

Batch and Continuous Process of Cyclohexanol Production

Abdul-Halim A-K Mohammed

Chemical Engineering Department – College of Engineering - University of Baghdad - Iraq

ABSTRACT

The dehydrogenation of phenol to cyclohexanol by continuous flow process using commercial Ni catalyst supported with charcoal and prepared Ni/Al₂O₃ catalyst was studied. It was found that the higher yield obtained from commercial catalyst is 53.1% at 160 °C, pressure 1.0 MPa, LHSV 0.5 h⁻¹ and H₂ to phenol ratio 1.5 mole/mole, while the prepared catalyst gave higher yield (73.3%) at 155 °C, pressure 1.5 MPa, LHSV 0.35 h⁻¹ and H₂ to phenol ratio 5 mole/mole.

Phenol was also hydrogenated to cyclohexanol by batch process at temperature range of 90-160 °C, pressure 1.5 MPa and prepared Raney nickel catalyst to phenol 7.3%. It was found that the increase in temperature had slight effect on the yield of cyclohexanol, while the residence time decreased from 100 to 50 minutes. Using the percentage of catalyst to phenol in the range of 3.2-7.3% increased the yield of cyclohexanol from 93.3 to 97.5%, while the residence time decreases from 110 to 80 minutes, respectively.

INTRODUCTION

It is possible to obtain a mixture of cyclohexanol-cyclohexanone by hydrogenation process using different types of catalyst based on Zn and Cu and temperature range of 400-450 °C.

There are numerous patents describing the production of mixture of cyclohexanol-cyclohexanone and cyclohexanol from phenol, but they differ by operating conditions and catalyst used.

US patent 3,998,884⁽¹⁾ and US patent 4,410,741⁽²⁾ study the use of Ni catalyst for cyclohexanol production, while US patent 2,794,056⁽³⁾ study the effect of different percentage of Ni to Ruthenium supported with chromium oxide catalyst using base media on the yield of cyclohexanol.

US patent 4,053,521⁽⁴⁾ describes the use of catalyst based on Ni, Mn, and Mg oxides.

US patent 4,409,401⁽⁵⁾ mentioned the preparation of 0.01-5% Pd catalysts supported with alumina-silica, alumina and silica promoted with sodium and improved with different organic sulfur compounds.

This investigation deals with the production of cyclohexanol from phenol using commercial and prepared catalysts, by a batch and continuous processes.

EXPERIMENTAL

Feedstock:

Phenol with purity of 99% was used for cyclohexanol production. The chromatographic analysis showed that this feedstock contained 0.7% cyclohexanol and 0.3% cyclohexanone.

Catalyst:

Catalyst for continuous operation

Ni supported with charcoal imported from Harshaw company and laboratory prepared catalyst were used for continuous production of cyclohexanol.

The catalyst preparation included calcination of 100 g γ -Alumina at 600 °C for four hours, cooling the calcined γ -Alumina to room temperature, controlled vacuum impregnation by 164.4 g of nickel nitrate in 25 ml of distilled water and then drying of the catalyst at 130 °C for 5 hours.

Catalyst for batch operation

Prepared Raney nickel was used for batch hydrogenation of phenol. Ni-Al alloy (BDH) was treated with 25% sodium hydroxide solution.

Sodium hydroxide solution was prepared by dissolving 380 g pure sodium hydroxide in 1.5 liter distilled water and the solution was cooled to 10 °C. 300 g of Ni-Al alloys powder was added slowly (about 2 hours) to the NaOH solution with continuous mixing. The temperature was kept at 25 °C. Then the content was heated up to 65 °C in water bath for 8 hours until the hydrogen evolution was discontinued.

In order to precipitate the Ni, the content was poured onto 50 g NaOH in 500 ml distilled water. After 10 minutes, Ni was washed ten times with distilled water until the pH value reaches 7, then washed 3 times with 95% ethanol (200 ml each wash), and repeated with 99% ethanol. The prepared Raney Ni was kept in 99% ethanol to protect it from oxidation. Table (1) shows some properties of the catalysts.

Table (1) Some Properties of the Catalysts

Properties	Ni/Charcol	Ni/Al ₂ O ₃
1 Nickel Content, %	60.6	12.5
2 Surface Area, m ² g ⁻¹	102.7	220
3 Apparent Density, g cm ⁻³	0.7	0.4
4 Pore Volume, cm ³ g ⁻¹	0.38	0.19

Hydrogenation Process:

Continuous hydrogenation

Phenols was hydrogenated with continuous flow, in a laboratory unit shown in Fig. (1). Phenol was preliminary melted to liquid, then it pumped into the reactor after being mixed with required quantity of hydrogen. Reaction takes place at the packed bed of

90 cm³ catalyst. The reactor was heated with four separated heating shells and the temperature was regulated in each of these four shells. The product was cooled and separated from H₂ through high pressure separator followed by low pressure separator. Finally the gas passed through wet gas meter.

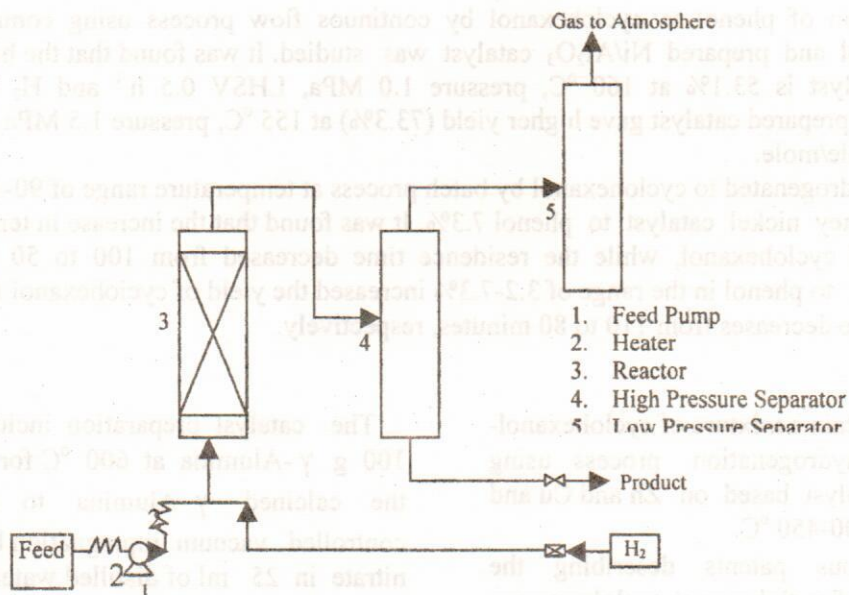


Figure (1) Laboratory Continuous Flow Hydrogenation Unit

Batch hydrogenation

1 liter high pressure (up to 20 MPa) stainless steel autoclave was used for batch operation.

Figure (2) showed a simplified scheme of the autoclave system. Autoclave was cleaned and charged with 94 g of phenol and calculated quantity of prepared Raney Ni (3.0-6.5 g). The autoclave was closed then discharged from air by H₂ and the required pressure of H₂ was obtained. Temperature was increased gradually until the desired level was reached.

Chromatographic Analysis:

The products were analyzed by gas chromatograph 204 Pye Unikamp connected with computer and recorder. Glass column diameter 1/4 in and length 2 m packed with 10% OV-101 was used. Pure N₂ was used as carrier gas with flow rate 20 ml min⁻¹. The temperature of ionization detector was kept at 250 °C, while column temperature was programmed to be fixed at 100 °C for 5 minutes, then increased by 16 °C per minute up to 150 °C. The quantity of injected sample was 0.15 microliter and the injector temperature was 250 °C.

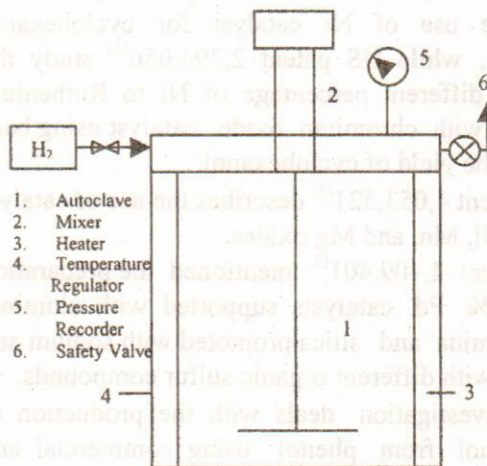


Figure (2) Laboratory Continuous Flow Hydrogenation Unit

RESULTS AND DISCUSSION

As it shown in Table (2) the yield of cyclohexanol and cyclohexanone using Ni-charcoal catalyst was increased by decreasing pressure from 1.0 to 0.5 MPa at constant temperature of 160 °C, LHSV of 0.5 h⁻¹ and H₂ to phenol ratio of 2.5 mole/mole.

Table (2) The Results of the Continuous Phenol Hydrogenation

No.	Operating Conditions					Chromatographic Analysis				
	T °C	P MPa	LHSV h ⁻¹	H ₂ to Phenol, mole/mole	Catalyst Type	Cyclo-hexanol	Cyclo-hexanone	Cyclo-hexane	Unknown	Phenol
1	160	0.5	0.5	2.5	Commercial	46.5	11.4	1.6	2.9	37.6
2	160	0.7	0.5	2.5	Ni-Charcoal	31.0	10.0	-	-	59.0
3	160	1.0	0.5	2.5	Ni-Charcoal	23.3	1.1	0.8	-	74.8
4	160	1.0	0.5	4.5	Ni-Charcoal	53.1	4.1	1.5	2.4	38.9
5	160	1.0	1.0	2.5	Ni-Charcoal	18.8	5.1	0.8	-	75.3
6	160	0.5	0.5	1.5	Ni-Charcoal	12.1	6.5	0.5	-	80.9
7	155	1.5	0.35	5.0	Prepared NI-Alumina	73.5	0.8	22.8	1.4	1.5

Table (3) The Results of the Batch Phenol Hydrogenation

No.	Operating Conditions				Chromatographic Analysis				
	T °C	P MPa	Residence Time	Catalyst to Phenol, wt%	Cyclo-hexanol	Cyclo-hexanone	Cyclo-hexane	Unknown	Phenol
1	90	1.5	100	7.3	97.5	-	1.9	0.6	-
2	100	1.5	80	7.3	97.5	-	1.8	0.7	-
3	120	1.5	70	7.3	98.1	-	1.9	-	-
4	135	1.5	60	7.3	97.0	-	2.3	0.7	-
5	160	1.5	50	7.3	97.1	-	2.2	0.7	-
6	100	1.5	90	5.9	97.8	-	1.9	0.3	-
7	100	1.5	100	4.8	96.7	-	1.9	-	1.2
8	100	1.5	110	3.2	93.3	-	1.9	-	4.8
9	100	1.5	80	5.9	38.3	7.3	1.7	-	52.7
10	100	1.5	80	3.2	11.5	9.0	1.2	-	78.3

The ratio of H₂ to phenol at the range 1.5 to 4.5 mole/mole, temperature 160 °C, pressure 1.0 MPa and LHSV 0.5 h⁻¹ increased the cyclohexanol yield from 12.1 to 53.1% by wt. While the use of Ni-Alumina catalyst at temperature of 155 °C, LHSV of 0.35 h⁻¹ pressure 1.5 MPa and H₂ to phenol ratio of 2.5 mole/mole gave 73.5% cyclohexanol with remarkable yield of cyclohexanone (22.8%).

Thus, the above experiments showed that the higher cyclohexanol yield requires low LHSV and high concentration of hydrogen.

Table (3) showed the effect of temperature in the range of 90-160 °C at pressure 1.5 MPa and percentage of Raney nickel catalyst to phenol 7.3% upon the cyclohexanol yield. The increasing of temperature from 90 to 160 °C had slight effect on the cyclohexanol yield (97.0-98.1%) while the residence time decreased from 100 to 50 minutes, as shown from Fig. (3). This is due to the increasing of reaction rate by temperature.

The study of the effect of catalyst to phenol percentage in the range of 3.2-7.3% showed that the yield of cyclohexanol increased from 93.3 to 97.5% although the residence time decreased from 110 to 80 minutes as shown in Fig. (4) and Table (3).

The change in the percentage of catalyst of phenol from 3.2 to 7.3% at temperature 100 °C and residence time 80 minutes increased the cyclohexanol from 11.5 to 97.5% as shown from Fig. (5).

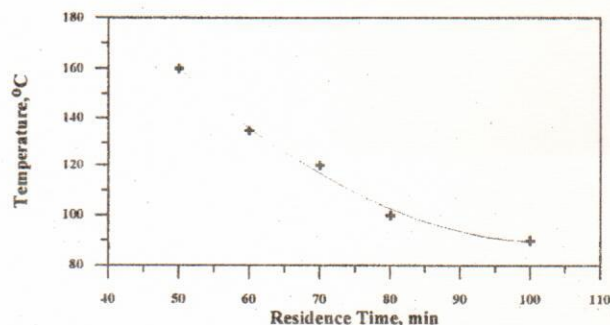


Fig.3 The Effect of Temperature on the Residence Time at 7.3 wt% of Catalyst to Phenol Percentage

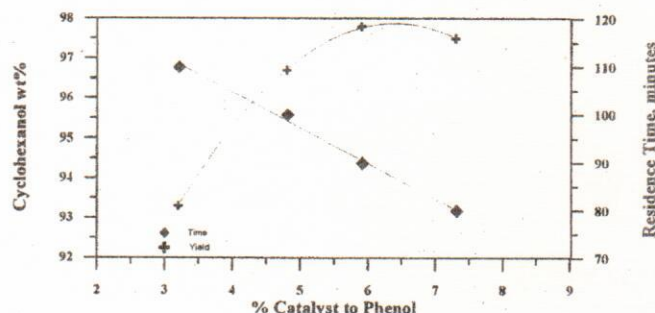


Fig.4 The Effect of Catalyst to Phenol Percentage on the cyclohexanol Yield and residence Time at 100 °C

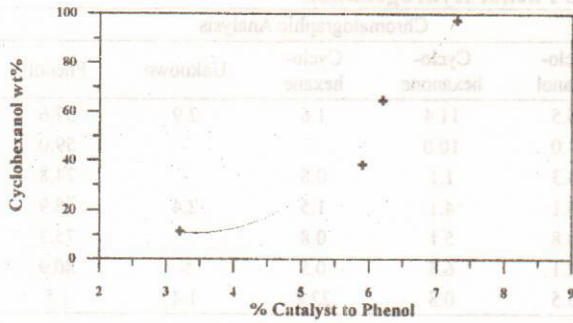


Fig.5 The Effect of Catalyst to Phenol Percentage on Cyclohexanol Yield at 100 °C and Residence Time 80 minutes

CONCLUSION

The recommended operating conditions for high yield of cyclohexanol using prepared Raney Ni and batch hydrogenation process are:

temperature 100 °C, pressure 1.5 MPa, Raney Ni to phenol 5.9% and residence time 90 minutes.

ACKNOWLEDGEMENT

The author wish to thank Fadia Sa'ab and Hussain Sahib for their participation in the experimental part of this investigation.

REFERENCES

1. US Patent 3,998,884, Dec., 21, 1976.
2. US Patent 4,410,741, Oct., 18, 1983.
3. US Patent 2,794,056, May, 28, 1957.
4. US Patent 4,053,521, Oct., 11, 1977.
5. US Patent 4,409,401, Oct., 11, 1981.

The ratio of H₂ to phenol in the range 1.5 to 4.5 mole/mole, temperature 160 °C, pressure 1.0 MPa and LHSV 0.5 h⁻¹ increased the cyclohexanol yield from 12.1 to 23.1% by wt. While the use of Ni-Alumina catalyst at temperature of 155 °C, LHSV of 0.25 h⁻¹ pressure 1.5 MPa and H₂ to phenol ratio of 2.5 mole/mole gave 73.2% cyclohexanol with remarkable yield of cyclohexanone (22.8%).

Thus, the above experiments showed that the higher cyclohexanol yield requires low LHSV and high concentration of hydrogen.

Table (3) showed the effect of temperature in the range of 90-160 °C at pressure 1.5 MPa and percentage of Raney nickel catalyst to phenol 7.3% upon the cyclohexanol yield. The increasing of temperature from 90 to 160 °C had slight effect on the cyclohexanol yield (57.0-92.1%) while the residence time decreased from 100 to 20 minutes, as shown from Fig. (3). This is due to the increasing of reaction rate by temperature.

The study of the effect of catalyst to phenol percentage in the range of 3.2-7.3% showed that the yield of cyclohexanol increased from 93.7 to 97.9% although the residence time decreased from 110 to 80 minutes as shown in Fig. (4) and Table (3).

The change in the percentage of catalyst of phenol from 3.2 to 7.3% at temperature 100 °C and residence time 80 minutes increased the cyclohexanol from 11.5 to 97.5% as shown from Fig. (5).



Fig.3 The Effect of Residence Time on the Cyclohexanol Yield at 100 °C and Catalyst to Phenol Percentage

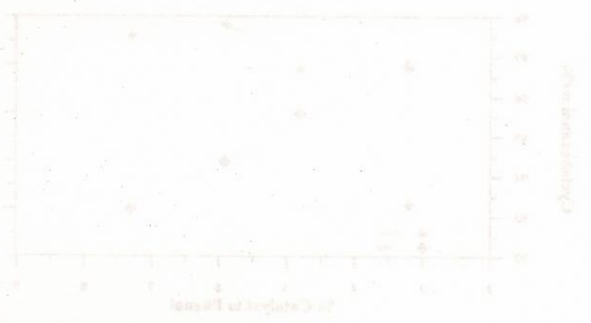


Fig.4 The Effect of Catalyst to Phenol Percentage on the Cyclohexanol Yield at 100 °C and Residence Time 80 minutes