CHAPTER IV

RESULTS AND DISCUSSIONS

In this study, the experiments will be catagorized into four sections. Experiments 1 to 9 are conducted to study the effect of temperatures and pressures. Experiments 10 to 12 are conducted to study the effect of the amount of catalyst. Experiments 13 and 14 are conducted in order to study the repeatability of the experiment at the conditions chosen. Experiments 15 to 22 are conducted to study the effect of nitrogen compounds on hydrogenation of benzene. Details of each experiment are given in Table 4.1.

In each experiment, approximately 300 cm^3 of solution of benzene (75 wt%) and n-hexane is used as a feedstock. n-Hexane is added in order to be a liquid carrier. The catalyst used is a commercial Raney nickel. The hydrogenation is performed in a batch reactor. During each experiment, liquid samples are taken at every 5 minute interval during the first hour and every 10 minute interval after that until the hydrogenation activity vanish or after six hours (for the effects of nitrogen compounds). The samples are analyzed for their composition by gas chromatographic analysis techniques. The outputs from chromatogram show that cyclohexane, which is identified from the standard retention time, is the only product observed from benzene hydrogenation. The outputs are used to calculate weight percent of benzene and

TABLE 4.1 Operating Conditions in Each Experiment

Exp. No.	Reactant	amt. of cat (gram)	Temperature (C)	Pressure (psig.)	Nitrogen compound
1	Benzene	1	120	150	-
2	Benzene	1	150	150	-
3	Benzene	1	180	150	-
4	Benzene	1	120	200	-
5	Benzene	1	150	200	-
6	Benzene	1	180	200	-
7	Benzene	1	120	250	-
8	Benzene	1	150	250	-
9	Benzene	1	180	250	-
10	Benzene	3	150	200	-
11	Benzene	2	150	200	-
12	Benzene	0.5	150	200	-
13	Benzene	1	150	200	-
14	Benzene	1	150	200	-
15	Benzene	1	150	200	pyridine
16	Benzene	1	150	200	quinoline
17	Benzene	1	150	200	butylamine
18	Benzene	1	150	200	pyrrole
19	Benzene	1	150	200	indole
20	Benzene	1	150	200	carbazole
21	Benzene	1	150	200	pyrrolidine
22	Benzene	1	150	200	pyrazine

cyclohexane in every samples, and then the concentration of benzene (C_B) at any time is calculated, by

$$\text{weight \% of benzene} = \frac{A_1}{A_1 + A_2} \times 100$$

$$\text{weight \% of cyclohexane} = \frac{A_2}{A_1 + A_2} \times 100$$

$$\text{and} \quad C_B = \frac{\text{Wt\% Benzene} \times 0.75 \times \text{density feed}}{10 \times 78.11} \quad (\text{mol/l})$$

where A_1 = peak area of benzene
A_2 = peak area of cyclohexane

Tables 4.2 to 4.5 show the concentration of benzene (mol/lite) at any time of each experiment. From benzene concentration data, the plots of benzene concentration versus time of each run are presented in Figures 4.1 to 4.6, Figures 4.8 to 4.9, and Figures 4.13 to 4.16., respectively.

From the literature, benzene hydrogenation reaction was reported as a zero-order reaction with respect to benzene (Amino, 1959; Vannice and Neikam, 1971; Moyes and Wells, 1973). Thus the rate of reaction is independent of the concentration of materials;

$$-r_B = \frac{-dC_B}{dt} = k'C_H$$

and the hydrogen flow in this study is excess, thus the reaction rate is independent of hydrogen partial pressure and then;

Table 4.2 Concentration of Benzene & Time
Effect of Temperature and Pressure

Time (min.)	concentration of benzene (mol/l)								
	150 psig.			200 psig.			250 psig.		
	120 C	150 C	180C	120 C	150 C	180 C	120 C	150 C	180 C
0	7.7775	7.7775	7.7775	7.7775	7.7775	7.7775	7.7775	7.7775	7.7775
5	7.5732	7.0740	7.5461	7.6202	7.2691	7.3450	7.6834	7.5743	6.6953
10	7.5447	7.2972	7.4035	7.5822	7.0637	7.3459	7.6441	7.5044	6.2057
15	7.4551	7.2177	7.2056	7.4816	7.0164	6.7270	7.4631	6.7938	5.9325
20	7.3507	7.1096	7.0787	7.3998	6.9186	6.3412	7.2403	6.4764	5.3859
25	7.2794	6.8551	6.9044	7.1853	6.4505	6.0074	7.0119	6.3265	5.0420
30	7.2184	6.7605	6.7534	7.0548	6.2543	5.7511	6.8905	6.0807	4.5782
35	7.1432	6.6739	6.5032	6.9303	6.0820	5.3346	6.7951	5.8169	4.1128
40	7.0638	6.4243	6.3081	6.6271	5.7269	5.0896	6.5522	5.2324	3.7151
45	7.0106	6.3227	6.1098	6.5151	5.4975	4.8172	6.3938	4.9223	3.1007
50	6.9378	5.9733	5.7978	6.3556	5.2942	4.5605	6.2602	4.6933	2.8574
55	6.9007	5.9431	5.5589	6.1955	5.0850	4.1374	6.1188	4.4370	2.3306
60	6.8107	5.8101	5.3949	6.1146	4.8067	3.9966	5.9879	4.2646	2.0955
70	6.7025	5.5854	4.9683	5.8209	4.5837	3.5110	5.7314	3.7977	1.5377
80	6.6165	5.2877	4.6969	5.7052	4.0731	3.0069	5.5339	3.1300	0.9720
90	6.5382	5.1069	4.2986	5.5836	3.6608	2.6008	5.2877	2.8043	0.4855
100	6.4855	4.7461	4.1271	5.1336	3.1851	2.1395	5.0739	2.1113	0.1078
110	6.4432	4.6286	3.8955	4.8123	2.9582	1.6866	4.7942	1.7562	0.0239
120	6.4195	4.1965	3.5119	4.5401	2.6917	1.3313	4.4561	1.4496	0.0075
130	6.3406	3.9965	3.2542	4.2741	2.4026	0.9416	4.2063	1.0545	
140	6.2955	3.6837	2.9535	3.9294	2.0552	0.8300	3.9912	0.7776	
150	6.2361	3.4575	2.6807	3.6729	1.5369	0.4251	3.8786	0.3856	
160	6.2216	3.3733	2.5789	3.4551	0.9774	0.2954	3.6068	0.1559	
170	6.1668	3.1515	2.1936	3.1667	0.6458	0.1713	3.4127	0.0141	
180	6.1362	2.9577	2.0338	2.8772	0.5083	0.0323	3.2657	0.0062	
190	6.0948	2.6187	1.5881	2.6575	0.3812	0.0541	3.1015	0.0541	
200	6.0218	2.4245	1.2092	2.4111	0.2409		2.9425		
210	5.9993	2.2781	1.0448	2.0230	0.0583		2.8399		
220	5.9891	1.9721	0.8110	1.9969	0.0073		2.7105		
230	5.9521	1.8330	0.5553	1.6320			2.5843		
240	5.9093	1.6670	0.3397	1.3457			2.4623		
250			0.1759	1.0760					
260	5.8648	1.1952	0.0677	0.9999			2.2592		
270			0.0586	0.7055					
280	5.8352	1.0174	0.0589	0.6745			2.0361		
290			0.0448	0.4438					
300	5.7661		0.0412	0.2624			1.8284		
310				0.0578					
320	5.6666			0.0456			1.6387		
330				0.0271					
340	5.6366			0.0154			1.4412		
350				0.0030					
360	5.5988	0.1052		0.0000			1.2645		

TABLE 4.3 Concentration of Benzene & Time.
Effect of Amount of Catalyst.

Time (min)	Concentration of benzene (mol/l)			
	cat. 3g	cat. 2g	cat. 1g	cat.0.5g
0	7.7775	7.7775	7.7775	7.7775
5	7.5008	-	7.2691	7.5692
10	7.4080	7.6606	7.0637	7.5246
15	7.1991	6.9618	7.0164	7.4572
20	6.2929	6.0963	6.9186	7.4178
25	5.8444	5.4436	6.4505	7.3488
30	4.8589	4.9655	6.2543	7.2782
35	3.6145	4.4356	6.0820	7.1718
40	3.0725	3.8960	5.7269	7.1076
45	2.5819	3.3659	5.4975	7.0329
50	2.0904	2.8409	5.2942	6.9719
55	1.5272	2.4166	5.0850	6.9016
60	1.1494	1.7937	4.8067	6.8965
70	0.6298	0.7306	4.5837	6.8838
80	0.2394	0.1281	4.0731	6.8055
90	0.1216	0.0100	3.6608	6.7430
100	0.0601	0.0044	3.1871	6.6931
110	0.0000	0.0035	2.9582	6.6802
120			2.6917	6.6143
130			2.4026	-
140			2.0552	-
150			1.5369	6.4457
160			0.9774	-
170			0.6478	-
180			0.5083	6.3714
190			0.3812	-
200			0.2409	-
210			0.0583	6.2283
220			0.0073	-
230			0.0000	-
240			0.0000	6.1818
250				-
260				-
270				6.0948

TABLE 4.4 Concentration of Benzene & Time Experimental Error

Time (min.)	Concentration of benzene (mol/l)			
	Exp. 5	Exp. 13	Exp. 14	Average
0	7.7775	7.7775	7.7775	7.7775
5	7.2691	7.5506	7.4630	7.4276
10	7.0367	7.3557	7.4799	7.2908
15	7.0164	7.1898	7.2334	7.1465
20	6.9186	6.8747	6.9063	6.8999
25	6.4505	6.5642	6.6350	6.5499
30	6.2543	6.2240	6.2433	6.2405
35	6.0820	6.0783	5.8565	6.0056
40	5.7269	5.8336	5.5439	5.7015
45	5.4975	5.4577	5.3103	5.4218
50	5.2942	5.2687	5.0775	5.2135
55	5.0850	5.0616	4.7830	4.9765
60	4.8067	4.7939	4.5739	4.7248
70	4.5837	4.4538	4.0929	4.3768
80	4.0731	4.0254	3.8170	3.9718
90	3.6608	3.5770	3.6024	3.6134
100	3.1871	3.3385	3.0776	3.2011
110	2.9582	2.9451	2.6258	2.8430
120	2.6917	2.5299	2.3637	2.5284
130	2.4026	2.3013	2.0240	2.2426
140	2.0552	1.8801	1.4627	1.7993
150	1.5369	1.6715	1.1612	1.4565
160	0.9774	1.2187	0.7162	0.9708
170	0.6478	0.9452	0.5548	0.7159
180	0.5038	0.5645	0.2679	0.4454
190	0.3812	0.2725	0.1083	0.2540
200	0.2409	0.2034	0.0246	0.1563
210	0.0583	0.0379	0.0133	0.0365
220	0.0073	0.0000	0.0000	0.0024
230	0.0000	0.0000	0.0000	0.0000
240				

TABLE 4.5 Concentration of Benzene & Time
Effect of Nitrogen Compounds

Time (mins)	Concentration of benzene (mol/l)								
	pure	pyridine	quinoline	butylamine	pyrrole	indole	carbazole	pyrrolidine	pyrazine
0	7.7775	7.7775	7.7775	7.7775	7.7775	7.7775	7.7775	7.7775	7.7775
10	7.2908	7.6823	7.5353	7.5869	7.7530	7.7012	7.5073	7.6531	7.7297
20	6.8999	7.6362	7.4780	7.5085	7.6817	7.6342	7.4215	7.6187	7.7200
30	6.2405	7.5915	7.5020	7.3434	7.6155	7.5702	7.3793	7.5624	7.7051
40	5.7015	7.5318	7.3178	7.0231	7.5544	7.4577	7.2300	7.4981	7.6980
50	5.2135	7.4721	7.1009	6.6214	7.4672	7.2678	7.0687	7.3428	7.6736
60	4.7248	7.4216	6.9750	6.4138	7.2433	7.1593	6.9615	7.0819	7.6672
70	4.3768	7.3647	6.8028	6.1623	7.0810	7.0696	6.8939	6.8727	7.6490
80	3.9718	7.2791	6.7108	6.9893	6.9671	6.9824	6.7879	6.7464	7.6280
90	3.6134	7.2360	6.5687	5.7780	6.9092	6.9181	6.7109	6.6048	7.5883
100	3.2011	7.1523	6.4731	5.4986	6.8462	6.9014	6.6379	6.4780	7.5549
110	2.8430	7.0780	6.3499	5.2713	6.7675	6.8909	6.5684	6.3590	7.4635
120	2.5284	7.0471	6.2809	5.1820	6.6907	6.7367	6.4965	6.2614	7.4228
140	1.7993	6.9630	6.1301	4.7725	6.6106	6.5907	6.3782	6.0352	7.3360
160	0.9708	6.8362	5.8779	4.4471	6.5260	6.5155	6.2443	5.8383	7.0981
180	0.4454	6.7855	5.6967	4.0100	6.3679	6.3868	6.1413	5.6478	7.0090
200	0.2540	6.7128	5.5248	3.6822	6.2333	6.2771	6.0086	5.4556	6.8913
220	0.0024	6.6291	5.0320	3.3699	6.1015	6.1691	5.9191	5.1021	6.8583
240	0.0000	6.5142	5.1768	3.0508	6.0203	6.1165	5.8330	4.9618	6.8167
260		6.4088	5.0130	2.8227	5.9127	6.0220	5.7343	4.7782	6.7881
280		6.2530	4.8548	2.5294	5.8186	5.9706	5.6606	4.6321	6.6525
300		6.2000	4.6746	2.2478	5.7284	5.8706	5.6115	4.4724	6.5696
320		6.0692	4.5199	2.1375	5.6370	5.8283	5.5426	4.3440	6.4903
340		5.9534	4.4153	1.8773	5.5574	5.7484	5.4839	4.1401	6.4566
360		5.8231	4.2719	1.4288	5.4594	5.6850	5.4105	4.0261	6.3993

$$-r_B = \frac{-dC_B}{dt} = k$$

then integrate the rate equation, we obtain

$$C_{BO} - C_B = kt$$

Therefore, a plot of benzene concentration versus time give a straight line with slope of -k. Tables 4.6 to 4.9 show the k values of each experiment sections and Figures 4.7, 4.10 to 4.12 show comparison of k values of each experiment sections.

There are many different types of nitrogen compounds in nature. They differ in their features, such as characteristic structure and basicity. In this study, the main effects of nitrogen compounds are catagorized as the following:

- the effects of basicity: pyridine, quinoline are compared with pyrrole, indole and carbazole.
- the effects of structures: pyridine, quinoline are compared with butylamine.
- the effects of ring saturation nitrogen compounds: pyrrole is compared with pyrrolidine.
- the effects of number of nitrogen atom in nitrogen compounds: pyridine is compared with pyrazine.

The results are compared with the average reference experiment result.

4.1 Effects of Temperature and Pressure.

A set of experiments, listed in Table 4.1 as experiments 1-9, is conducted to study the effects of operating temperature and pressure. The catalyst used in this set weighs 1 gram. raney nickel. The temperatures are varied from 120°C to 180°C (at an increment of 30°C) and pressures are varied from 150 psig. to 250 psig. (at an increment of 50 psig). Figures 4.1 to 4.6 show comparison of benzene concentration at any time. The results show that the reaction rates depend on operating temperature and pressure; as temperature and pressure increase, the reaction rate increase. This result is in accordance with the Arrhenius relationship, $k = Ae^{-E/RT}$, where E is the activation energy and R is the gas constant. Similar results were also observed by Proskurnin et al. (1972) and Franco et al.(1980).

From this set of experiments, the suitable temperature and pressure are chosen. The suitable operating temperature and pressure are the ones that give a moderate rate of reaction. This can be observed from a total reaction time whicn is not too long or too short. It is also possible to determine from k values which the rate reaction is a function of this term. The reason for choosing a moderate rate of reaction is that the effect of addition of nitrogen compound, either increasing or decreasing, would be easily identified.

From the reaction rate as a function of k values, the operating temperature and pressure chosen are 150°C and 200 psig, respectively. These conditions are subsequently used to study the effect of the amount of catalyst.

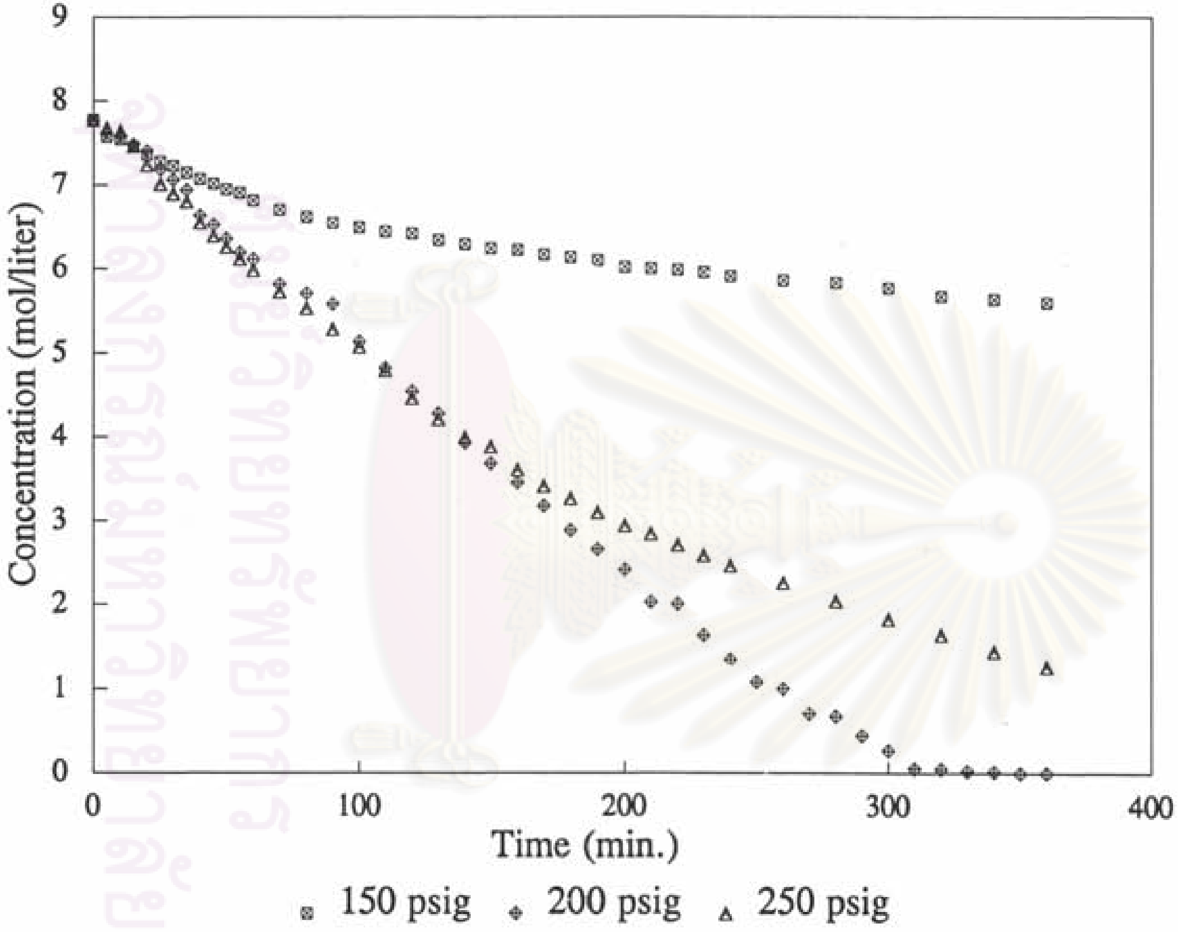

Figure 4.1 Concentration of Benzene at Temperature 120°C and Various Pressures

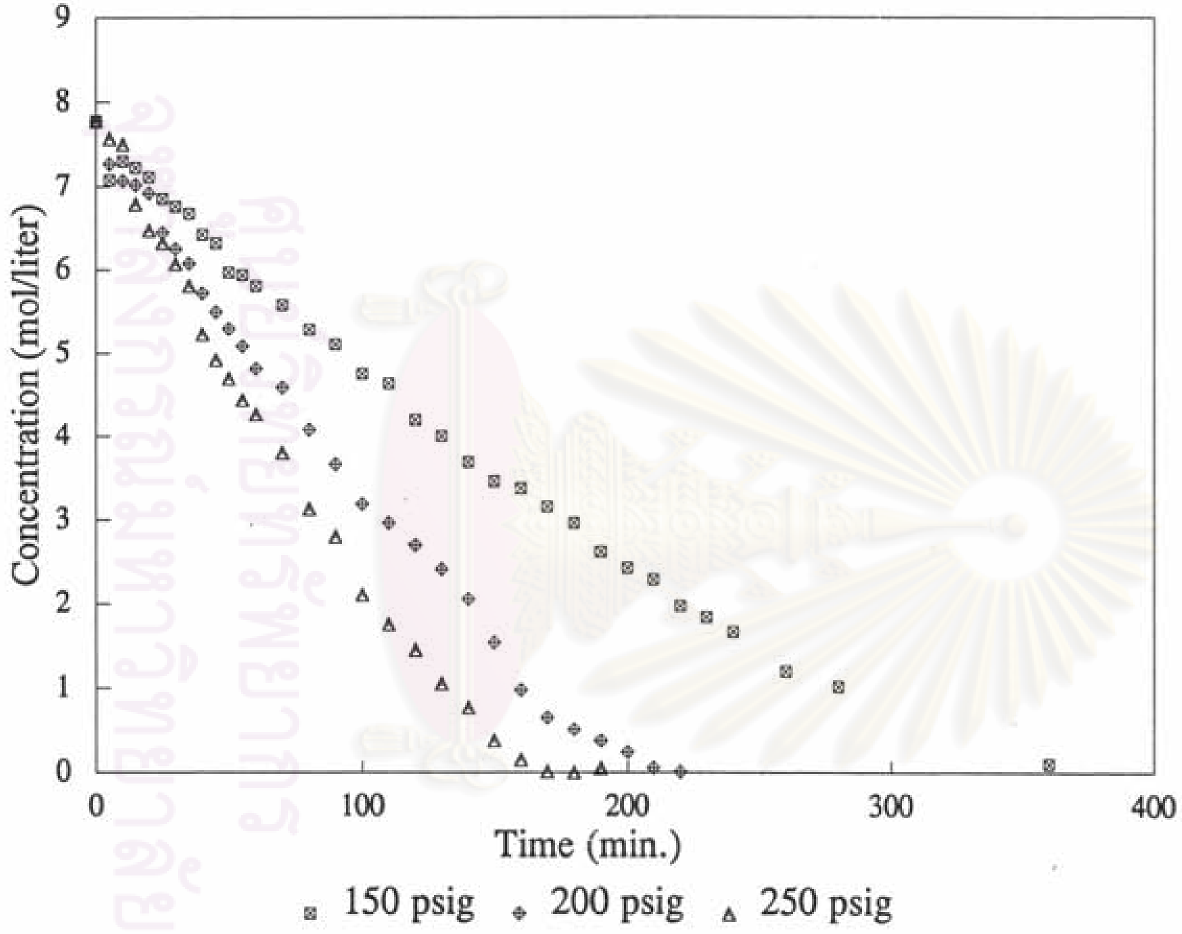

Figure 4.2 Concentration of Benzene at Temperature 150°C and Various Pressures

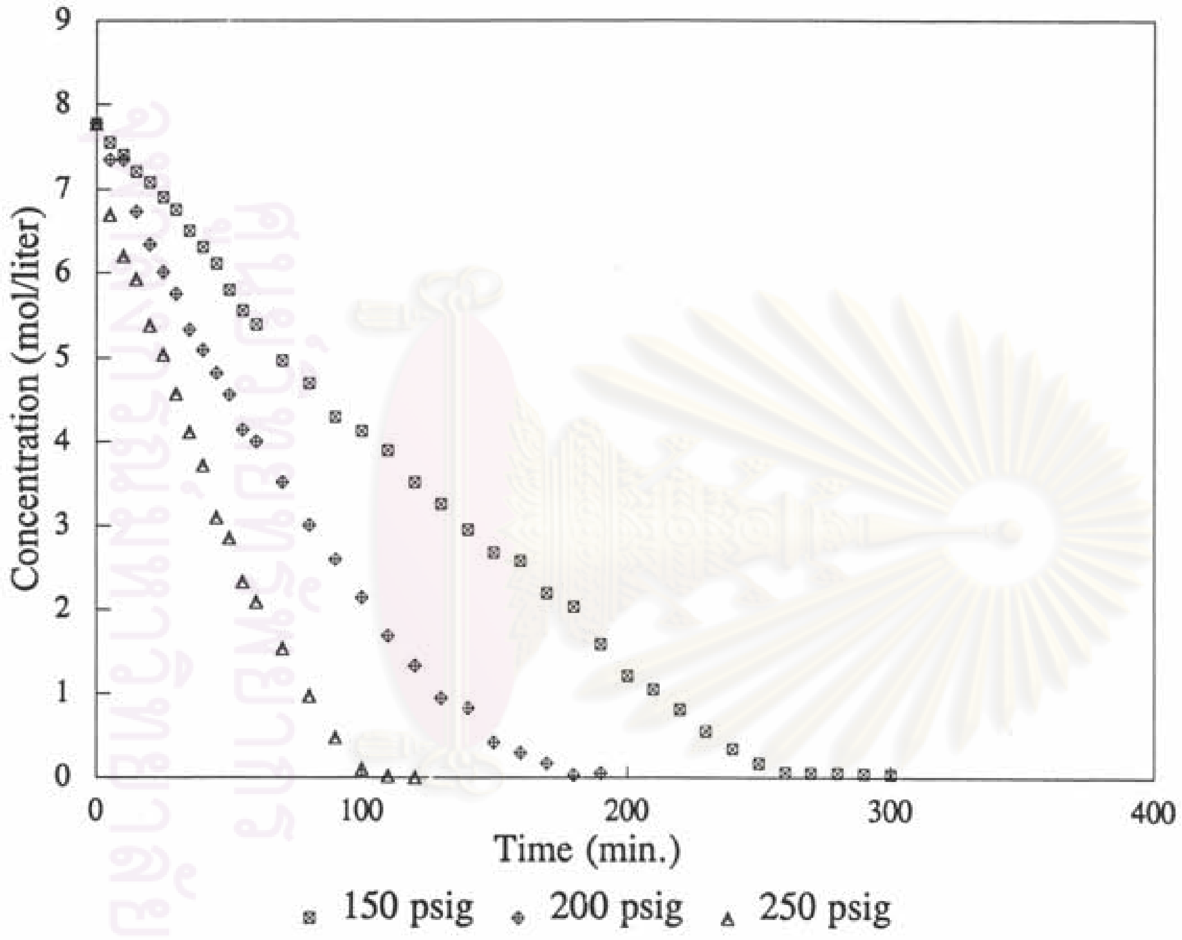

Figure 4.3 Concentration of Benzene at Temperature 180°C and Various Pressures

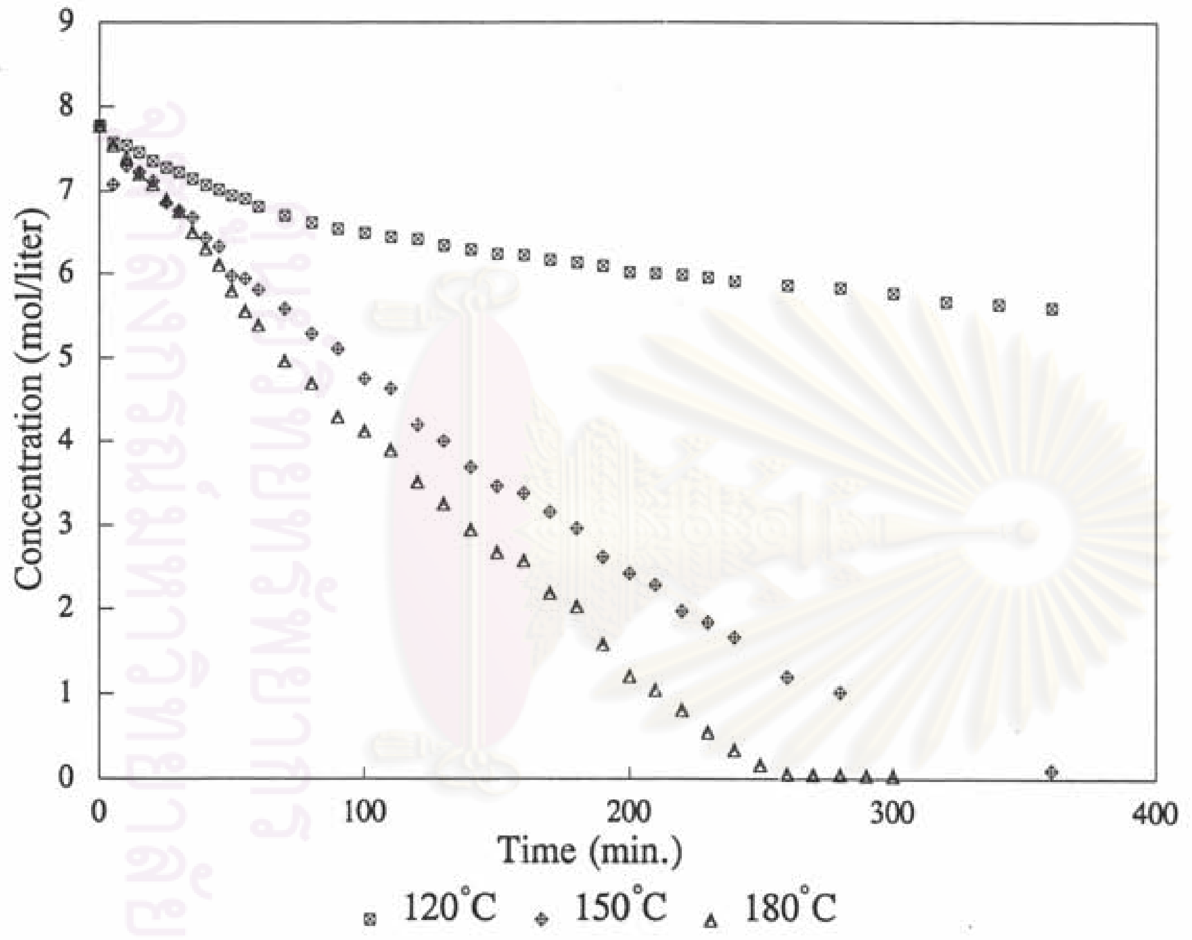

Figure 4.4 Concentration of Benzene at Pressure 150 psig. and Various Temperatures

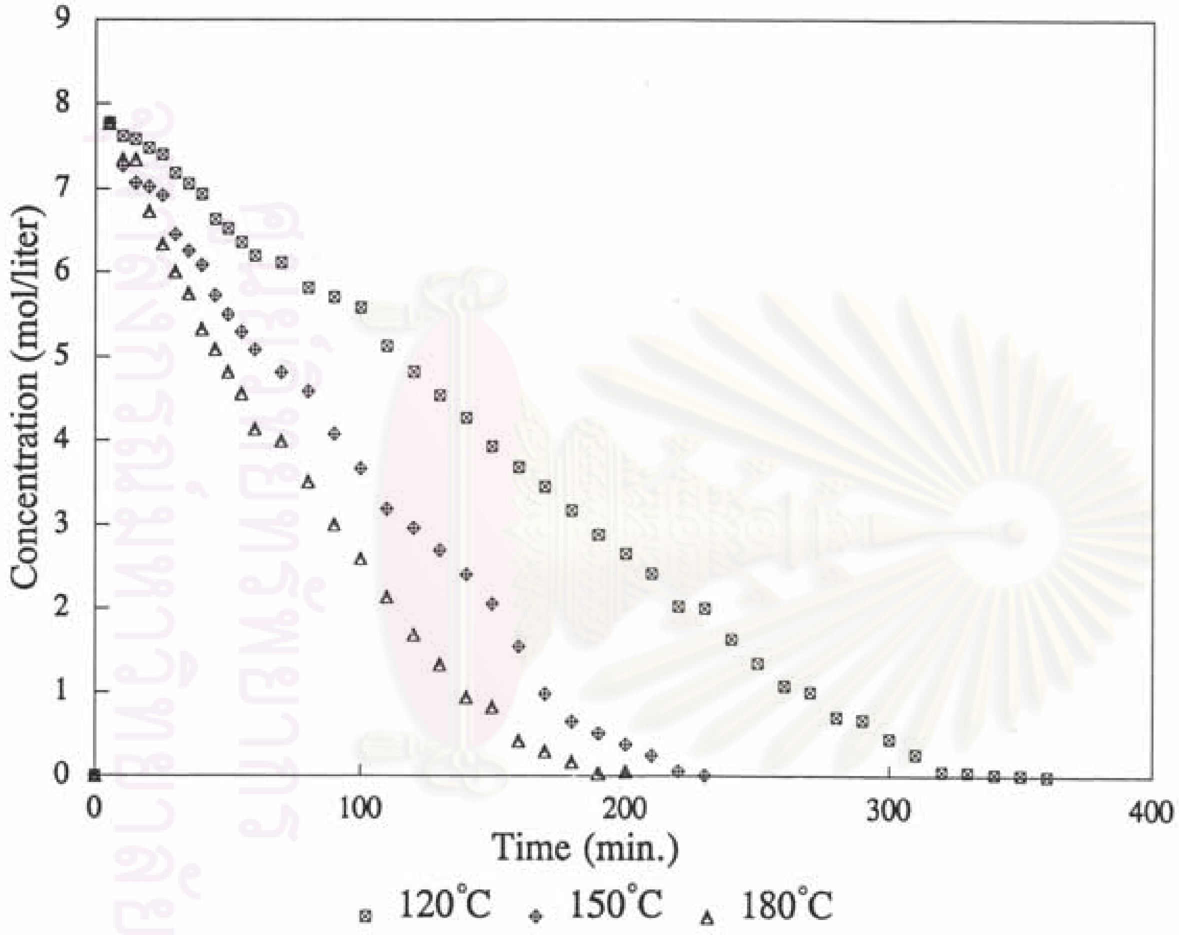

Figure 4.5 Concentration of Benzene at Pressure 200 psig. and Various Temperatures

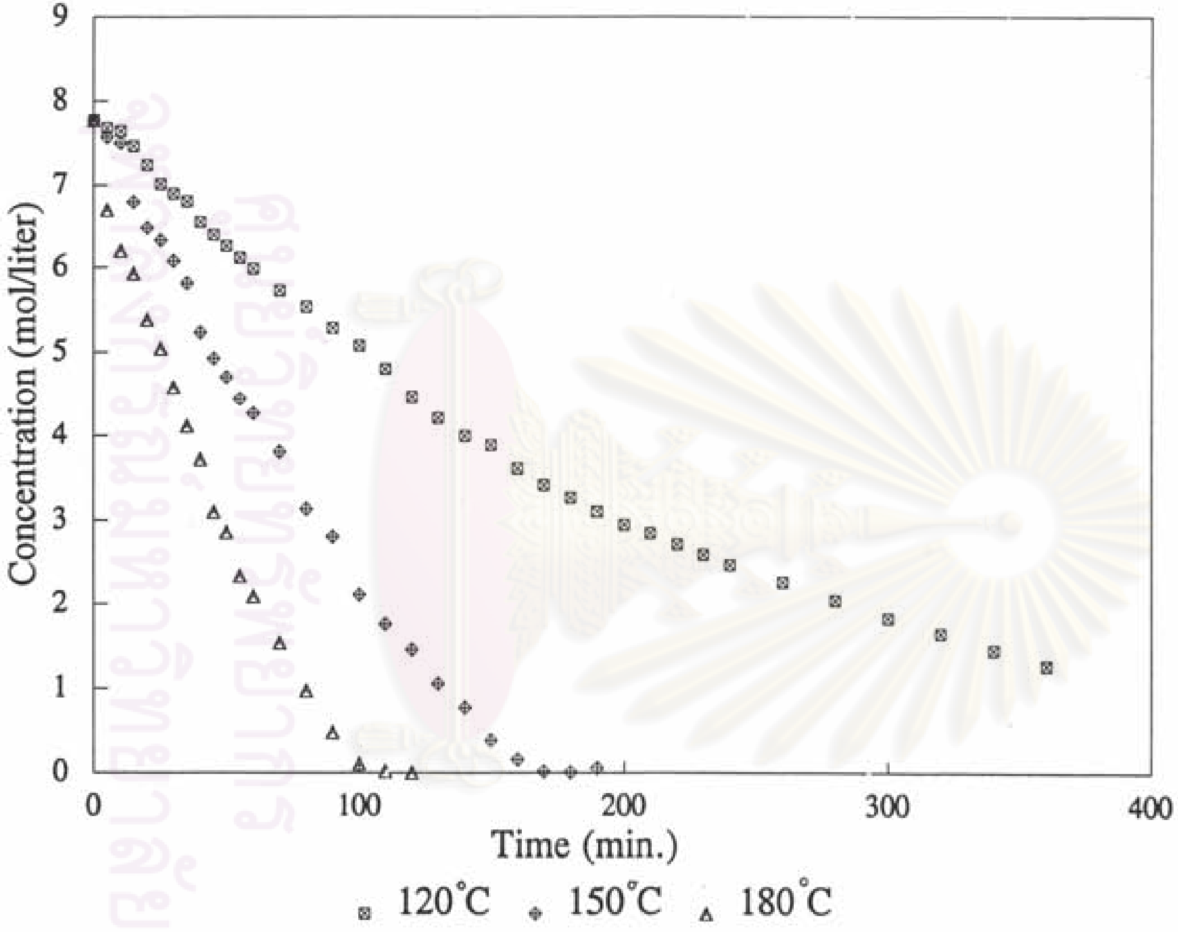

Figure 4.6 Concentration of Benzene at Pressure 250 psig. and Various Temperatures

Table 4.6 k Values of the Reaction at Various Temperatures and Pressures

temperature (°C)	pressure (psig.)	k values (* 10^{-2} mol/l.sec)
120	150	0.69
120	200	1.35
120	250	1.36
150	150	1.06
150	200	1.67
150	250	2.26
180	150	1.64
180	200	2.58
180	250	4.51

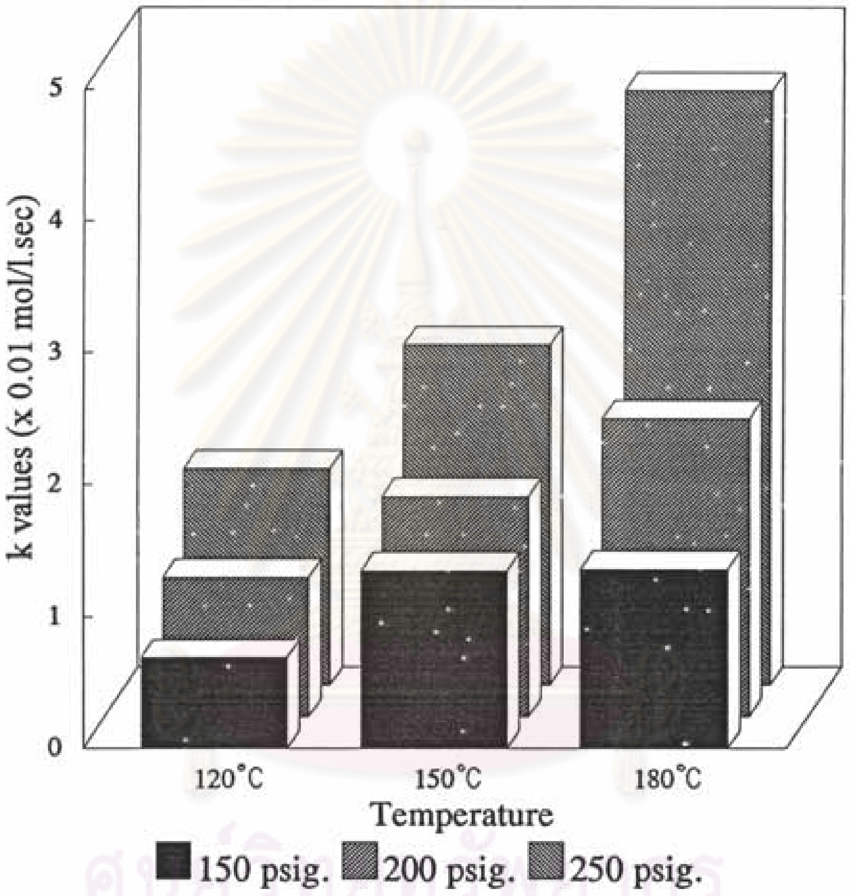

Figure 4.7 Comparison of k Values of Reaction at Various Temperatures and Pressures

4.2 Effects of Amount of Catalyst.

A set of experiments, listed in Table 4.1 as experiments 5, 10, 11 and 12, is conducted to study the effect of the amount of catalyst. The reaction is performed at 150°C and 200 psig. The amounts of catalyst are varied from 3 gm., 2 gm., 1 gm., and 0.5 gm. The major product shown on the chromatogram is cyclohexane. Figure 4.8 and Table 4.7 show a comparison of benzene concentration at any time and k values of this set of experiments, respectively. The results indicate that the reaction rate is a function of the amount of catalyst, i.e. reaction rate increases when the amount of catalyst increase. When 3 gm and 2 gm of catalyst are used, the reaction rates are rather high and the total reaction times are approximately the same, 1.5 hours. While at amount of 0.5 gm catalyst, the rate of reaction is rather slow. Consequently, the amount chosen is 1 gm of catalyst. These operating conditions, 150°C and 200 psig. and 1 gm of catalyst, are subsequently used as a reference experiment.

4.3 Experimental Error

Experiments 13 and 14 are conducted at the same conditions as the experiment chosen, 150°C and 200 psig and 1 gm of catalyst, in order to study the repeatability of the experiments. The results are nearly the same as shown in Figure 4.9. The k values are shown in Table 4.8. From these experiments, average benzene concentration at any time and k values are calculated and are used as reference data. An experimental error is calculated

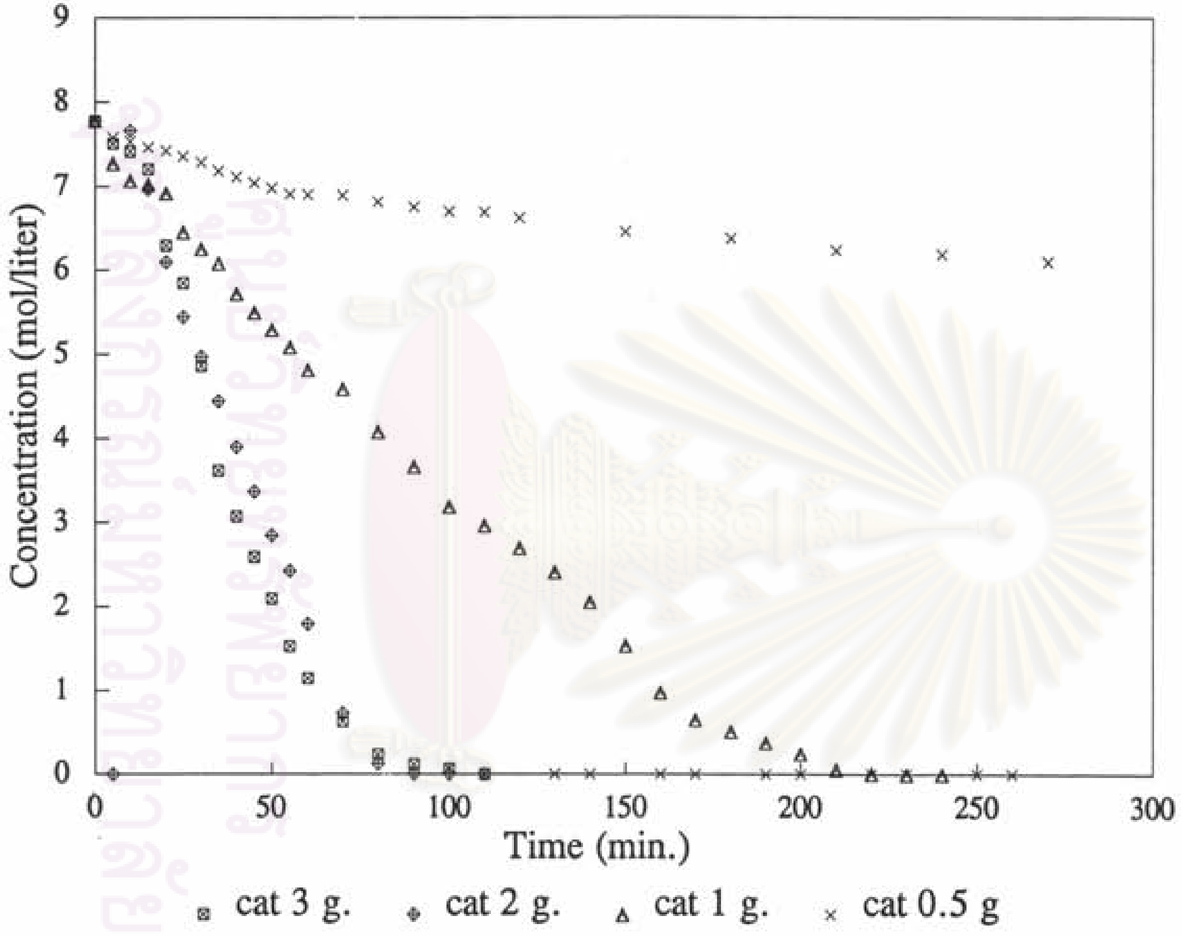

Figure 4.8 Effect of Amount of Catalyst on Concentration of Benzene

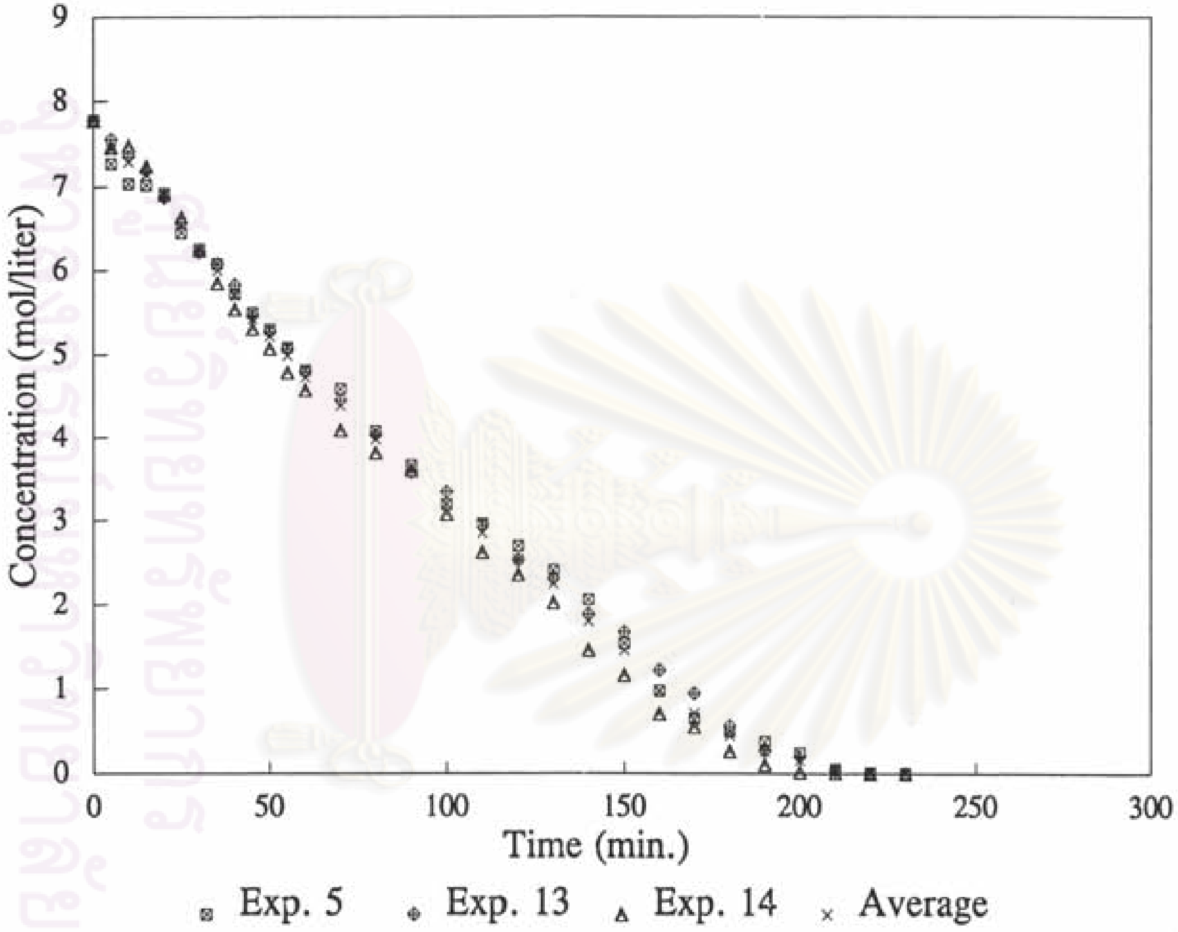

Figure 4.9 Concentration of Benzene at 150°C and 200 psig.

Table 4.7 k Values of the Reaction at Various Amounts of Catalyst

amount of catalyst (grams)	k values (* 10^{-2} mol/l.sec)
3	2.86
2	2.50
1	1.67
0.5	0.16

Table 4.8 k Values of the Reaction at 150°C and 200 psig.

Experiment	k values (* 10^{-2} mol/l.sec)
5	1.67
13	1.52
14	1.62
average	1.60
max. error	+4.38 %
min. error	-5.00 %

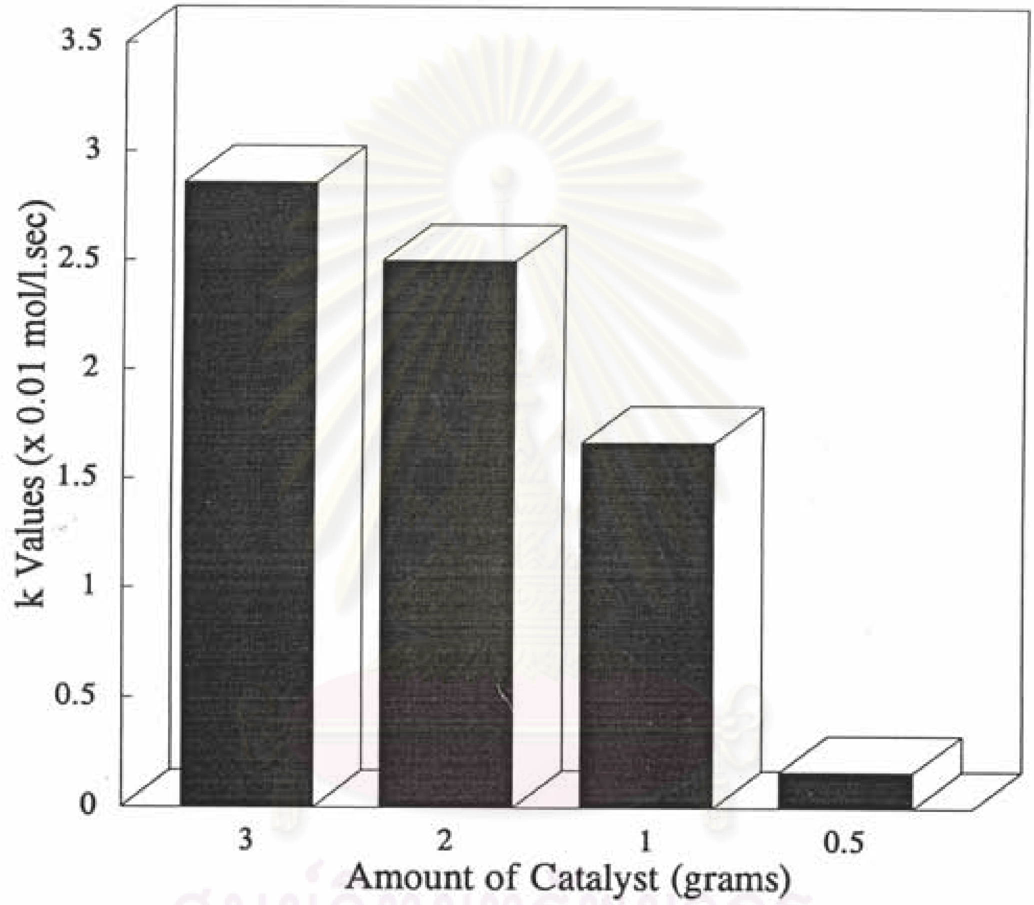

Figure 4.10 Comparison of Reaction Rate Constant (k values) at Various Amounts of Catalyst

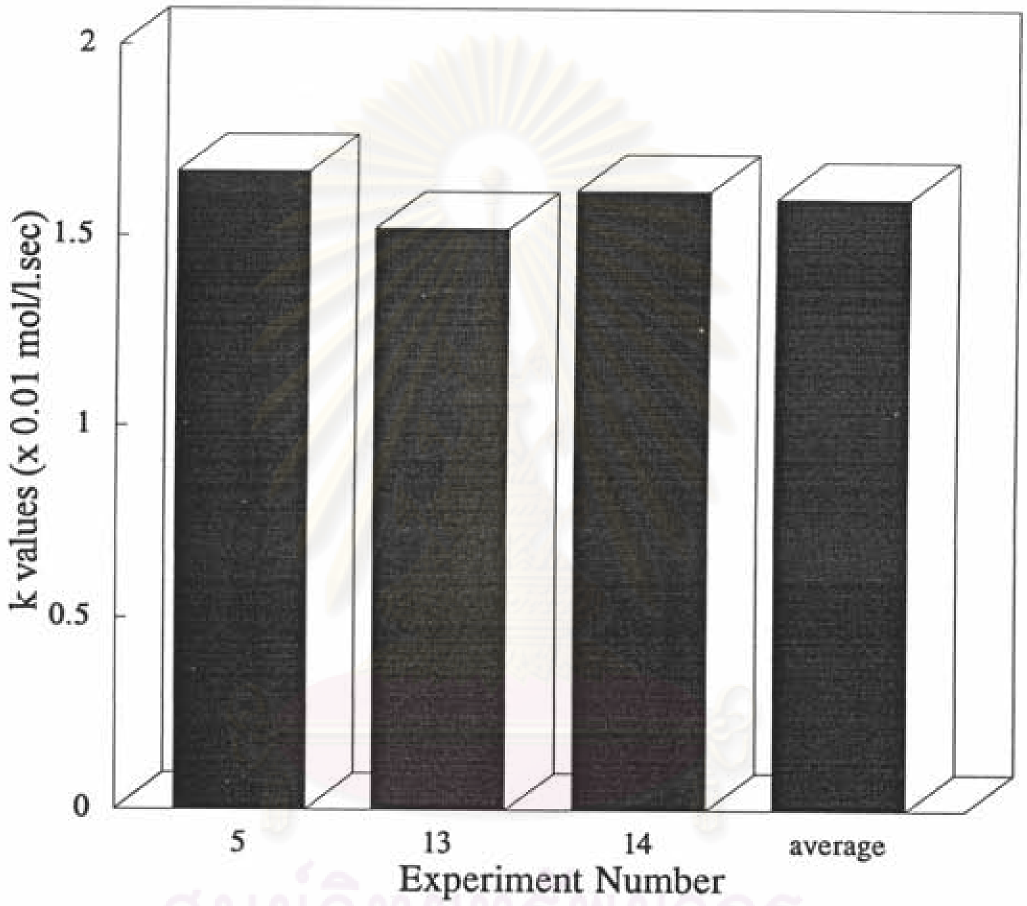

Figure 4.11 Comparison of Reaction Rate Constant (k values) at 150°C and 200 psig.

to be in the range of ± 5 %.

4.4 Effects of Nitrogen Compounds

Selected nitrogen compound is added to the benzene solution to make a solution containing 0.0015% N as nitrogen compounds and is hydrogenated at the same operating condition as in the reference experiment. Nitrogen compounds used in this set of experiments are pyridine, quinoline, butylamine, pyyrole, indole, carbazole, pyrrolidine, and pyrazine, respectively.

The changes in benzene concentration at any time are shown in Figures 4.13 to 4.16 and k values are shown in Table 4.9. The results show that the addition of nitrogen compound even at low concentration affects hydrogenation of benzene. All reaction rates are obviously lower than the ones in the reference experiments. This indicates that these compounds adsorb on active sites of the catalyst, resulting in the reduction of the reactant being adsorbed on the catalytic sites which in turn reduces the total conversion of the reactant. Furthermore, the poisoning effect of nitrogen compounds on benzene hydrogenation depend upon the nature of nitrogen compounds type as in the following.

4.4.1 Effect of Basicity of Nitrogen Compounds

Basic nitrogen compounds used in this study are pyridine and quinoline, and non-basic nitrogen compounds used are pyrrole, indole, and carbazole. Figure 4.13 shows a comparison of benzene concentration at any time taken from experiments using pure feedstock, and the

Table 4.9 k Values of the Reaction at Various Nitrogen Compounds

nitrogen compounds	k values (* 10^{-2} mol/l.sec)
pure	1.60
pyridine	0.222
quinoline	0.476
butylamine	0.759
pyrrole	0.255
indole	0.230
carbazole	0.292
pyrrolidine	0.573
pyrazine	0.211

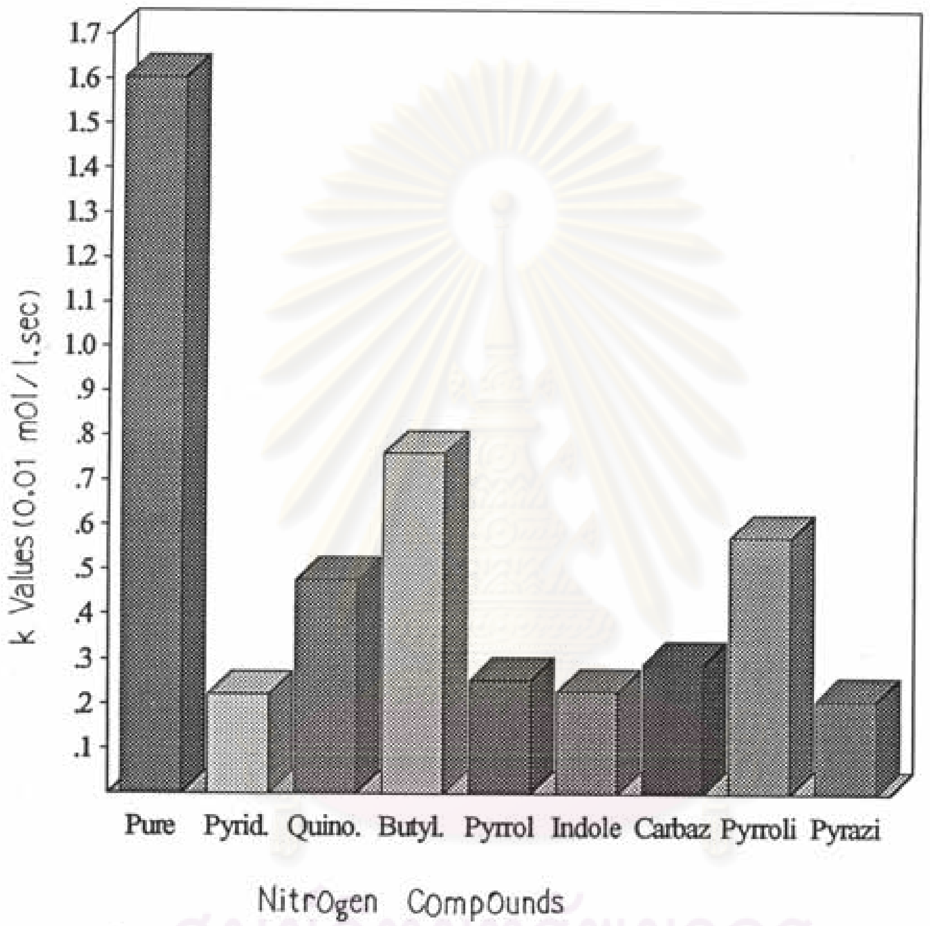

Figure 4.12 Comparison of Reaction Rate Constants (k values) at various nitrogen compounds.

feedstock mixed with nitrogen compounds and Table 4.9 shows k values of the reaction. The pKa values given in Table 4.10 represent the basic strength of various nitrogen compounds in water (the higher the pKa, the greater the basic strength). The results show that the addition of pyridine increases the concentration of unreacted benzene more than the results from three non-basic nitrogen compounds. This indicates that basic nitrogen compounds have stronger inhibition characteristics than non-basic nitrogen compounds due to the acidity characteristic of the surface of the catalyst.

The effect agreed with the results of La Vopa and Satterfield (1988) who studied the poisoning of thiophene by nitrogen compounds over $NiMo/Al_2O_3$. They found that nitrogen compounds were selective poisons for thiophene hydrogenation , but not for desulfurization. The degree of inhibition of the nitrogen compounds was correlated with the strength of their basicities. Deactivation was generally greater when the basicity of nitrogen compounds increase. The result also agreed with the Masatoshi Nagai (1986) studies.

However, from the results as shown in Figure 4.13 quinoline has lower poisoning effect on the reaction rate than pyridine and the three non-basic compounds. The fact that quinoline has lower poisoning effect than pyridine may be due to the effect of basicity of pyridine. But the reason why this compound has lower poisoning effect than non-basic nitrogen compounds is still a confusion. This shows that thier is a complexity in the characteristic of the nitrogen compounds.

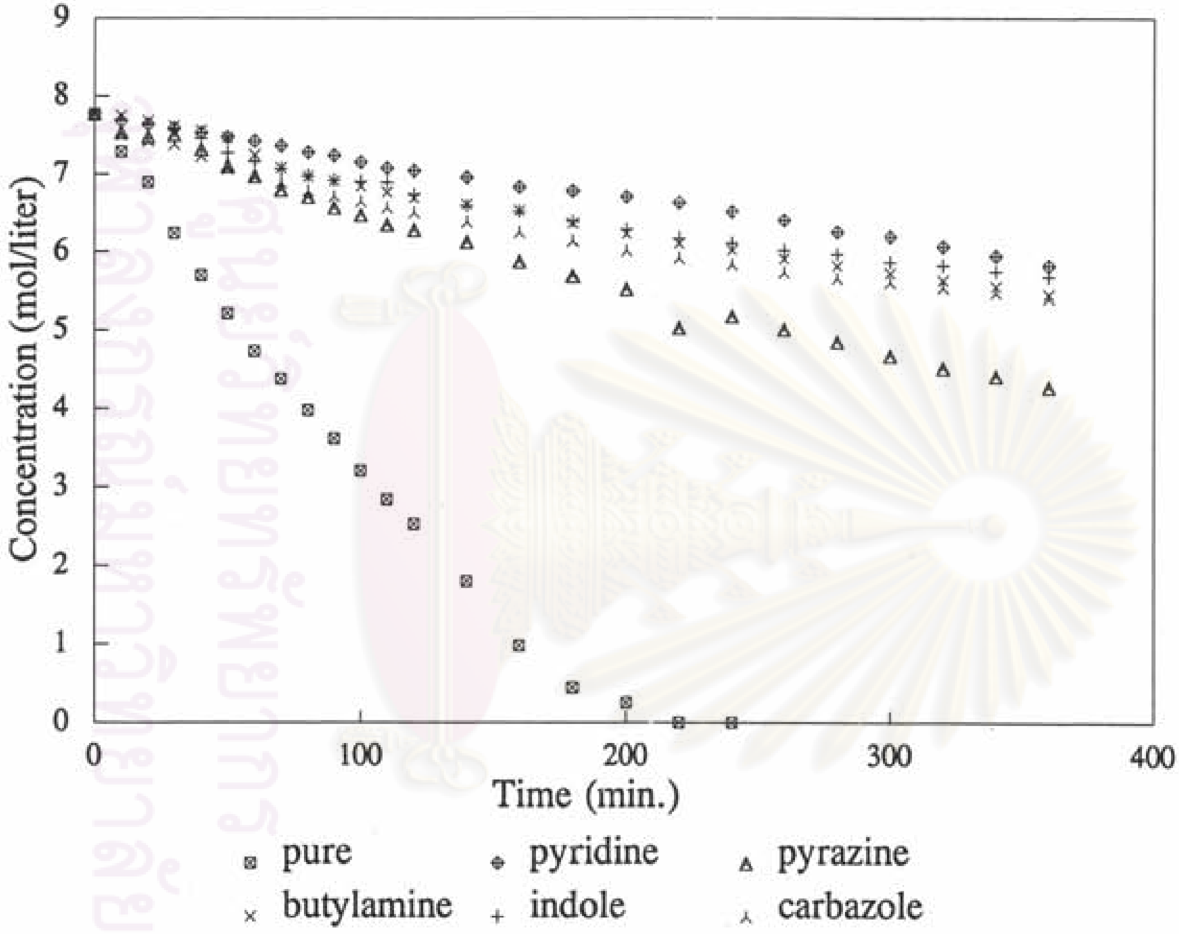

Figure 4.13 Effect of Basicity of Nitrogen Compounds on Concentration of Benzene

Table 4.10 pKa Values of Nitrogen Compounds

name	pKa*
pyridine	5.3
quinoline	4.9
butylamine	10.27
pyrrole	-
indole	-
carbazole	-
pyrrolidine	11.27
pyrazine	0.65

*From Handbook of Chemistry and Physics, Chemical Rubber Company, 60th Ed., 1975. d-161

4.4.2 The Effect of the Structure of Nitrogen Compounds.

These experiments are conducted to investigate the effect of structure of nitrogen compound, i.e. the effect of ring structure and straight chain structure of nitrogen compounds. Butylamine is chosen as a chain structure model compound, pyridine and quinoline are chosen as a ring structure model compound. Figure 4.14 shows that the poisoning effects increase in the order butylamine < quinoline < pyridine. The lowest poisoning effect of linear amine compare to cyclic nitrogen compounds can be explained by their higher dissociation accompanied by evolution of alkanes. These results agreed with the study of Marecot et al. (1992) who studied the effect of sulfur compounds on nickel catalyst in benzene hydrogenation. They found that the toxicity of sulfur compounds were in the order thiophene ~ thiolane > propane-thiol ~ hexane-thiol > hydrogen sulfide.

4.4.3 The Effect of Ring Saturation of Nitrogen Compounds.

Pyrrole and pyrrolidine are chosen to represent a saturated and unsaturated model compounds, respectively. Figure 4.15 and Table 4.9 show a concentration of benzene versus time and k values with the addition of these two compounds in the feed compare with the case of pure benzene. The results show that pyrrolidine has lower the reaction rate than pyrrole , in spite of being a stronger base than pyrrole. ($pKa_{pyrrole}$= -3.8, $pKa_{pyrrolidine}$ =

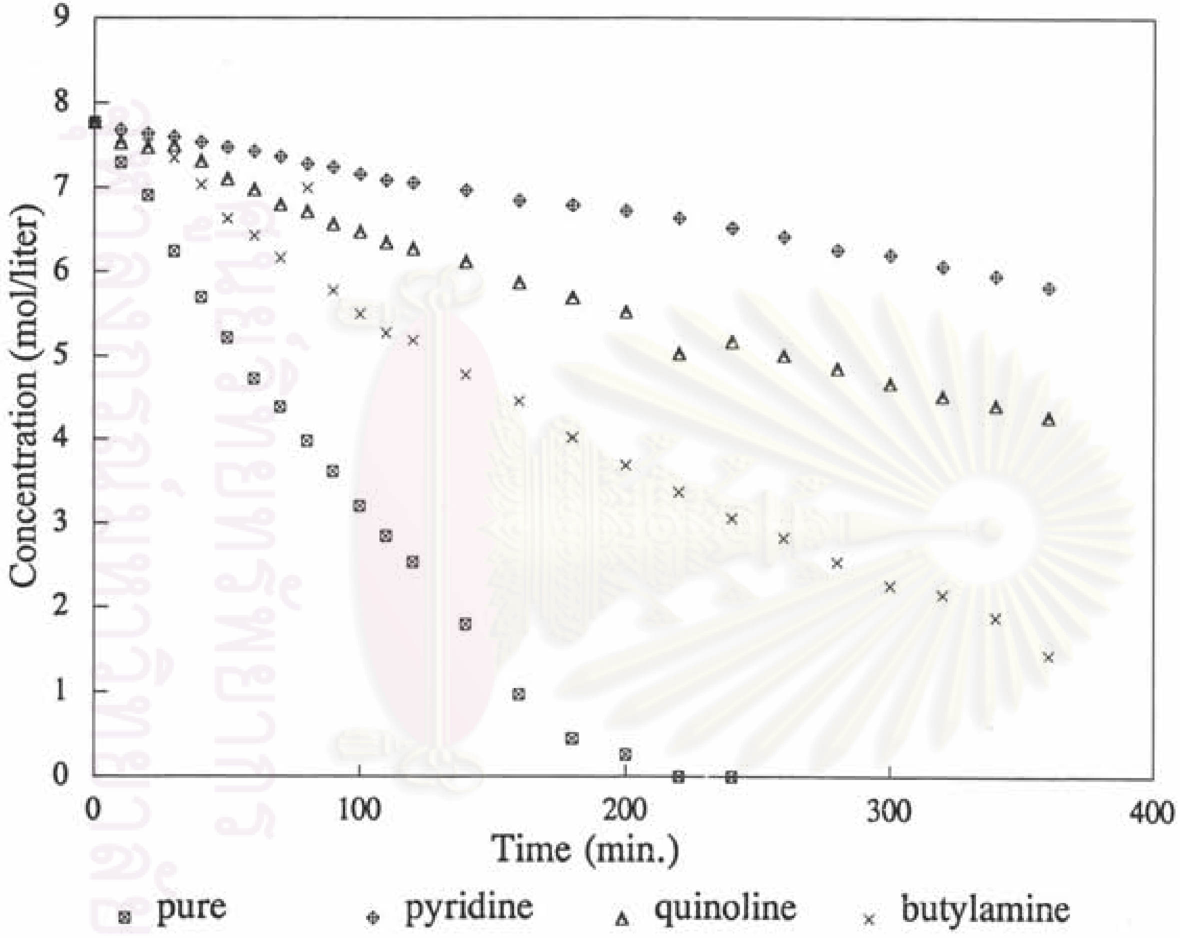

Figure 4.14 Effect of Structure of Nitrogen Compounds on Concentration of Benzene

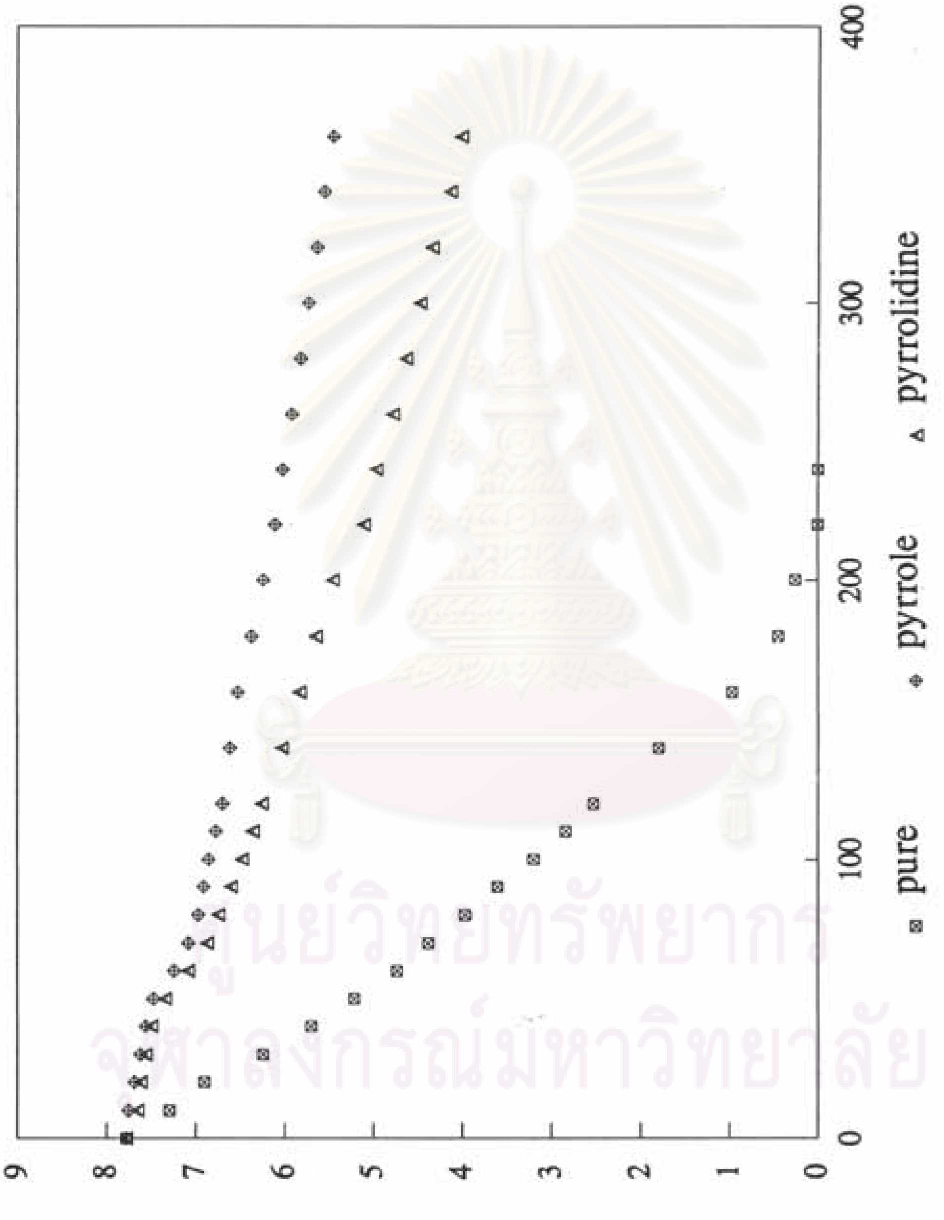

Figure 4.15 Effect of Ring Saturation of Nitrogen Compounds on Concentration of Benzene

11-12). This can be explained that aliphatic cyclic compounds have lower adsorption constants than the heterocyclic aromatic compounds. The effect agreed with the work of Masatoshi Nagai et al. (1986). They studied the poisoning effect of nitrogen compounds on dibenzothiophene hydrodesulfurization on sulfide NiMo/Al_2O_3 catalysts. The poisoning effect of N-compounds in reducing hydrogenation functionality increase in the order: acridine> quinoline > pyridine > piperidine > cyclohexylamine > γ-picoline > aniline. They explained that the adsorption constants of acridine was higher than those of pyridine and quinoline despite similar pKa values. Furthermore, γ - picoline, which has the methyl group in the para position of pyridine, has lower adsorption constant that pyridine. Thus, there is a great gap between the adsorption constants of the various added nitrogen compounds and their solution basicities.

4.4.4 The Effect of Number of Nitrogen Atom.

From Figure 4.16, pyrazine which has two nitrogen atoms in the molecule has slightly lower rate of reaction of benzene hydrogenation than pyridine. The different in rate constants (k values) fall in the experimental error range, thus it is difficult to conclude that the different in the number of nitrogen atom in the molecule affect the reaction rate of benzene hydrogenation. However, Gonzalez-Tejuca, et al. (1977) proposed that H_2S and COS deactivated Pt/Al_2O_3 and Pt/SiO_2 catalysts for hydrogenation of olefins and benzene less than CS_2.

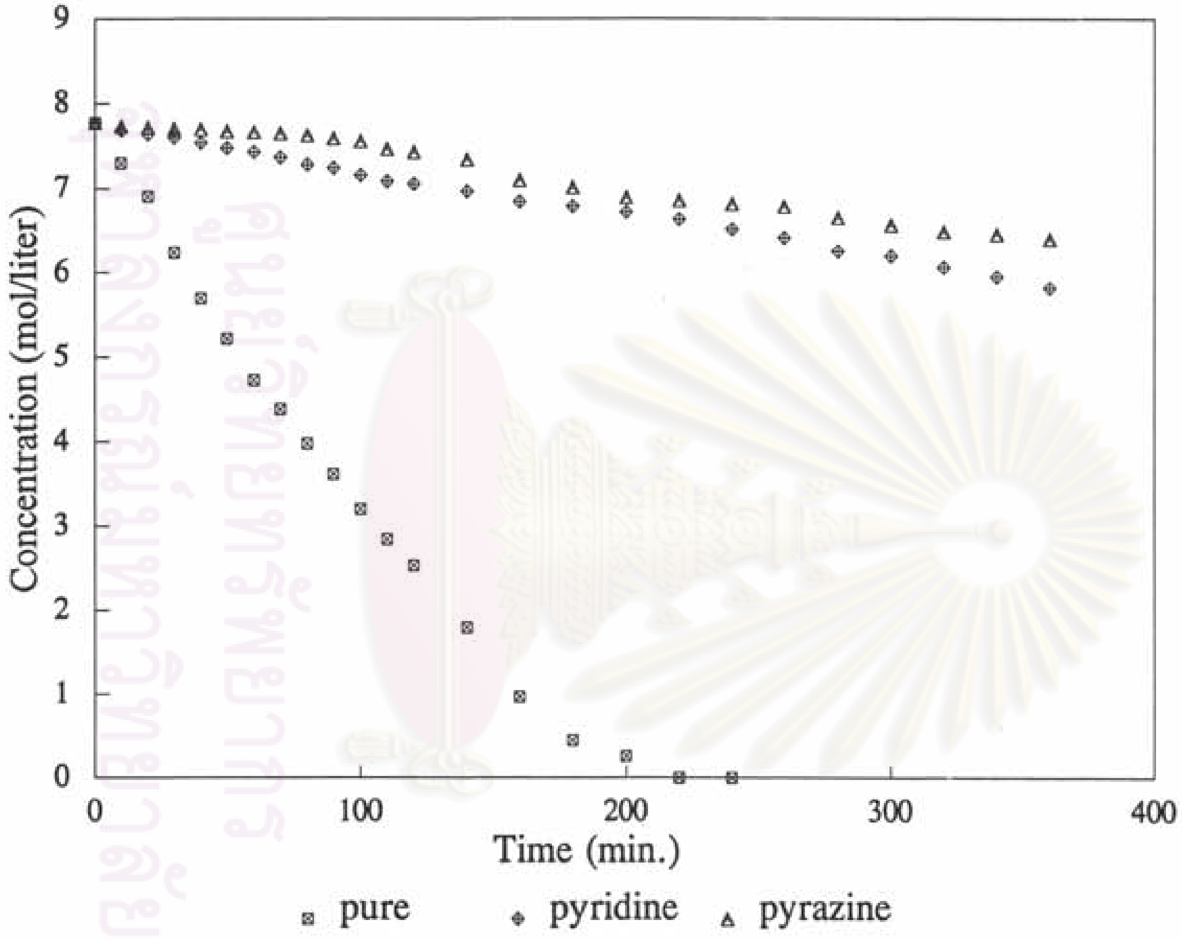

Figure 4.16 Effect of Number of Nitrogen Atom in Nitrogen Compounds on Concentration of Benzene

The reason was due to H_2S and COS deactivated one platinum site per molecole adsorbed, whereas CS_2 generally deactivated two platinum sites per adsorbed molecule. Thus, the effect of the number of nitrogen atom on the reaction rate of benzene hydrogenation should have the similar result.

In summary, from this study, the deactivation effect of nitrogen compounds are in the following order pyrazine ~ pyridine > pyrrole ~ indole ~ carbazole > quinoline > pyrrolidine > butylamine.