange resin (Rohm and Haas, Amberlyst 36), and anhydrous ethanol (analytically pure, Zibo Linzi Tiande Fine Chemical Research Institute).

### Analytical procedure

The composition of the samples was determined by gas chromatography (flame ionization detector). The gas chromatograph PANNA 91 gas chromatograph (with autosampler B75) made by Changzhou Pannuo Instrument Co., Ltd. was used. The chromatographic conditions were as follows: capillary column (FFAP capillary column,  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ ), column temperature  $110 \text{ }^\circ\text{C}$ , detector temperature  $200 \text{ }^\circ\text{C}$ , injection port temperature  $260 \text{ }^\circ\text{C}$ ,  $\text{N}_2$  as a carrier gas,  $\text{N}_2$  flow rate  $30 \text{ mL min}^{-1}$ , sample size  $0.6 \text{ }\mu\text{L}$ , quantitative analysis by internal standard method, toluene as the internal standard, and detection time 10 min.

### Experimental device

The experimental device is shown in Fig. 1. In this device, the inner diameter of the catalytic distillation column was 32 mm. The entire catalytic distillation column could be divided into three parts, namely the upper rectification section (0.5 m in height), the middle reaction section (1.0 m in height), and the lower stripping section (0.5 m in height). Spiral triangular packing purchased from the manufacturer was used in the upper and lower sections, and the intermediate two-stage reaction section was filled with a cationic exchange resin catalyst. A thermal insulation sleeve was used to wrap the outside of the tower, and the whole tower was connected to the computer for control. The temperature distribution in the column was measured using thermocouples, and the column temperature was measured at four temperature-measuring ports. Cyclohexene, water, and isophorone were mixed and added at the top of the reaction section. When the catalytic distillation process reached stability, the composition and temperature of the products at the top and bottom of the tower remained unchanged, and it was considered that the unit was in steady state.

### Model building

#### Process flowsheet setup

In order to simulate the synthesis of cyclohexanol by catalytic distillation, the temperature and concentration distribution profiles of the tower were studied. The process flowsheet of the Aspen Plus software is presented in Fig. 2. The reaction raw

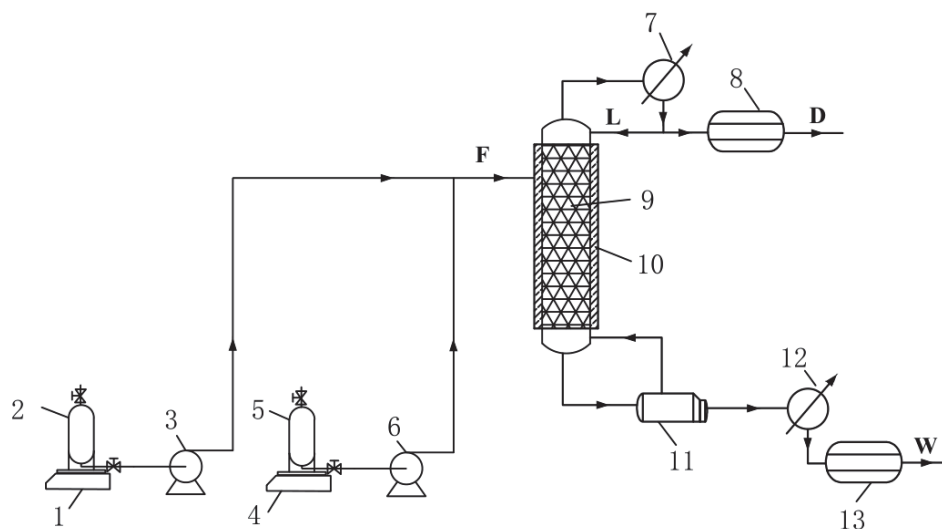


Fig. 1 – Schematics of the catalytic distillation experiment; 1,4 – Platform scale; 2,5 – Raw material tank; 3,6 – Raw material pump; 7 – Condenser; 8 – Column top product tank; 9 – Catalytic distillation column; 10 – Thermal insulation sleeve; 11 – Column reboiler; 12 – Condenser; 13 – Product storage tank

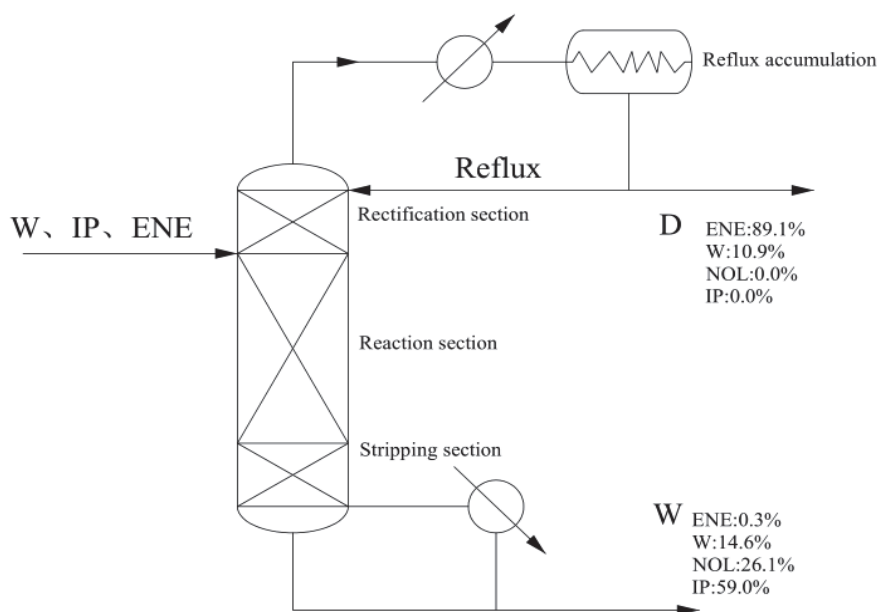


Fig. 2 – Process flowsheet for the simulation of catalytic hydration of cyclohexene in a distillation column  
W:  $H_2O$ ; ENE: Cyclohexene; NOL: Cyclohexanol; IP: Isophorone

materials cyclohexene, water, and the cosolvent were fed at the top of the reaction section. Since the boiling points of cyclohexanol and isophorone were significantly higher than those of cyclohexene and water, unreacted cyclohexene and water could be recovered at the top of the column. In addition, since the boiling point of the water-cyclohexanol azeotrope (118.40 °C, 2 atm) was lower than the boiling point of water, a mixture containing the four components was produced at the bottom of the column.

#### Kinetic equation parameters

The hydration of cyclohexene to form cyclohexanol is an exothermic reaction, and so an increase in temperature results in the reaction equilibrium shifting to the left. Through previous experimental determination,<sup>17</sup> and in accordance with the chemical reaction shown in Fig. 3, the kinetic equation for the hydration of cyclohexene obtained using an A-36 cation exchange resin as the catalyst was found to be as follows:

$$-r_A = -\frac{dc_A}{mdt} = 54775.19 \exp(-57894.54/RT) c_A c_B - 1.7327 \exp(-16451.74/RT) c_C \quad (1)$$

$r_A$  – Reaction rate, mol L<sup>-1</sup> s<sup>-1</sup> g<sup>-1</sup> (cat.)

$m$  – Mass of the catalyst, g

$T$  – Temperature, K

$c_A$  – Water concentration at time  $t$ , mol L<sup>-1</sup>

$c_B$  – Concentration of cyclohexene at time  $t$ , mol L<sup>-1</sup>

$c_C$  – Concentration of cyclohexanol at time  $t$ , mol L<sup>-1</sup>.

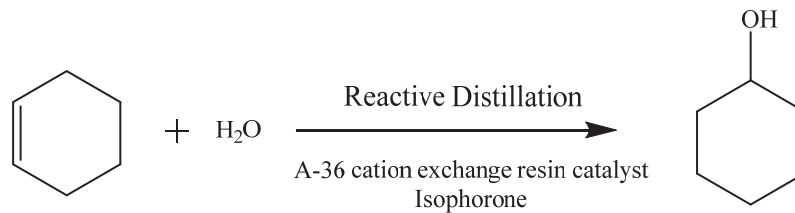


Fig. 3 – Reaction of cyclohexene hydration to prepare cyclohexanol

### Vapour-liquid equilibrium activity coefficient model

It is well known that the mutual solubility of cyclohexene and water is very low, and so to enhance the conversion of the hydration reaction, this mutual solubility has to be improved. For example, the addition of isophorone as a cosolvent can improve the mutual solubility of cyclohexene and water to increase the reaction rate. It can be noted that the NRTL activity coefficient model can be used to fairly describe the non-ideality of liquid mixtures as well as gas-liquid and liquid-liquid equilibrium in the system.

The NRTL equation has the advantages of high fitting degree and great prediction accuracy. At the same time, the parameters fitted by the binary system data can predict the activity coefficient of the multi-component system, with good prediction accuracy.<sup>17,18</sup>

The NRTL model equations used in the Aspen Plus software are:

$$\ln \gamma_i = \frac{\sum_{j=1}^N x_j \tau_{ji} G_{ji}}{\sum_{k=1}^N x_k G_{kj}} + \sum_{j=1}^N \frac{x_j G_{ij}}{\sum_{k=1}^N x_k G_{kj}} \left[ \tau_{ij} - \frac{\sum_{k=1}^N x_k \tau_{kj} G_{kj}}{\sum_{k=1}^N x_k G_{kj}} \right] \quad (2)$$

With:

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}); \quad \tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T;$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15 \text{ K}); \quad \tau_{ii} = 0;$$

$$G_{ii} = 1; \quad a_{ii} \neq a_{ji}; \quad b_{ii} \neq b_{ji}; \quad d_{ii} \neq d_{ji}.$$

$\gamma_i$  – Activity coefficient

$a_{ij}, b_{ij}, c_{ij}, d_{ij}, e_{ij}, f_{ij}$  – Binary parameters

$T$  – Temperature, K.

The binary parameters  $a_{ij}, b_{ij}, c_{ij}, d_{ij}, e_{ij}$  and  $f_{ij}$  are determined from the regression of vapour-liquid equilibrium data. The NRTL interaction parameters

were obtained based on the vapour-liquid phase equilibrium data determined in Sun<sup>19</sup> and related experimental work. The experimentally measured temperature and azeotropic composition, and the values simulated by the NRTL model are listed in Table 1.

It may be seen from Table 1 that the temperature and azeotrope composition values simulated by the NRTL model parameters do not differ much from the literature values, indicating that the selected thermodynamic model is suitable for steady-state simulation.<sup>20</sup>

### Model verification

According to the kinetic equation, Sun<sup>19</sup> created diagrams of the conversion and reaction rate at temperatures of 105 °C, 110 °C, 115 °C, and 120 °C. The results showed that the model could describe well the process of cyclohexene-water-cosolvent hydration to produce cyclohexanol.

In an attempt to describe the used experimental device in ASPEN, the distillation and reaction processes simulation was carried out in the Rad Frac module, and the Decanter module was used to simulate the liquid-liquid separation device. The detailed flowsheet is outlined in Fig. 2. It was noted that the catalytic distillation process uses 22 theoretical trays (including the theoretical tray of the column reboiler), and the feed position is the eighth theoretical tray.

Under the experimental conditions employed herein, namely a fixed water and cyclohexene ratio of 3, a space velocity of 0.213 m<sup>3</sup> m<sup>-3</sup> h<sup>-1</sup>, a feed temperature of room temperature, and a reflux ratio of 1, the process model of cyclohexanol synthesis by catalytic distillation was verified, the temperature and concentration distribution profiles in the

Table 1 – Comparison of experimental values and analogue values

Components	References value		NRTL Calculated value	
	$T/^\circ\text{C}$	Molar composition	$T/^\circ\text{C}$	Molar composition
Cyclohexene	82.9	–	82.88	–
Water	100	–	100.02	–
Cyclohexene-water	70.8	(0.310, 0.690)	70.75	(0.318, 0.682)
Cyclohexanol	160.1	–	160.84	–
Cyclohexanol-water	98.1	(0.930, 0.070)	97.8	(0.927, 0.073)
Isophorone	215.2	–	215.23	–
Isophorone-water	99.5	(0.976, 0.024)	99.31	(0.974, 0.026)

Table 2 – Comparison of experimental and simulated values of temperature profile

Theoretical trays position	$T/^\circ\text{C}$		Percent error/%
	Experimental value	Simulated value	
4	91.6	89.36	2.44
6	91.4	90.5	0.97
11	108.2	110.66	-2.27
19	110.5	113.13	-2.38
Maximum error			2.44
Average error			2.02

From Fig. 4 and Table 1, it is apparent that the maximum relative error between the temperature experimental results and the simulation results is 2.44 %, the average error is 2.02 %, and the average relative error between the composition results and the simulation results is within 5 %. These results confirm that the established process can accurately simulate the synthesis of cyclohexanol by catalytic distillation in the presence of isophorone.

## Result and discussion

### Optimisation of the process conditions for catalytic distillation

In order to improve the conversion of cyclohexene and at the same time reduce the energy consumption of the catalytic distillation column, the number of trays in the rectification section, the number of trays in the reaction section, the number of trays in the stripping section, the product to feed ratio, and the position of the cyclohexene, water and the isophorone feed were varied. The main parameters of the catalytic distillation model for the synthesis of cyclohexanol are presented in Table 3.<sup>21</sup>

### Effect of the number of rectification section trays on cyclohexene conversion

The main function of the rectification section is to increase the concentrations of cyclohexene and water, and to reduce the concentration of cyclohexanol in the top product of the column. As such, a lower number of trays will lead to increased concentration of cyclohexanol in the top product of the column, thereby influencing its concentration in the bottom product as well. However, higher numbers of trays will lead to increased energy consumption, in addition to higher equipment costs. For the purpose of this simulation, the cyclohexene to water feed ratio was 0.6, the cyclohexene to isophorone feed ratio was 1.5, the number of reaction section trays was 13, the number of stripping section trays was 5, the cyclohexene feed position was the 18th

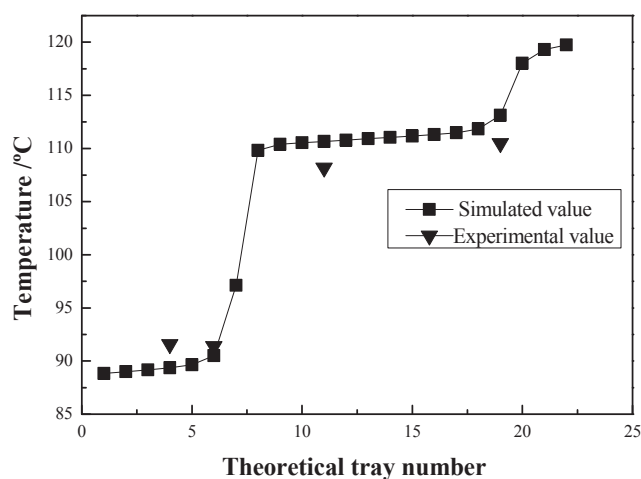


Fig. 4 – Temperature distribution profile in the reactive distillation column

column were studied, and the simulated value was compared with the experimental value. The temperature results are presented in Fig. 4, the relative error, maximum error, and average errors of the experimental and simulated values are listed in Table 2. The distribution profiles of cyclohexene, water, cyclohexanol, and isophorone are given in Figs. 5 to 8, respectively.

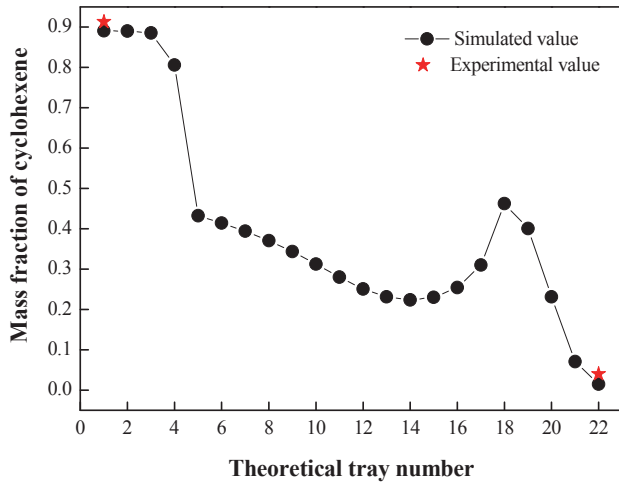


Fig. 5 – Cyclohexene concentration distribution profile

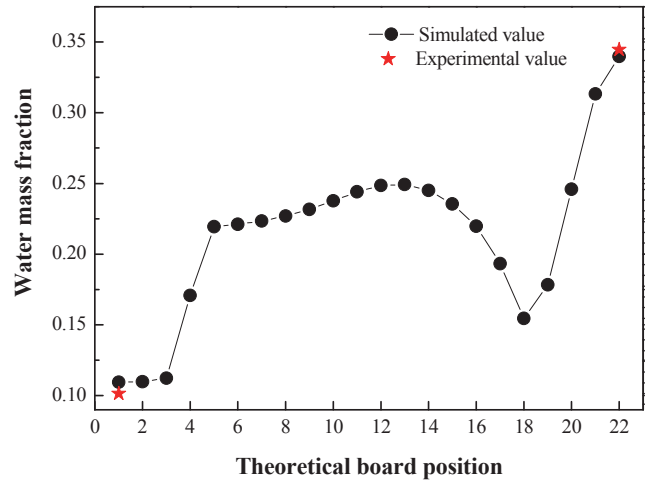


Fig. 6 – Water concentration distribution profile

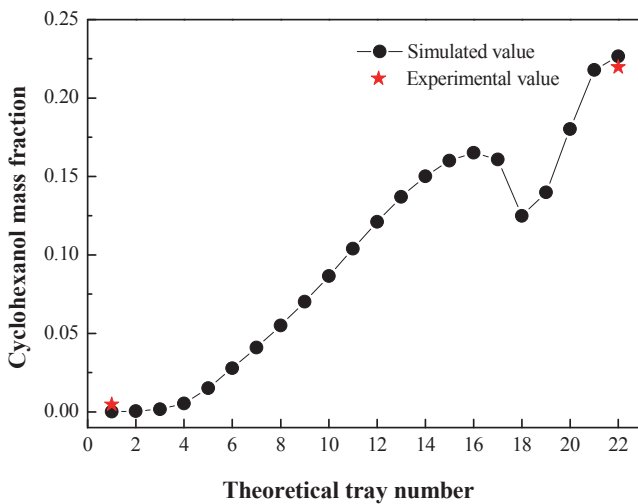


Fig. 7 – Cyclohexanol concentration distribution profile

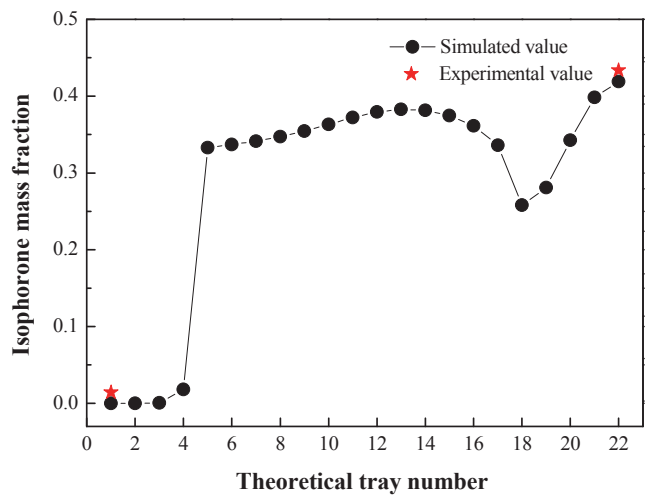


Fig. 8 – Isophorone concentration distribution profile

Table 3 – Main parameters of the model for the simulation of catalytic hydration of cyclohexene in a distillation column

Total number of theoretical trays	22 trays
Number of trays in stripping section	1–4 trays
Number of trays in reaction section	5–17 trays
Number of trays in distillation section	18–22 trays
Raw material feed position	5 trays
Reflux ratio	3
Thermodynamic calculation model	NRTL-HOC

tray, the water and isophorone feed position was the 5th tray, the reflux ratio was 3, and the product to feed ratio (D/F) was 0.25. The number of rectification trays in the catalytic distillation column was varied to examine its influence on the cyclohexene

conversion and the energy consumption of the column, and the results are shown in Figs. 9(a) and 9(b).

As presented in Fig. 9(a), an increase in the number of trays in the rectification section resulted in an initial increase in the cyclohexene conversion, followed by a slight decrease. In addition, as shown in Fig. 9(b), the energy consumption of the system increased continuously upon increasing the number of trays in the distillation section, with four trays being considered optimal.

#### Effect of the number of reaction section trays on cyclohexene conversion

For this investigation, the feed ratio of cyclohexene to water was fixed at 0.6, the cyclohexene to isophorone feed ratio was 1.5, the number of rectification section trays was 4, the number of stripping section trays was 5, the cyclohexene feed position was the 18th tray, the water and isophorone feed position was the 5th tray, the reflux ratio was 3, and

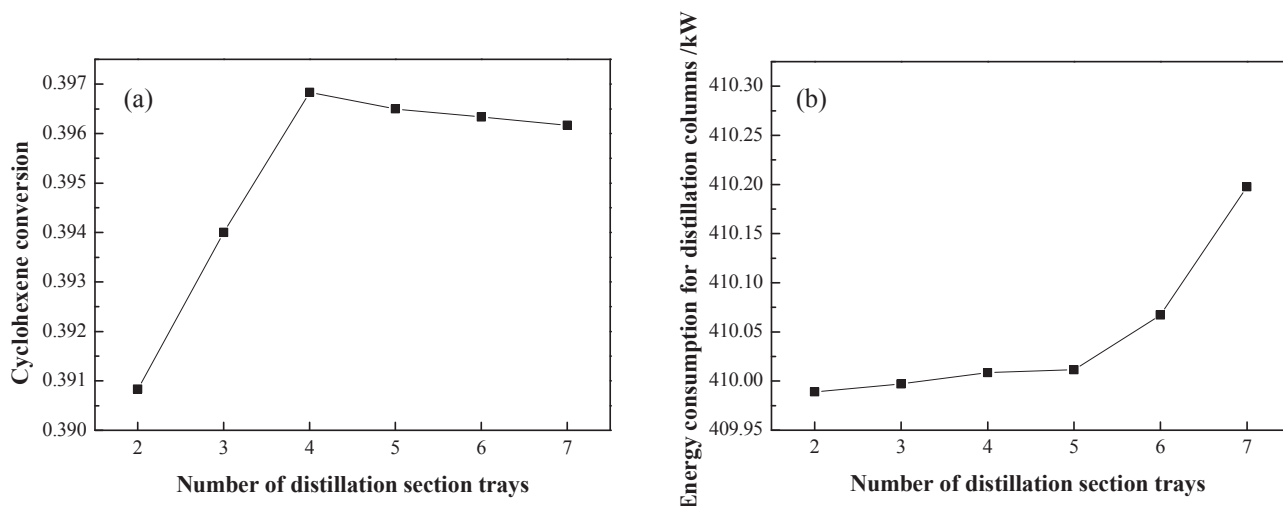


Fig. 9 – Effect of the number of trays in the rectification section on (a) conversion of cyclohexene, and (b) energy consumption of the distillation column

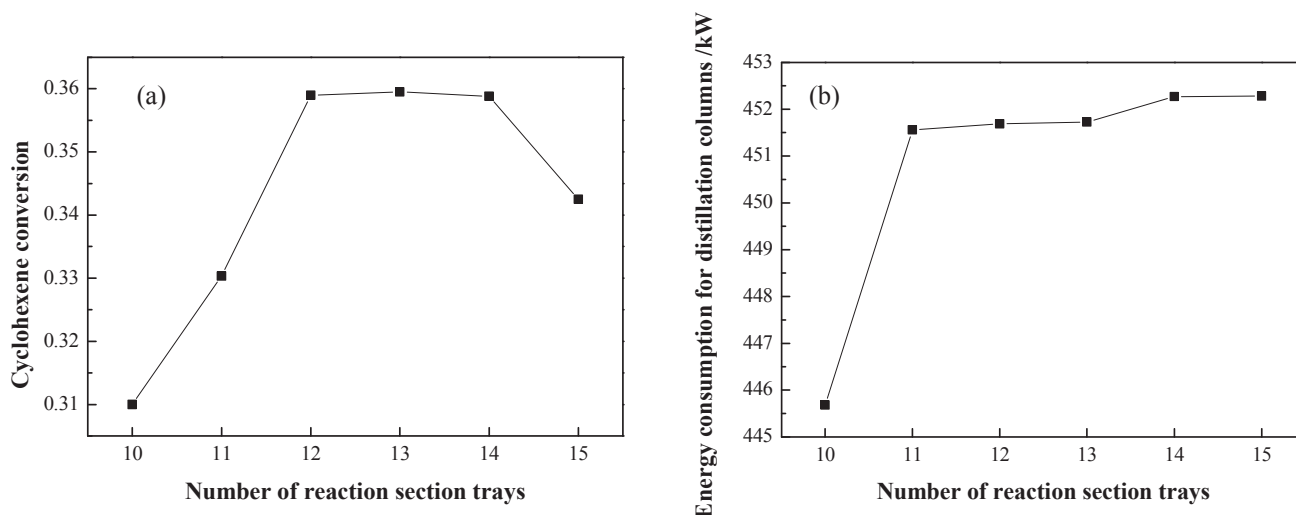


Fig. 10 – Effect of the number of reaction section trays on (a) conversion of cyclohexene, and (b) energy consumption of the distillation column

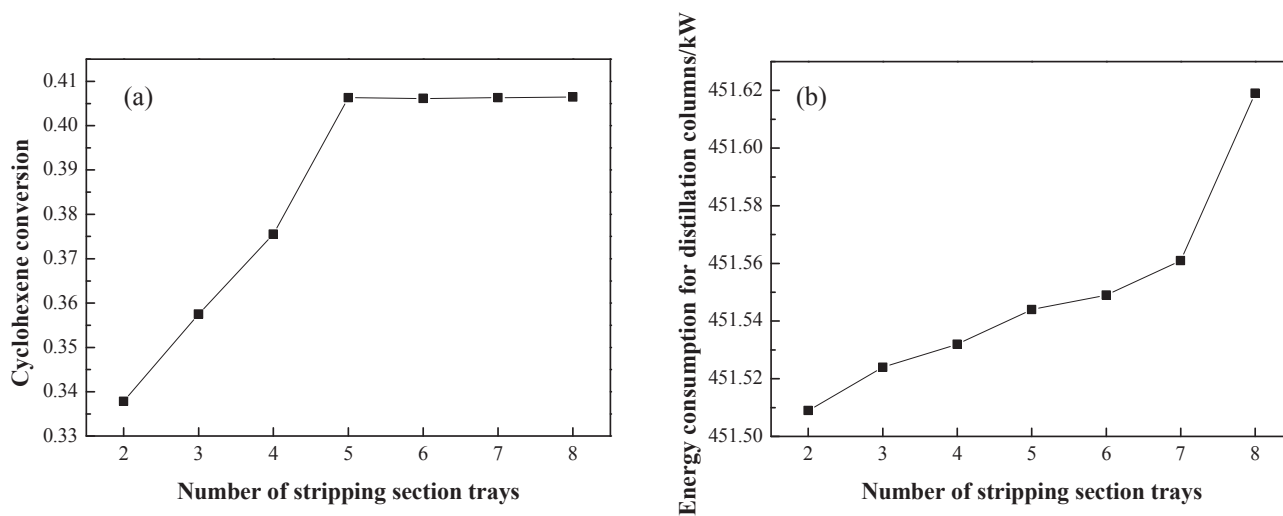


Fig. 11 – Effect of the number of trays in the stripping section on (a) conversion of cyclohexene, and (b) energy consumption of the distillation column

the D/F ratio was 0.25. The number of reaction section trays was varied to determine the effect on the cyclohexene conversion and the energy consumption of the column, as presented in Figs. 10(a) and 10(b).

It is known that the number of trays in the reaction section determines the amount of product in the reactive distillation process. As seen in Fig. 10(a), an increase in the number of trays in the reaction section resulted in an initial increase in the cyclohexene conversion followed by a subsequent decrease. A maximum conversion was reached with 13 trays. Since the cyclohexene hydration reaction is reversible, an increased number of trays in the reaction section may have led to the reverse reaction, thereby accounting for the latter observed decrease in the cyclohexene conversion. An increased number of trays also resulted in an initial increase in the energy consumption of the system, as seen in Fig. 10(b). Since any further increase in the number of trays would also lead to increased equipment costs, a total of 13 trays in the reaction section was considered optimal.

#### **Effect of the number of trays in the stripping section on cyclohexene conversion**

The cyclohexene to water feed ratio were fixed at 0.6, the cyclohexene to isophorone feed ratio was 1.5, the number of distillation section trays was 4, the number of reaction section trays was 13, the cyclohexene feed position was the 18th tray, the water and isophorone feed position was the 5th tray, the reflux ratio was 3, and the D/F ratio was 0.25. The number of stripping section trays was varied to examine its effect on the conversion of cyclohexene and energy consumption of the column, and the results are shown in Figs. 11(a) and 11(b).

The main function of the stripping section is to separate and purify the unreacted cyclohexene and return it to the reaction section to continue the reaction and ultimately improve the cyclohexene conversion. The product cyclohexanol and isophorone have higher boiling points, and so belong to the heavy components of the system, which have to be withdrawn as the bottom product of the column. An increase in the number of trays in the stripping section is therefore beneficial to the separation of the light and heavy components. It can thus reduce the loss of light components in the bottom product, allowing for greater quantities of the cyclohexene and water reactants to return to the reaction section. It may be seen from Fig. 11(a) that the conversion of cyclohexene increased upon increasing the number of trays in the stripping section. However, after 5 trays, no further increase in the cyclohexene conversion was observed, but the energy consumption of the catalytic distillation column increased, as seen

in Fig. 11(b). Thus, an optimal number of 5 trays in the stripping section was found.

#### **Effect of the cyclohexene to water feed ratio on cyclohexene conversion**

The cyclohexene to isophorone feed ratio was fixed at 1.5, the number of distillation section trays was 5, the number of reaction section trays was 12, the number of stripping section trays was 6, the cyclohexene feed position was the 18th tray, the water and isophorone feed position was the 5th tray, the reflux ratio was 3, the D/F ratio was 0.25. The cyclohexene to water feed ratio was varied to examine its effect on the conversion rate of cyclohexene, and the results are presented in Fig. 12.

It may be seen from Fig. 12 that a cyclohexene to water feed ratio of 0.5 was optimal. More cyclohexene in the feed decreased its conversion.

#### **Effect of the cyclohexene to isophorone feed ratio on cyclohexene conversion**

The cyclohexene to water feed ratio was fixed at 0.5, the number of distillation section trays was 5, the number of reaction section trays was 12, the number of stripping section trays was 6, the cyclohexene feed position was the 18th tray, the water and isophorone feed position was the 5th tray, the reflux ratio was 3, and the D/F ratio was 0.25. The cyclohexene to isophorone feed ratio was varied to examine its effect on the conversion rate of cyclohexene, and the results are shown in Fig. 13.

It may be seen from Fig. 13 that the optimal cyclohexene to isophorone feed ratio was 1.5. Upon increasing the amount of isophorone, the solubility of cyclohexene and water increased, thereby promoting the conversion of cyclohexene. However, beyond a certain point, increased solvent volumes resulted in dilution of the reactants, thereby lowering the conversion.

#### **Effect of the cyclohexene feed position on its conversion**

The cyclohexene to isophorone feed ratio was fixed at 1.5, the cyclohexene to water feed ratio were 0.5, the number of distillation section trays was 5, the number of reaction section trays was 12, the number of stripping section trays was 6, the cyclohexene feed position was the 18th tray, the water and isophorone feed position was the 5th tray, the reflux ratio was 3, and the D/F ratio was 0.25. The feed location of cyclohexene was varied to examine its effect on the conversion rate of cyclohexene, and the results are shown in Fig. 14. As indicated, the optimal cyclohexene feed position was the 18th tray. When cyclohexene was fed at a higher or lower tray, the reaction was incomplete and the conversion low.



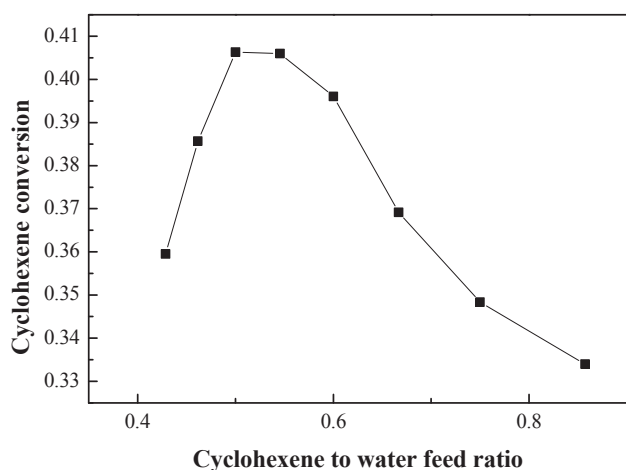


Fig. 12 – Effect of cyclohexene to water feed ratio on cyclohexene conversion

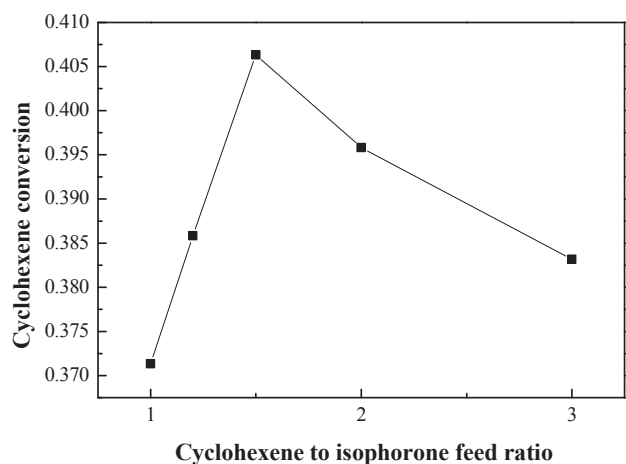


Fig. 13 – Effect of cyclohexene to isophorone feed ratio on cyclohexene conversion

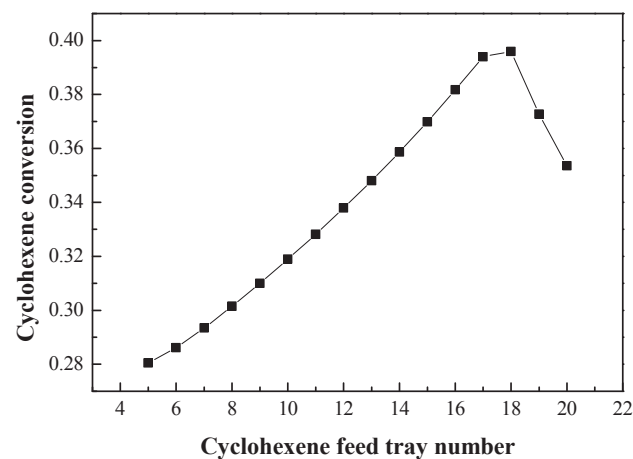


Fig. 14 – Effect of cyclohexene feed position on cyclohexene conversion

## Conclusions

In order to improve the conversion of cyclohexene and reduce the energy consumption of the catalytic distillation column, different variables were optimized, such as the number of trays in the rectification, reaction, and stripping sections, the product to feed ratio, as well as the position of cyclohexene, water and isophorone feed. Following the optimization of the cyclohexene hydrate catalytic distillation column model, the optimal operating conditions were found, as follows: cyclohexene to isophorone feed ratio 1.5; cyclohexene to water feed ratio 0.5; 5, 12, and 6 trays in the rectification, reaction, and stripping sections, respectively; 18th tray as the cyclohexene feed position; 5th tray as the water and isophorone feed position. In all calculations, reflux ratio of 3 and D/F ratio of 0.25 were used. Under these process conditions, the conversion of cyclohexene was 40.63 %, the top condenser heat duty was 206.34 kW, and the reboiler heat duty was 245.20 kW.

The new catalytic distillation process using isophorone as a cosolvent, A-36 cation exchange resin as a catalyst, and operating at optimal reaction conditions, as obtained by the simulation study, significantly improved the cyclohexene conversion in comparison with the previous processes using isophorone as a cosolvent and ZSM-5 as a catalyst or using other cosolvents. The results of the simulation study were also confirmed experimentally.

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