CHAPTER II

CONVERSION OE CYCLOHEXENE TO CYLOHEXANOL IN A CHROMATOGRAPHIC REACTOR

Conversion of Cyclohexene to Cyclohexanol in a Chromatographic Reactor

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Abstract

Cyclohexanol is mainly used for the production of adipic acid, which is an intermediate for the production of nylon-6,6. The production of cyclohexanol through the hydration of cyclohexene with an acidic catalyst, e.g., ZSM-5, is an important process in the petrochemical industry. However, this process yields low cyclohexene conversion, i.e. 7-10%, due to thermodynamic equilibrium of the reaction. In this work, to improve the yield of cyclohexene conversion, the reaction was carried out at 80, 100, 120 and 140 °C in a chromatographic reactor, in which the reaction and separation of the product took place, simultaneously. Results from this reactive separation system indicated that the thermodynamic equilibrium could be overcome with essentially 100 %. With water as a continuos phase, only 0.56 wt% (ZSM-5) and 0.73 wt % (Amberlyst-15) of cyclohexanol was obtained while with cyclohexene, up to 1.89 wt% (Amberlyst-15) of cyclohexanol was achived. The effect of catalyst acidity on the cyclohexene hydration was also studied in a batch system with different catalysts, i.e., Amberlyst-15 and ZSM-5, at 80, 100, 120 and 130 °C. The results showed that for the catalyst acidity did affect the conversion of cyclohexanol.

1. Introduction

Cyclohexanol has its place in various industrial applications, such as the production of adipic acid, a raw material of nylon 66. It is also used as a solvent for lacquers, shellacs, varnishs, cellulose nitrate and resin solutions. Moreover, the chemical is a starting raw material in the preparation of esters for plasticizers, e.g., dicyclohexyl phthalates.

Cyclohexanol is commercially produced from phenol hydrogenation or air oxidation of cyclohexane. In the former, 80% of phenol is hydrogenated to cyclohexanol and cyclohexanone as a by-product by using a metal-catalyst such as Pd/MgO under mild conditions [1]. In the latter, cyclohexane is oxidized with air to a mixture of cyclohexanone and cyclohexanol, known as K/A oil, as major products and by-products are alcohols, aldehydes, and ketones. In the oxidation method, the K/A oil selectivity is as high as 75-80%; however, the conversion of cyclohexane is only 4-6% due to the thermodynamic equilibrium of the reaction. Furthermore, the treatment of by-products is expensive [2].

Attempts to obtain high conversion of cyclohexane and selectivity of K/A oil have been made through the oxidation under mild conditions. An example is the cyclohexane oxidation using N-hydroxyphthalimide (NHPI) combined with a metal-catalyst such as Co or Mn. This process gives higher conversion of cyclohexane of 40–50% and higher selectivity to K/A oil and adipic acid under mild conditions without toxic by-products [3-4]. Another new technology for the cyclohexanol production is cyclohexene hydration using zeolite with the reactive separation technique, which overcomes the thermodynamic equilibrium limitation, resulting in nearly 80% conversion to cyclohexanol and cyclohexane as a by-product [5-6].

However, because of the slurry characteristic of this process, the catalyst separation becomes a problem.

In order to avoid the catalyst separation problem, a zeolite packed-bed reactor was used in this work for the hydration of cyclohexene to cyclohexanol. The main objective of this work was to use a chromatographic reactor for the cyclohexene hydration. With the reactor, not only can the thermodynamic equilibrium limitation be overcome through the reactive separation technique but also the catalyst separation is not necessary. In addition, effects of different catalysts, ZSM-5 and Amberlyst-15, on the hydration were also investigated.

2. Experimental Section

2.1. Materials

2.1.1 Gases

Ultra high purity (UHP) hydrogen was used as a fuel for FID detector.

Air zero grade was used for the FID detector. High purity (HP) helium was used as a carrier gas for a Fison gas chromatograph.

2.1.2. Chemicals

Acetone (C_3H_6O) of min 99.9 % purity was obtained from Labscan Asia co., Ltd. (Bangkok, Thailand).

Cyclohexane (C_6H_{12}) of min 99 % purity was obtained from Labscan Asia co., Ltd. (Bangkok, Thailand).

Cyclohexene (C_6H_{10}) of min 99 % purity was obtained from Asia Pacific Specialty (Seven Hill, Australia).

Cyclohexanol ($C_6H_{12}O$) of min 98 % purity was obtained from Carlo Erba Reagenti (Milano, Italy).

n-Hexane (C_6H_{14}) of min 99 % purity was obtained from Merck (Darmstadt, Germany).

Methanol (C_3H_4O) of min 99.9 % purity was obtained from Labscan Asia co., Ltd. (Bangkok, Thailand).

2.1.3. Catalysts

Amberlyst-15 with the average pore diameter of 250 A° and in the hydrogen form was obtained from Rohm and Hass (Philadephia, USA).

ZSM-5 with 40 SiO_2/Al_2O_3 and the average pore size diameter of 5.4 A° and in the hydrogen form was obtained from UOP LLC (Illinois, USA).

2.2 Cyclohexene Hydration Experiments

2.2.1. In a Batch Reactor

Experiments were performed using a stirred-well batch reactor at atmospheric pressure and 80, 100, 120, and 130 °C with different catalysts. The batch reactor was made of stainless steel 316 with 10 mm in thickness. The volume was about 200 cm^3 with 8.3 and 5.5 cm as the height and inside diameter. The top plate of the reactor was held in place with eight bolts. Heat was provided by a heating coil and controlled by a PID temperature controller in the temperature range of 80-140 °C. The reactor was connected with a K-type thermocouple through the top plate. An o-ring was placed between the top plate and the reactor to prevent any leak. Solution inside the reactor was constantly stirred. A sample from the reactor was drawn through the tube, connected at the bottom of the reactor (See Fig. 1). The samples were automatically injected into a Fison gas chromatograph equipped with an FID detector.

An experiment was started by adding cyclohexene, water, and a catalyst at the ratio of 2.4:2.7:1.0 by weight into the reactor. The type of catalysts and temperature were used according to Table 1. The system was left until it reached equilibrium. The equilibrium of the system was observed by measuring the liquid solution in the oil phase with the GC/FID until a constant concentration of each species was observed. Only the composition in the oil phase was analyzed because

cyclohexene and cyclohexanol are slightly soluble in water and can be negligible when the ratio of the oil and aqueous phases are almost equal [6].

2.2.2. In a Chromatographic Reactor

A catalyst was packed into a 70 cm³ column with 0.75 and 158 cm as the inside diameter and length. Quartz wool was used to block the catalyst at both ends of the column. After the column was connected to the test unit, the continuous phase reactant pump was turned on. A continuous phase reactant was passed through the packed column at a constant flow rate of 0.8 cm³ /min. Another reactant, the injected reactant, of 2 cm³ was injected through a six-ports valve with a 10-minutes interval. The operating temperature was varied from 80–140 °C with a temperature controlled hot box. A fan was used to circulate the air in order to unitize the temperature. A schematic diagram of the experimental set-up is shown in Fig. 2. During the injection, the fraction collector was started to collect the system effluent every 2 minutes. Each fraction containing approximately 1.6 cm³ of the sample was then analyzed for its concentration by means of the same GC. The experiment was performed with different catalysts, temperatures and the mode of operations as in Table 2.

2.3 Equilibrium Adsorption Experiments

The experiment was performed by packing Amberlyst-15 in the same column as mentioned in the previous section. 100 cm³ of the feed consisting of 85% cyclohexene. Ten % cyclohexanol and 5% n-hexene was passed through the packed column at a constant flow rate of 1.2 cm³/min. After that, 100 cm³ of the desorbent (water) was fed into the reactor at the same flow rate through a three-ways valve. The fraction collector started to collect the system effluent every 2 minutes. Each fraction, approximately 2.4 cm³, was analyzed for its concentration with the GC. The operating temperature was 120 °C. The pressure in the reactor was maintained at 500 psig by a back-pressure valve. The system was left until it reached steady state.

3. Results and Discussion

3.1. Effect of Catalysts

The cyclohexene hydration was performed in the batch reactor at 120 °C with either ZSM-5 (Si/Al$_2$:40) or Amberlyst-15 as a catalyst. The comparison of the cyclohexene conversion and cyclohexanol concentration at equilibrium from this work to that from Ishida *et al.* [7] is shown in Table 3. It can be clearly seen that for ZSM-5 the higher acidity of the catalysts, the higher cyclohexene conversion and cyclohexanol concentration. Moreover, the results from the table also shows that the cyclohexanol selectivity using ZSM-5, with 5.4 A° pore size, as a catalyst, is not significantly different from the cyclohexanol selectivity using Amberlyst-15 with 250 A° pore size as a catalyst. So, it can be postulated that the pore size of the catalysts does not affect the cyclohexanol selectivity.

The kinetics of the hydration was derived for the cyclohexene hydration in the batch reactor at 120 °C. The reaction is assumed to proceed reversibly with the first order with respect to both cyclohexene and cyclohexanol, according to eqn. (1).

$$\bigcirc + H_2O \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \bigcirc^{OH} \tag{1}$$
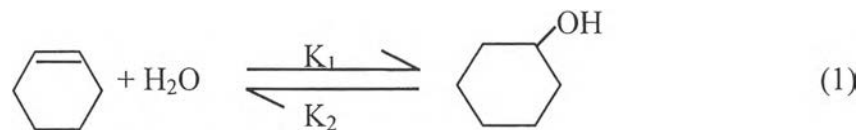
The rate equation is

$$-r_{HE} = K_1 . C_{HE} - K_2 C_{HL} \tag{2}$$

The cyclohexanol selectivity is 100 %, so eqn. (2) can be rearranged to

$$-r_{HE} = K_1 . C_{HE} \times \{1 - X_{HE}(1 + \frac{1}{K_c})\} \tag{3}$$

where

C_{HE0}	Initial concentration of cyclohexene
C_{HE}	Concentration of cyclohexene at time t
C_{HL}	Concentration of cyclohexanol at time t

X_{HE} Conversion of cyclohexene

K_C $K_1/K_2 = $ [cyclohexanol]/[cyclohexene] at equilibrium

$-r_{HE}$ Rate of reaction

K Reaction rate constant at 120 °C

The rate eqn. (3) is integrated to

$$t = -k \times \ln(1 - (1 + \frac{1}{K_c}) X_{HE})$$

(4)

K_C is 0.051, as obtained from the experimental data of cyclohexene hydration in the batch reactor at 120 °C. The experimental data can then be plotted versus time as shown in Fig. 6, and the reaction rate constant, k, was determined to be 0.0056 mol/l.min from the slope.

The cyclohexene hydration with ZSM-5 (Si/Al$_2$:40) and Amberlyst-15was also performed in the chromatographic reactor. Water was used as a continuous phase reactant with cyclohexene injection, Experiment No.1 and 2 in Table 2. The results are shown in Table 3. With Amberlyst-15 as a catalyst, the average conversion of cyclohexene is 12.45% and the average concentration of cyclohexanol in the eluted solution is 0.73 wt%. The results are approximately the same when ZSM-5 was used, 13.77 % conversion and 0.56 wt% of cyclohexanol. The results indicate that the chromatographic reactor can overcome the thermodynamic equilibrium limitation of the cyclohexene hydration. However, the chromatographic reactor resulted in a low cyclohexanol concentration in the eluted solution, posing a problem in the separation of cyclohexanol. To increase the cyclohexanol concentration, the effect of using different continuous phase reactants on the cyclohexanol concentration was investigated.

3.2 . Effect of a continuous phase reactant

Three continuous phase reactants 1) water, 2) cyclohexene, and 3) 50:50 of cyclohexene:cyclohexane, were used to investigate the effect of different continuous phases on the cyclohexene hydration with Amberlyst-15 as the catalyst. Fig. 3 shows the comparison of cyclohexanol concentration in the eluted solution from the

different continuous phases in the chromatographic reactor according to Experiment No. 2, 3 and 4 in Table 2. The average cyclohexanol concentrations are 0.73, 1.89 and 0.89 wt% with water, cyclohexene and the mixture of cyclohexene and cyclohexanol as the continuous phases, respectively. The highest concentration of cyclohexanol was obtained with cyclohexene as a continuous phase reactant. So, effect of temperature on cyclohexene hydration was investigated with cyclohexene.

The effect of temperature on cyclohexene hydration in the chromatographic reactor is shown in Fig. 4. The results are also compared to those from the equilibrium data from the batch reactor. It can be clearly seen that the conversion of cyclohexene in the chromatographic reactor increases with the increase of the reaction temperature, unlike those from the equilibrium in the batch reactor

Interestingly, when the temperature is higher than 130 °C, cyclohexene conversion in the chromatographic reactor is higher than the equilibrium conversion from the batch experiment. In other words, the equilibrium limited conversion of cyclohexene can be overcome at 130 °C or higher. The above results have posed a question on the lower cyclohexene conversion for the chromatographic reactor than that from the batch reactor at the temperature lower than 130 °C. It was postulated that cyclohexanol, the product of cyclohexene hydration, is strongly adsorbed on Amberlyst-15. To elucidate that, cyclohexene and cyclohexanol adsorption experiments on Amberlyst-15 in the chromatographic reactor at 120 °C was carried out.

Fig. 5 shows the cyclohexene and cyclohexanol concentration as a fraction of retention time. The results indicate that cyclohexanol is adsorbed more strongly than cyclohexene by Amberlyst-15. At the beginning, cyclohexene was adsorbed and later replaced by cyclohexanol as indicated by the roll-up on the cyclohexene conversion. With this, the postulate has been verified; that is, cyclohexanol being adsorbed on the catalyst as the hydration takes place and certain high temperature is required for the desorption of cyclohexanol.

4. Conclusions

Cyclohexene hydration with ZSM-5 and Amberlyst-15 in both batch and chromatographic reactors was investigated. With ZSM-5 as a catalyst, acidity played an important role in the hydration. In the chromatographic reactor, with the same conditions as in the batch reactor (120 °C), the thermodynamic limitation was overcome with low cyclohexanol concentration (0.56 and 0.73 wt%) when water was used as a continuous phase reactant. Nevertheless, with cyclohexene as a continuous phase reactant, the thermodynamic limitation of the cyclohexene hydration was overcome with high concentration of cyclohexanol (1.89 wt %) at temperature higher than 130 °C. A suitable desorbent is needed to increase the cyclohexene conversion at lower temperature.
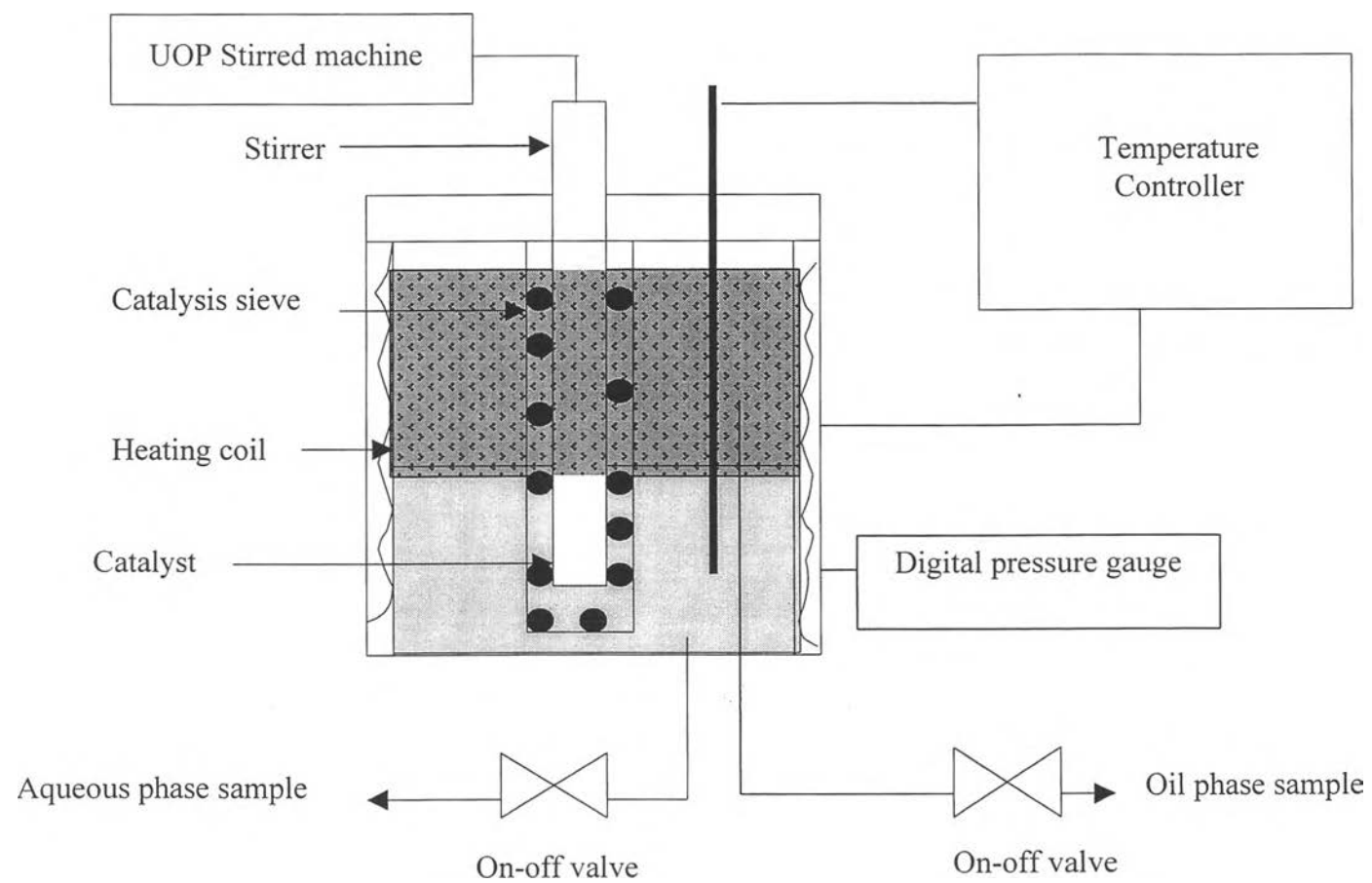
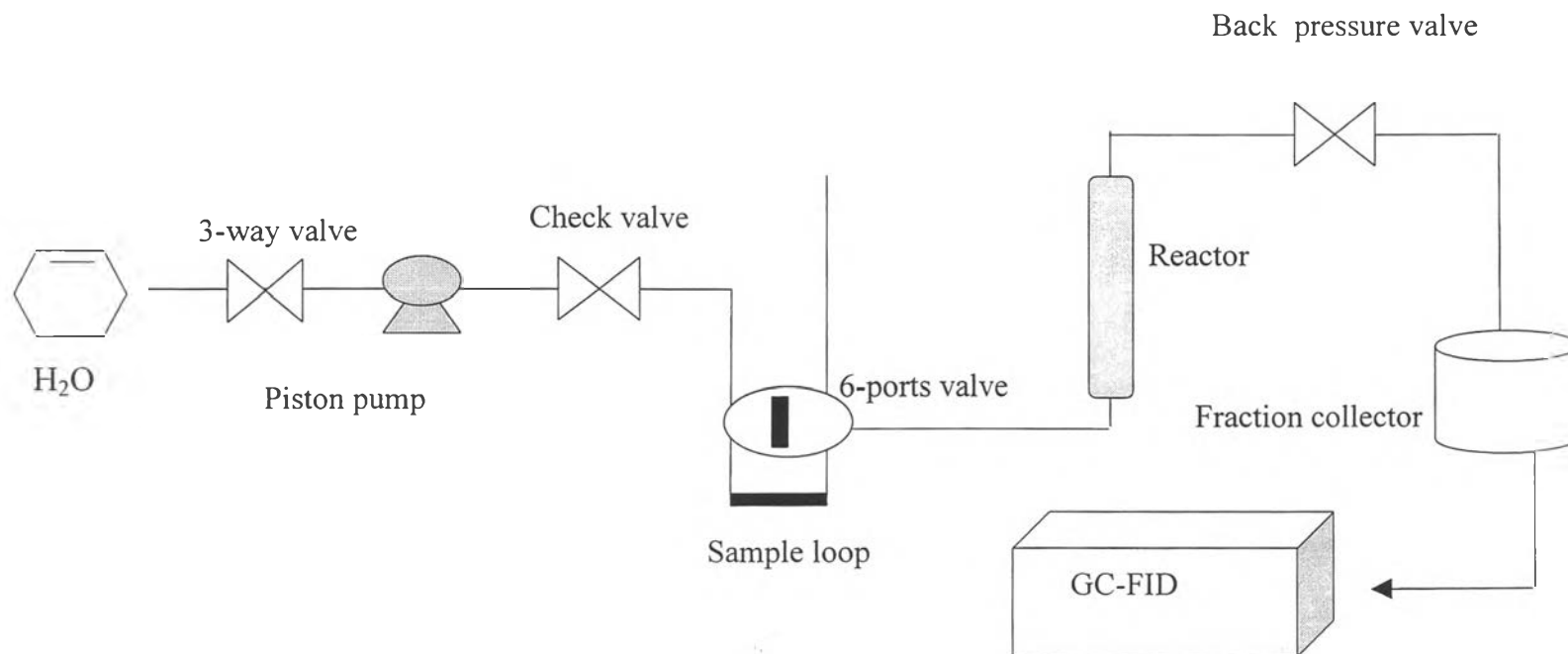Fig. 1. A schematic diagram of the set-up of the batch reactor.

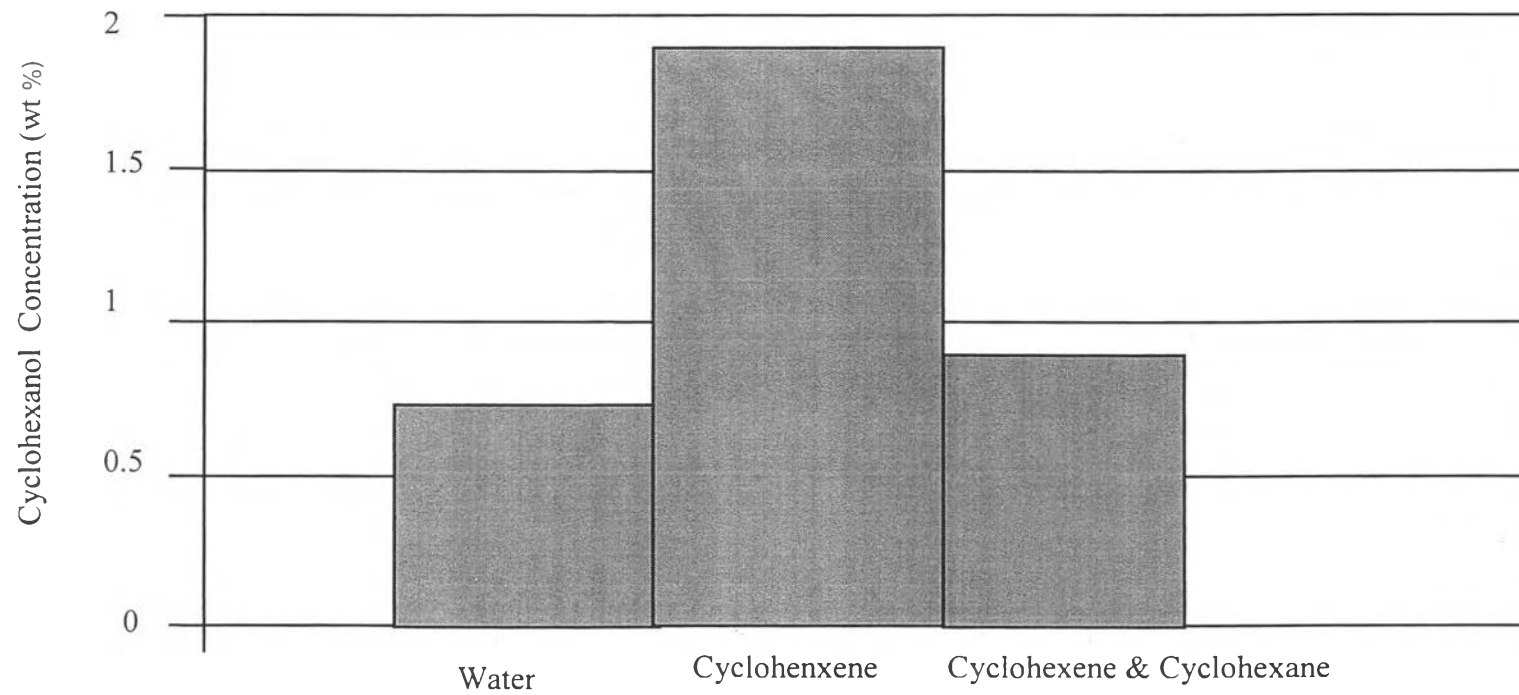Fig. 2. A schematic diagram of the chromatographic reactor for the cyclohexene hydration.

Fig. 3. Cyclohexene hydration with Amverlyst-15 at 120 °C with different continuous phase reactants in the chromatographic reactor.
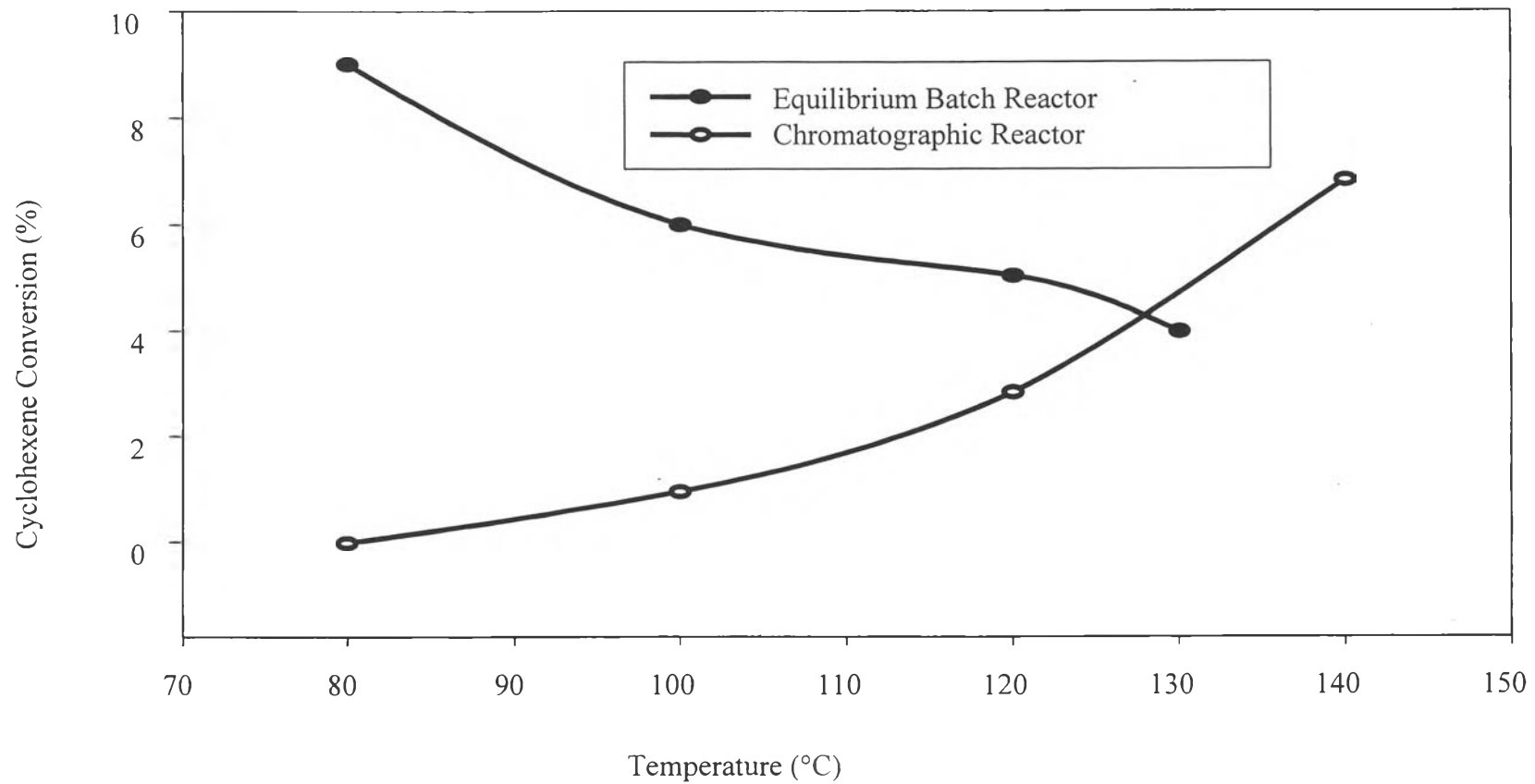
Fig. 4. The comparison of cyclohexene conversion with Amberlyst-15 as a catalyst from the batch reactor and the chromatographic reactor with cyclohexene as a continuous phase.
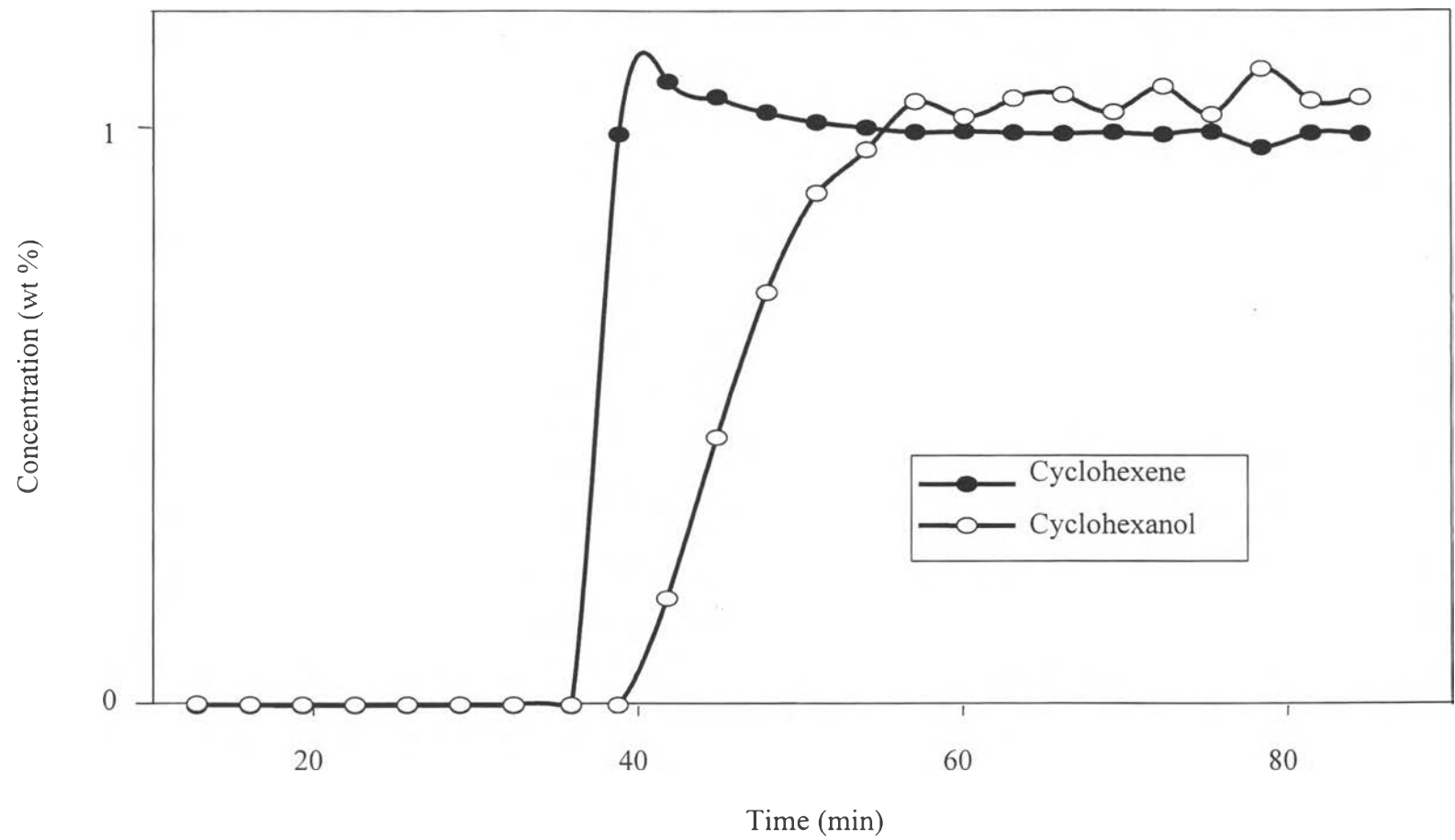
Fig. 5. The cyclohexene and cyclohexanol adsorption on Amberlyst-15 at 120 °C in the chromatographic reactor.
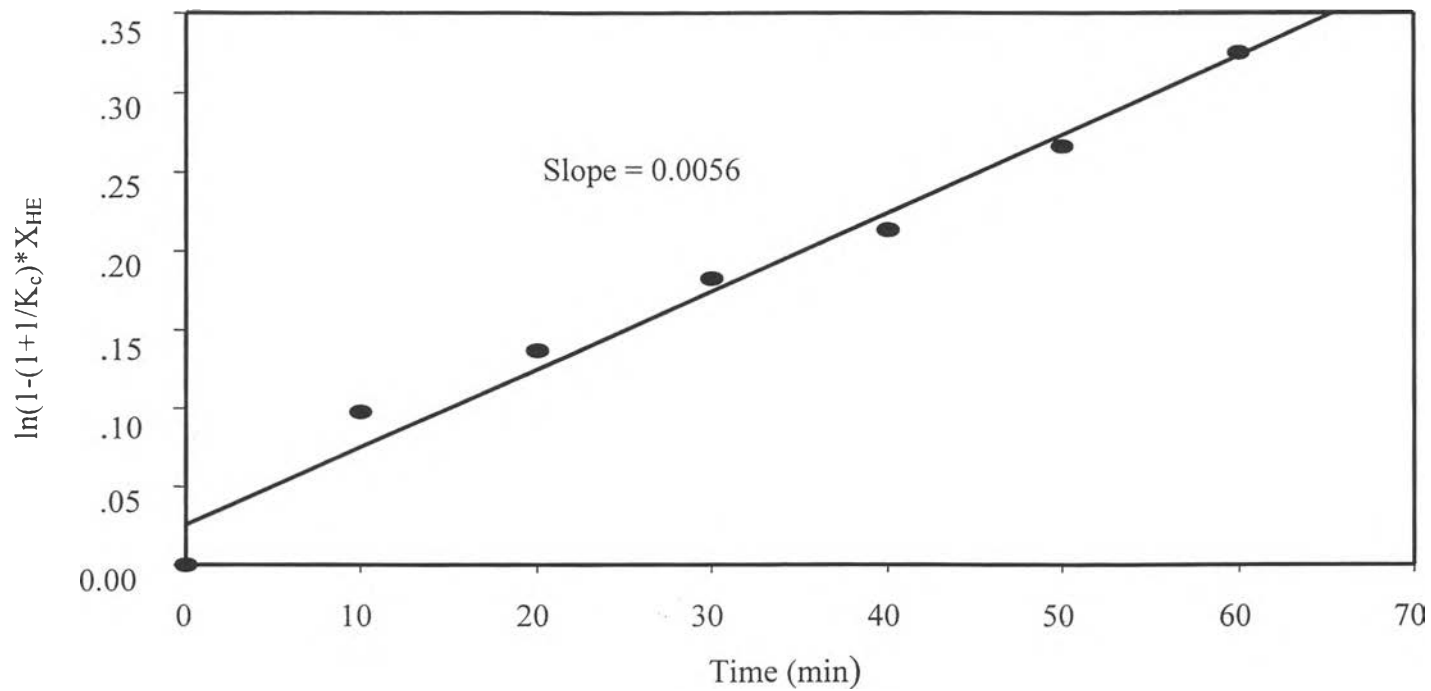
Fig. 6. The plot $-\ln(1-(1+1/K_c)*X_{HE}$ vs time (min) from the cyclohexene hydration in the batch reactor at 120 ° C.

Table 1

The experimental conditions for the cyclohexene hydration experiments in the batch reactor

Experiment No.	Catalyst	Temperature (°C)
1	ZSM-5	120
2	Amberlyst-15	80
3		100
4		120
5		130

Table 2

The experimental conditions for the cyclohexene hydration experiments in the chromatographic reactor

Experiment No.	Catalyst	Temperature (°C)	Continuous Flow Reactant	Injected Reactant
1	ZSM-5	120	Water	Cyclohexene
2	Amberlyst-15		Water	Cyclohexene
3			Cyclohexene	Water
4			Cyclohexene & Cyclohexane (50:50 %wt)	Water
5		80	Cyclohexene	Water
6		100		
7		140		

Table 3

The cyclohexene hydration with ZSM-5 and Amberlyst-15 at 120 °C

Catalyst	Si/Al$_2$	Batch Reactor (Equilibrium)		Chromatographic Reactor	
		Cyclohexene Conversion (%)	Cyclohexanol Concentration (wt%)	Cyclohexene Conversion (%)	Cyclohexanol Concentration (wt%)
ZSM-5	25.0	10.7	6.0[7]	-	-
	30.0	7.5	4.2[7]	-	-
	40.0	7.1	3.9	13.77	0.56
Amberlyst -15	-	5.1	2.9	12.45	0.73

Note: Cyclohexanol selectivity is 100%.

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