Chapter 6

DISCUSSION AND COMPARISON OF EXPERIMENTAL RESULTS

Appendix B summarizes the results of analysis of experimental data for the case of the isopropanol synthesis catalyst no. 1-3. The results of NaY, offretite/erionite and Na-mordenite (the last one studied by W.Tanthapanichakoon) are plotted in Figs. 6.1-6.63 to show the effects of reaction pressure, temperature, space velocity by each catalyst on the C_3H_6 conversion per pass, product selectivity, space time yield of isopropanol, and product distribution.

6.1 Discussion of Experimental Results for Catalyst No.1

Here catalyst no.1 means a NaY catalyst composed of SiO_2 = 66.7 %, Al_2O_3 = 20.3 %, Na_2O = 12.3 % by wt., SiO_2/Al_2O_3 = 5.6/1 by mole. To investigate the effects of temperature, pressure and space velocity on isopropanol synthesis using this catalyst, experiments were carried out under the conditions summarized in Table 6.1. The catalyst powder was pelletized to obtain a density of 0.866 gm/cm^3 and then screened between meshes #10 and #15. Then 2 ml of the screened catalyst was packed in the tubular reactor for isopropanol synthesis from propylene.

6.1.1 Total C_3H_6 Conversion

Figs. 6.1-6.3 show that the total conversion of C_3H_6 increased smoothly with temperature. At a high temperature (230 -250 °C) intermolecular distance of reactants was closer and the

Table 6.1 Summary of Experimental Conditions for Catalyst no.1 (NaY ; SiO_2: Al_2O_3 = 5.6:1)

Pressure (psig)	Space Velocity (hr^{-1})	Temperature Range (°C)
45	2000	150-300
	5000	150-300
	8000	150-300
75	2000	150-300
	5000	150-300
	8000	150-300
105	2000	150-300
	5000	150-300
	8000	150-300

reactants were more activated than at a low temperature. At a high space velocity, total conversion of C_3H_6 decreased against increasing space velocity, because there was less time for C_3H_6 and water to react. The results suggested that the optimum space velocity of isopropanol synthesis is 5,000 hr^{-1}.

Figs. 6.7-6.12 indicate that space time yield (STY) of isopropanol generally increased with temperature between 230-250 °C, and with space velocity between 2000-8000 hr^{-1}. However STY of isopropanol decreased as temperature rose above 250 °C because the selectivity of isopropanol decreased greatly while more by-products were produced.

6.1.2 Isopropanol Selectivity

Figs. 6.4-6.6 show the results obtained using a NaY catalyst with mole ratios of SiO_2/Al_2O_3 = 5.6/1. They indicate that isopropanol selectivity increased with space velocity in the range of 2000-8000 hr^{-1} and decreased as temperature increased as it became easier for the disproportionation of propylene to ethylene and butene. Therefore a selective catalyst was required for isopropanol synthesis. Figs. 6.4-6.6 and 6.13-6.21 also indicate that isopropanol selectivity became favorable at low pressure when the temperature was in the range of 200-260 °C. Above 260 °C the selectivity began to decrease and below 200 °C little isopropanol was synthesized. Thus the optimum temperature for isopropanol selectivity for this catalyst was between 230-250 °C. Variation in reaction pressure seemed to have little effect on the isopropanol synthesis.

6.1.3 Product Distribution

Figs. 6.13-6.21 show the distribution of all observed products at each temperature. The main (desired) isopropanol product and by-products were obtained as follows:

$$2C_3H_6 \rightleftharpoons C_2H_4 + C_4H_8$$

$$C_3H_6 + H_2O \rightleftharpoons i\text{-}C_3H_7OH \quad \text{(major product)}$$

$$C_3H_6 + H_2O \rightleftharpoons n\text{-}C_3H_7OH \quad \text{(minor product)}$$

$$C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$$

$$i\text{-}C_4H_8 + H_2O \rightleftharpoons t\text{-}C_4H_9OH$$

$$n\text{-}C_4H_8 + H_2O \rightleftharpoons 2\text{-}C_4H_9OH \quad \text{(major product)}$$

$$n\text{-}C_4H_8 + H_2O \rightleftharpoons 1\text{-}C_4H_9OH \quad \text{(minor product)}$$

As for ethylene and butene their selectivities decreased as space velocity became high because there was not enough time for propylene to disproportionate to ethylene and butene.

As for C_2H_5OH, C_3H_7OH, t-butanol, sec-butanol and n-butanol, their selectivities usually increased with temperature and space velocity. The influence of pressure however was not remarkable. It was surmised that these alcohols came mainly from the reactions above. If this be correct, then the yield of C_2H_5OH, $t\text{-}C_4H_9OH$, $2\text{-}C_4H_9OH$ and $n\text{-}C_4H_9OH$ should depend on the availability of C_2H_4, butylene and the concentration of H_2O. It was observed that the more C_2H_4 and C_4H_8 detected, the higher the concentration of C_2H_5OH and C_4-alcohols, and vice versa. At high temperatures, total C_3H_6 conversion as well as C_2H_4 and C_4H_8 selectivity were found to be high, thus resulting in more C_2H_5OH and C_4 alcohols. When the space velocity was high, there was not enough time for C_3H_6 to disproportionate to become C_2H_4 and C_4H_8 and further hydrated to C_2H_5OH and C_4-alcohols, so less C_2H_5OH and C_4-alcohols were obtained.

Conclusions of Isopropanol Synthesis Results for Catalyst No.1

The main conclusions are:

1. A high propylene/water mole ratio was expected to increase polymer formation. However a low ratio would adversely affect plant size, thus increasing investment costs and operating costs. The ratio studied varied from 1 : 4 to 1 : 10 in this work.

2. A high temperature would increase the formation of C_2H_4, C_4 olefins and C_4 alcohols. Below 200°C, little reaction occurred.

3. Pressure ranging from 45 to 105 psig had no remarkable effect on isopropanol synthesis.

4. Decreasing the space velocity had a negative effect on isopropanol yield. Increasing the space velocity would be expensive because of the increasing costs of product separation and recycling of unreacted propylene.

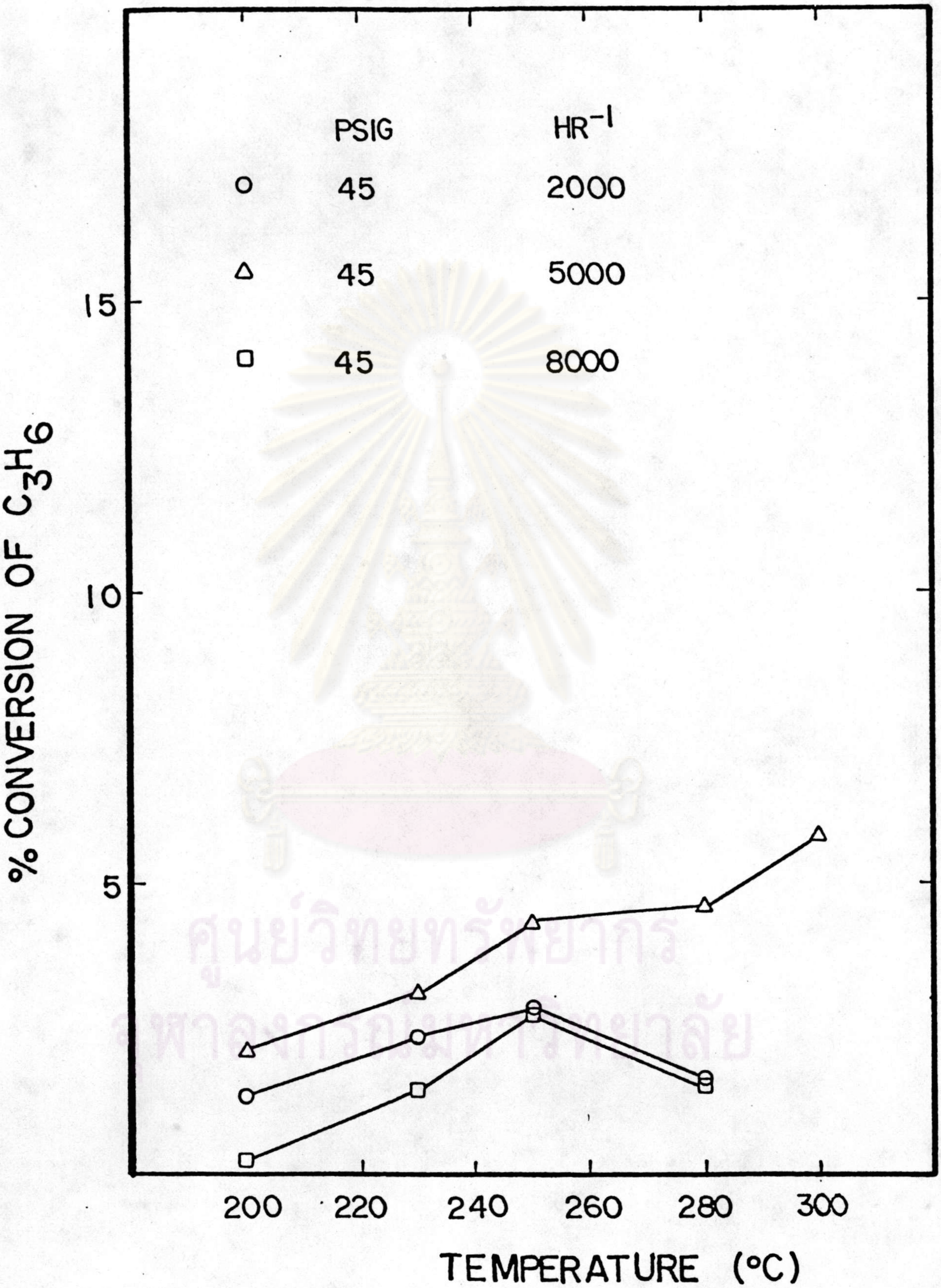

Figure 6.1 Effect of Temperature (200-300°C) on Total Propylene Conversion (at 45 psig, 2000-8000 hr^{-1}) for Catalyst no.1

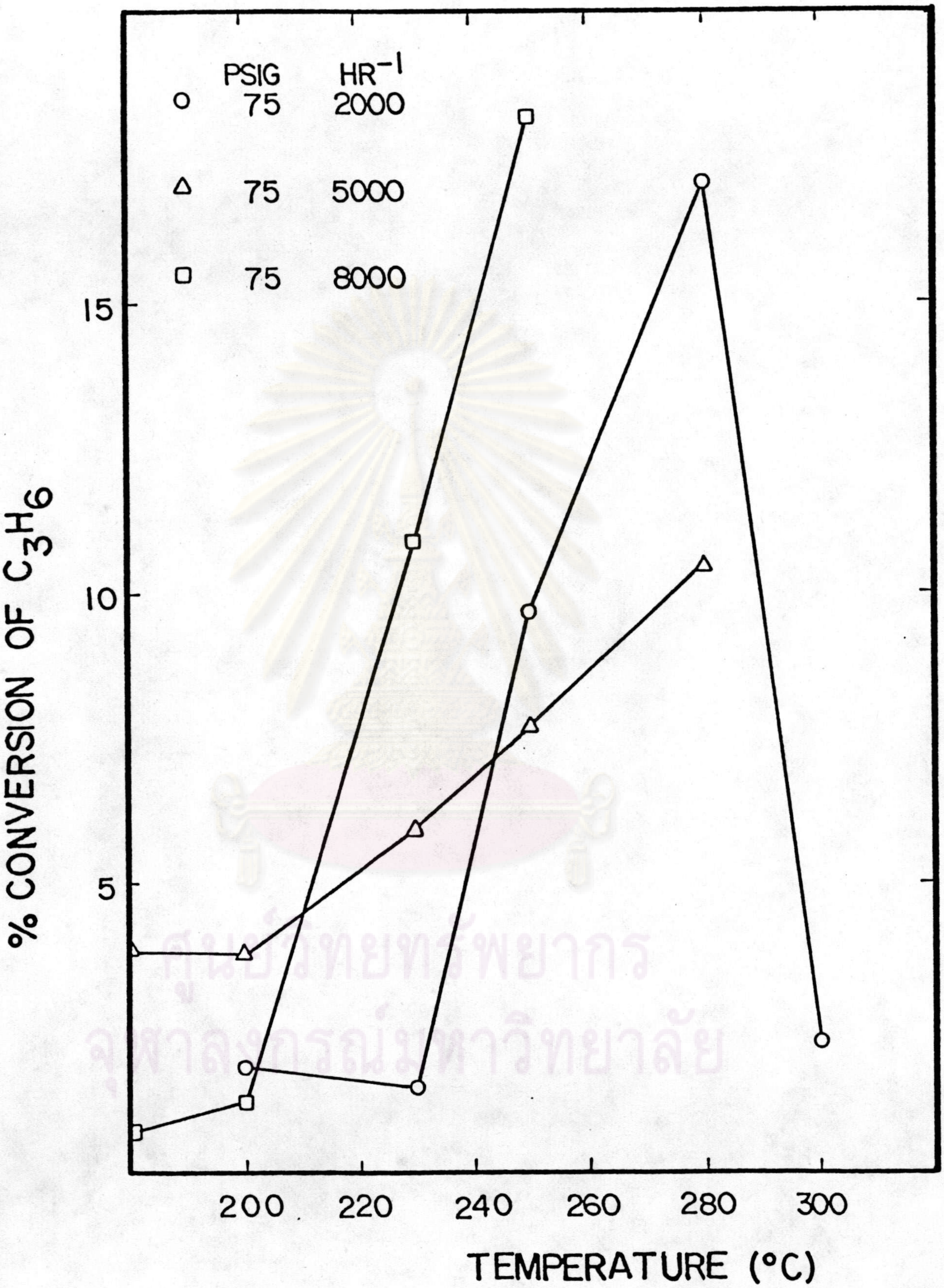

Figure 6.2 Effect of Temperature (200-300°C) on Total Propylene Conversion (at 75 psig, 2000-8000 hr^{-1}) for Catalyst no.1

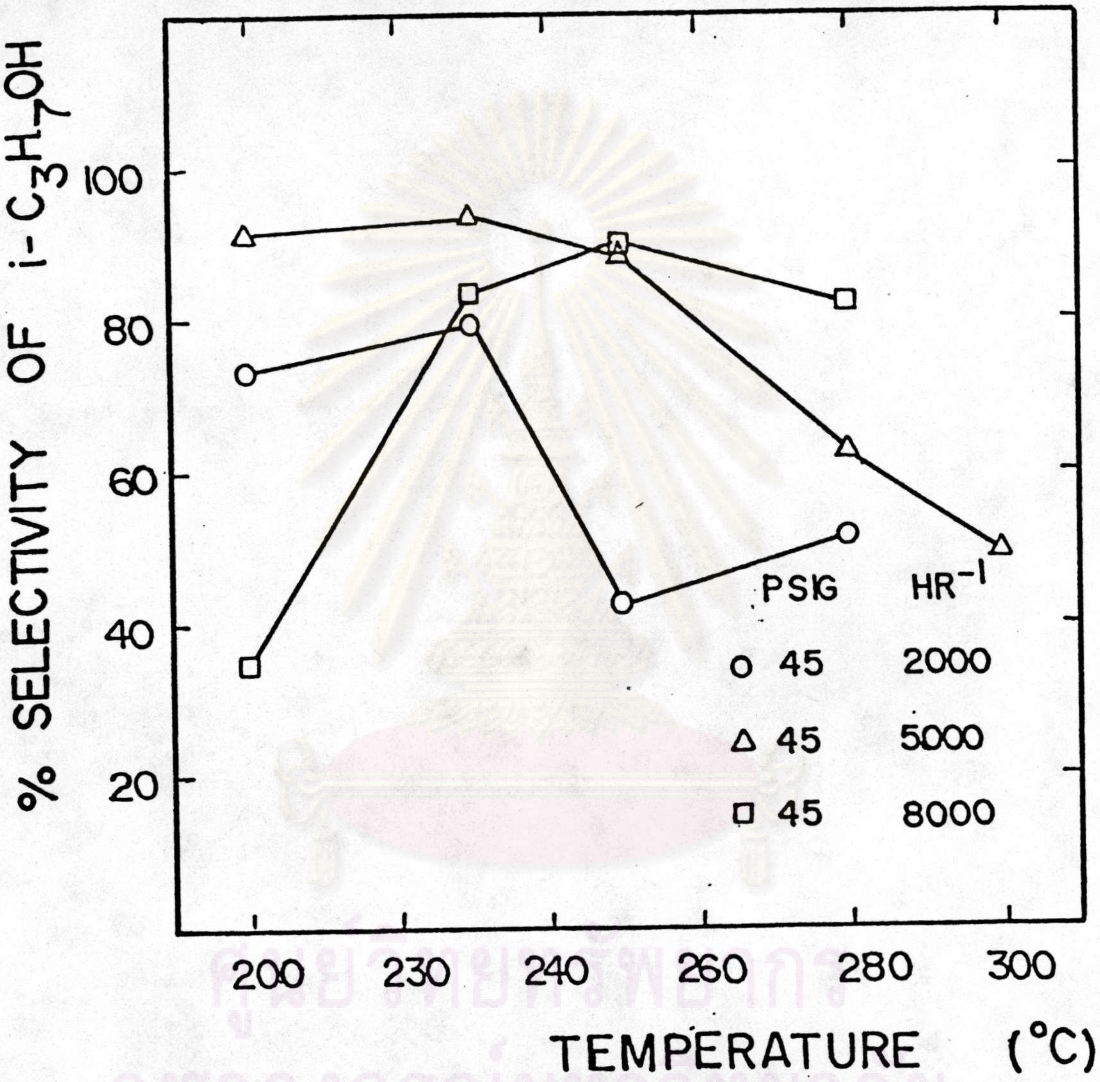

Figure 6.4 Effect of Temperature (200-300°C) on Selectivity of Isopropanol (at 45 psig, 2000-8000 hr^{-1}) for Catalyst no.1

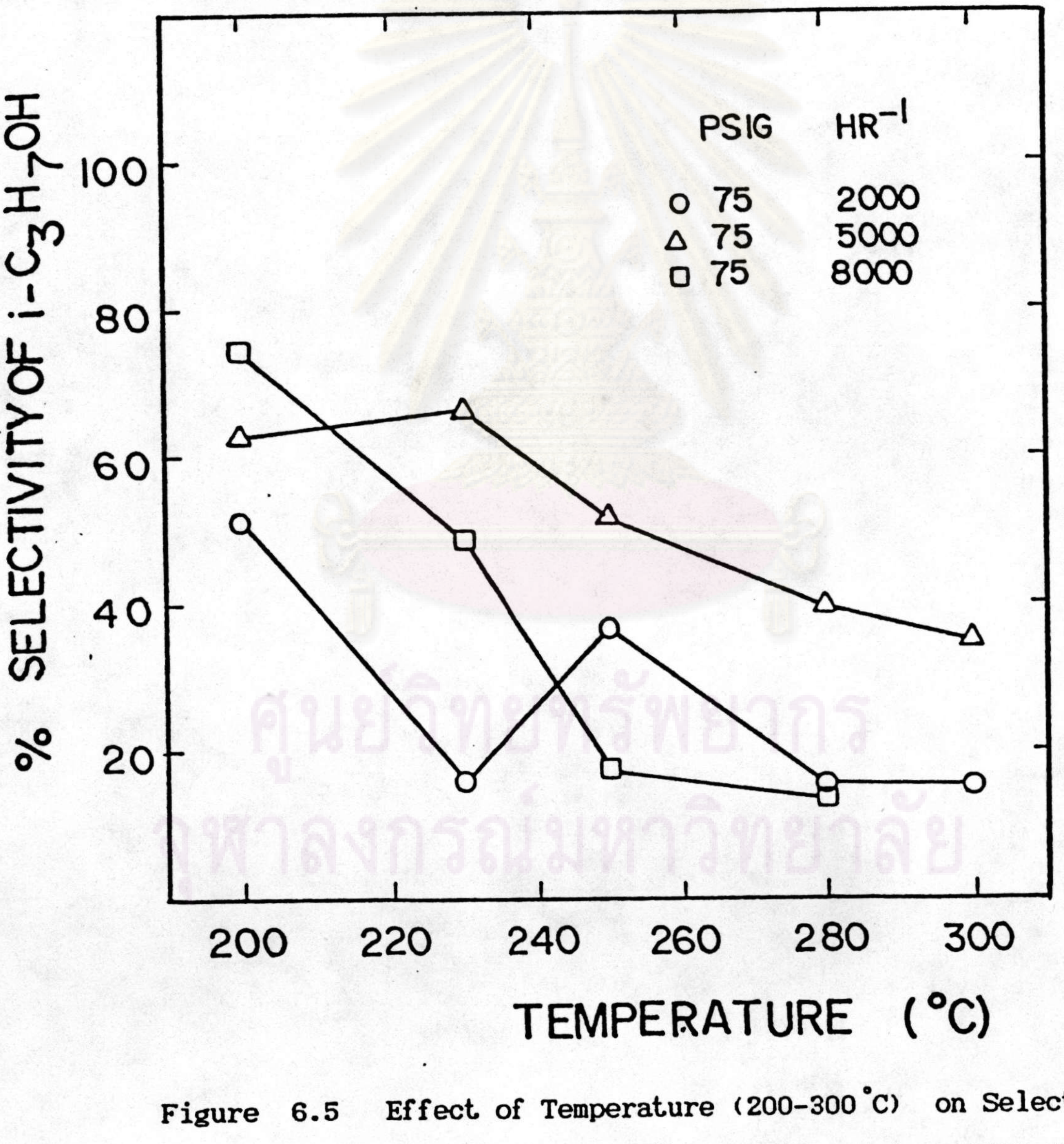

Figure 6.5 Effect of Temperature (200-300 °C) on Selectivity of Isopropanol (at 75 psig, 2000-8000 hr^{-1}) for Catalyst no.1

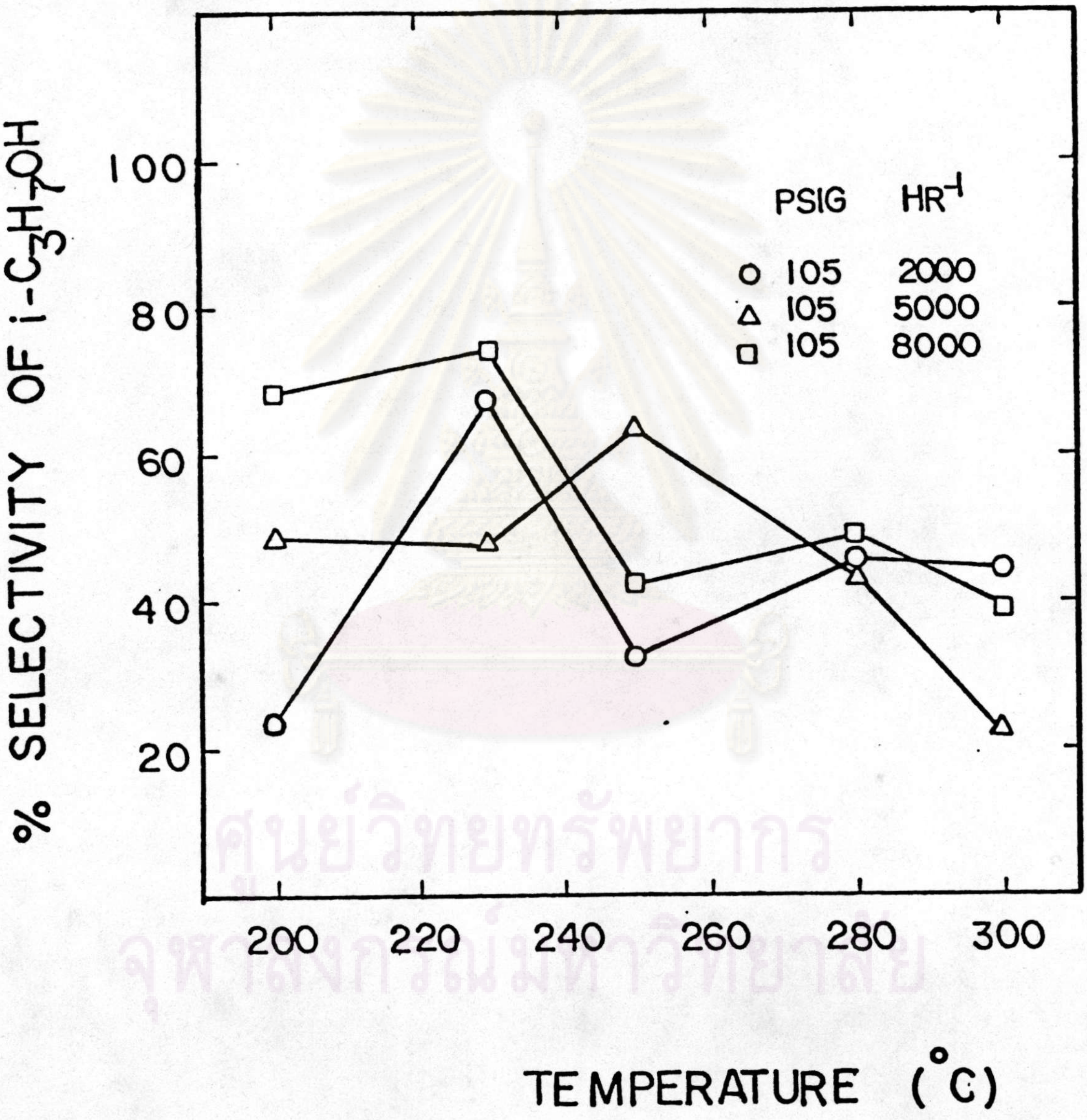

Figure 6.6 Effect of Temperature (200-300 °C) on Selectivity of Isopropanol (at 105 psig, 2000-8000 hr^{-1}) for Catalyst no.1

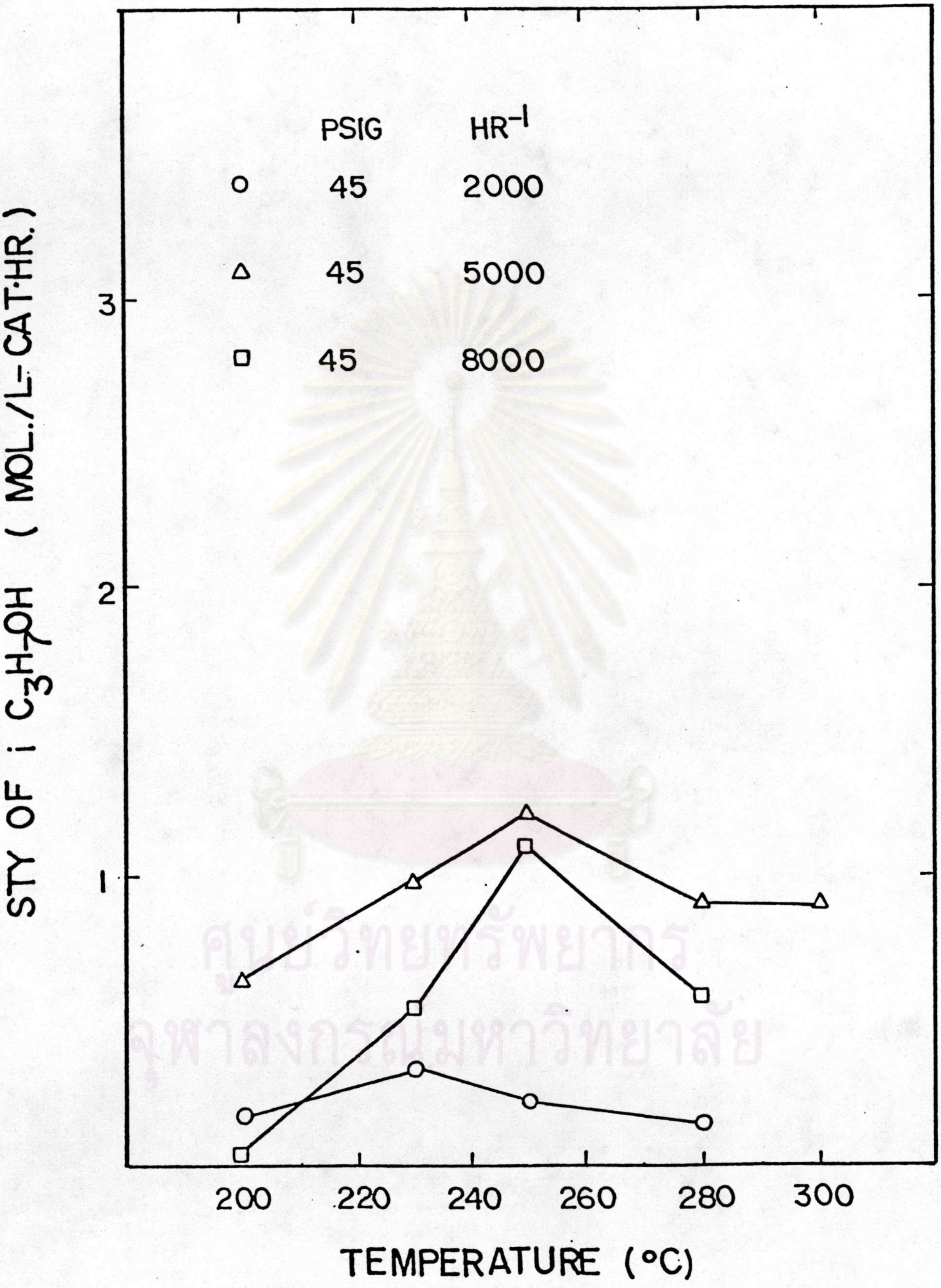

Figure 6.7 Effect of Temperature (200-300 °C) on Space Time Yield of Isopropanol (at 45 psig, 2000-8000 hr^{-1}) for Catalyst no.1

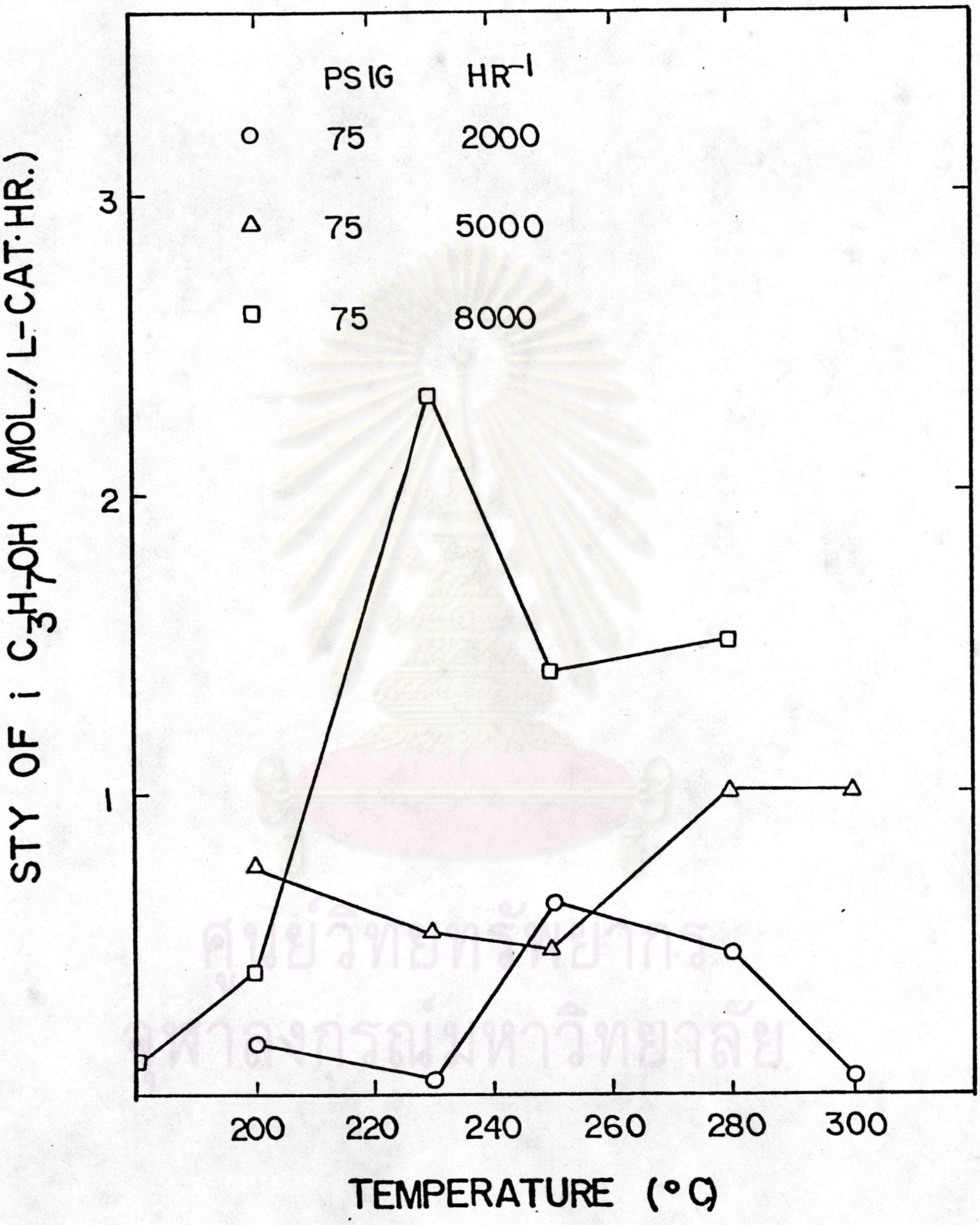

Figure 6.8 Effect of Temperature (200-300 °C) on Space Time Yield of Isopropanol (at 75 psig, 2000-8000 hr^{-1}) for Catalyst no.1

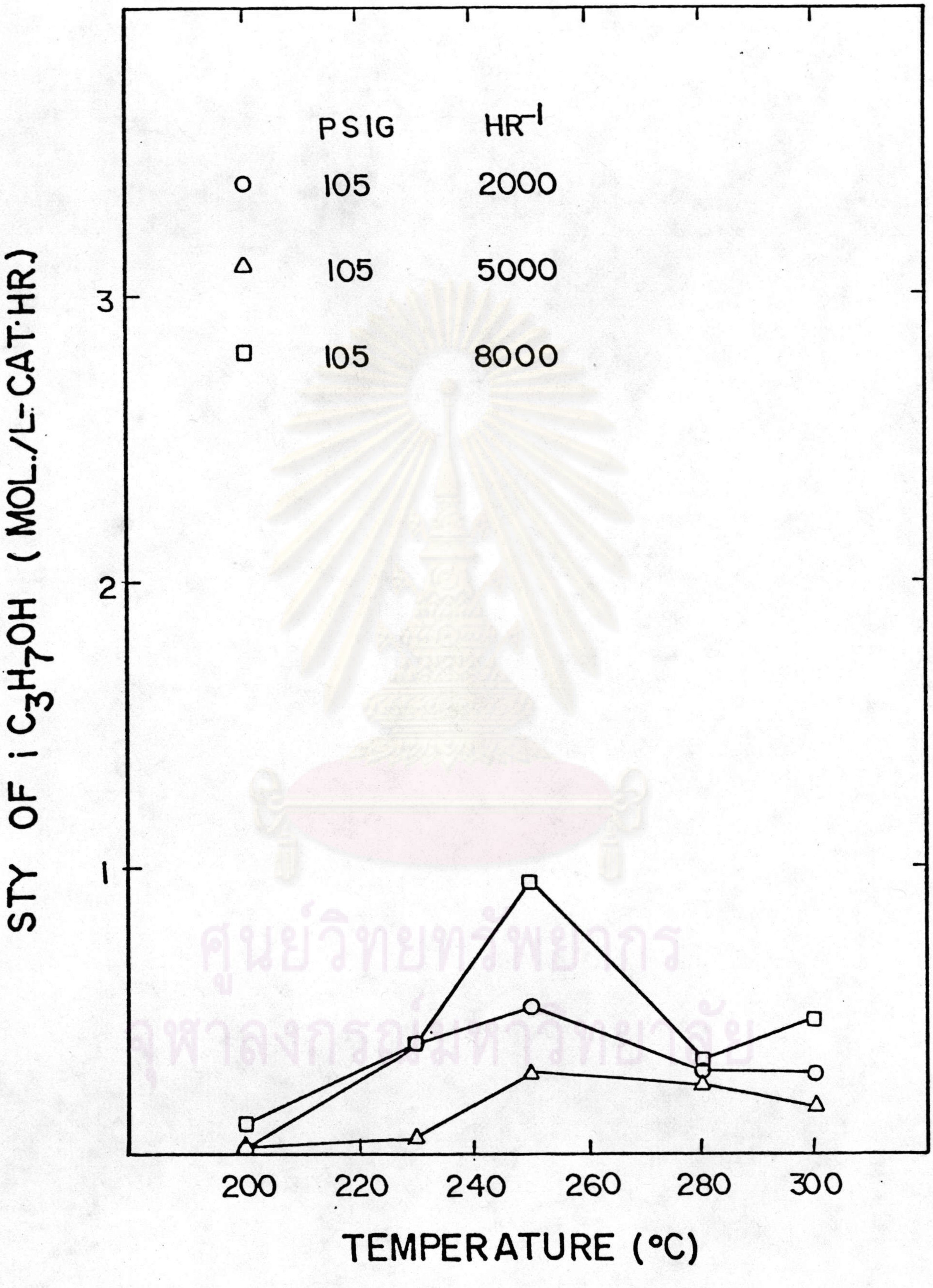

Figure 6.9 Effect of Temperature (200-300°C) on Space Time Yield of Isopropanol (at 105 psig, 2000-8000 hr^{-1}) for Catalyst no.1

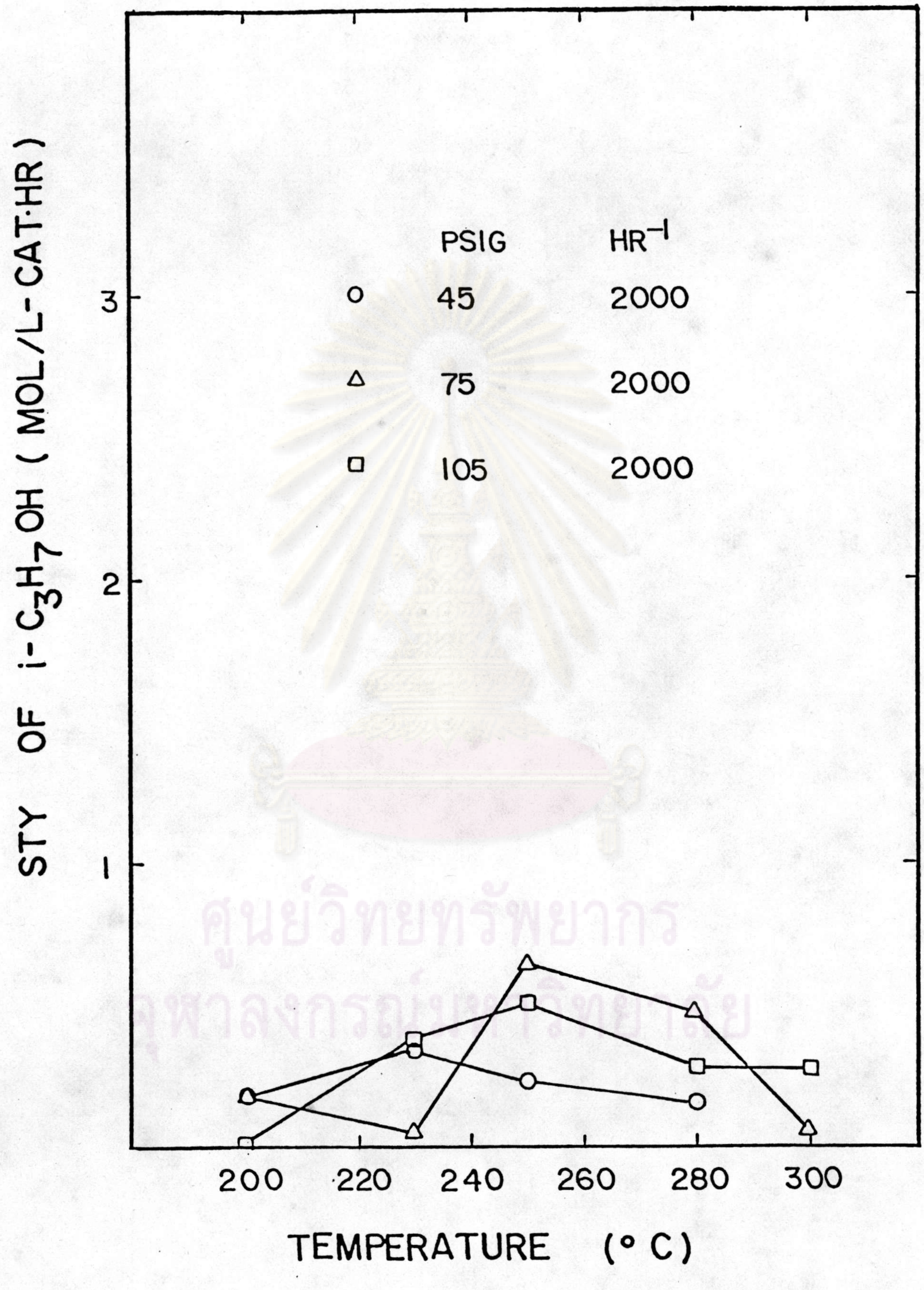

Figure 6.10 Effect of Temperature (200-300 °C) on Space Time Yield of Isopropanol (at 45-105 psig, 2000 hr^{-1}) for Catalyst no.1

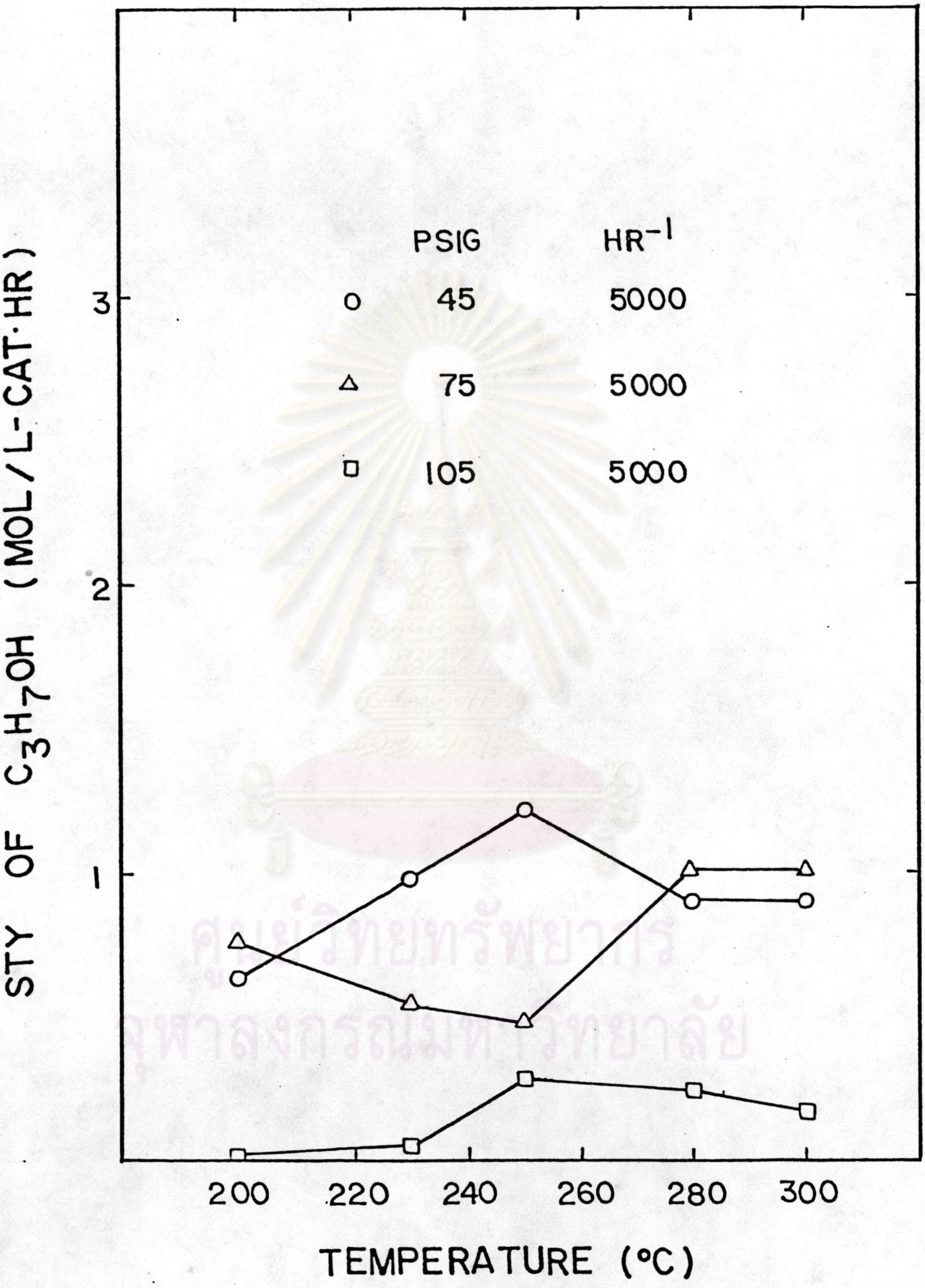

Figure 6.11 Effect of Temperature (200-300°C) on Space Time Yield of Isopropanol (at 45-105 psig, 5000 hr^{-1}) for Catalyst no.1

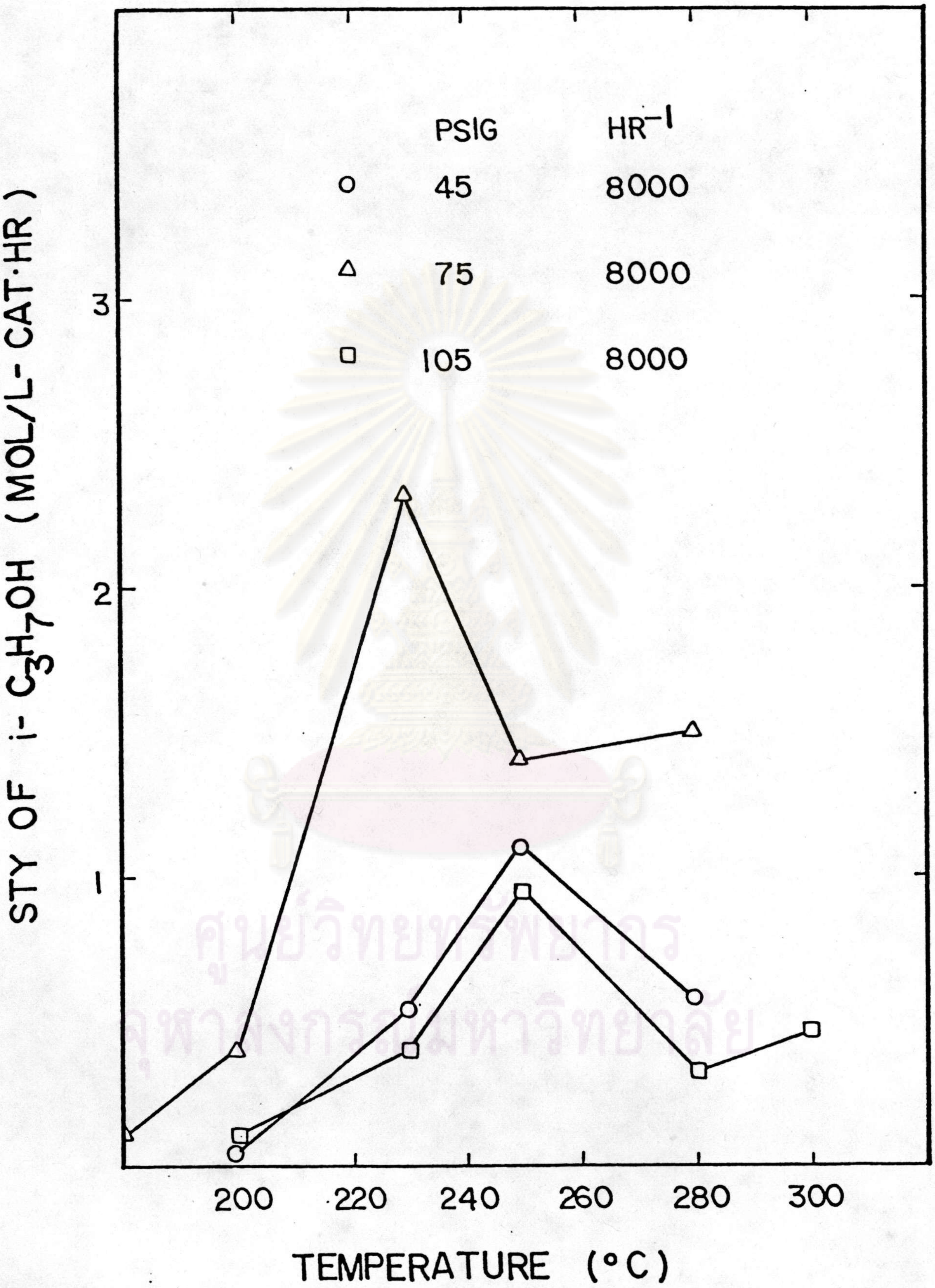

Figure 6.12 Effect of Temperature (200-300 °C) on Space Time Yield of Isopropanol (at 45-105 psig, 8000 hr^{-1}) for Catalyst no.1

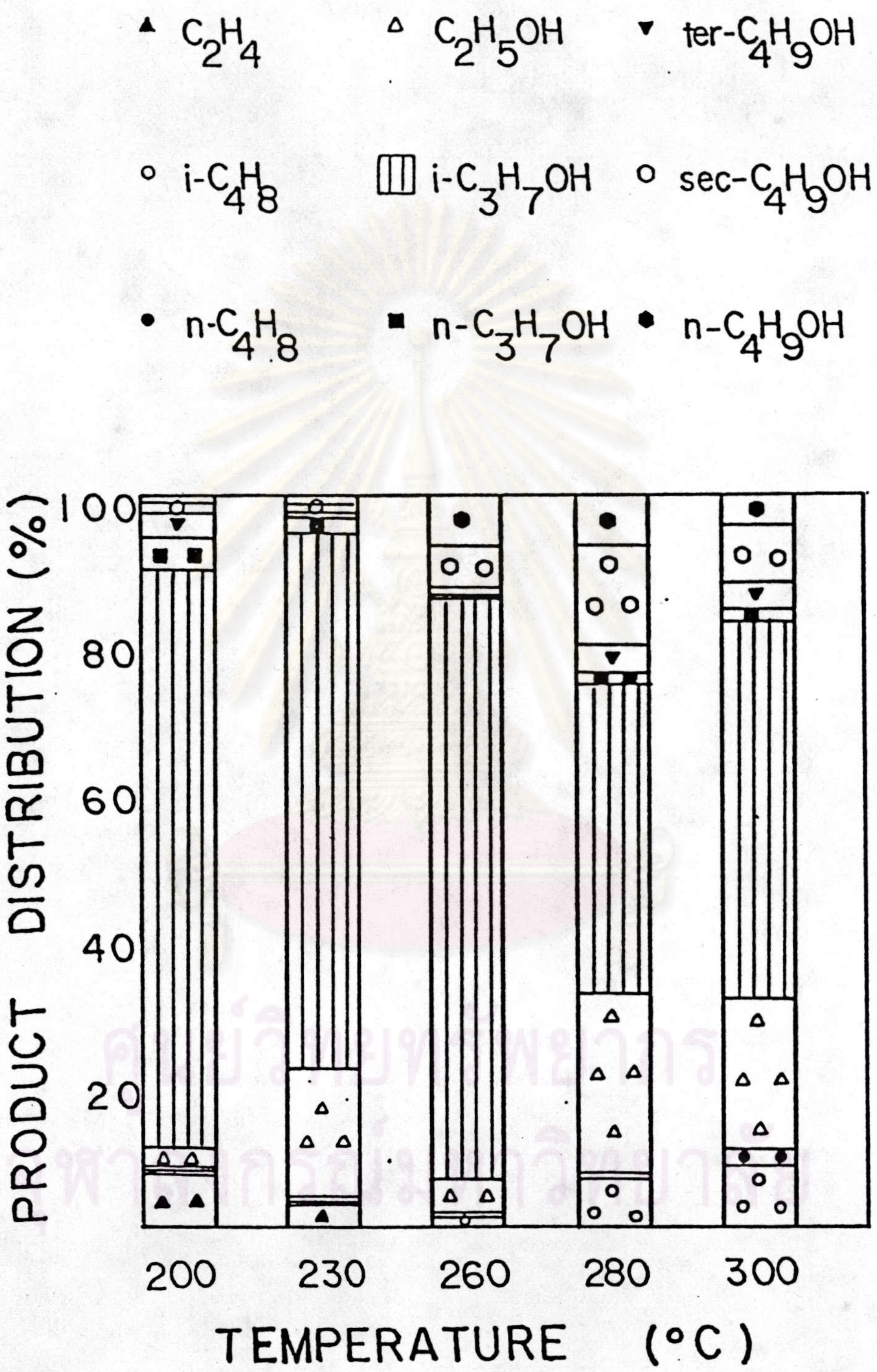

Figure 6.13 Effect of Temperature (200-300 °C) on Product Distribution (at 45 psig, 2000 hr^{-1}) for Catalyst no.1

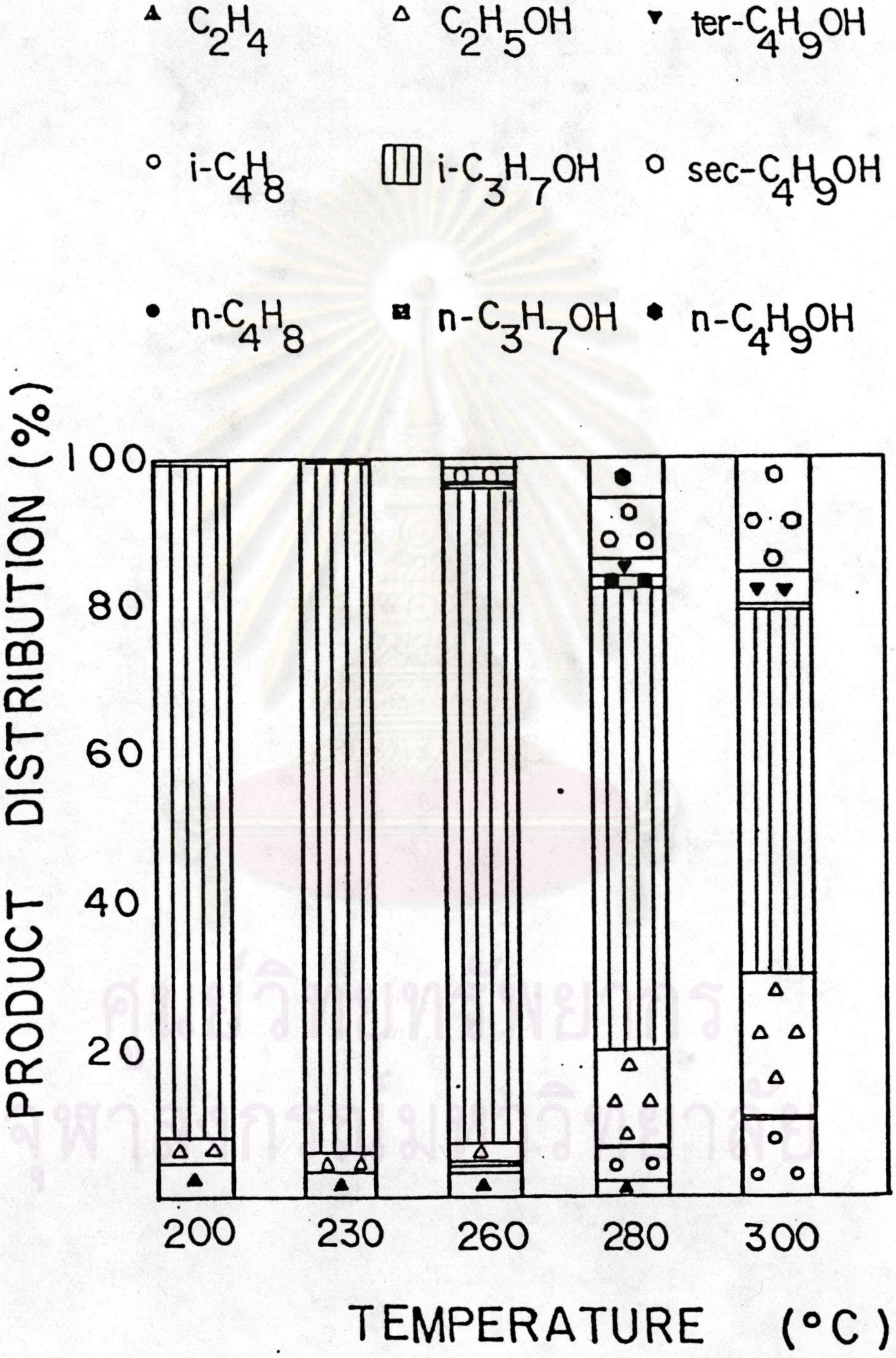

Figure 6.14 Effect of Temperature (200-300 °C) on Product Distribution (at 45 psig, 5000 hr^{-1}) for Catalyst no.1

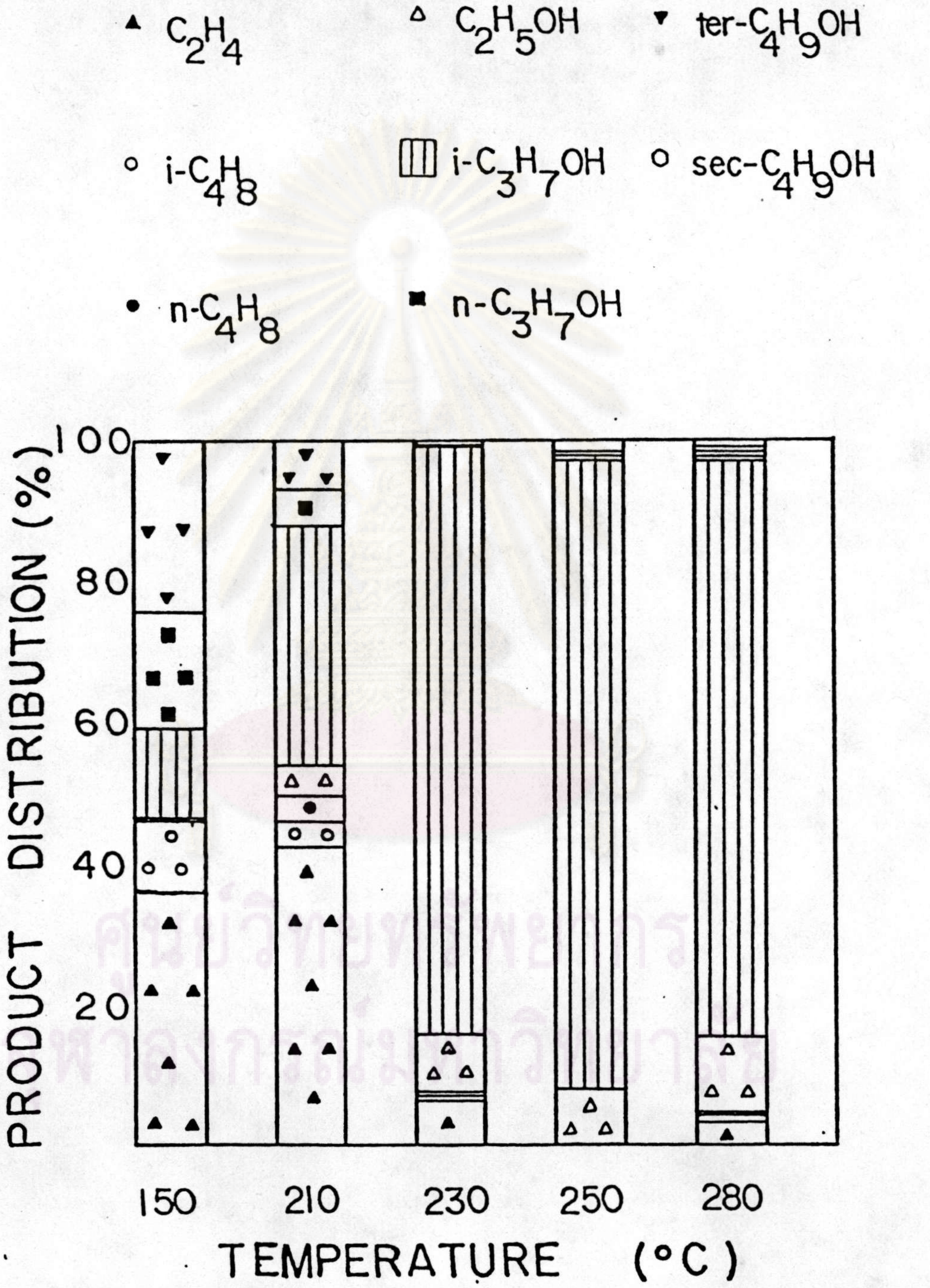

Figure 6.15 Effect of Temperature (150-280 °C) on Product Distribution (at 45 psig, 8000 hr^{-1}) for Catalyst no.1

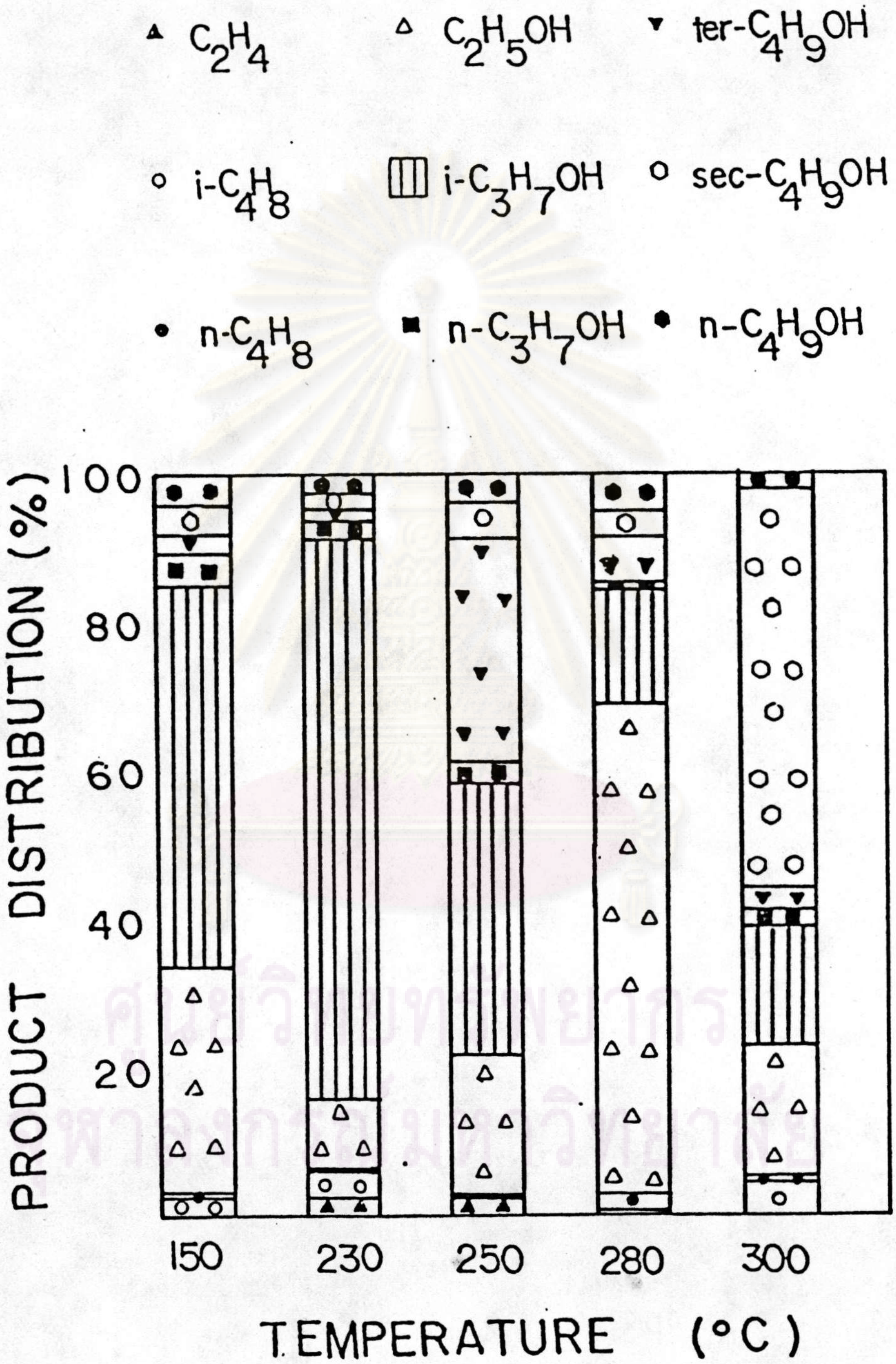

Figure 6.16 Effect of Temperature (150-300 °C) on Product Distribution (at 75 psig, 2000 hr^{-1}) for Catalyst no.1

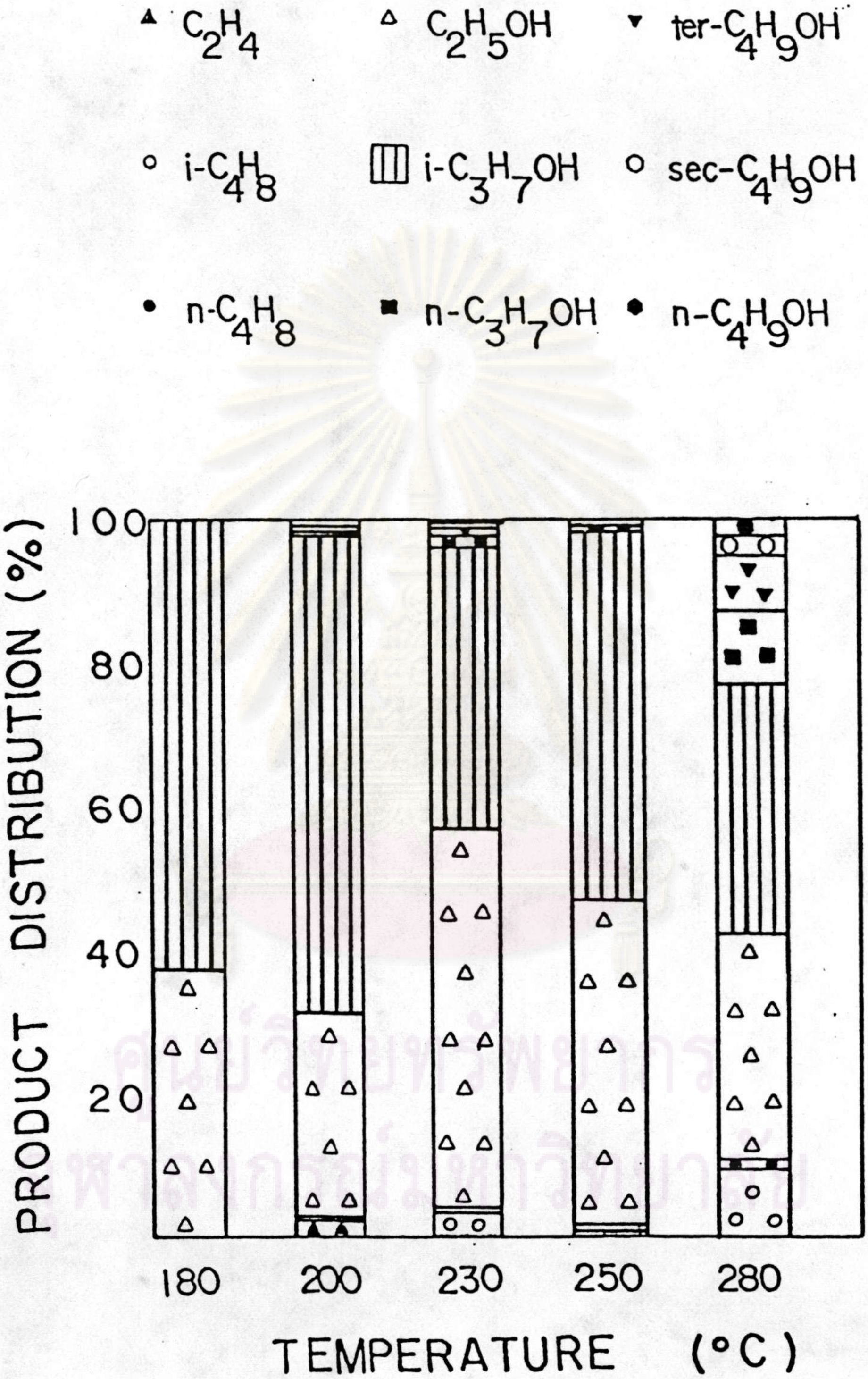

Figure 6.17 Effect of Temperature (180-280 °C) on Product Distribution (at 75 psig, 5000 hr^{-1}) for Catalyst no.1

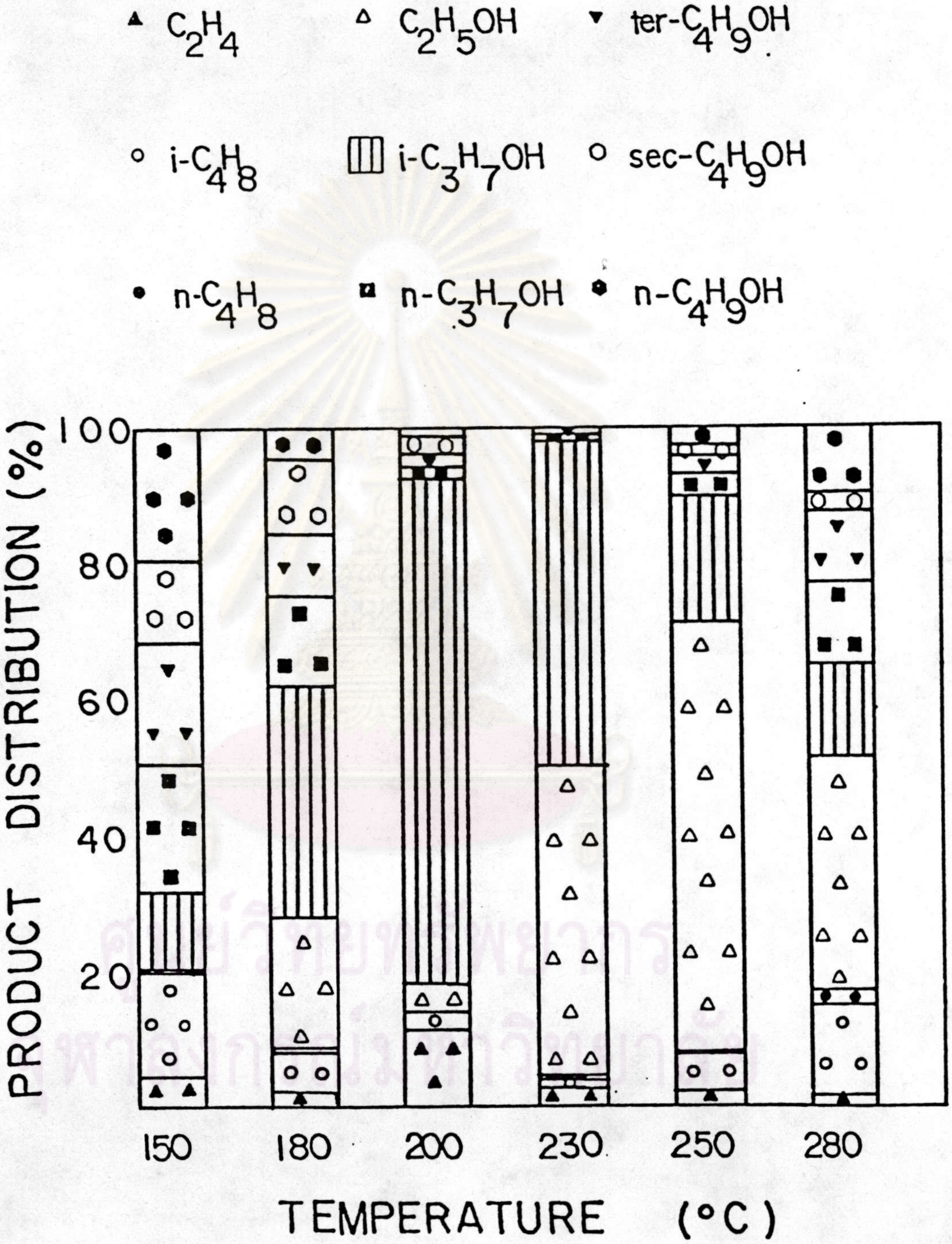

Figure 6.18 Effect of Temperature (150-280 °C) on Product Distribution (at 75 psig, 8000 hr^{-1}) for Catalyst no.1

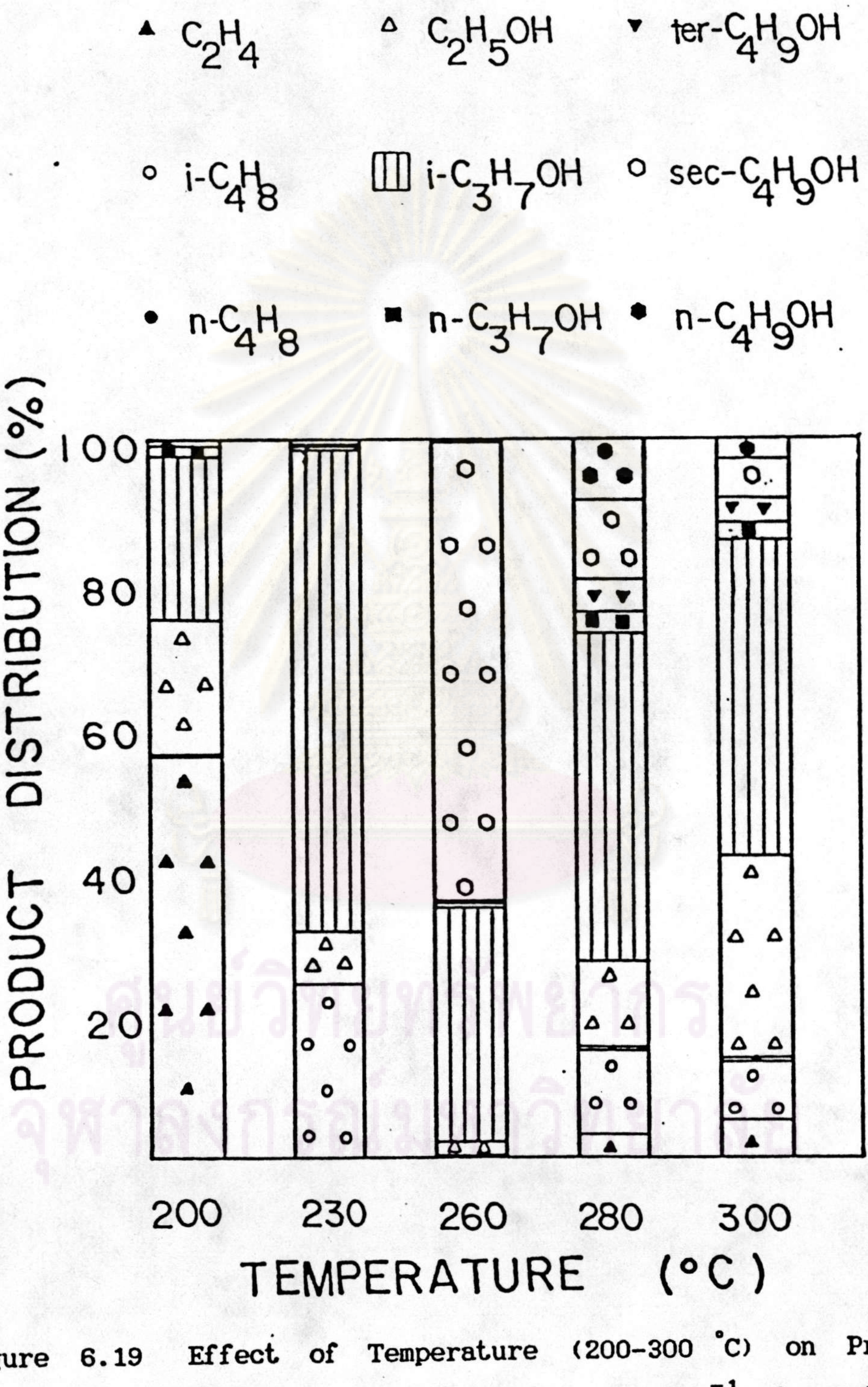

Figure 6.19 Effect of Temperature (200-300 °C) on Product Distribution (at 105 psig, 2000 hr^{-1}) for Catalyst no.1

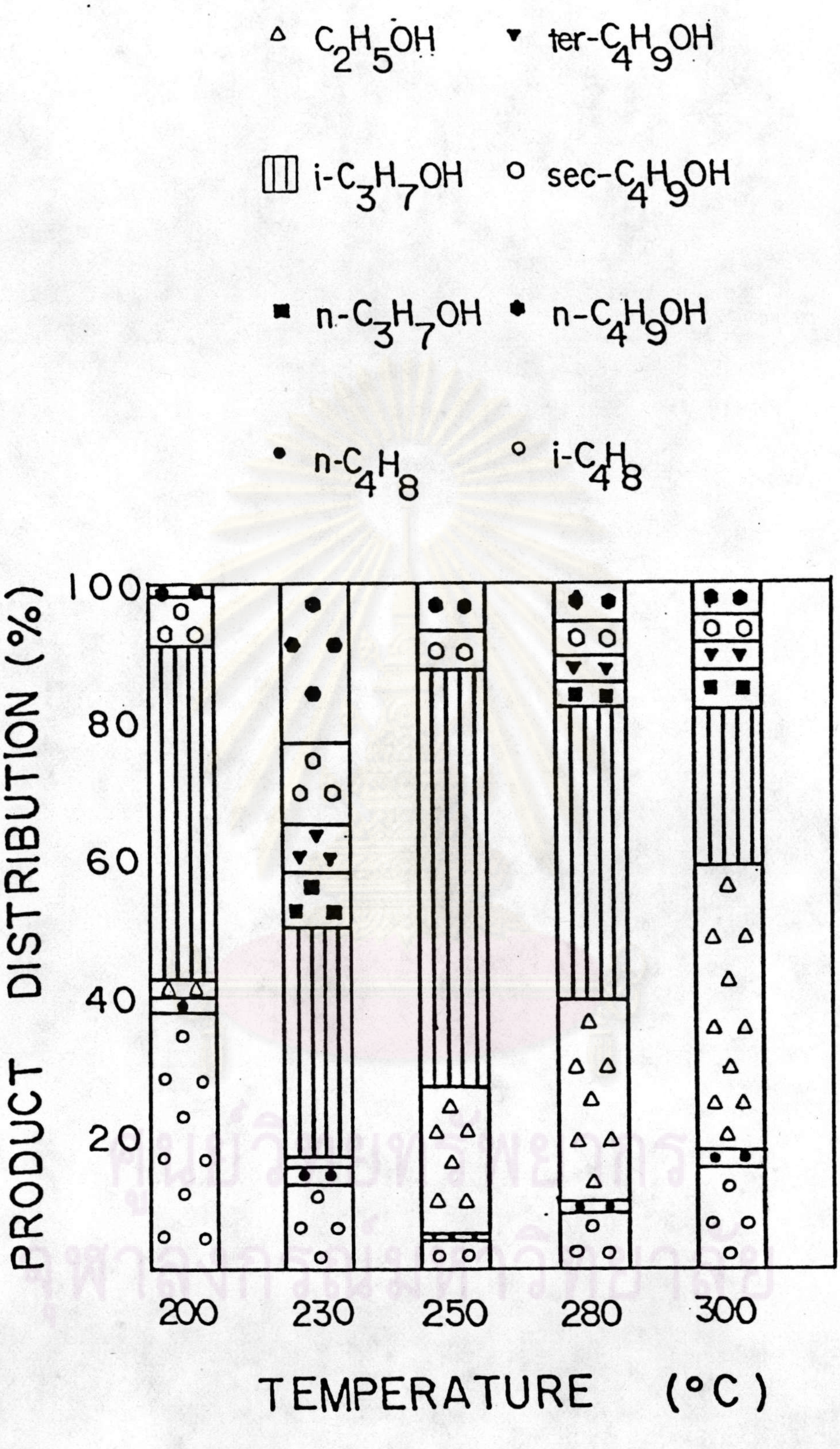

Figure 6.20 Effect of Temperature (200-300 °C) on Product Distribution (at 105 psig, 5000 hr^{-1}) for Catalyst no.1

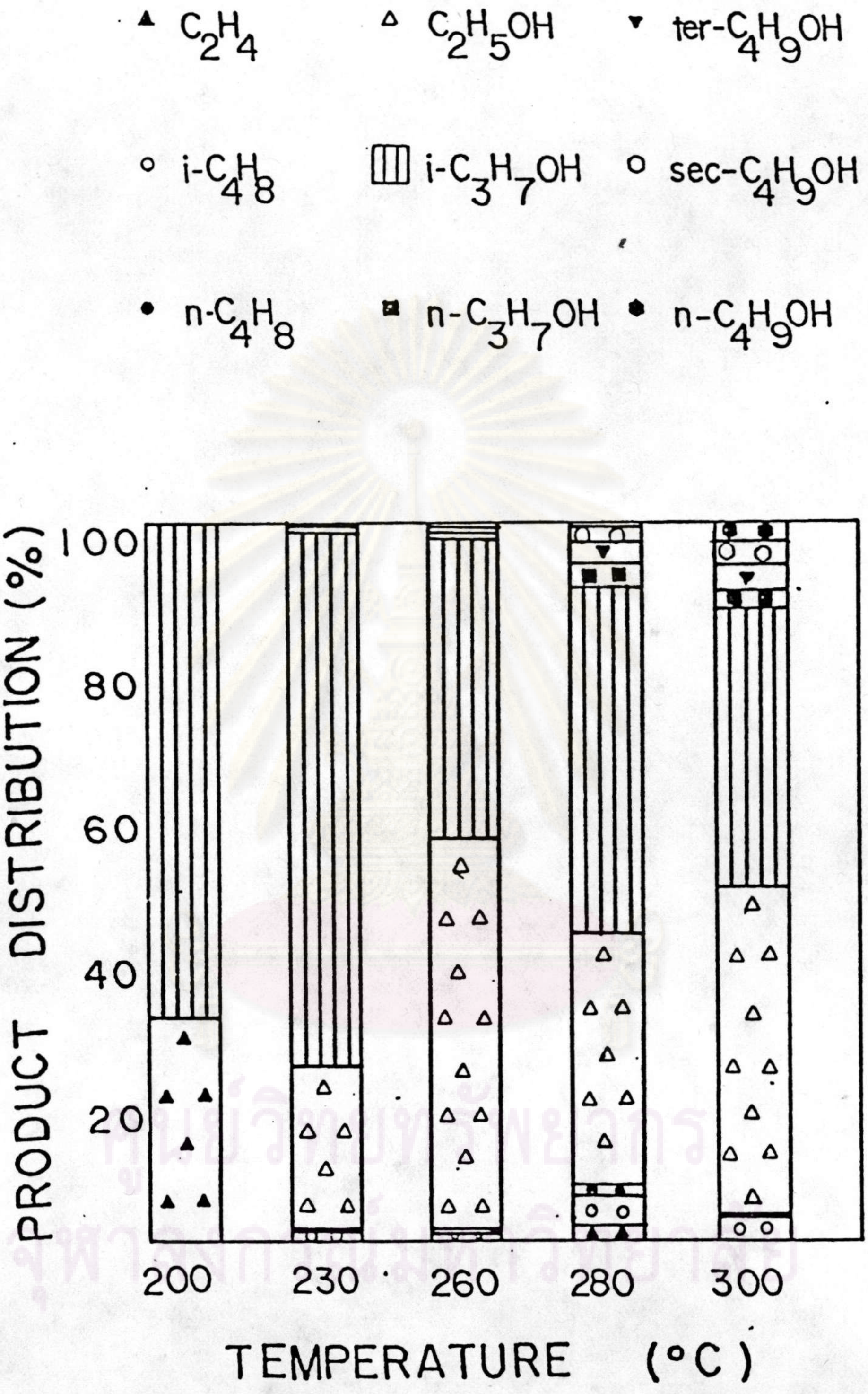

Figure 6.21 Effect of Temperature (200-300 °C) on Product Distribution (at 105 psig, 8000 hr^{-1}) for Catalyst no.1

6.2 Comparison of Experimental Results between Catalysts No.1 and No.2

Catalysts no.1 and no.2 were both zeolite catalysts but with different composition of SiO_2 : Al_2O_3. In addition catalyst no.2 contained K_2O 11.2 wt% in its composition.

Catalyst no.1 was NaY with SiO_2 : Al_2O_3 = 5.6 : 1 (mole ratio) where as catalyst no.2 was a mixture of offretite/erionite with mole ratio of SiO_2 : Al_2O_3 = 7.7 : 1 and K_2O : Al_2O_3 = 0.78 : 1. Only experimental results under comparable conditions will be compared quantitatively. Nevertheless, the general qualitative effects of pressure, temperature and space velocity will also be compared.

6.2.1 Total Propylene Conversion

The qualitative effects of temperature and pressure at a fixed space velocity on isopropanol synthesis were the same for both catalysts. Total propylene conversion increased with temperature from 200°C up to 280°C and decreased beyond that as more by products were instead obtained (see Figs. 6.1-6.3 and Figs. 6.22-6.24). An optimum space velocity existed around 5000 hr^{-1}, above which total propylene conversion would decrease. Thus we may conclude that the effects of temperature, pressure and space velocity on total propylene conversion were qualitatively the same for catalyst no.1 and no.2. Maximum observed total propylene conversion for catalyst no.1 was 25.9 % at 75 psig, 280°C, 8000 hr^{-1} while it was 18.02 % at 45 psig, 230°C, 5000 hr^{-1} for catalyst no.2. On the other hand, at 45 psig, 250°C, 5000 hr^{-1}, for example, total propylene conversion (4.3 %) for catalyst no.1 was lower than total conversion (9.84 %) for catalyst no.2.

Table 6.2 Comparison of Total Propylene Conversion between Catalysts no.1 and no.2

Experimental Conditions	Total Propylene Conversion (%)	
	Catalyst no.1	Catalyst no.2
45 psig 200°C 5000 hr^{-1}	2.18	10.36
45 psig 250°C 5000 hr^{-1}	4.30	9.84
75 psig 200°C 5000 hr^{-1}	3.01	5.16
75 psig 250°C 5000 hr^{-1}	7.64	15.92
105 psig 200°C 5000 hr^{-1}	.23	1.72
105 psig 250°C 5000 hr^{-1}	2.18	2.19

6.2.2 Isopropanol Selectivity and Space Time Yield of Isopropanol

Isopropanol selectivity for both catalysts generally decreased with increasing temperature, while the effect of pressure was not remarkable. The selectivity tended to rise at first with temperature, then decreased as temperature became too high. With respect to isopropanol selectivity, the optimum space velocity was 5000 hr^{-1} for catalyst no.1. At space velocity = 2000 hr^{-1} the selectivity of isopropanol was low because there was too much time for by-products to form. For catalyst no.2, isopropanol selectivity increased with increasing space velocity all the way to 5000 hr^{-1} (see Figs. 6.4-6.6 and Figs. 6.25-6.27).

Table 6.3 compares isopropanol selectivity between catalysts no.1 and no.2 under similar experimental conditions, as obtained from Figs. 6.4-6.6 and Figs. 6.25-6.27. It is obvious from Table 6.3 that catalyst no.2, except at 105 psig, 200°C and 5000 hr^{-1} where very little product and by products were obtained.

Table 6.3 Comparison of Isopropanol Selectivity Between Catalysts no.1 and no.2

Experimental Conditions	Isopropanol Selectivity (%)	
	Catalyst no.1	Catalyst no.2
45 psig 200°C 5000 hr^{-1}	91.59	69.52
45 psig 250°C 5000 hr^{-1}	88.68	45.57
75 psig 200°C 5000 hr^{-1}	66.0	51.36
75 psig 250°C 5000 hr^{-1}	39.13	4.40
105 psig 200°C 5000 hr^{-1}	48.58	93.71
105 psig 250°C 5000 hr^{-1}	63.75	45.96

In general, space time yield (STY) of isopropanol for both catalyst increased with space velocity. (2000-8000 hr^{-1}). One exception occured at 45 psig, where both catalysts had a maximum STY at space velocity 5000 hr^{-1} (see Figs. 6.7-6.12 and Figs. 6.28-6.33). With respect to temperature, STY of isopropanol for catalyst no.1 increased as temperature increased from 220 - 250°C but decreased at temperature above 250 °C because total propylene conversion and isopropanol selectivity dropped rapidly above 250°C. On the other hand, STY of isopropanol for catalyst no.2 increased from 180-210 °C and decreased above 230°C [Note that (STY) = (space velocity) x (total propylene conversion) x (isopropanol selectivity) x (mole ratio of $C_3H_6 : H_2O$)]

Table 6.4 compares the STY of isopropanol under similar experimental conditions. Obviously, catalyst no.2 had higher STY of isopropanol than catalyst no.1 except at 75 psig, 250°C, 5000 hr^{-1}, in which case the optimum STY of catalyst no.2 occured at a lower temperature than catalyst no.1.

6.2.3 Product Distribution

At high temperatures C_2H_4 selectivity generally increased with temperature, although in the temperature range between 230-300°C, some experimental results showed a decrease in C_2H_4 selectivity due to increased ethanol selectivity. Apparently some of the C_2H_4 was converted to C_2H_5OH as in the reaction $C_2H_4 + H_2O \longrightarrow C_2H_5OH$. The effect of space velocity and temperature on C_2H_4 selectivity are shown in Figs. 6.13-6.21 and 6.34-6.42. For both catalysts the effect of pressure was not remarkable at low space velocity or high temperature, though there were more by-products, especially olefins and higher alcohols, probably as follows:

$$2C_3H_6 \longrightarrow C_2H_4 + C_4H_8$$

$$C_4H_8 + H_2O \longrightarrow 2 - C_4H_9OH \text{ (major product).}$$

$$i - C_4H_8 + H_2O \longrightarrow t - C_4H_9OH$$

$$C_4H_8 + H_2O \longrightarrow n - C_4H_9OH \text{ (minor product)}$$

Table 6.4 Comparison of Space Time Yield of Isopropanol between Catalysts no.1 and no.2

Experimental Conditions	STY of Isopropanol (mol/l-cat.hr.)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	0.64	2.29
45 psig 250 °C 5000 hr^{-1}	1.21	1.36
75 psig 200 °C 5000 hr^{-1}	.55	.85
75 psig 250 °C 5000 hr^{-1}	1.09	.23
105 psig 200 °C 5000 hr^{-1}	.03	.51
105 psig 250 °C 5000 hr^{-1}	.27	.32

Table 6.5 Comparison of Ethene Selectivity Between Catalysts no.1 and no.2

Experimental Conditions	Ethene Selectivity (%)	
	Catalyst no.1	Catalyst no. 2
45 psig 200°C 5000 hr^{-1}	4.72	1.49
45 psig 250°C 5000 hr^{-1}	3.13	5.18
75 psig 200°C 5000 hr^{-1}	2.61	1.76
75 psig 250°C 5000 hr^{-1}	.287	.507
105 psig 200°C 5000 hr^{-1}	-	-
105 psig 250°C 5000 hr^{-1}	-	-

Table 6.6 Comparison of Isobutene Selectivity between Catalysts no.1 and no.2

Experimental Conditions	Isobutene Selectivity (%)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	-	.85
45 psig 250 °C 5000 hr^{-1}	.424	3.64
75 psig 200 °C 5000 hr^{-1}	.31	.638
75 psig 250 °C 5000 hr^{-1}	3.5	20.64
105 psig 200 °C 5000 hr^{-1}	37.4	.94
105 psig 250 °C 5000 hr^{-1}	4.74	2.58

Table 6.7 Comparison of 1-Butene Selectivity between Catalysts no.1 and no.2

Experimental Conditions	Selectivity of 1-Butene (%)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	-	3.42
45 psig 250 °C 5000 hr^{-1}	.079	12.0
75 psig 200 °C 5000 hr^{-1}	-	.85
75 psig 250 °C 5000 hr^{-1}	.076	1.34
105 psig 200 °C 5000 hr^{-1}	2.06	.142
105 psig 250 °C 5000 hr^{-1}	1.01	.148

Table 6.8 Comparison of Ethanol Selectivity between Catalysts no.1 and no.2

Experimental Conditions	Ethanol Selectivity (%)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	3.28	14.76
45 psig 250 °C 5000 hr^{-1}	2.5	10.82
75 psig 200 °C 5000 hr^{-1}	28.9	9.58
75 psig 250 °C 5000 hr^{-1}	45.53	-
105 psig 200 °C 5000 hr^{-1}	2.58	1.91
105 psig 250 °C 5000 hr^{-1}	22.52	2.75

Table 6.9 Comparison of n-Propanol Selectivity between Catalysts no.1 and no.2

Experimental Conditions	n-Propanol Selectivity (%)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	-	1.85
45 psig 250 °C 5000 hr^{-1}	.576	2.06
75 psig 200 °C 5000 hr^{-1}	.38	2.0
75 psig 250 °C 5000 hr^{-1}	.88	10.74
105 psig 200 °C 5000 hr^{-1}	-	.23
105 psig 250 °C 5000 hr^{-1}	-	1.453

Table 6.10 Comparison of ter-Butanol Selectivity between Catalysts no.1 and no.2

Experimental Conditions	ter- Butanol Selectivity (%)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	-	3.98
45 psig 250 °C 5000 hr^{-1}	.5	6.48
75 psig 200 °C 5000 hr^{-1}	.89	8.94
75 psig 250 °C 5000 hr^{-1}	.55	19.67
105 psig 200 °C 5000 hr^{-1}	-	-
105 psig 250 °C 5000 hr^{-1}	-	1.87

Table 6.11 Comparison of 2-Butanol Selectivity between Catalysts no.1 and no.2

Experimental Conditions	2-Butanol Selectivity (%)	
	Catalyst no.1	Catalyst no.2
45 psig 200°C 5000 hr^{-1}	.39	1.34
45 psig 250°C 5000 hr^{-1}	2.56	5.26
75 psig 200°C 5000 hr^{-1}	.31	12.86
75 psig 250°C 5000 hr^{-1}	.505	18.96
105 psig 200°C 5000 hr^{-1}	7.38	3.03
105 psig 250°C 5000 hr^{-1}	4.81	28.97

Table 6.12 Comparison of n-Butanol Selectivity between Catalysts no.1 and no.2

Experimental Conditions	n-Butanol Selectivity (%)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	-	.95
45 psig 250 °C 5000 hr^{-1}	-	4.3
75 psig 200 °C 5000 hr^{-1}	.49	11.9
75 psig 250 °C 5000 hr^{-1}	.38	20.24
105 psig 200 °C 5000 hr^{-1}	1.98	-
105 psig 250 °C 5000 hr^{-1}	6.82	16.3

Table 6.13 Comparison of STY of Ethene between Catalysts no.1 and no.2

Experimental Conditions	STY of Ethene (mol/l-cat.hr)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	.032	.049
45 psig 250 °C 5000 hr^{-1}	.042	.155
75 psig 200 °C 5000 hr^{-1}	.021	.028
75 psig 250 °C 5000 hr^{-1}	6.99×10^{-3}	.025
105 psig 200 °C 5000 hr^{-1}	-	-
105 psig 250 °C 5000 hr^{-1}	-	-

Table 6.14 Comparison of STY of Isobutene between Catalysts no.1 and no.2

Experimental Conditions	STY of Isobutene (mol/l-cat.hr.)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	-	.028
45 psig 250 °C 5000 hr^{-1}	$5.81x10^{-3}$	.109
75 psig 200 °C 5000 hr^{-1}	$2.6x10^{-3}$	.01
75 psig 250 °C 5000 hr^{-1}	.011	1.04
105 psig 200 °C 5000 hr^{-1}	.026	$5.15x10^{-3}$
105 psig 250 °C 5000 hr^{-1}	.021	.018

Table 6.15 Comparison of STY of n-Butene between Catalysts no.1 and no.2

Experimental Conditions	STY of n-Butene (mol/l-cat hr)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	-	.112
45 psig 250 °C 5000 hr^{-1}	$1.08x10^{-3}$	.36
75 psig 200 °C 5000 hr^{-1}	-	.013
75 psig 250 °C 5000 hr^{-1}	$1.62x10^{-3}$	.068
105 psig 200 °C 5000 hr^{-1}	$1.47x10^{-3}$	$7.78x10^{-4}$
105 psig 250 °C 5000 hr^{-1}	$4.57x10^{-3}$	$1.03x10^{-3}$

Table 6.16 Comparison of STY of Ethanol between Catalysts no.1 and no. 2

Experimental Conditions	STY of Ethanol (mol/l-cat. hr.)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	.022	.48
45 psig 250 °C 5000 hr^{-1}	.034	.324
75 psig 200 °C 5000 hr^{-1}	.55	.157
75 psig 250 °C 5000 hr^{-1}	1.09	-
105 psig 200 °C 5000 hr^{-1}	$1.86x10^{-3}$	.010
105 psig 250 °C 5000 hr^{-1}	.102	.019

Table 6.17 Comparison of STY of n-Propanol between Catalysts no.1 and no.2

Experimental Conditions	STY of n-Propanol(mol/l-cat.hr.)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	-	.061
45 psig 250 °C 5000 hr^{-1}	7.89×10^{-3}	.061
75 psig 200 °C 5000 hr^{-1}	3.19×10^{-3}	.034
75 psig 250 °C 5000 hr^{-1}	.018	.545
105 psig 200 °C 5000 hr^{-1}	-	1.26×10^{-3}
105 psig 250 °C 5000 hr^{-1}	-	.010

Table 6.18 Comparison of STY of ter-Butanol between Catalysts no.1 and no.2

Experimental Conditions	STY of ter-Butanol(mol/l-cat.hr.)	
	Catalyst no.1	Catalyst no.2
45 psig 200°C 5000 hr^{-1}	-	.131
45 psig 250°C 5000 hr^{-1}	$6.85x10^{-3}$	.194
75 psig 200°C 5000 hr^{-1}	$7.47x10^{-3}$	.147
75 psig 250°C 5000 hr^{-1}	.011	.998
105 psig 200°C 5000 hr^{-1}	-	-
105 psig 250°C 5000 hr^{-1}	-	.013

Table 6.19 Comparison of STY of 2-Butanol between Catalysts no.1 and no.2

Experimental Conditions	STY of 2-Butanol (mol/l-cat.hr.)	
	Catalyst no.1	Catalyst no.2
45 psig 200 °C 5000 hr^{-1}	2.71×10^{-3}	.044
45 psig 250 °C 5000 hr^{-1}	.035	.157
75 psig 200 °C 5000 hr^{-1}	2.6×10^{-3}	.211
75 psig 250 °C 5000 hr^{-1}	.010	.962
105 psig 200 °C 5000 hr^{-1}	5.20×10^{-3}	.016
105 psig 250 °C 5000 hr^{-1}	.021	.198

Table 6.20 Comparison of STY of n-Butanol between Catalysts no.1 and no.2

Experimental Condition	STY of n-Butanol (mol/l-cat.hr.)	
	Catalyst no.1	Catalyst no.2
45 psig 200°C 5000 hr^{-1}	-	.031
45 psig 250°C 5000 hr^{-1}	.02	.129
75 psig 200°C 5000 hr^{-1}	$4.11x10^{-3}$	.195
75 psig 250°C 5000 hr^{-1}	$8.1x10^{-3}$	1.02
105 psig 200°C 5000 hr^{-1}	$6.42x10^{-3}$	-
105 psig 250°C 5000 hr^{-1}	.03	.113

Table 6.5 shows that temperature and space velocity slightly affected C_2H_4 selectivity for both catalysts.

As seen from Table 6.6, at pressure 45-75 psig i-C_4H_8 selectivity of catalyst no.2 was higher than that of no.1, but at 105 psig the reverse was true. The contradiction was caused by the pressence of numerous by-products which were also reaction intermediates. Overall the i-C_4H_8 selectivity of catalyst no.2 was higher than catalyst no.1. Tables 6.7-6.12 show the selectivity of 1-C_4H_8, C_2H_5OH, n-C_3H_7OH, t-C_4H_9OH and 2-C_4H_9OH, respectively. The results of Tables 6.7-6.12 are qualitatively the same as Table 6.6.

6.2.4 Space Time Yield of By-Products

Tables 6.13-6.20 show that space time yields of C_2H_4, i-C_4H_8, 1-C_4H_8, C_2H_5OH, n-C_3H_7OH, t-C_4H_9OH and n-C_4H_9OH for catalyst no.2 were generally higher than those for catalyst no.1. The exceptions were space time yields of i-C_4H_8, 1-C_4H_8 and C_2H_5OH at 105 psig, 5000 hr^{-1}, 200°C and 250°C. So it may be concluded that catalyst no.2, which is offretite/erionite with mole ratio of SiO_2/Al_2O_3 = 7.7, Na_2O/Al_2O_3 = 0.25, K_2O/Al_2O_3 = 0.78, performed better than H-Y, which has mole ratio of SiO_2/Al_2O_3 = 6.0.

Because of the difference in SiO_2/Al_2O_3, the "optimum" condition of isopropanol synthesis for the two catalysts turned out to be somewhat different in the present study. To maximize isopropanol selectivity and space time yield for catalyst no.1, synthesis should be carried at a low pressure and medium space velocity with temperature ranging from 250-280°C. For catalyst no.2, the optimum conditions for isopropanol selectivity and space time yield were similar to those of catalyst no.1 except that the temperature range should be 200-230°C. For both catalysts the optimum space velocity was around 5000 hr^{-1}, and pressure around 45-75 psig.

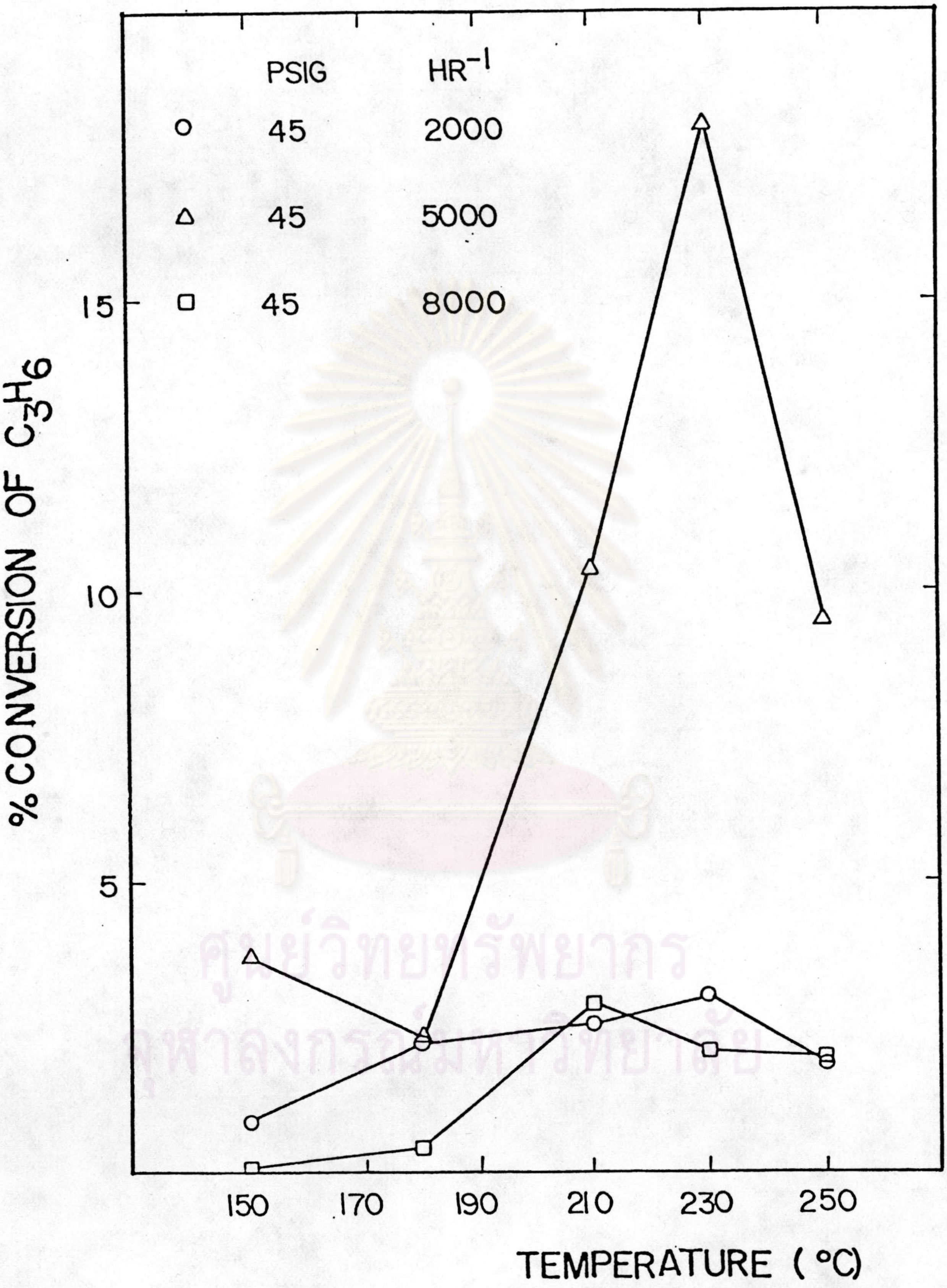

Figure 6.22 Effect of Temperature (150-250 °C) on Total Conversion of Propylene (at 45 psig, 2000-8000 hr^{-1}) for Catalyst no.2

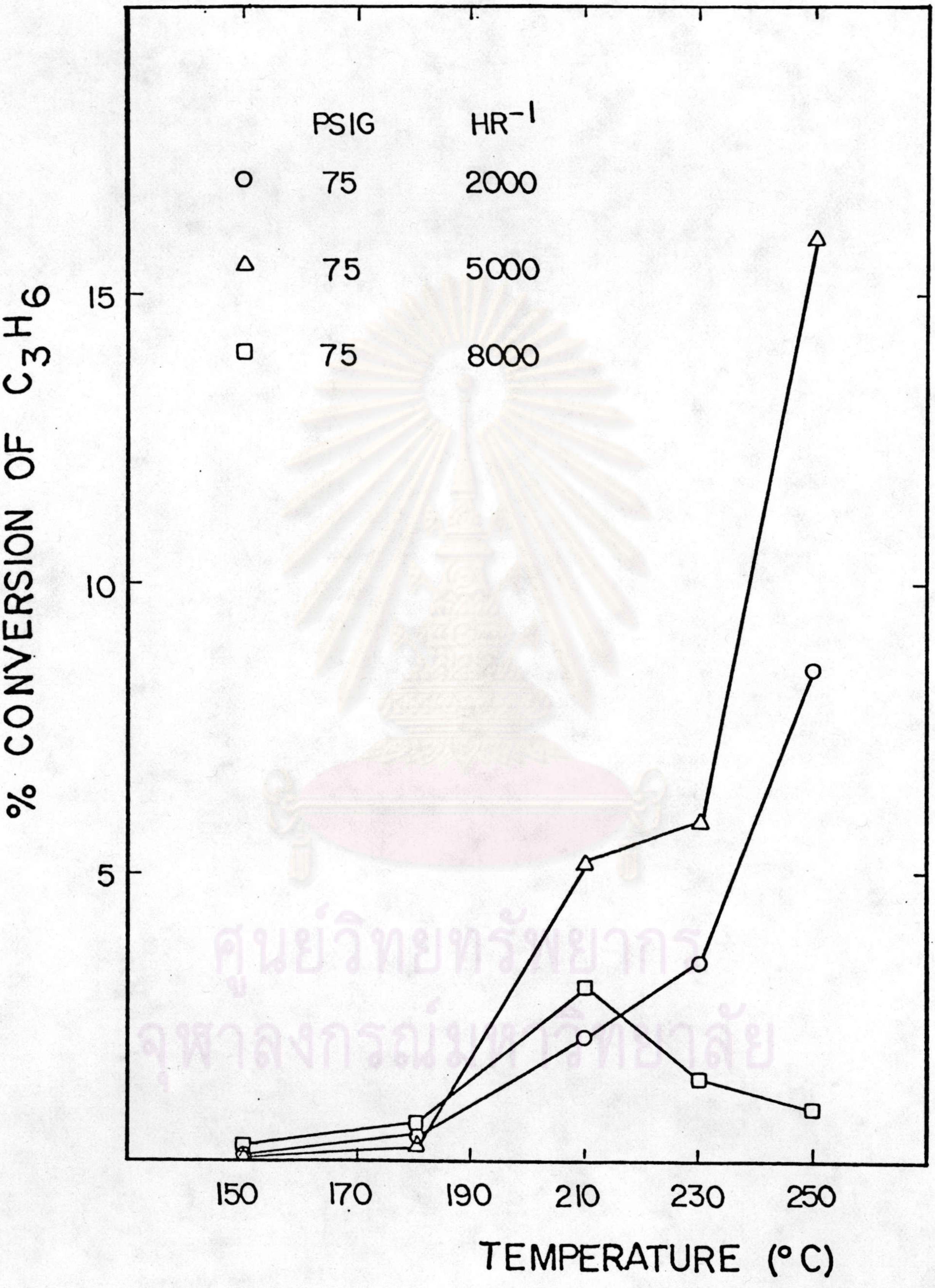

Figure 6.23 Effect of Temperature (150-250 °C) on Total Conversion of Propylene (at 75 psig, 2000-8000 hr^{-1}) for Catalyst no.2

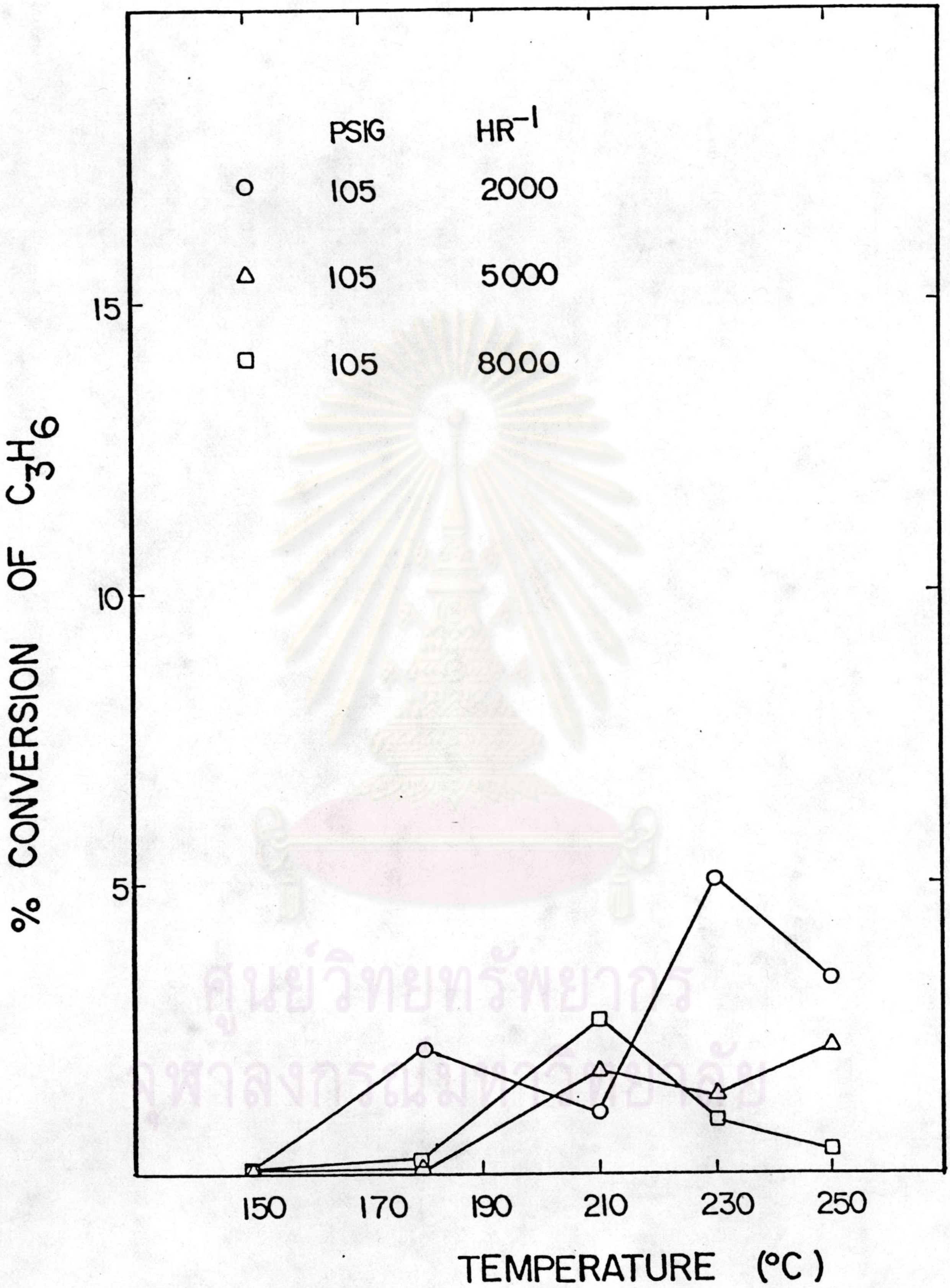

Figure 6.24 Effect of Temperature (150-250 °C) on Total Conversion of Propylene (at 105 psig, 2000-8000 hr^{-1}) for Catalyst no.2

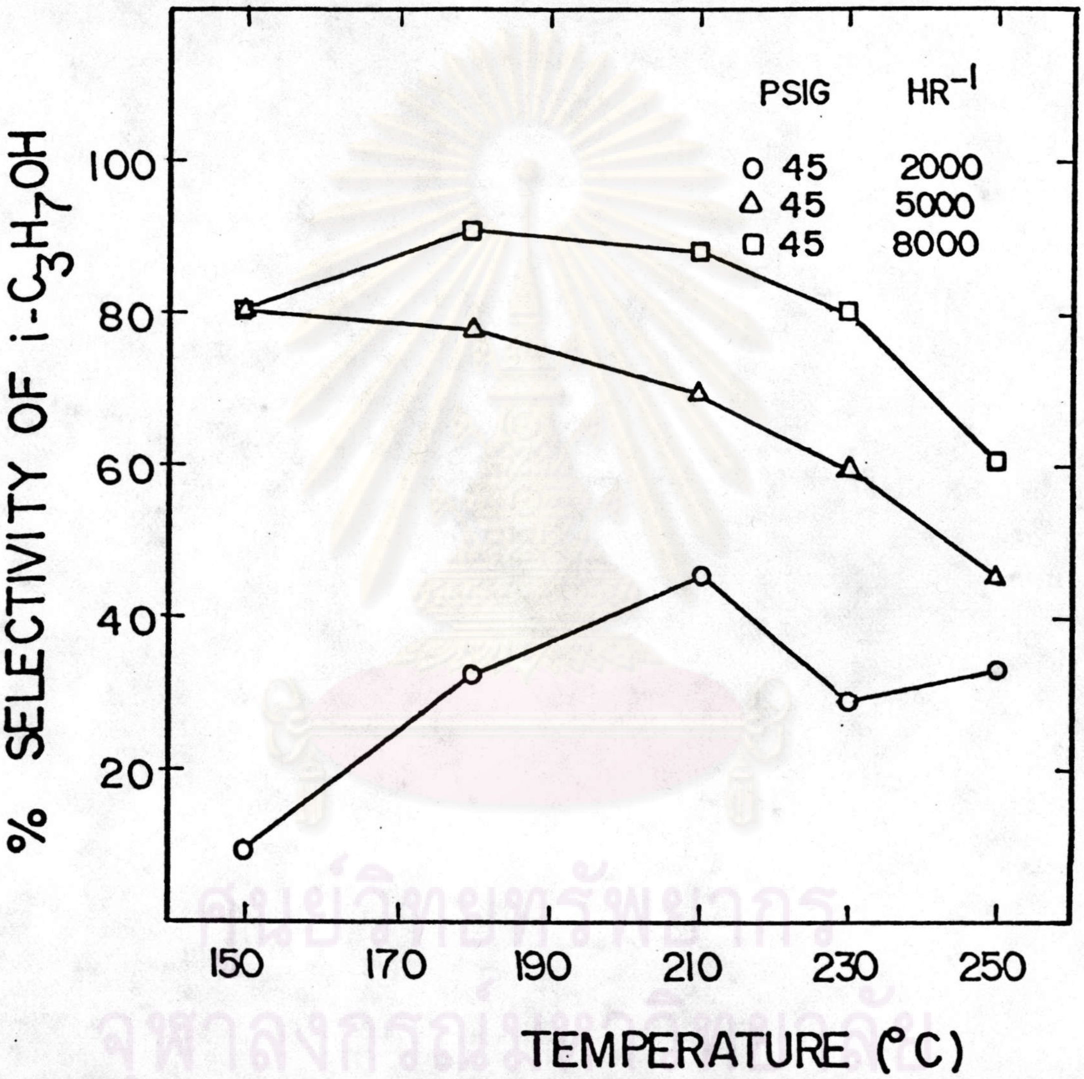

Figure 6.25 Effect of Temperature (150-250 °C) on Selectivity of Isopropanol (at 45 psig, 2000-8000 hr^{-1}) for Catalyst no.2

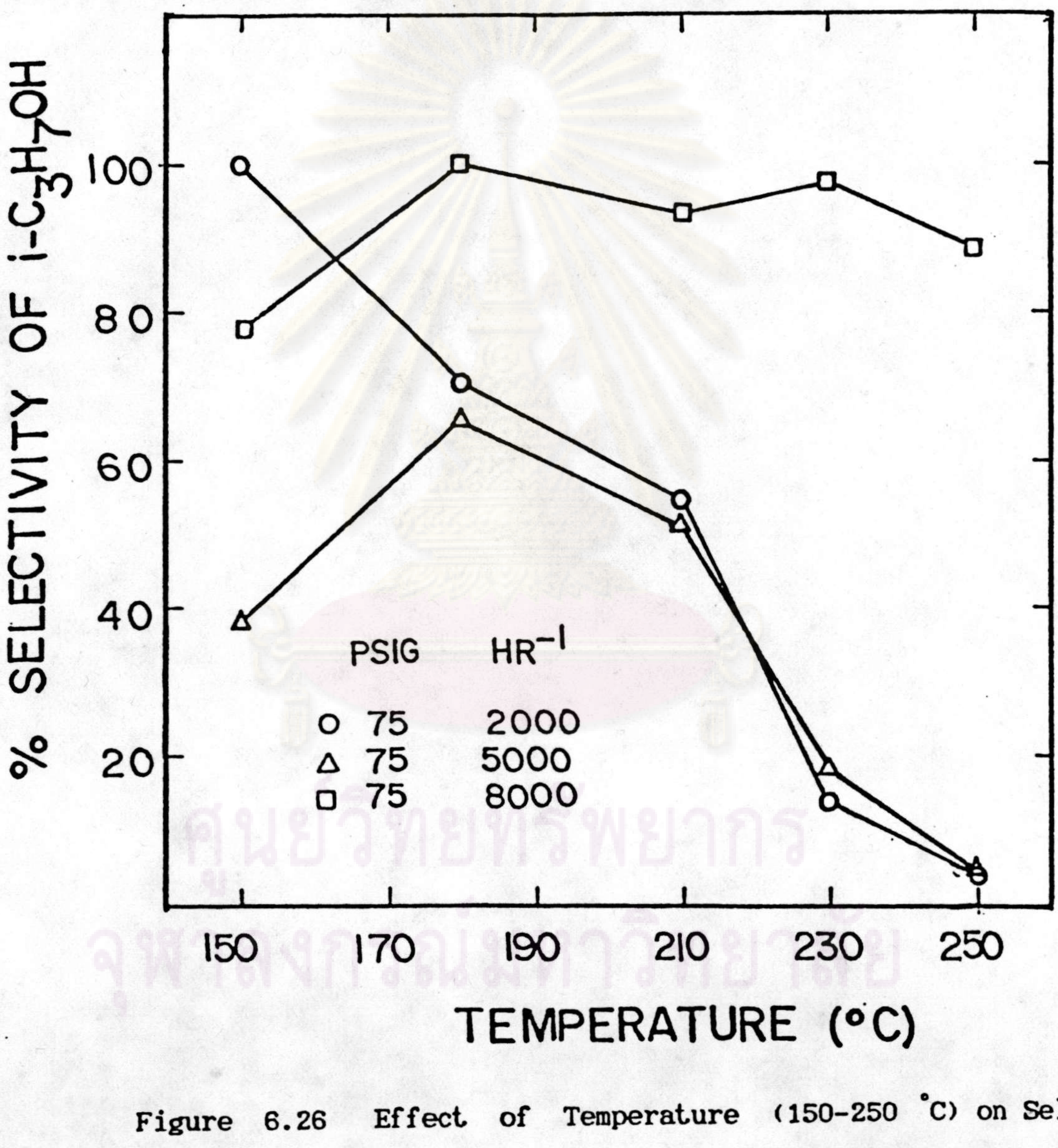

Figure 6.26 Effect of Temperature (150-250 °C) on Selectivity of Isopropanol (at 75 psig, 2000-8000 hr^{-1}) for Catalyst no.2

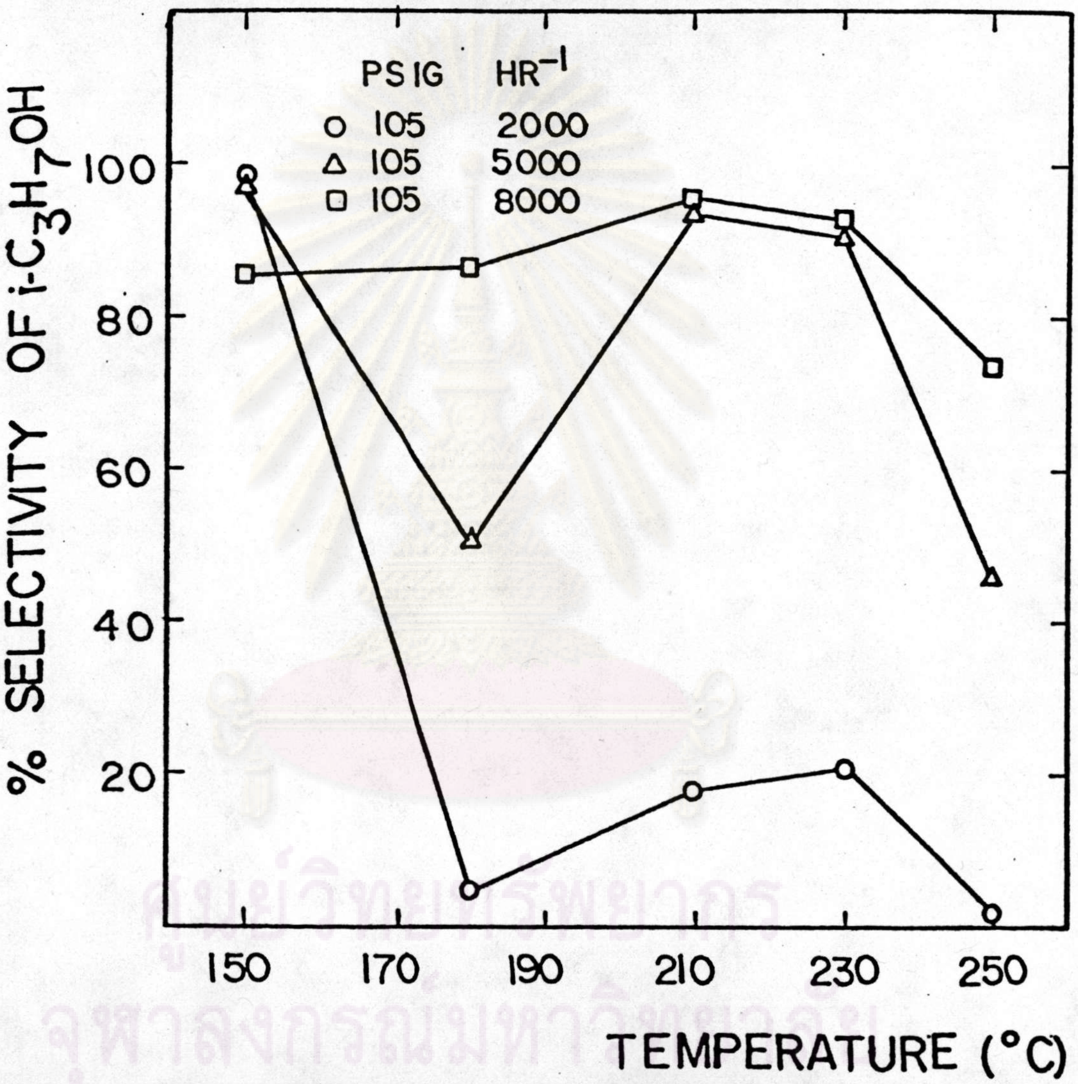

Figure 6.27 Effect of Temperature (150-250 °C) on Selectivity of Isopropanol (at 105 psig, 2000-8000 hr^{-1}) for Catalyst no.2

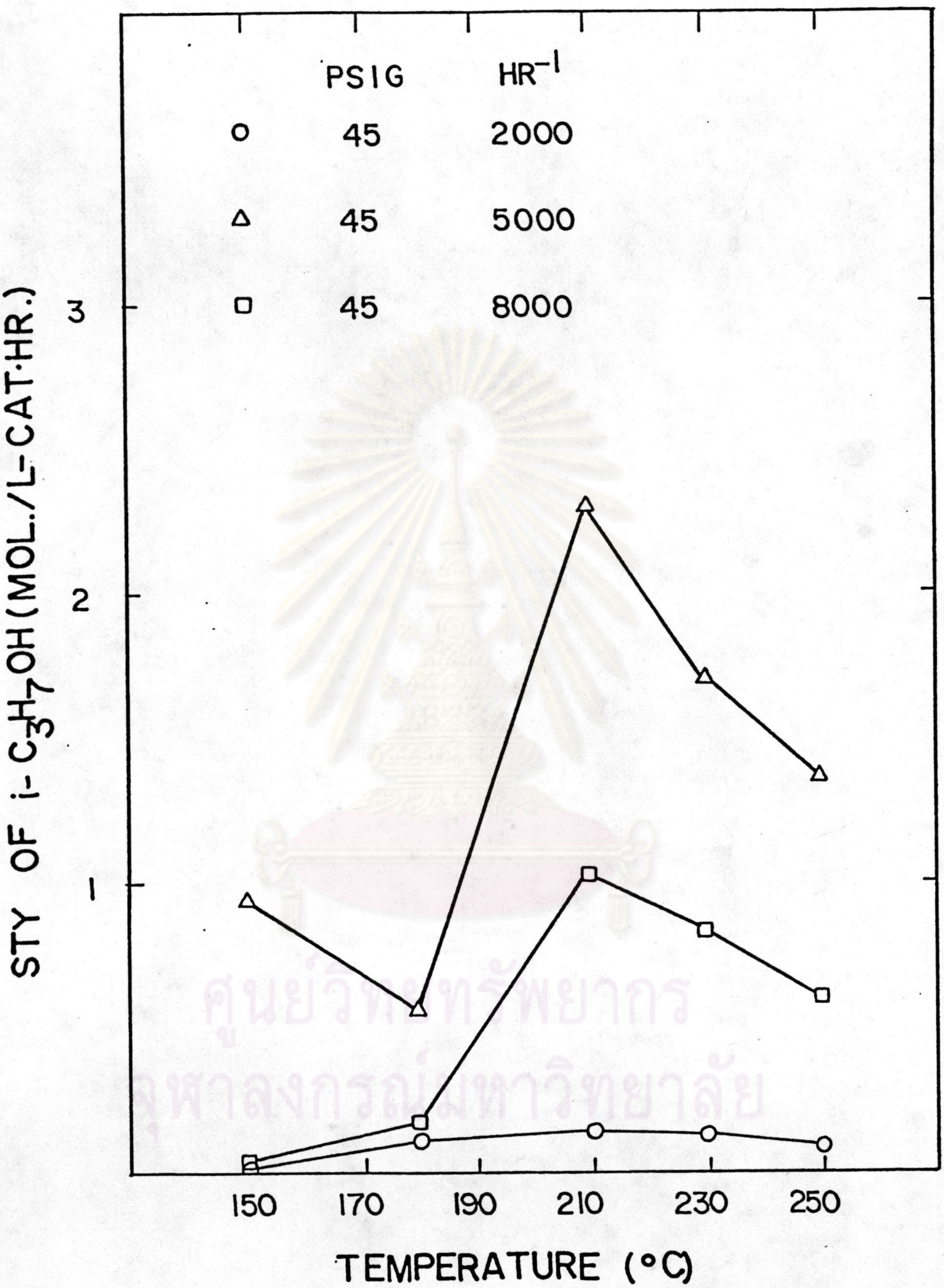

Figure 6.28 Effect of Temperature (150-250 °C) on Space Time Yield of Isopropanol (at 45 psig, 2000-8000 hr^{-1}) for Catalyst no.2

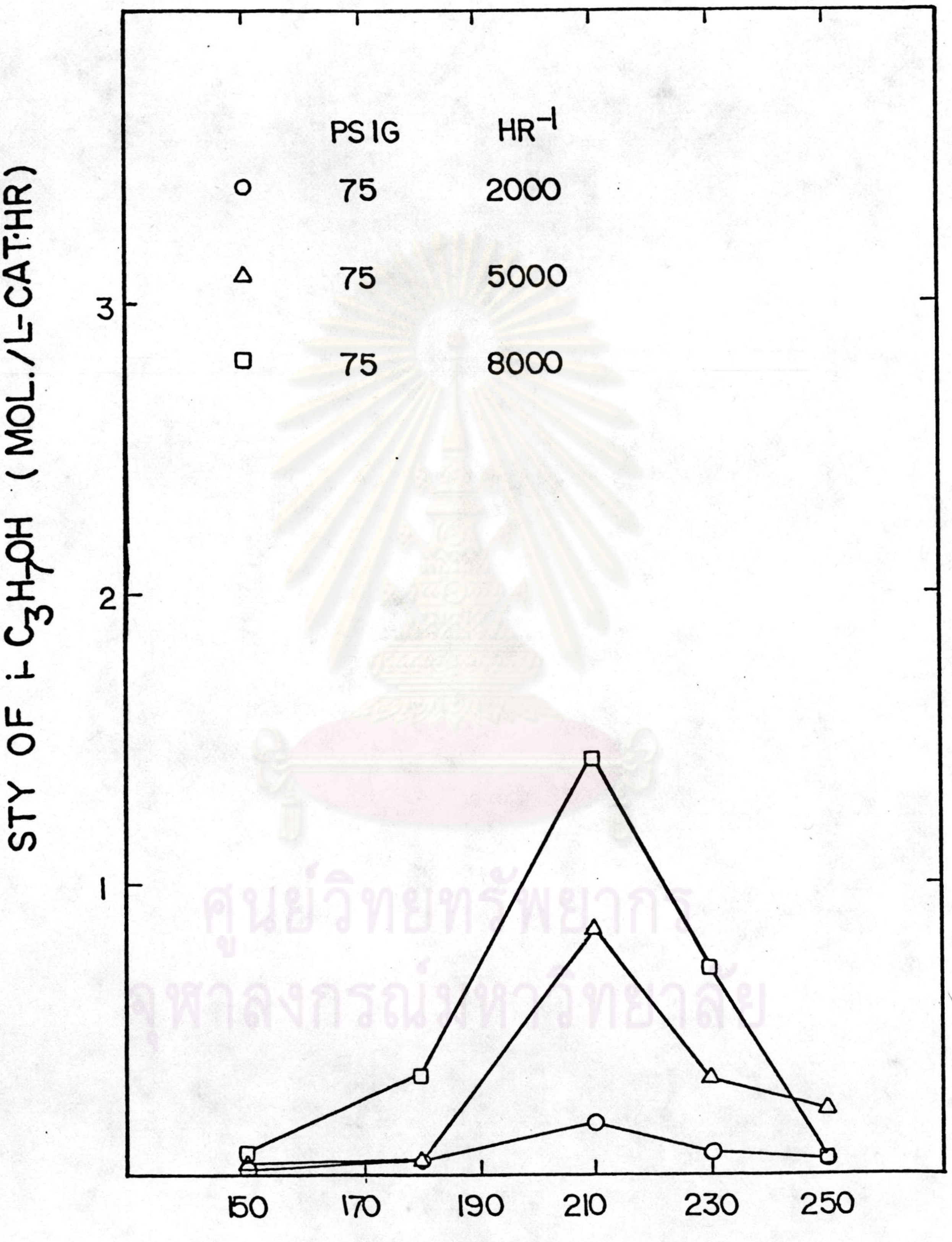

Figure 6.29 Effect of Temperature (150-250 °C) on Space Time Yield of Isopropanol (at 75 psig, 2000-8000 hr^{-1}) for Catalyst no.2

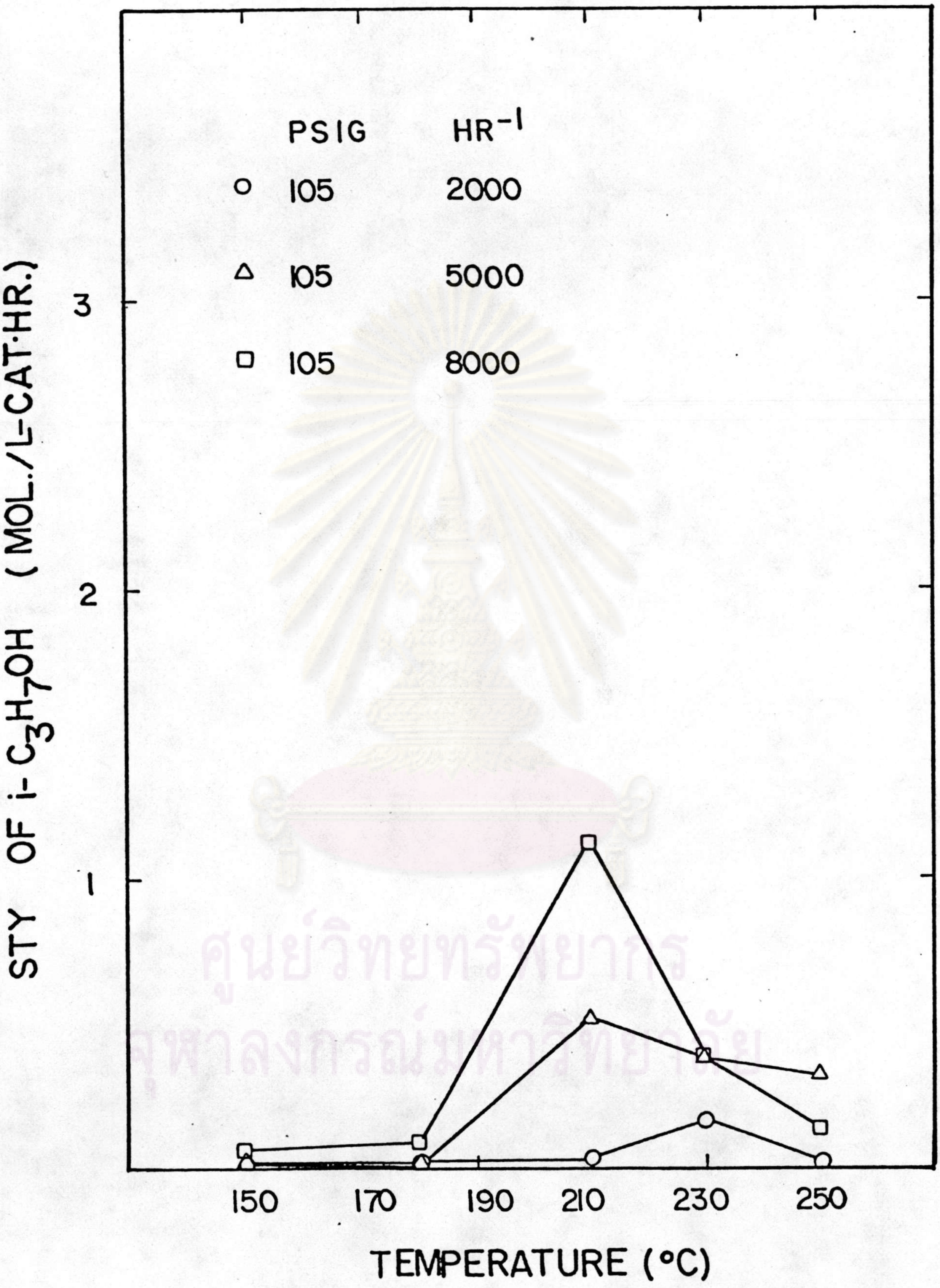

Figure 6.30 Effect of Temperature (150-250 °C) on Space Time Yield of Isopropanol (at 105 psig, 2000-8000 hr^{-1}) for Catalyst no.2

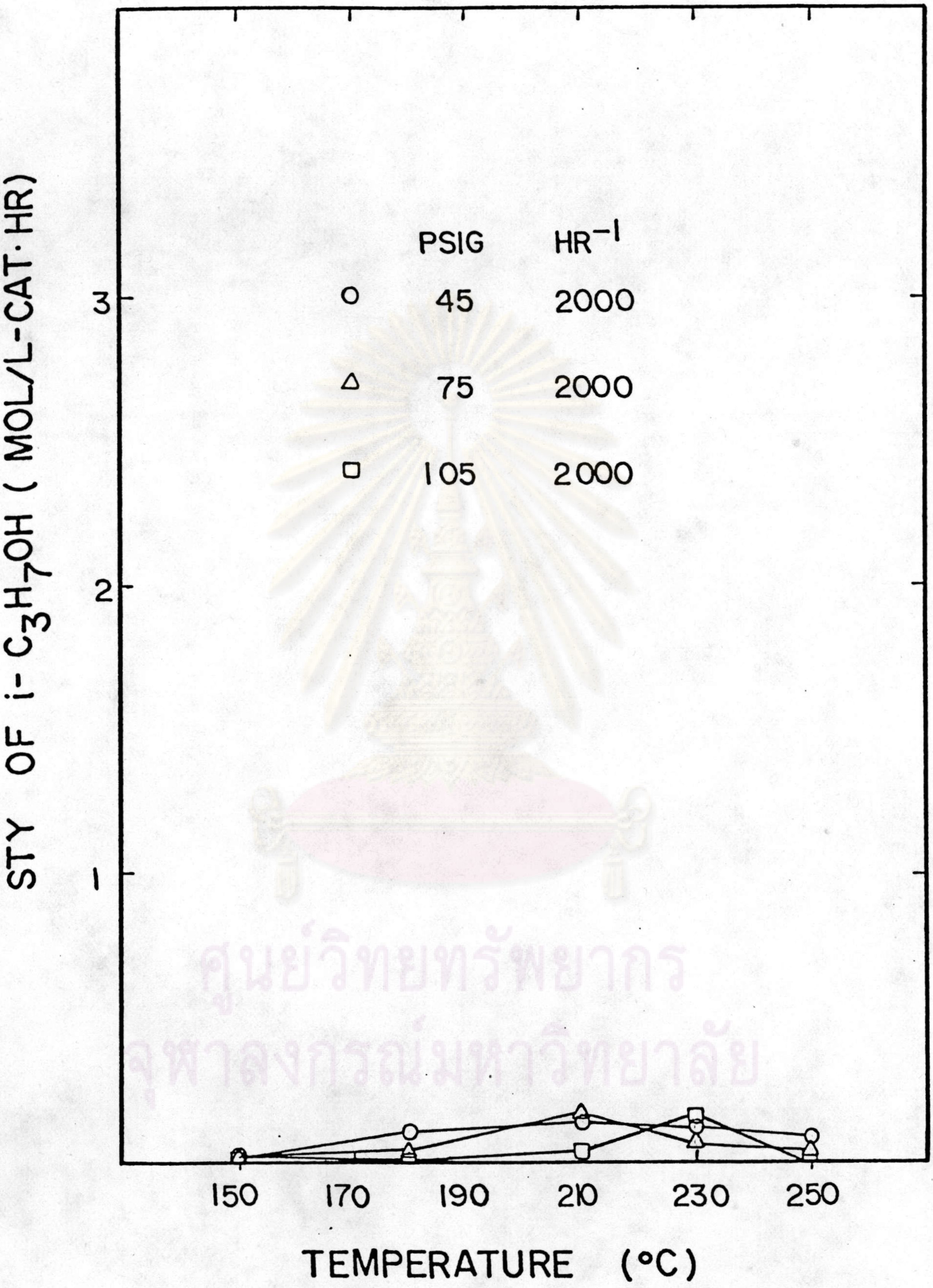

Figure 6.31 Effect of Temperature (150-250°C) on Space Time Yield of Isopropanol (at 45-105 psig, 2000-8000 hr^{-1}) for Catalyst no.2

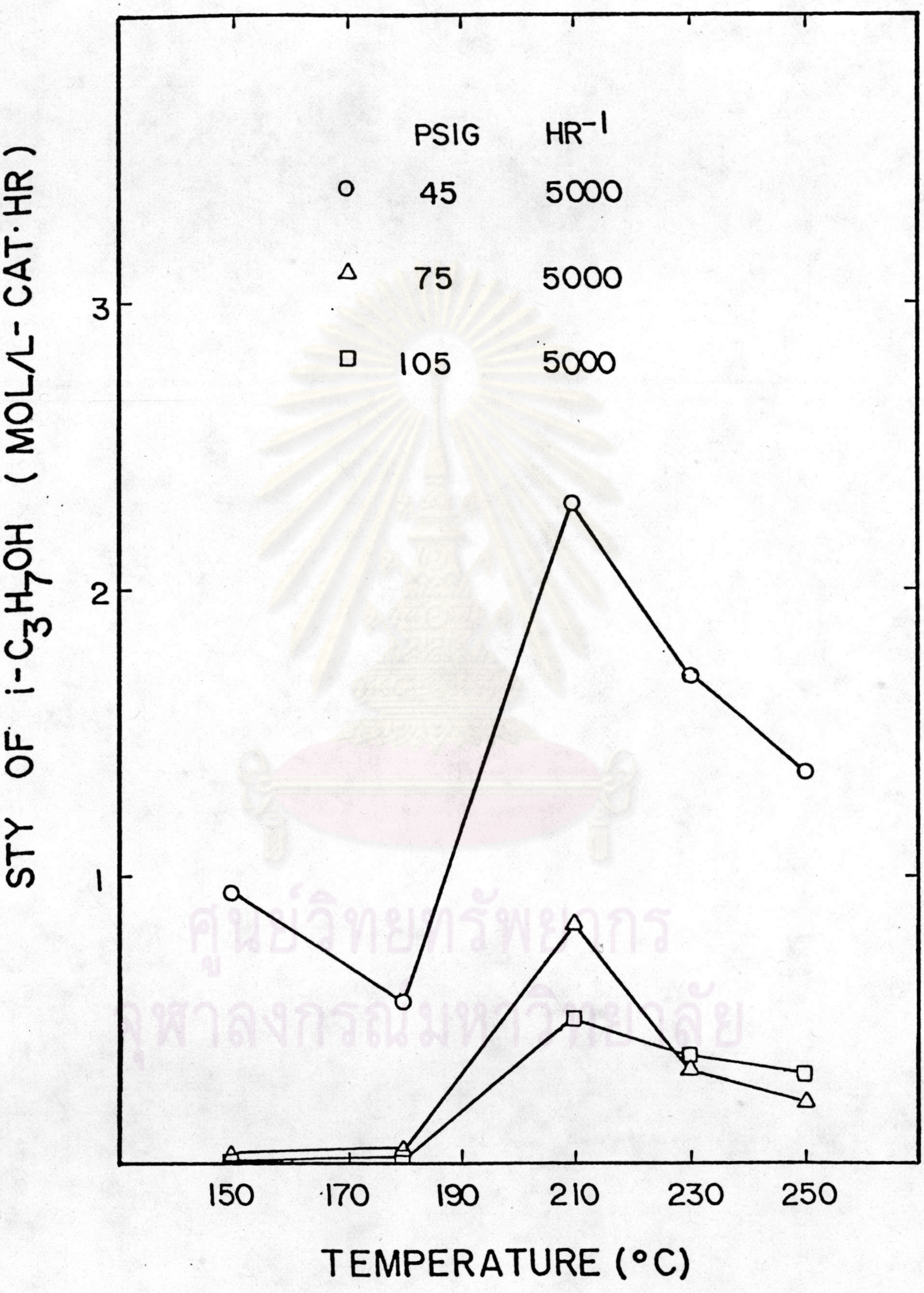

Figure 6.32 Effect of Temperature (150-250 °C) on Space Time Yield of Isopropanol (at 45-105 psig, 5000 hr^{-1}) for Catalyst no.2

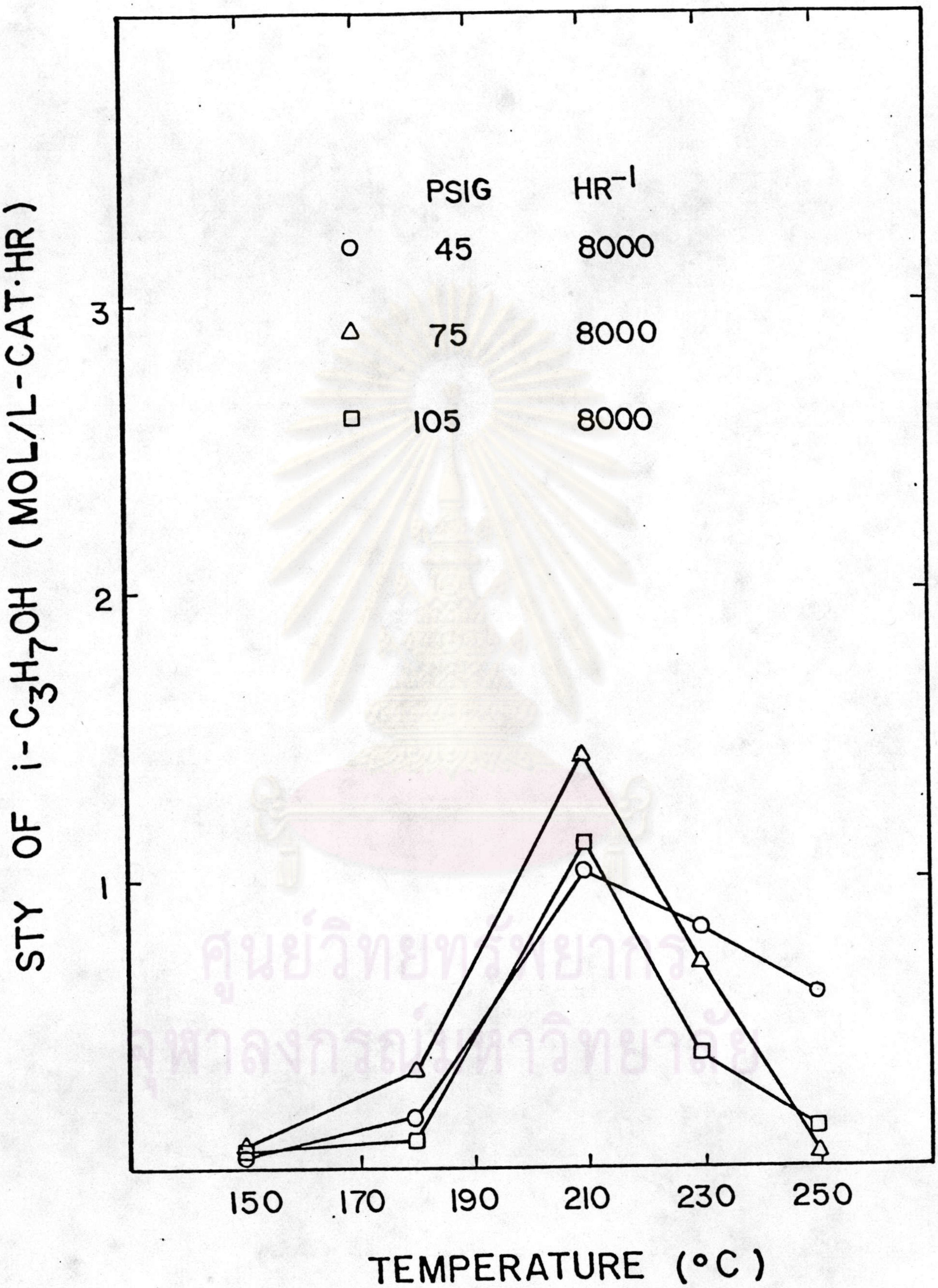

Figure 6.33 Effect of Temperature (150-250°C) on Space Time Yield of Isopropanol (at 45-105 psig, 8000 hr^{-1}) for Catalyst no.2

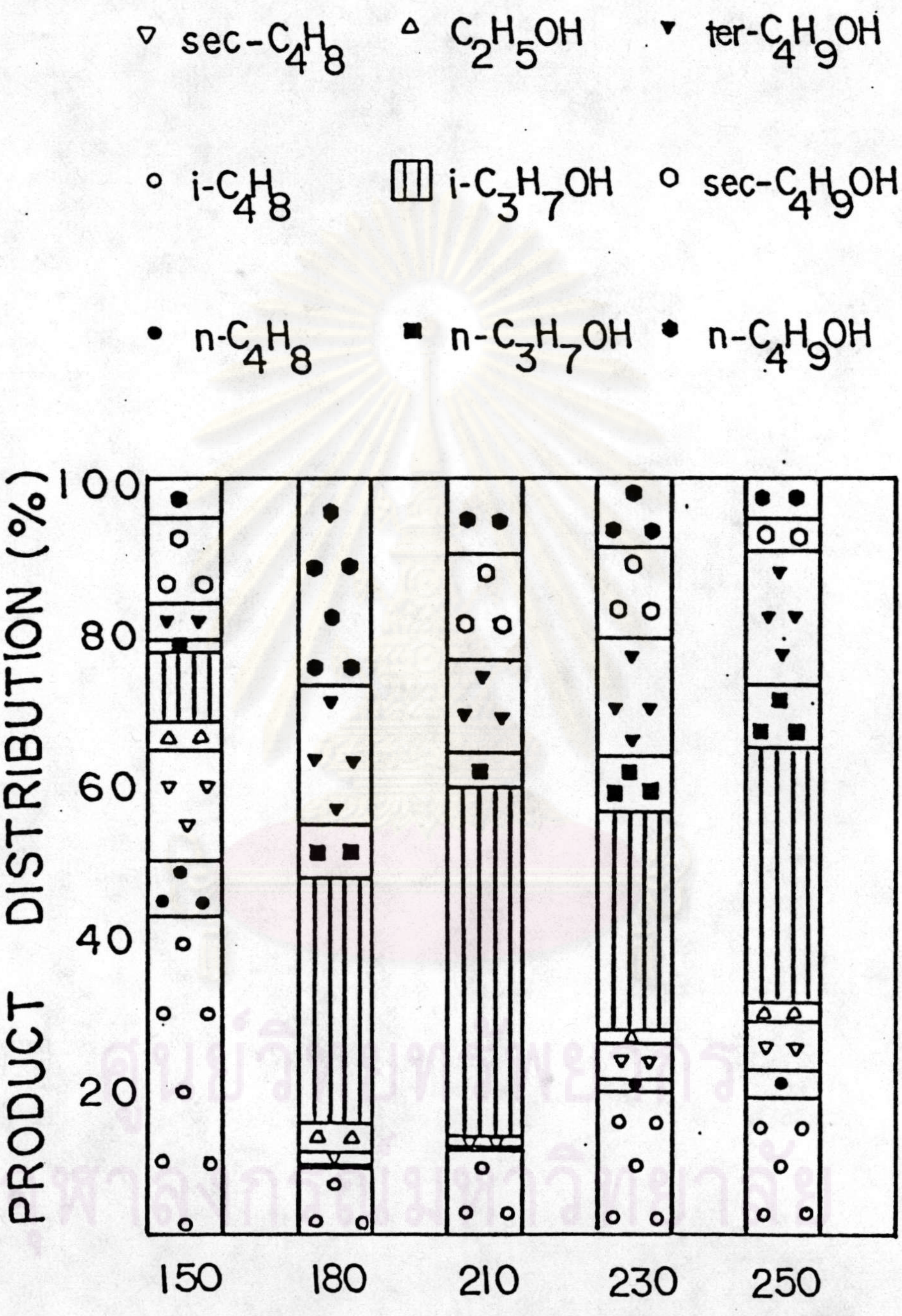

Figure 6.34 Effect of Temperature (150-250 °C) on Product Distribution (at 45 psig, 2000 hr^{-1}) for Catalyst no.2

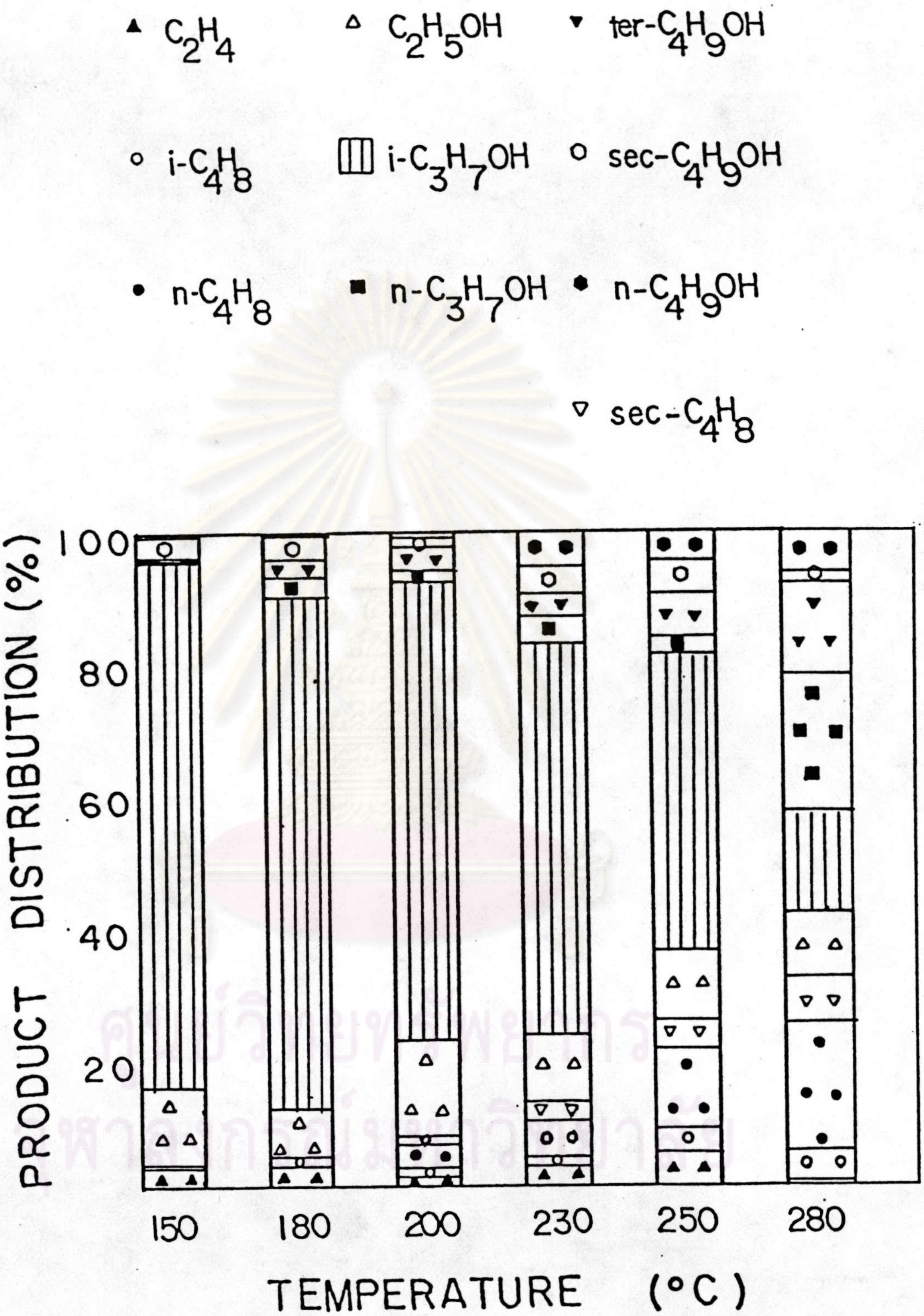

Figure 6.35 Effect of Temperature (150-250 °C) on Product Distribution (at 45 psig, 5000 hr^{-1}) for Catalyst no.2

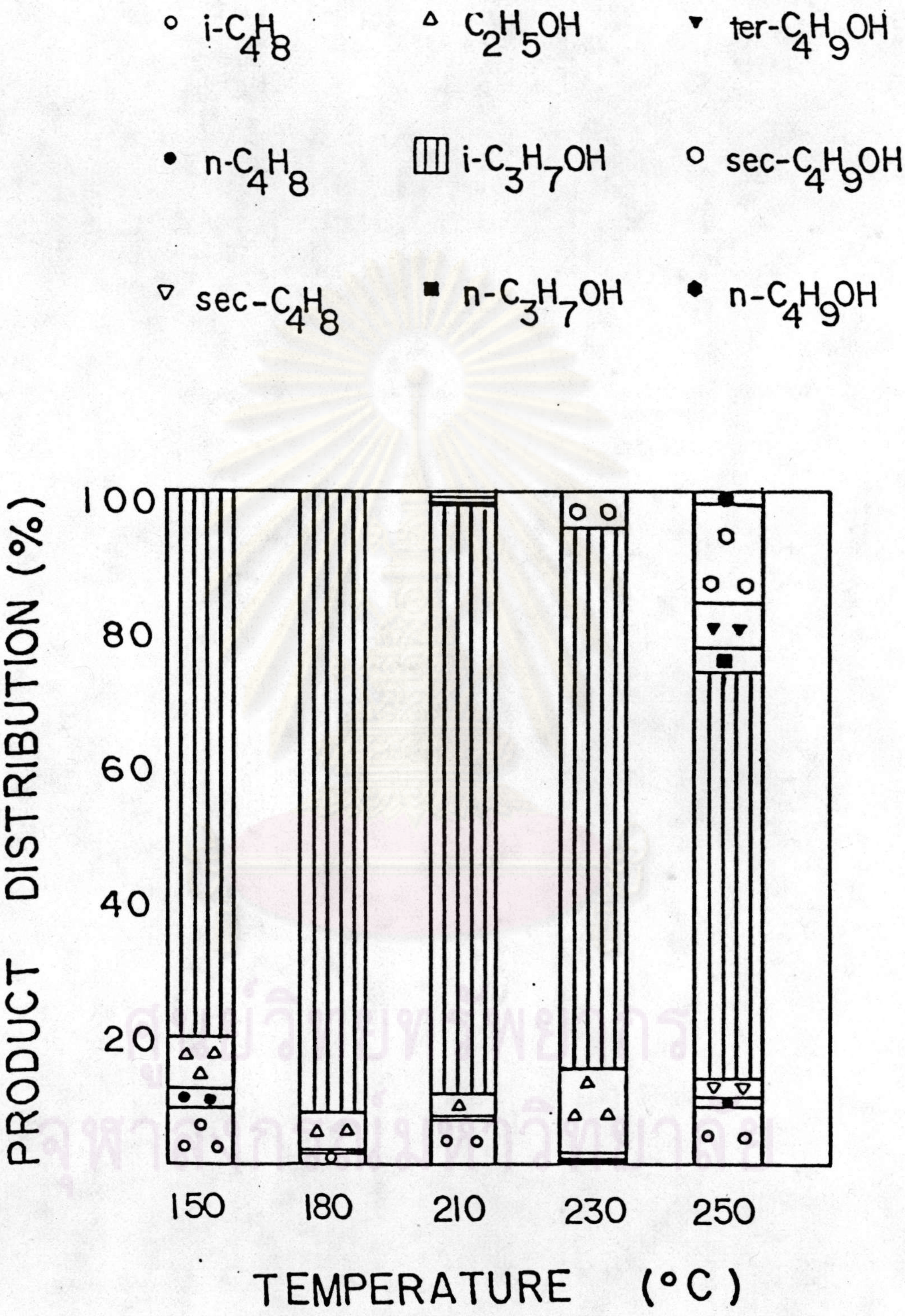

Figure 6.36 Effect of Temperature (150-250 °C) on Product Distribution (at 45 psig, 8000 hr^{-1}) for Catalyst no.2

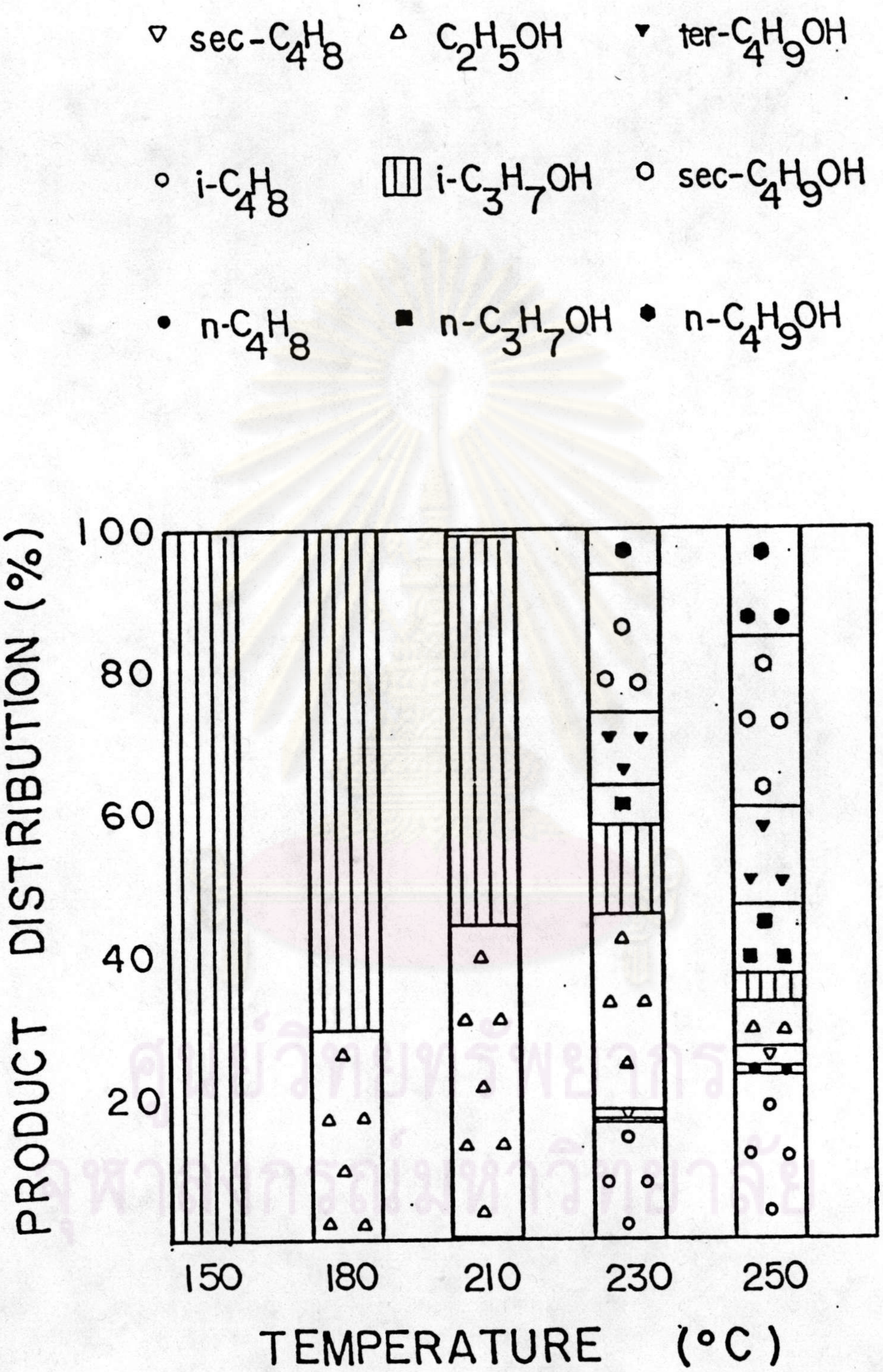

Figure 6.37 Effect of Temperature (150-250 °C) on Product Distribution (at 75 psig, 2000 hr^{-1}) for Catalyst no.2

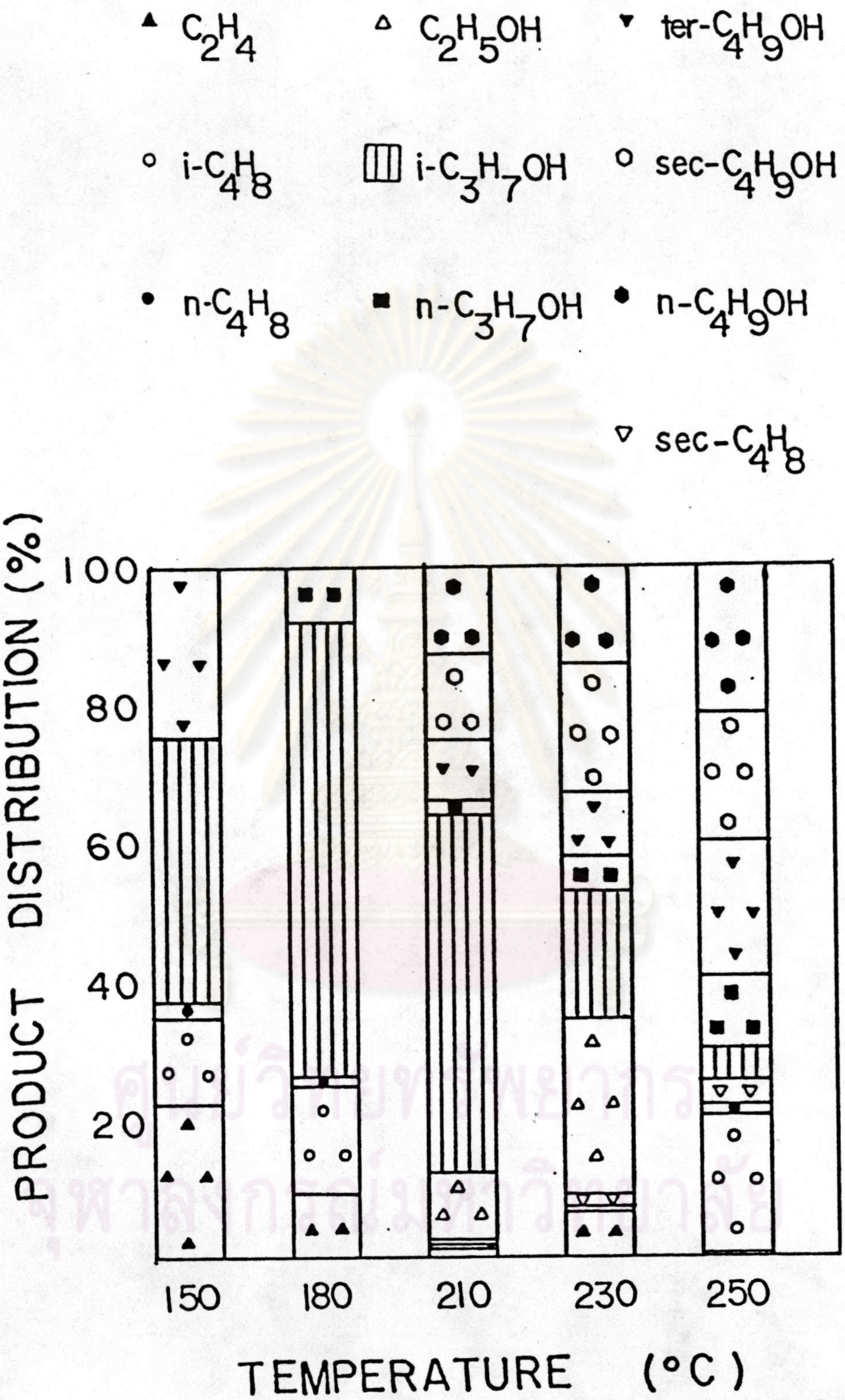

Figure 6.38 Effect of Temperature (150-250 °C) on Product Distribution (at 75 psig, 5000 hr^{-1}) for Catalyst no.2

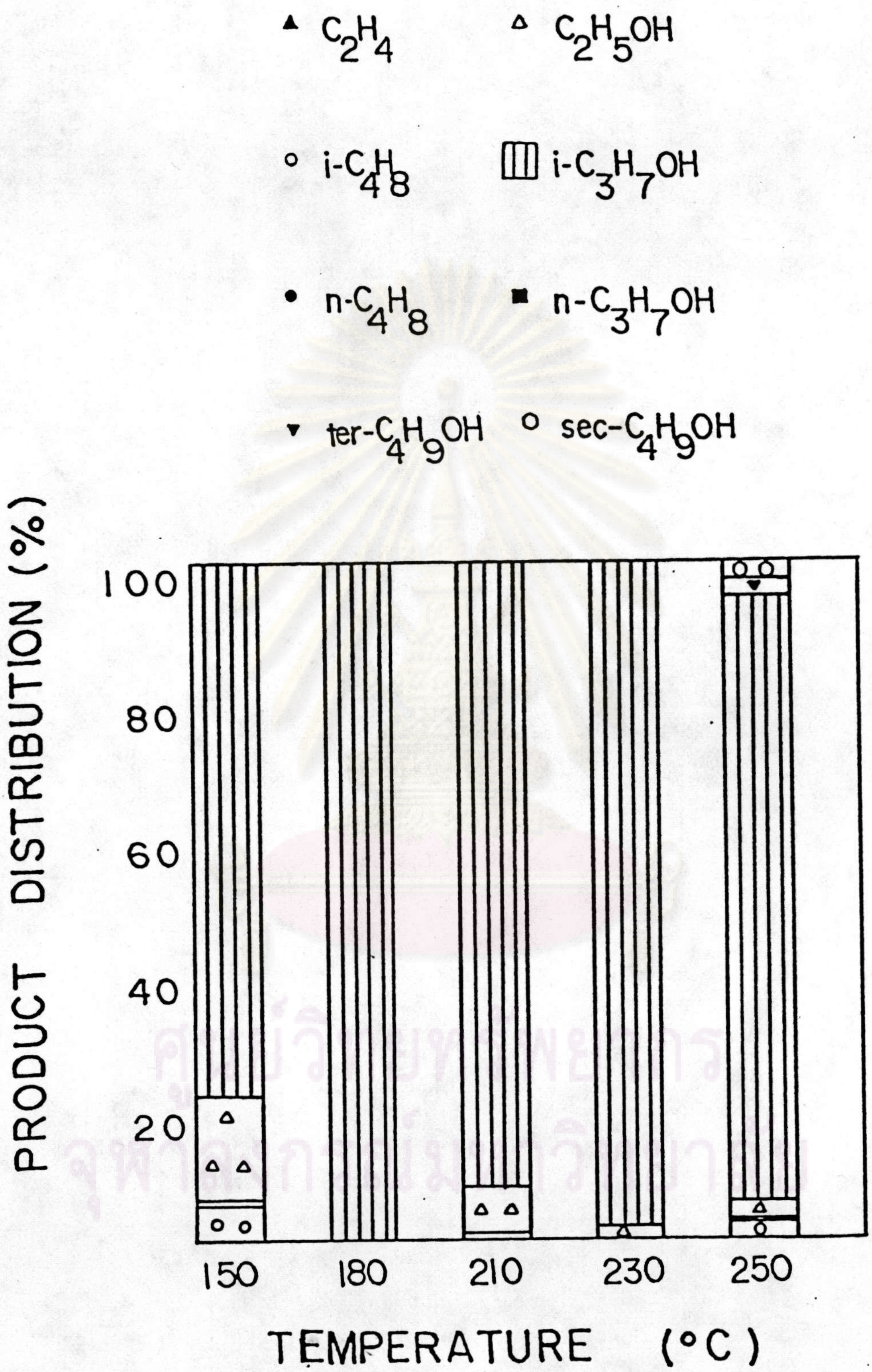

Figure 6.39 Effect of Temperature (150-250 °C) on Product Distribution (at 75 psig, 8000 hr^{-1}) for Catalyst no.2

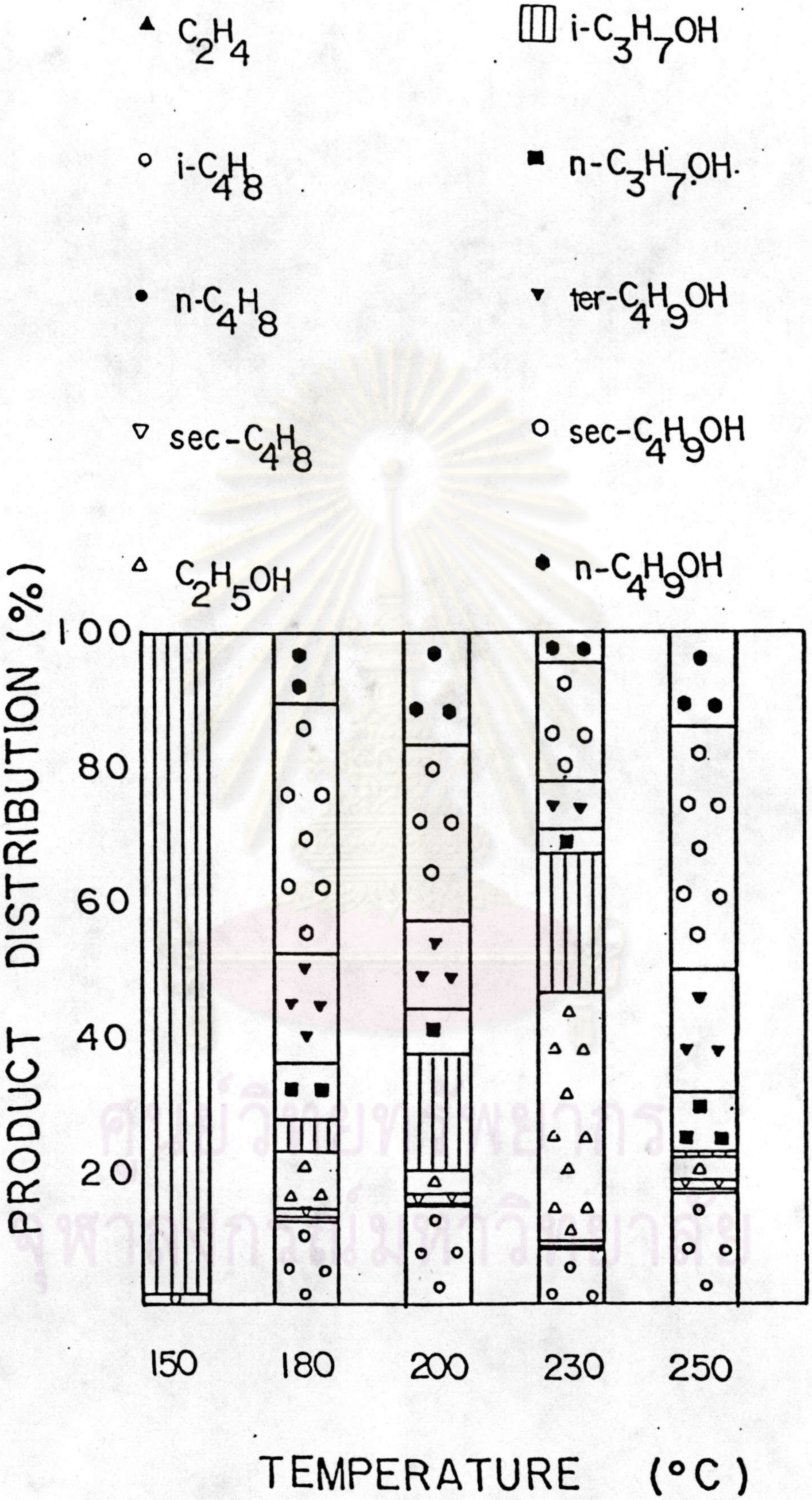

Figure 6.40 Effect of Temperature (150-250 °C) on Product Distribution (at 105 psig, 2000 hr^{-1}) for Catalyst no.2

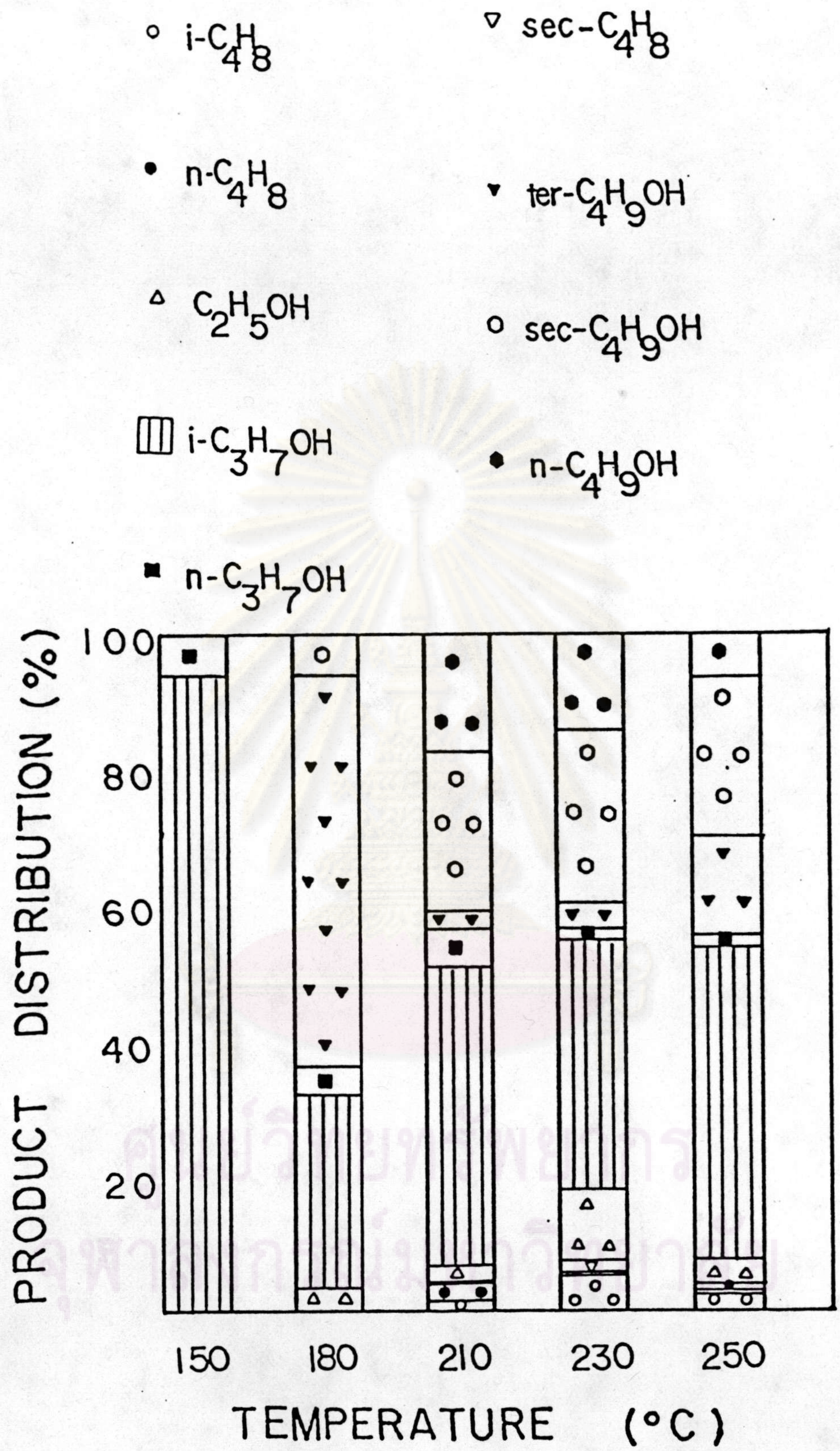

Figure 6.41 Effect of Temperature (150-250 °C) on Product Distribution (at 105 psig, 5000 hr^{-1}) for Catalyst no.2

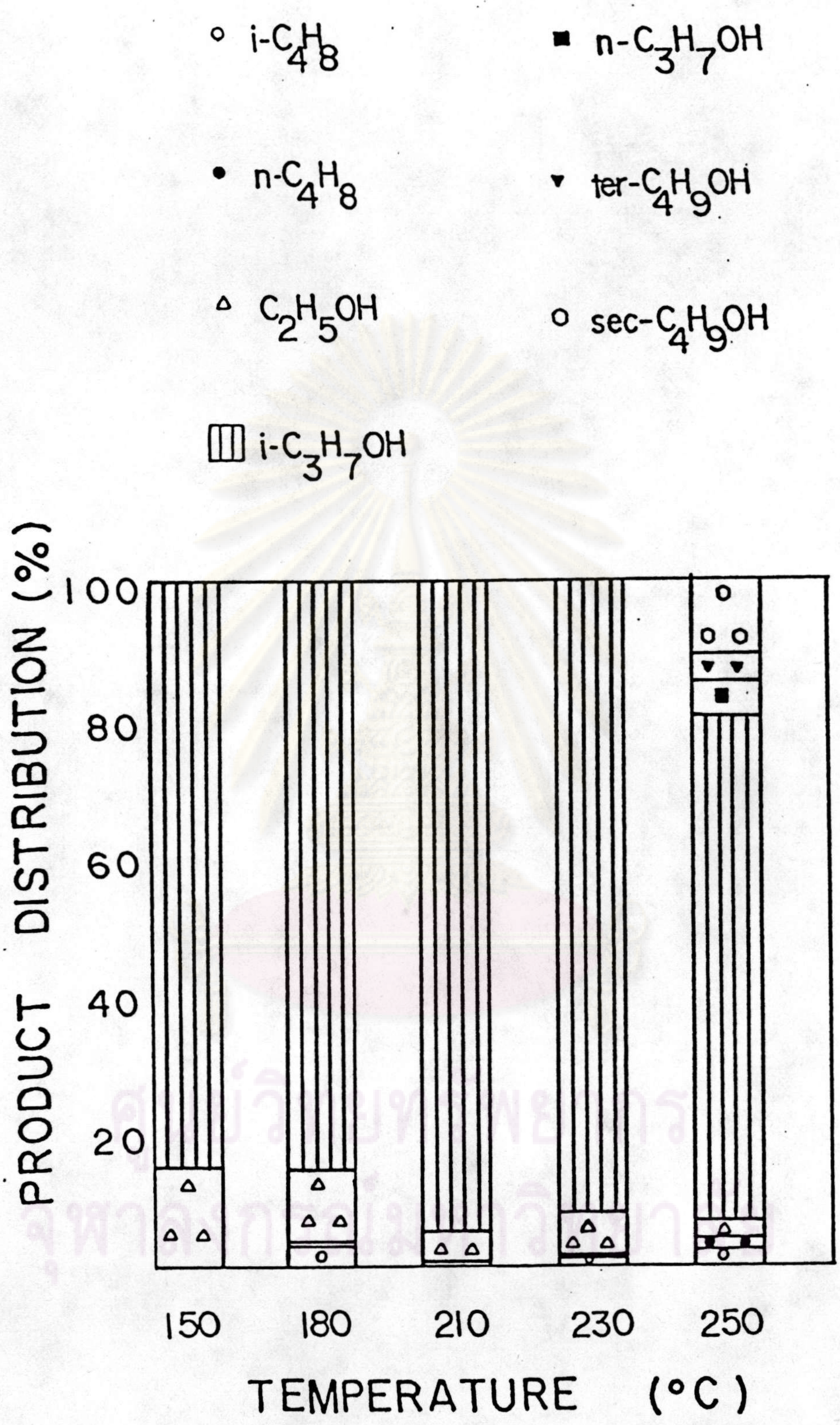

Figure 6.42 Effect of Temperature (150-250 °C) on Product Distribution (at 105 psig, 8000 hr^{-1}) for Catalyst no.2

6.3 Comparison of Experimental Results among Catalysts No.1, No.2 and No.3

Since catalysts no.1 and no.2 were the same zeolite differing only in the presence or absence of K_2O and in the mole ratio of SiO_2/Al_2O_3, they exhibited similar effects of temperature, pressure and space velocity on isopropanol synthesis. Thus it suffices to compare catalysts no.1 and no.2 and to compare either of them to catalyst no.3. The former comparison has been made previously. Here we choose to compare mainly catalysts no.2 and no.3.

Catalyst no.3 was Na-mordenite obtained from the Chemical Research Laboratory of Toyo Soda Manufacturing Co.Ltd,. It consisted of SiO_2 87.7 %, Al_2O_3 7.3 % and Na_2O 5.1 %. All synthesis experiments were carried out at medium pressures (45-105 psig). The range of space velocity was from 2000 to 8000 hr^{-1} and the temperature range was from 200 to 300 °C.

6.3.1 Comparison of Total C_3H_6 Conversion between Catalysts No.2 and No.3

The total C_3H_6 conversion for catalyst no.2 generally increased with temperature but decreased as pressure or space velocity increased (see Figs.6.22-6.24) Catalyst no.3 exhibited the similar trend as catalyst no.2 (see Figs. 6.43-6.45).

With respect to space velocity, the total C_3H_6 conversion for both catalysts tended to decrease as space velocity increased. The effect of space velocity for catalyst no.3 was less than that for catalyst no.2 when the temperature was low (200-250 °C). On the other hand, at a higher temperature (280-300 °C) the total conversion of C_3H_6 for catalyst no.3 was higher.

In general catalyst no.3 was found to give a lower total C_3H_6 conversion than catalyst no.1 and no.2. In terms of STY of isopropanol, the order of ranking was : catalyst no.2 > no.1 > no.3.

6.3.2 Comparison of Isopropanol Selectivity and STY of Isopropanol between Catalysts No.2 and No.3

Isopropanol selectivity for catalyst no.2 generally increased as space velocity increased, but decreased when temperature increased (see Figs. 6.25-6.27) The effect of pressure however was not significant. For catalyst no.3 isopropanol selectivity was high at 230-280 °C but it was hard to discern the effect of temperature. The results of both catalysts indicated that as space velocity increased or as temperature decreased, isopropanol selectivity generally increased. The optimum temperature for isopropanol selectivity was 180-230 °C for catalyst no.2 and 230-280 °C for catalyst no.3. In any case, we may conclude that the effects of pressure, temperature and space velocity on isopropanol selectivity were qualitatively similar for the two catalysts. When the observed maximum values of isopropanol selectivity were compared among catalyst no.1, no.2 and no.3, it was found that catalyst no.3 usually performed the worst (73.43 % compared to 80.24 % and 93.59 % for catalysts no.2 and no.1, respectively)

The effect of pressure on STY of isopropanol was the same for all three catalysts. It was hard to compare because they were not significant (see Figs. 6.7-6.12, 6.28-6.33 and 6.49-6.54). With respect to space velocity, both catalysts no.2 and no.3 exhibited a positive effect on the STY of isopropanol. Except at 45 psig, the maximum STY was observed at 5000 hr^{-1} and 180-230 °C for catalyst no.2 and at 2000 hr^{-1} and 260-280 °C for catalyst no.3.

Comparison of the observed maximum values of STY of isopropanol revealed that catalyst no.2 had a much higher STY than catalyst no.3 (3.42 mol/l-cat.hr compared to 0.65 mol/l-cat.hr at the same pressure 45 psig and space velocity 5000 hr^{-1}. Note that the applicable temperature ranges were different (230 °C for no.2 and 280 °C for no.3).

6.3.3 Comparison of Product Distribution among Catalysts No.1, No.2 and No.3

For all the three catalysts, when temperature increased or space velocity decreased, olefinic products would increase. The effect of space velocity on olefinic products was more significant than that of temperature because a low space velocity allowed enough time to produce olefins and to decompose isopropanol. At a temperature lower than 180 °C, isopropanol could hardly be detected. The suitable temperature range was 230-250 °C for catalyst no.1, 210-230 °C for no.2 and 260-280 °C for no.3. Below the suitable temperatures, little olefins or isopropanol were observed. Above the suitable temperature ranges such by-product as higher olefins and higher alcohols were observed.

In summary, we might conclude that in terms of isopropanol STY and selectivity, the order of ranking was : catalyst no.2 > no.1 > no.3.

It should be noted that only catalyst no.2 had K_2O as a compositon, which was not present in catalysts no.1 and no.3. The experimental results seemed to indicate that having K_2O as composition and smaller pore size were best for isopropanol synthesis.

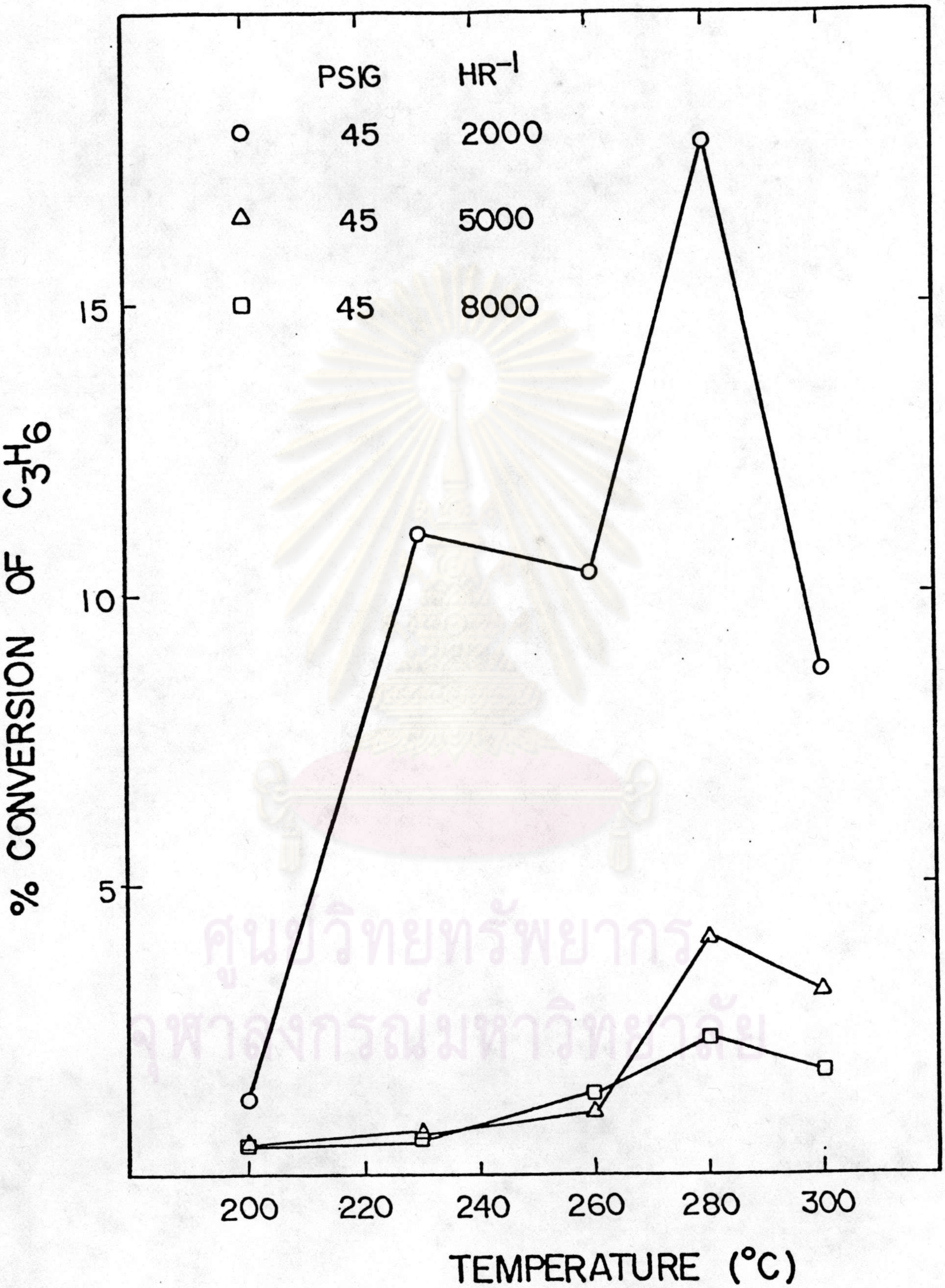

Figure 6.43 Effect of Temperature (200-300 °C) on Total Conversion of Propylene (at 45 psig, 2000-8000 hr^{-1}) for Catalyst no.3

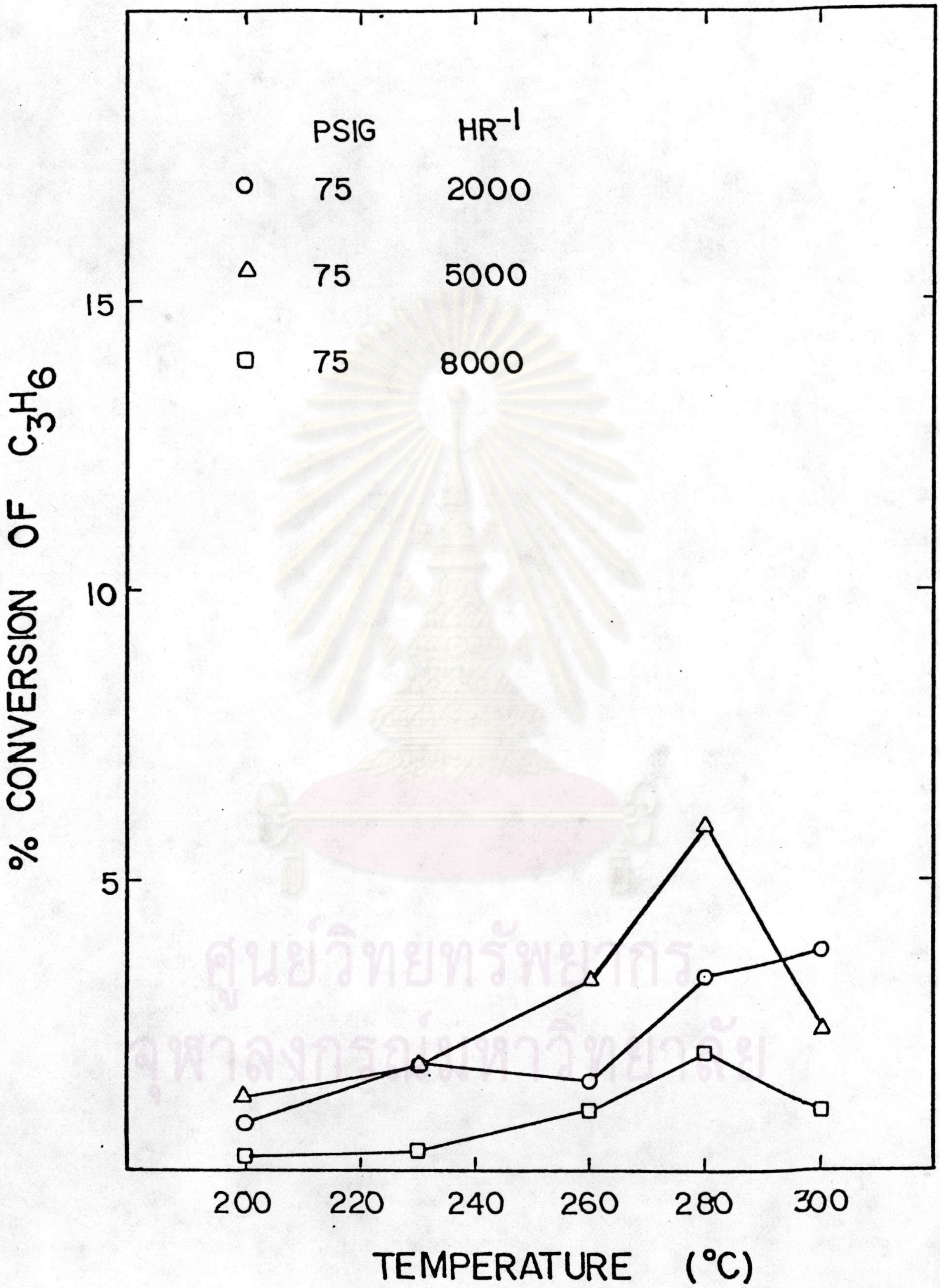

Figure 6.44 Effect of Temperature (200-300 °C) on Total Conversion of Propylene (at 75 psig, 2000-8000 hr^{-1}) for Catalyst no.3

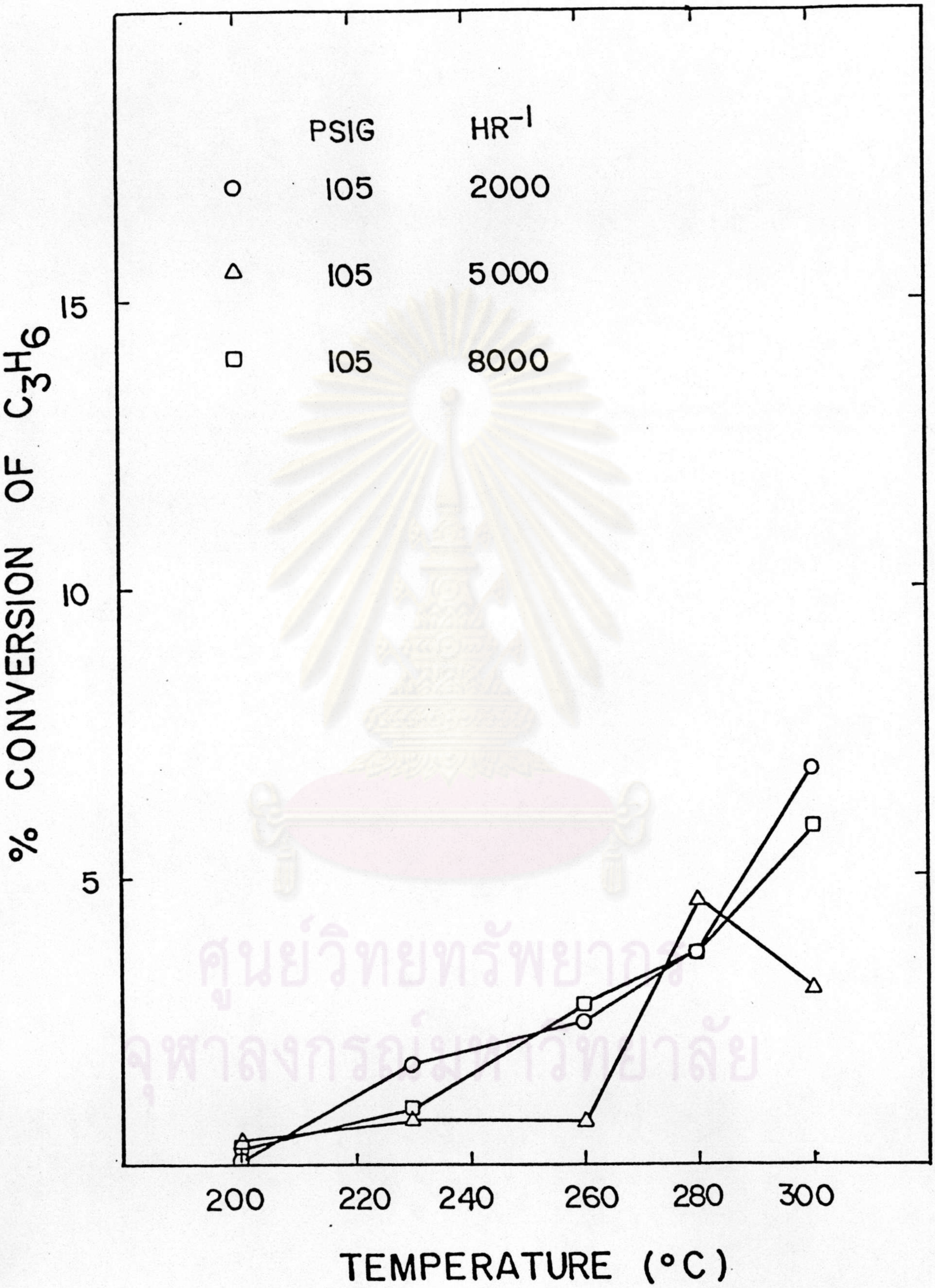

Figure 6.45 Effect of Temperature (200-300 °C) on Total Conversion of Propylene (at 105 psig, 2000 -8000 hr^{-1}) for Catalyst no.3

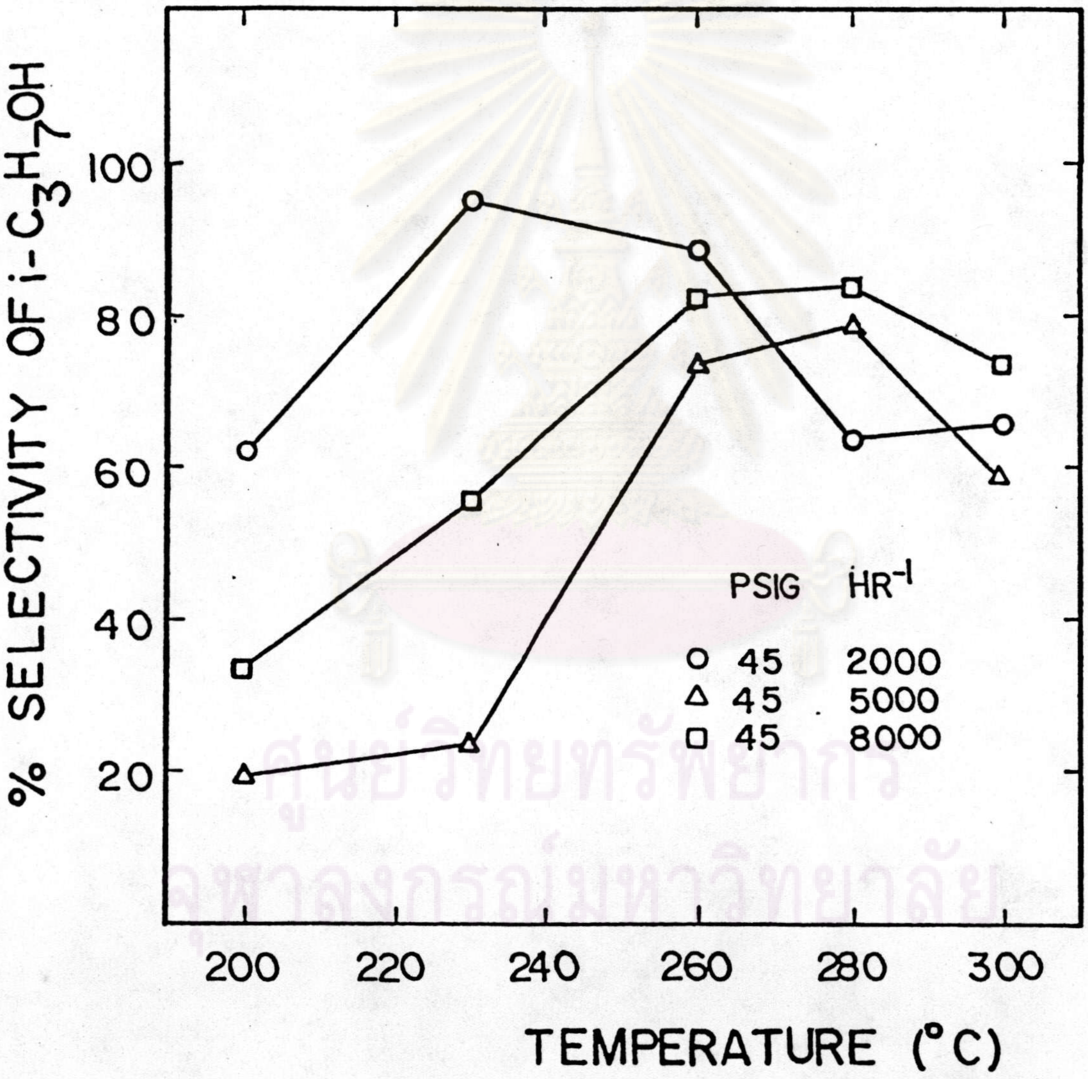

Figure 6.46 Effect of Temperature (200-300 °C) on Selectivity of Isopropanol (at 45 psig, 2000-8000 hr^{-1}) for Catalyst no.3

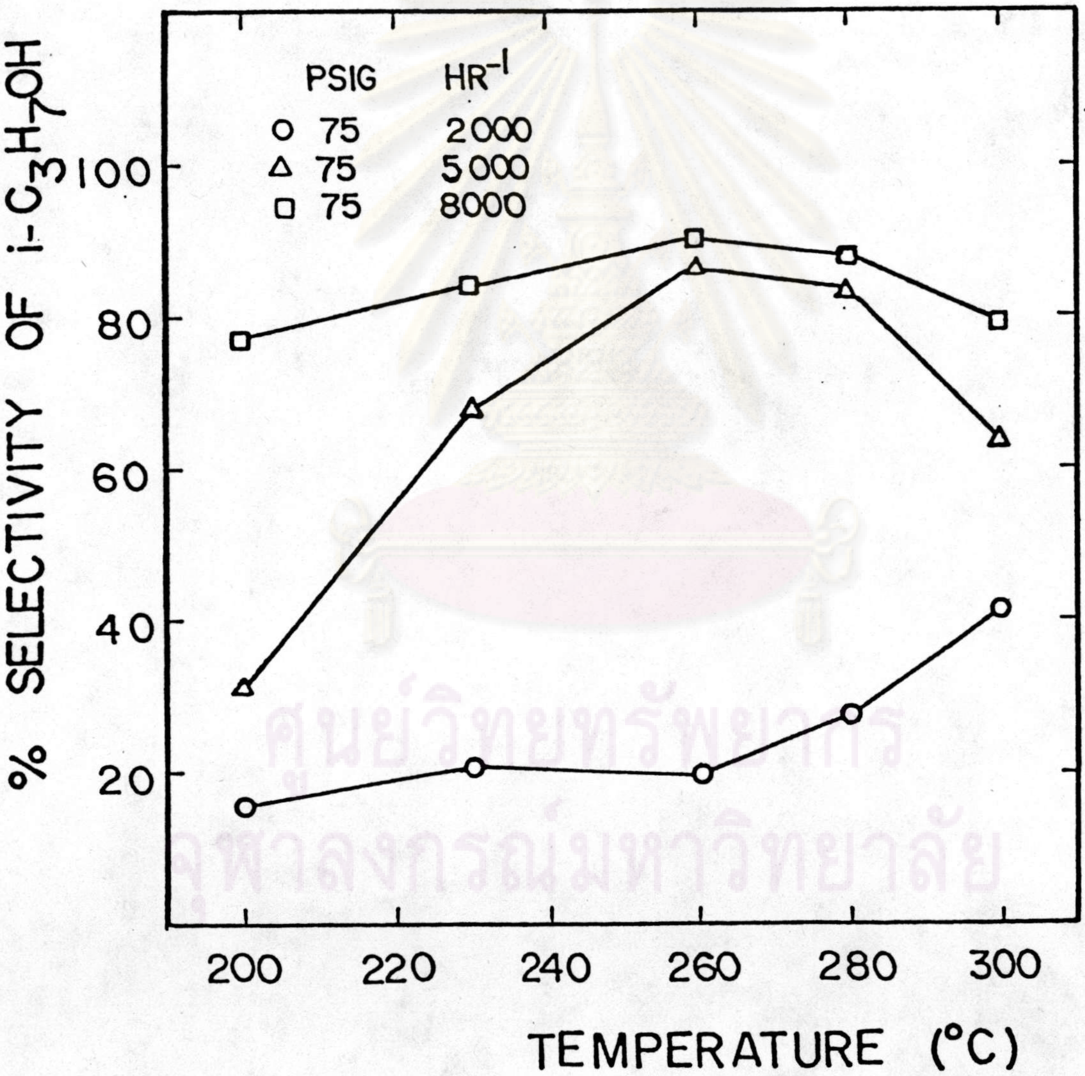

Figure 6.47 Effect of Temperature (200-300°C) on Selectivity of Isopropanol (at 75 psig, 2000-8000 hr^{-1}) for Catalyst no.3

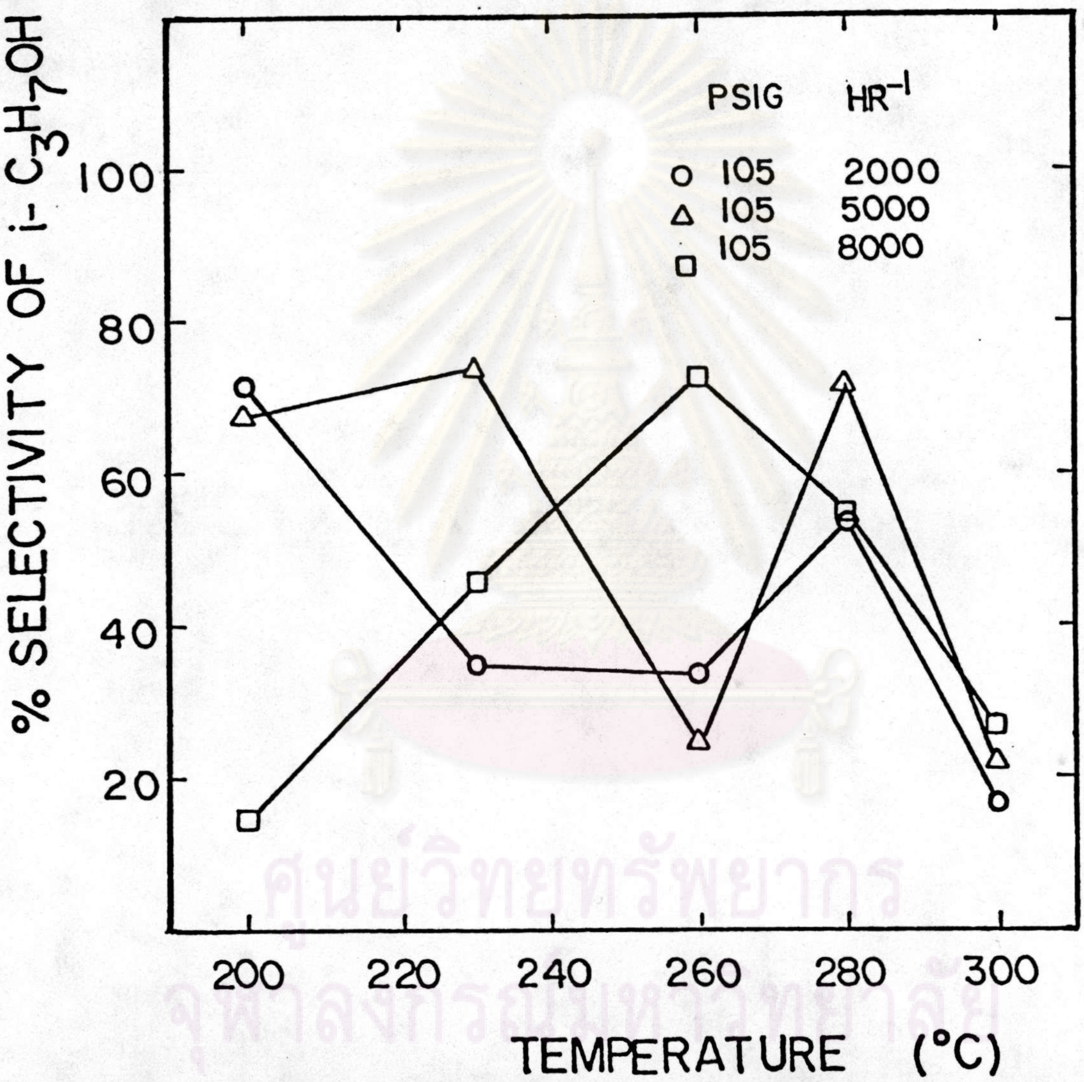

Figure 6.48 Effect of Temperature (200-300 °C) on Selectivity of Isopropanol (at 105 psig, 2000-8000 hr^{-1}) for Catalyst no.3

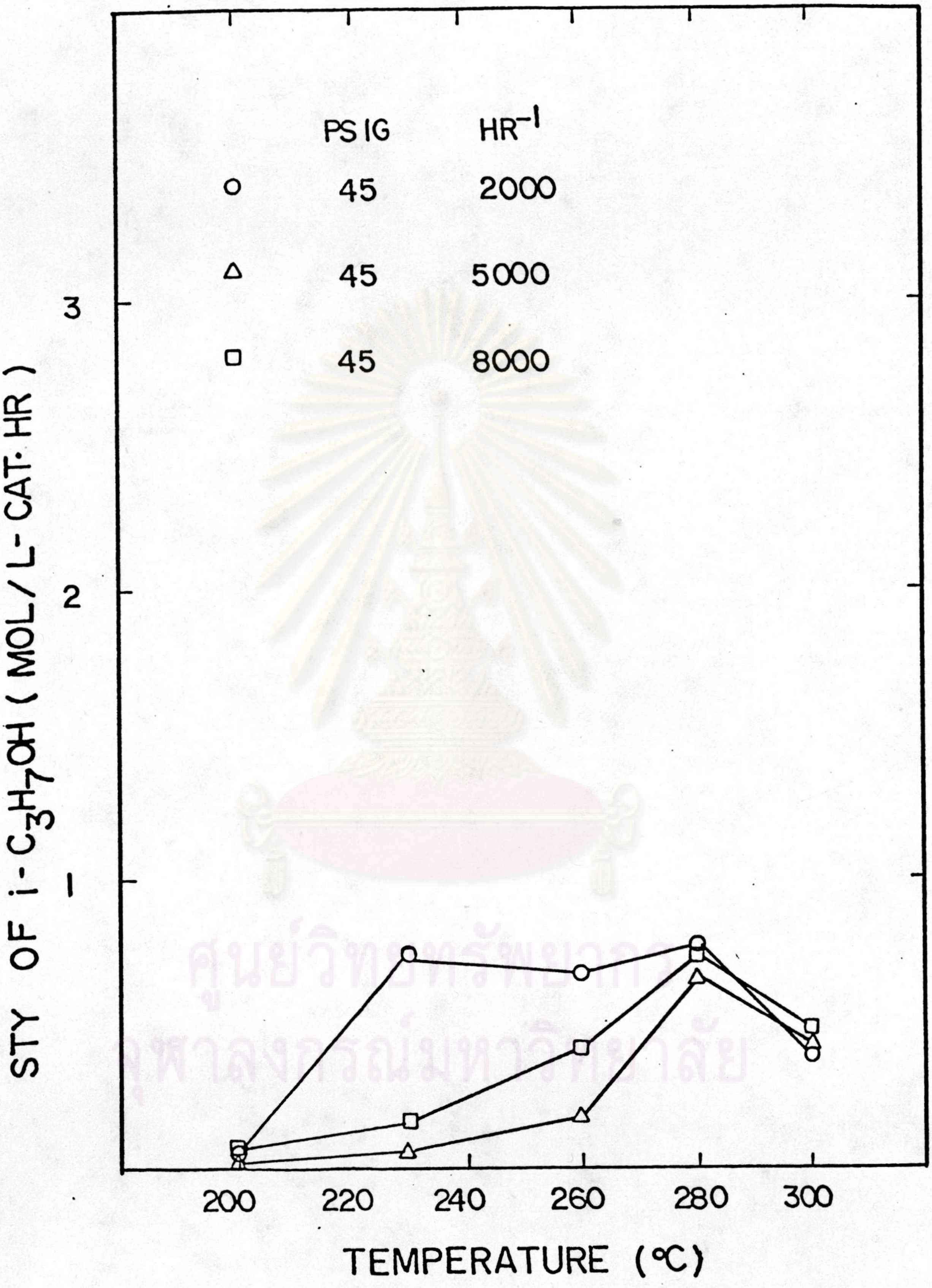

Figure 6.49 Effect of Temperature (200-300°C) on Space Time Yield of Isopropanol (at 45 psig, 2000-8000 hr^{-1}) for Catalyst no.3

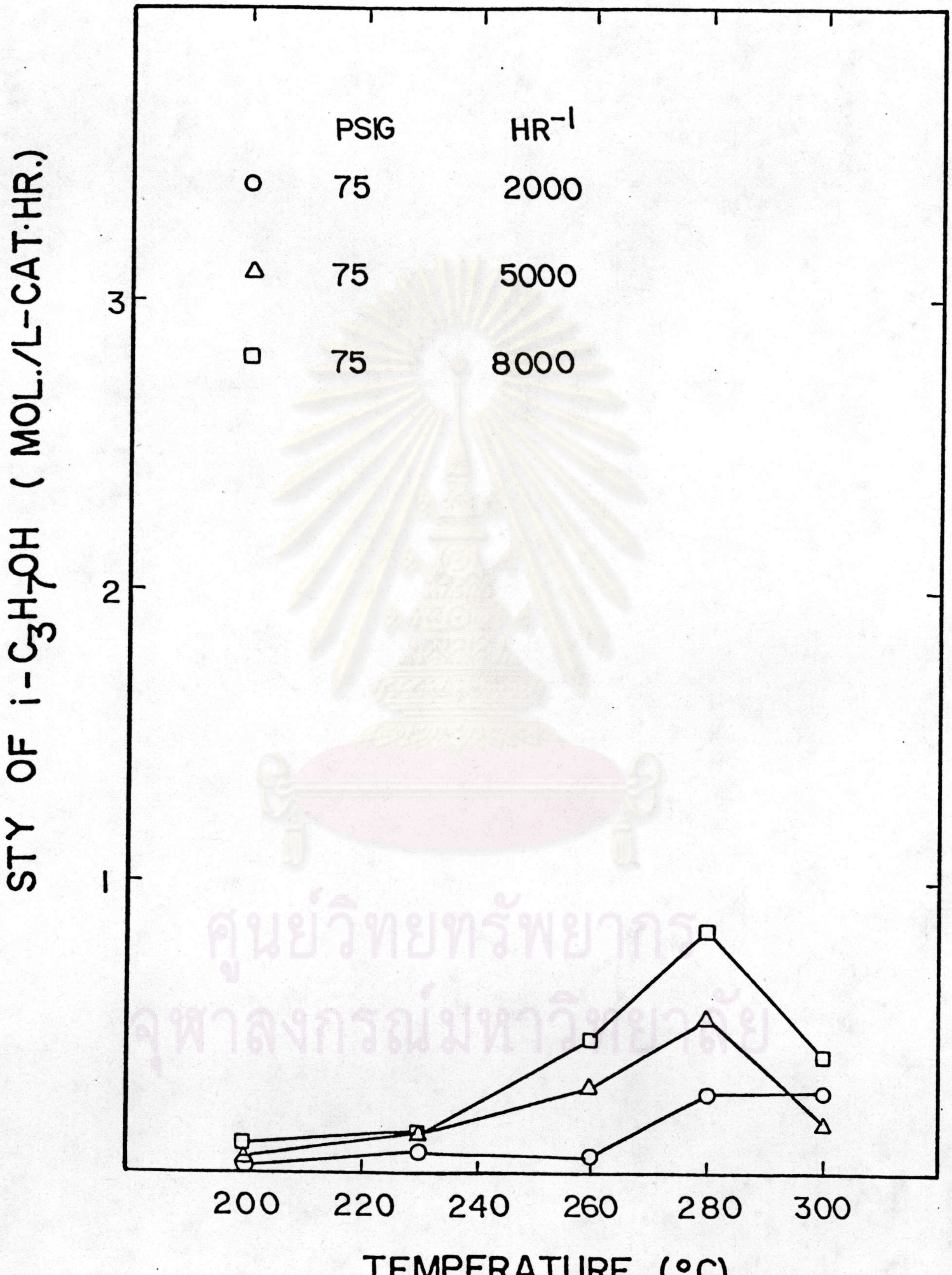

Figure 6.50 Effect of Temperature (200-300°C) on Space Time Yield of Isopropanol (at 75 psig, 2000-8000 hr^{-1}) for Catalyst no.3

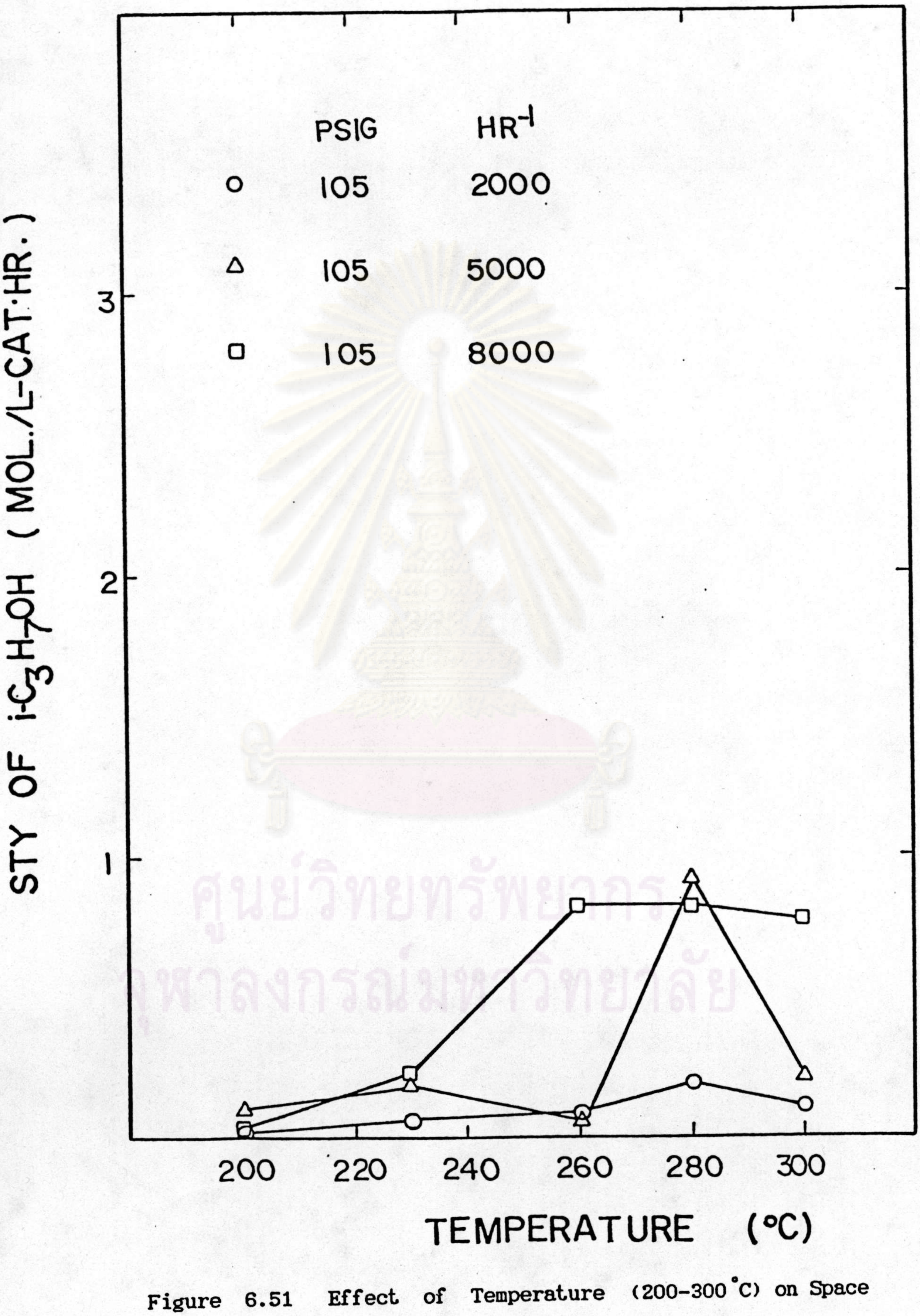

Figure 6.51 Effect of Temperature (200-300 °C) on Space Time Yield of Isopropanol (at 105 psig, 2000-8000 hr^{-1}) for Catalyst no.3

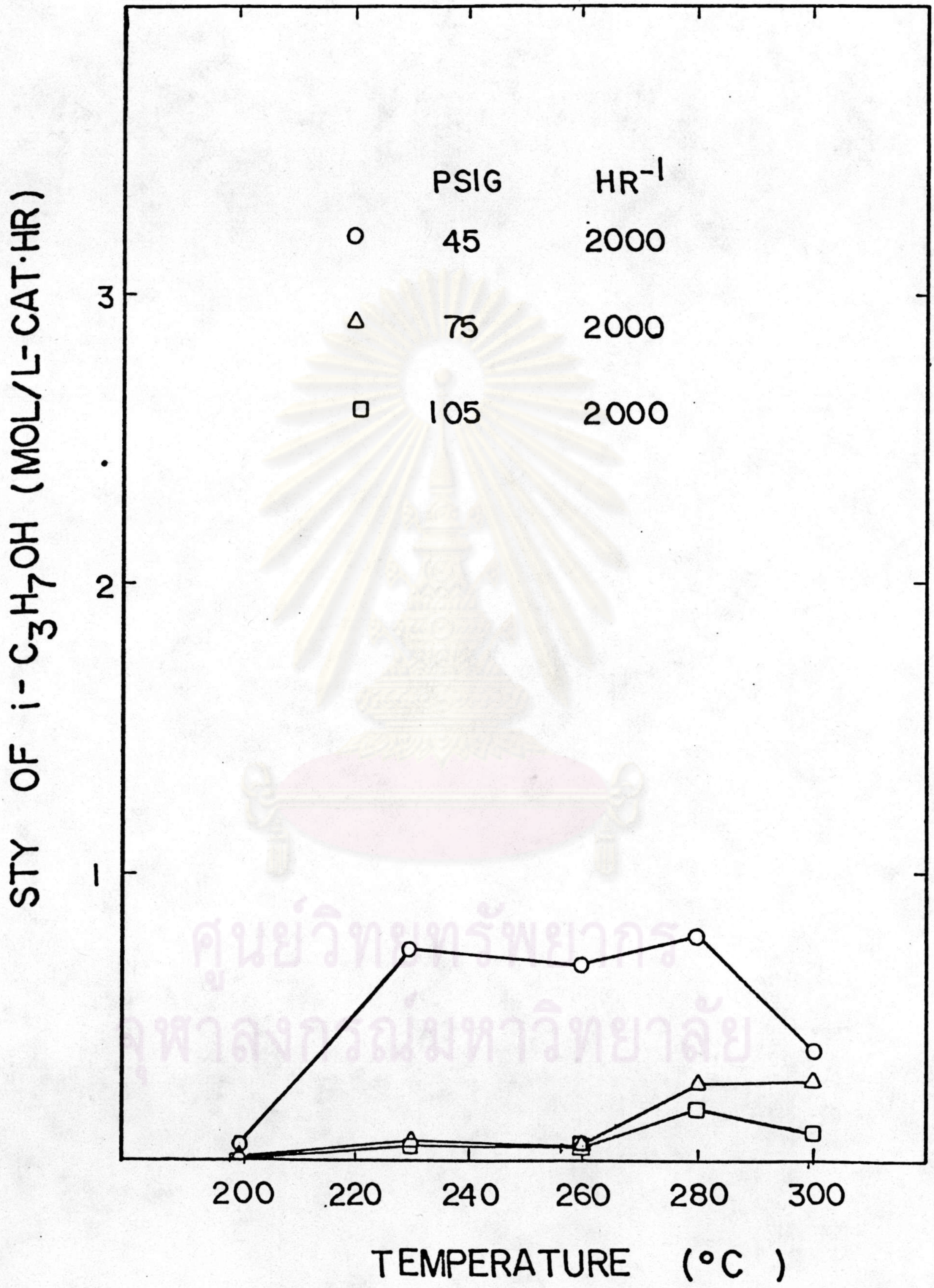

Figure 6.52 Effect of Temperature (200-300 °C) on Space Time Yield of Isopropanol (at 45-105 psig, 2000 hr^{-1}) for Catalyst no.3

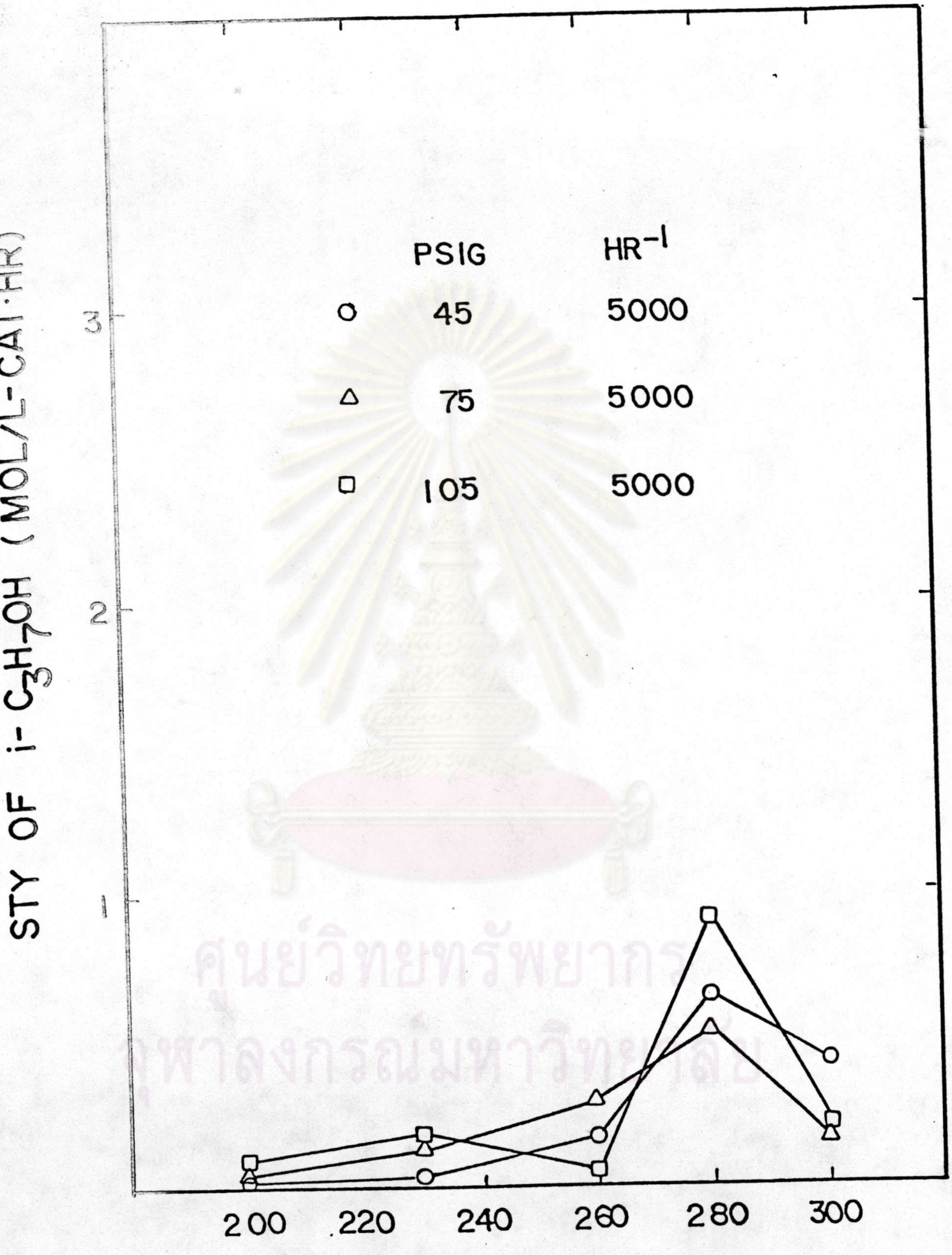

Figure 6.53 Effect of Temperature (200-300 °C) on Space Time Yield of Isopropanol (at 45-105 psig, 5000 hr^{-1}) for Catalyst no.3

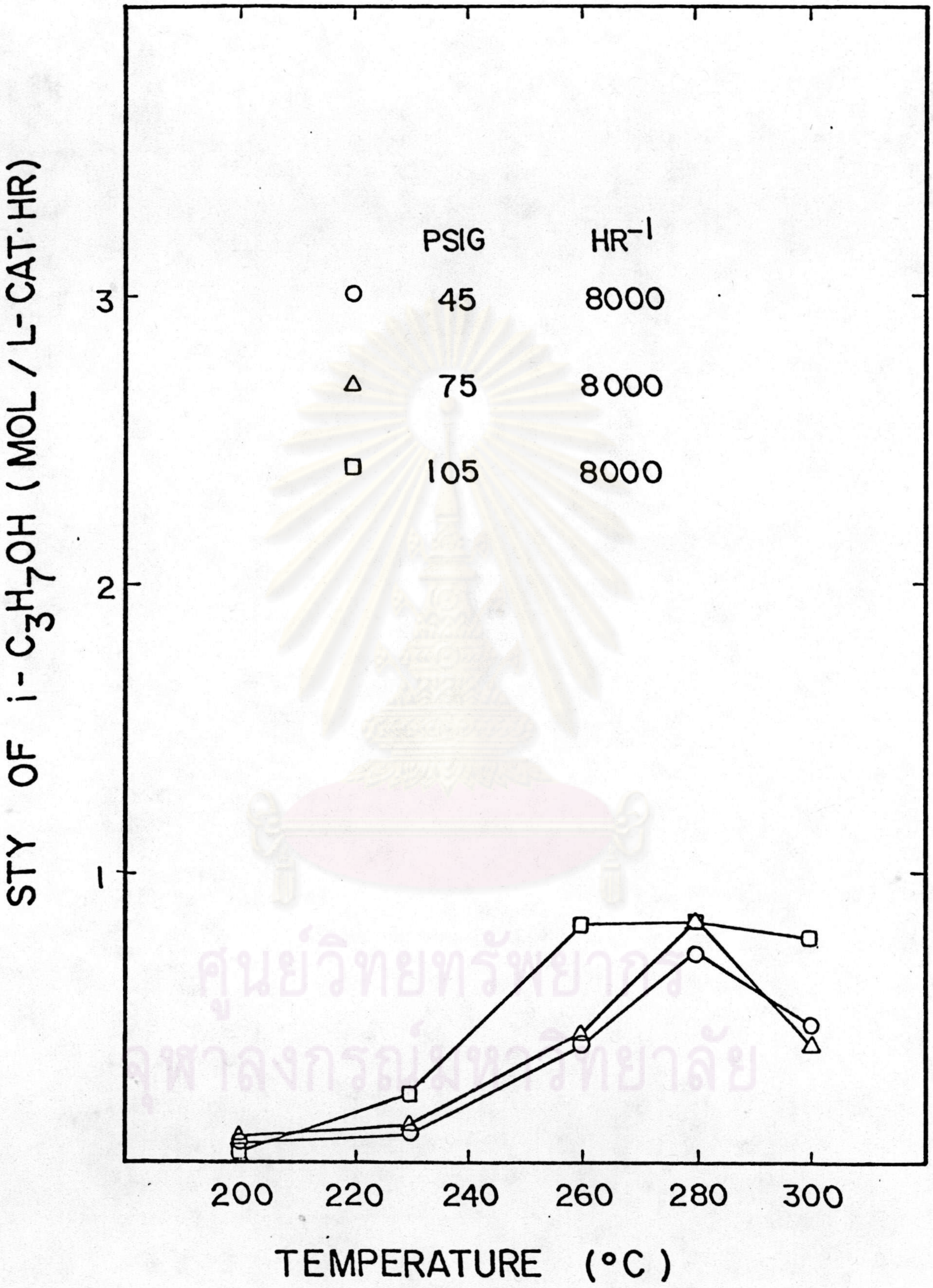

Figure 6.54 Effect of Temperature (200-300°C) on Space Time Yield of Isopropanol (at 45-105 psig, 8000 hr^{-1}) for Catalyst no.3

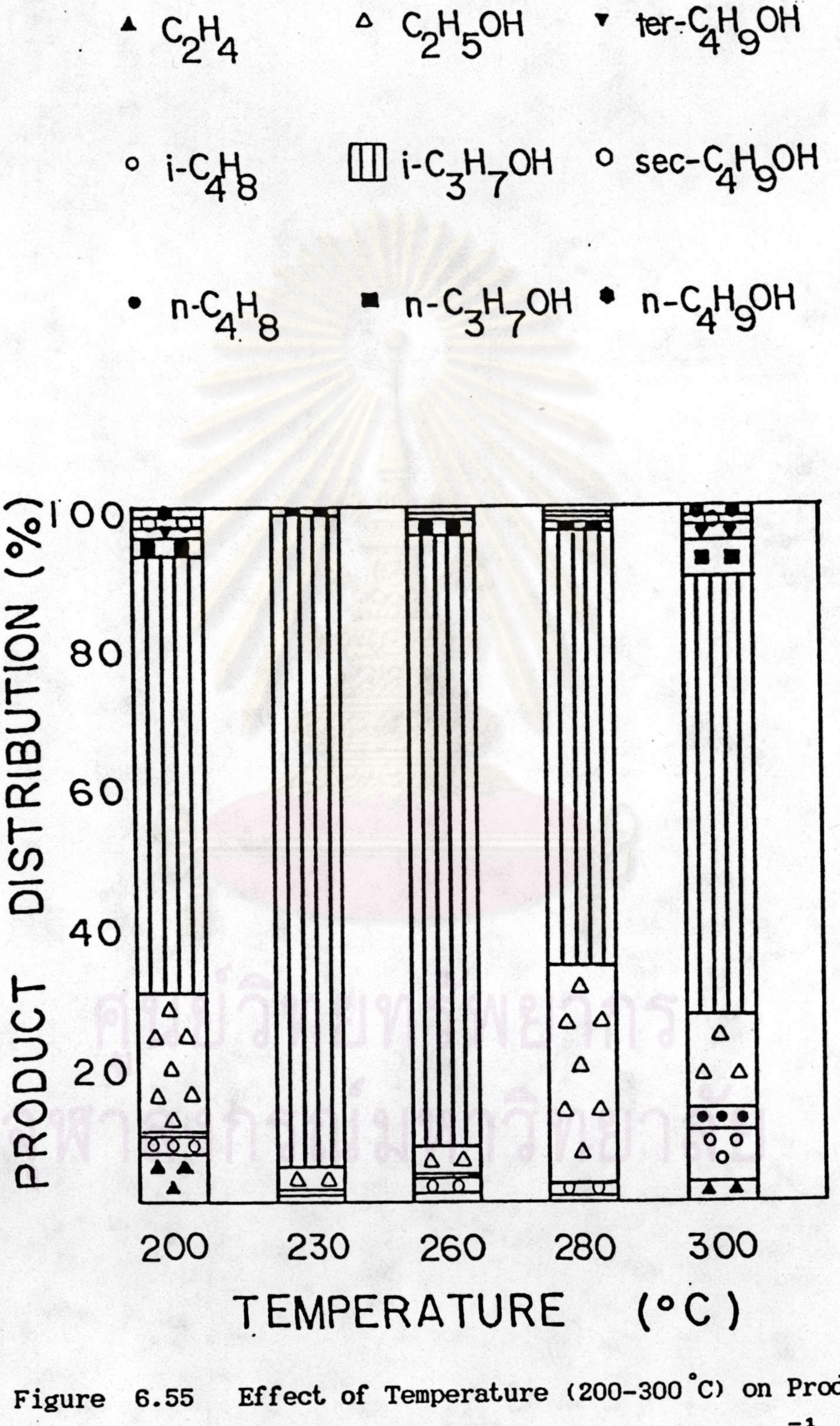

Figure 6.55 Effect of Temperature (200-300 °C) on Product Distribution (at 45 psig, 2000 hr^{-1}) for Catalyst no.3

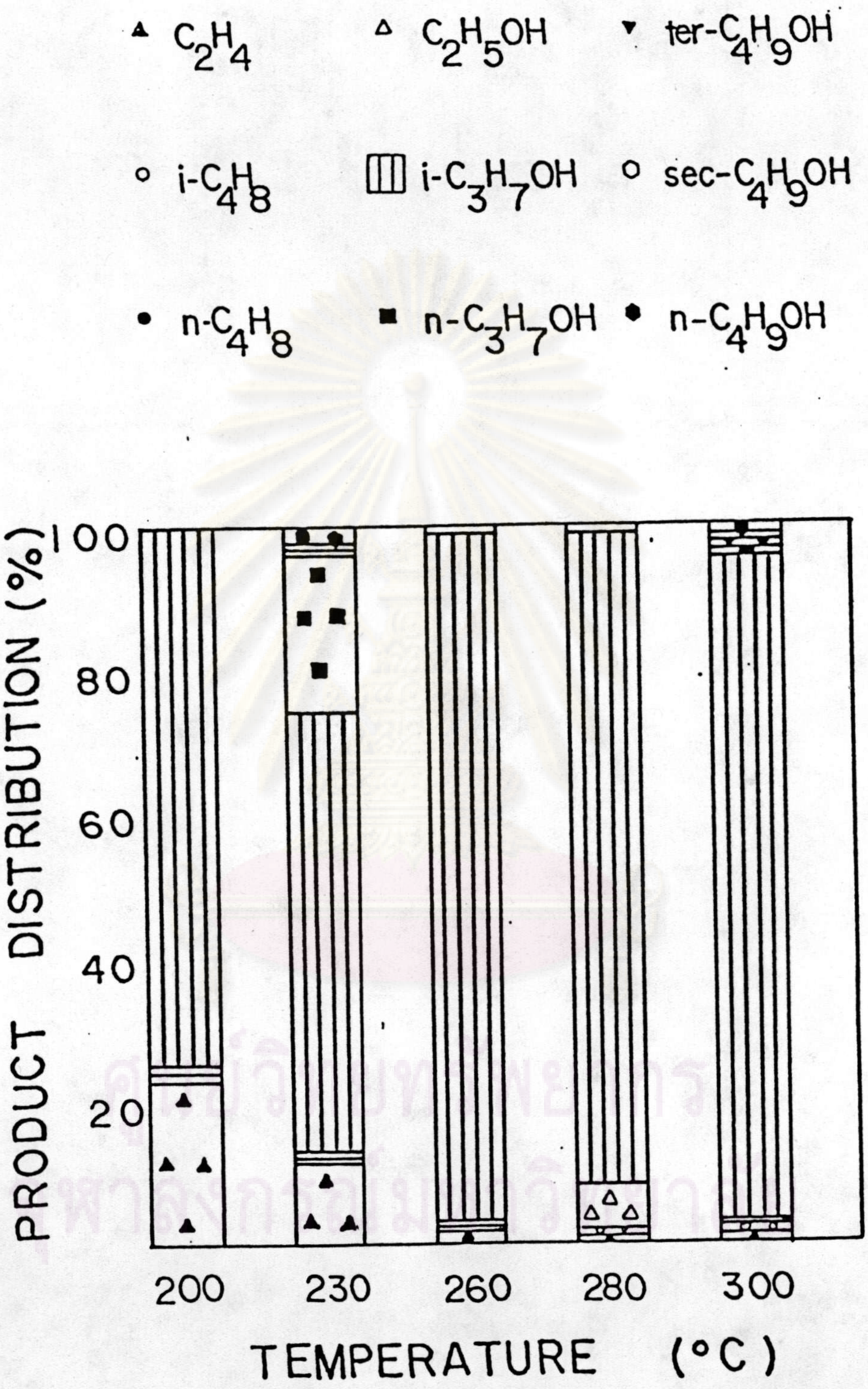

Figure 6.56 Effect of Temperature (200-300 °C) on Product Distribution (at 45 psig, 5000 hr^{-1}) for Catalyst no.3

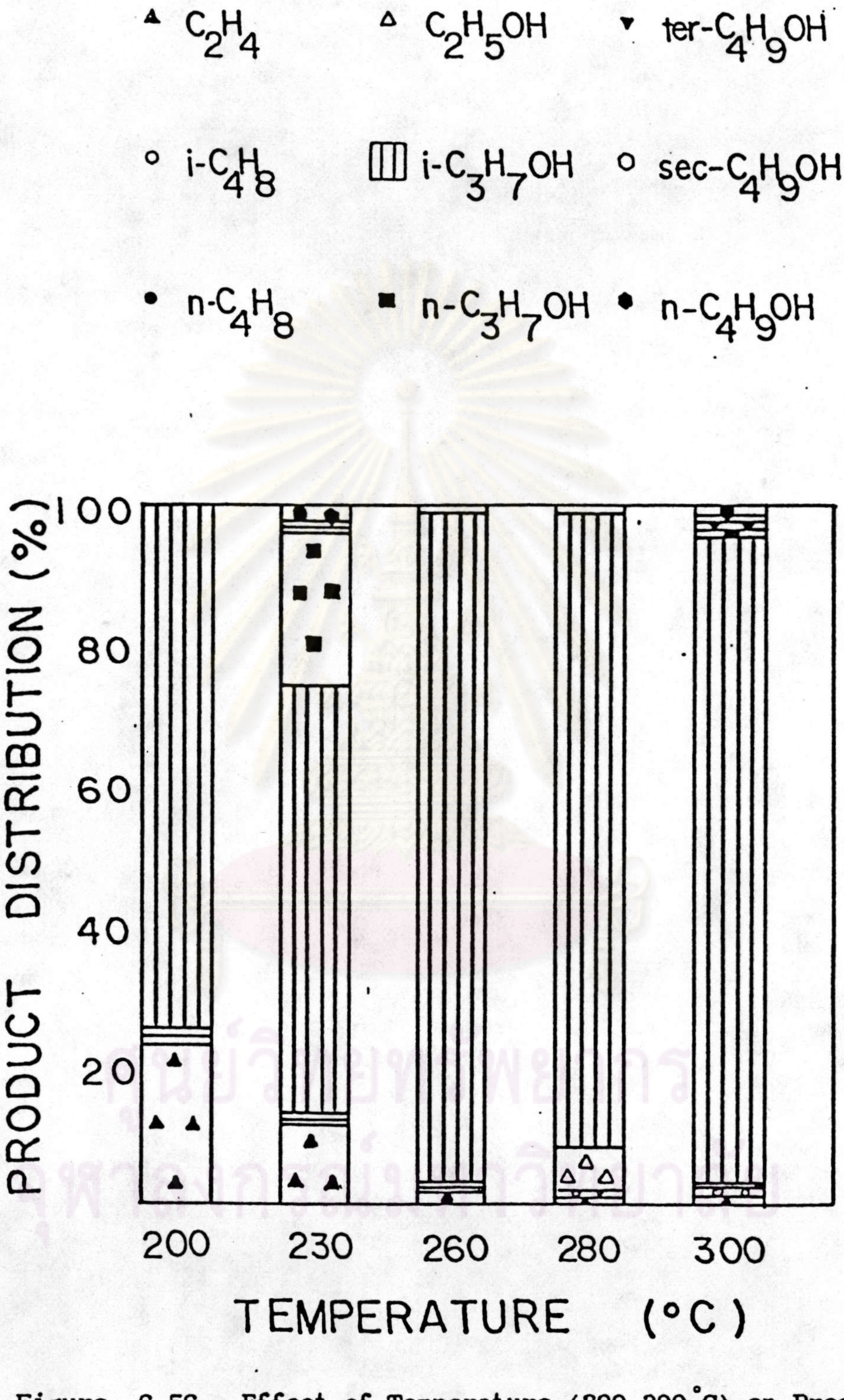

Figure 6.56 Effect of Temperature (200-300 °C) on Product Distribution (at 45 psig, 5000 hr^{-1}) for Catalyst no.3

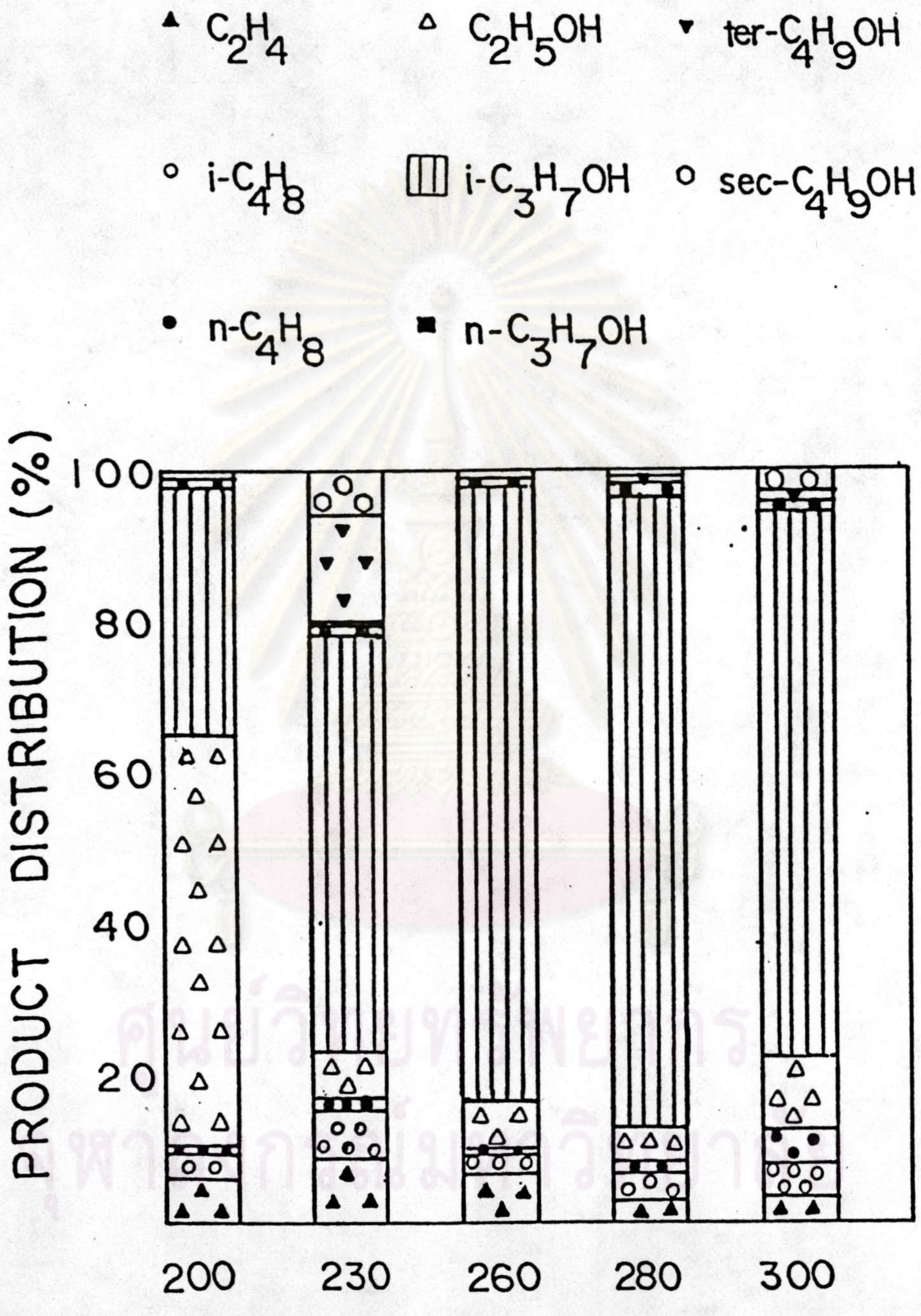

Figure 6.57 Effect of Temperature (200-300 °C) on Product Distribution (at 45 psig, 8000 hr^{-1}) for Catalyst no.3

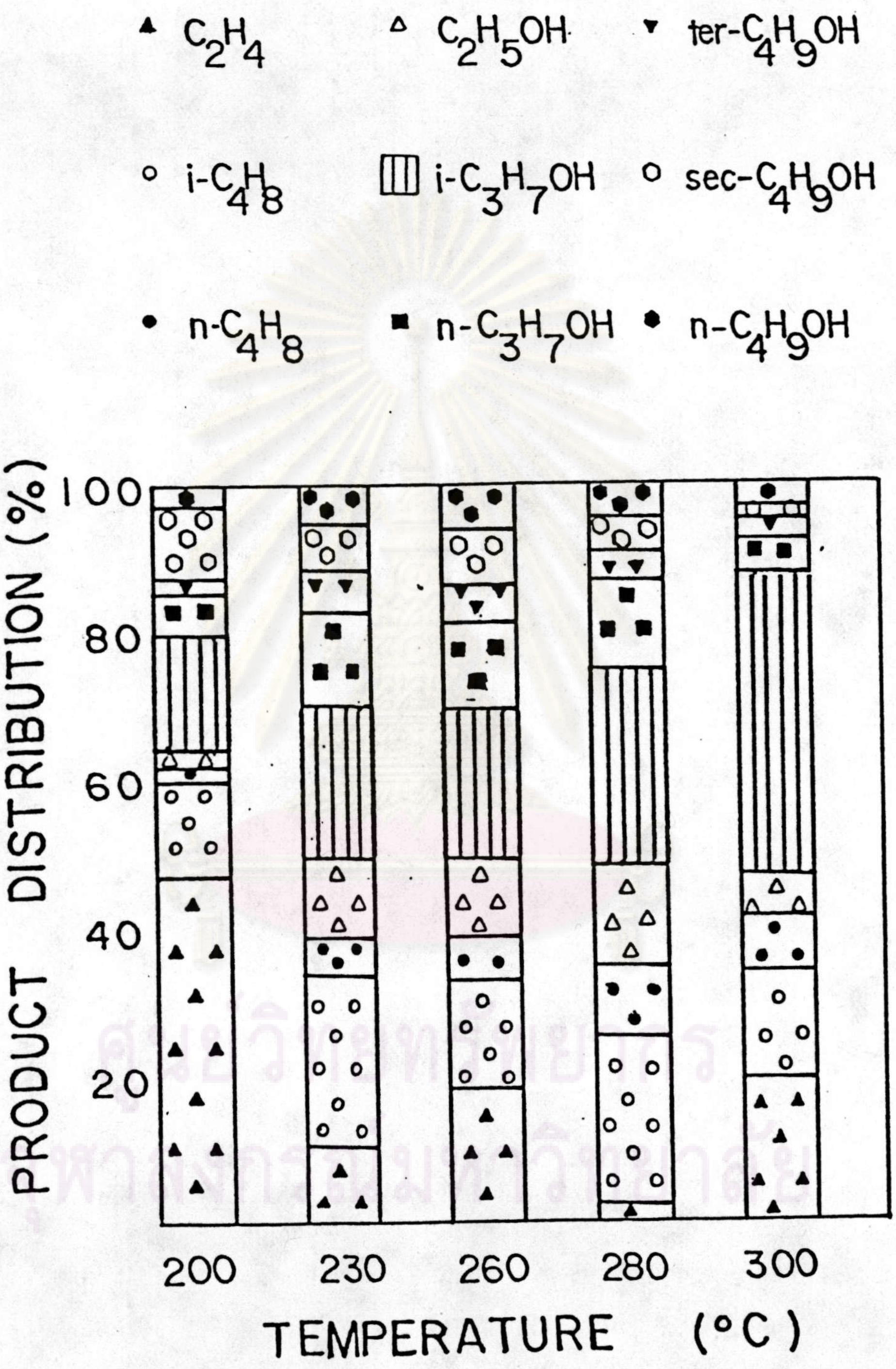

Figure 6.58 Effect of Temperature (200-300 °C) on Product Distribution (at 75 psig, 2000 hr^{-1}) for Catalyst no.3

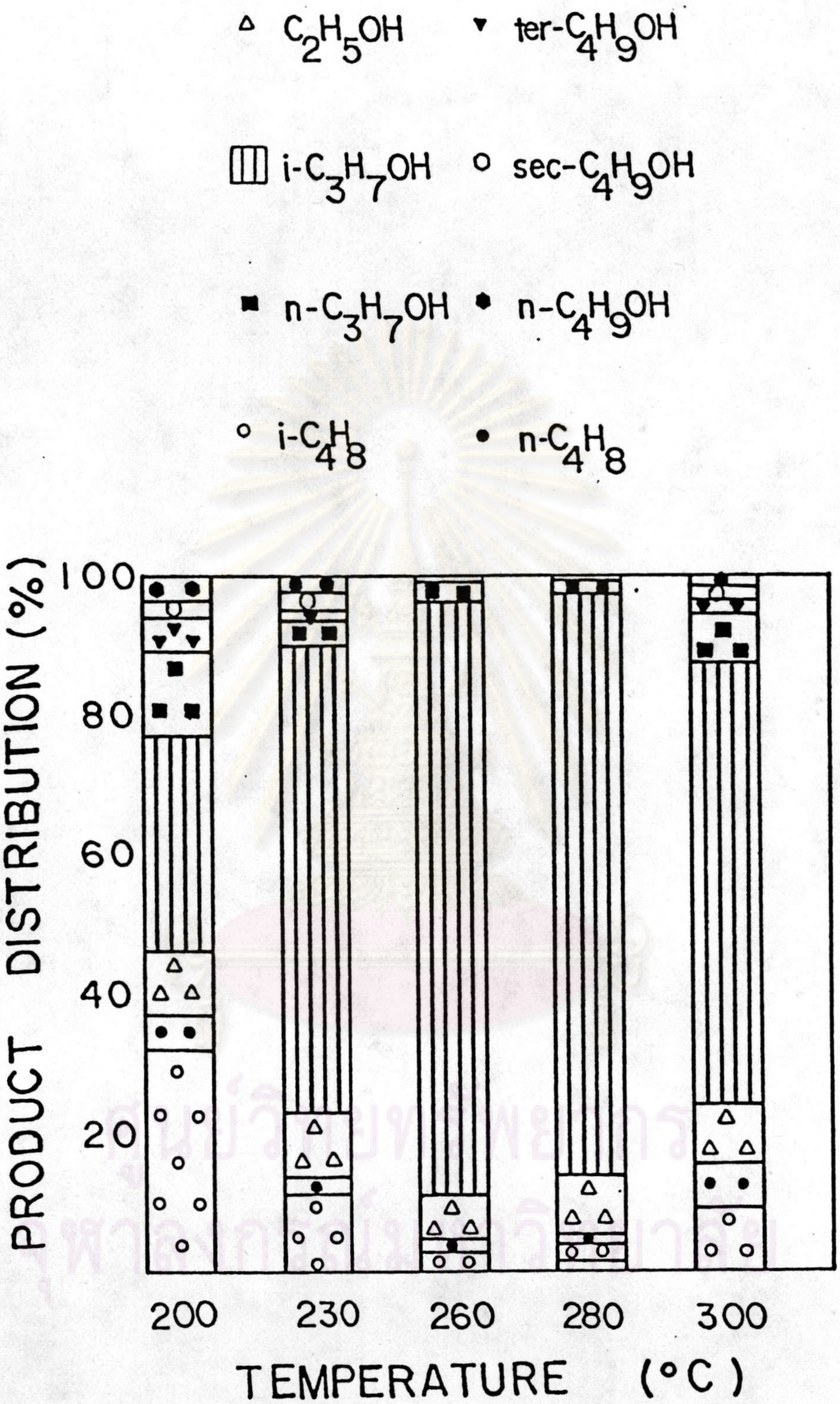

Figure 6.59 Effect of Temperature (200-300 °C) on Product Distribution (at 75 psig, 5000 hr^{-1}) for Catalyst no.3

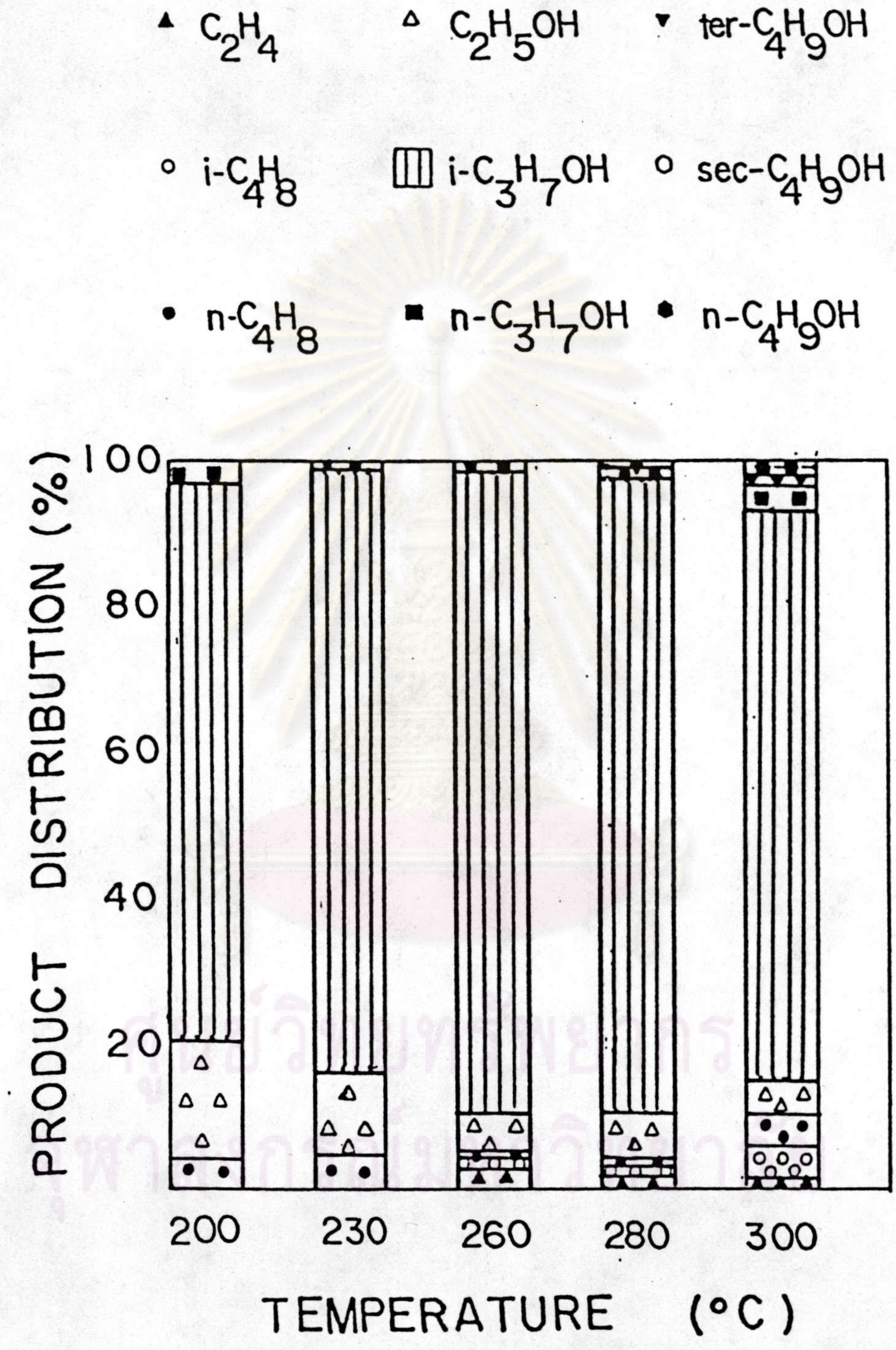

Figure 6.60 Effect of Temperature (200-300 °C) on Product Distribution (at 75 psig, 8000 hr^{-1}) for Catalyst no.3

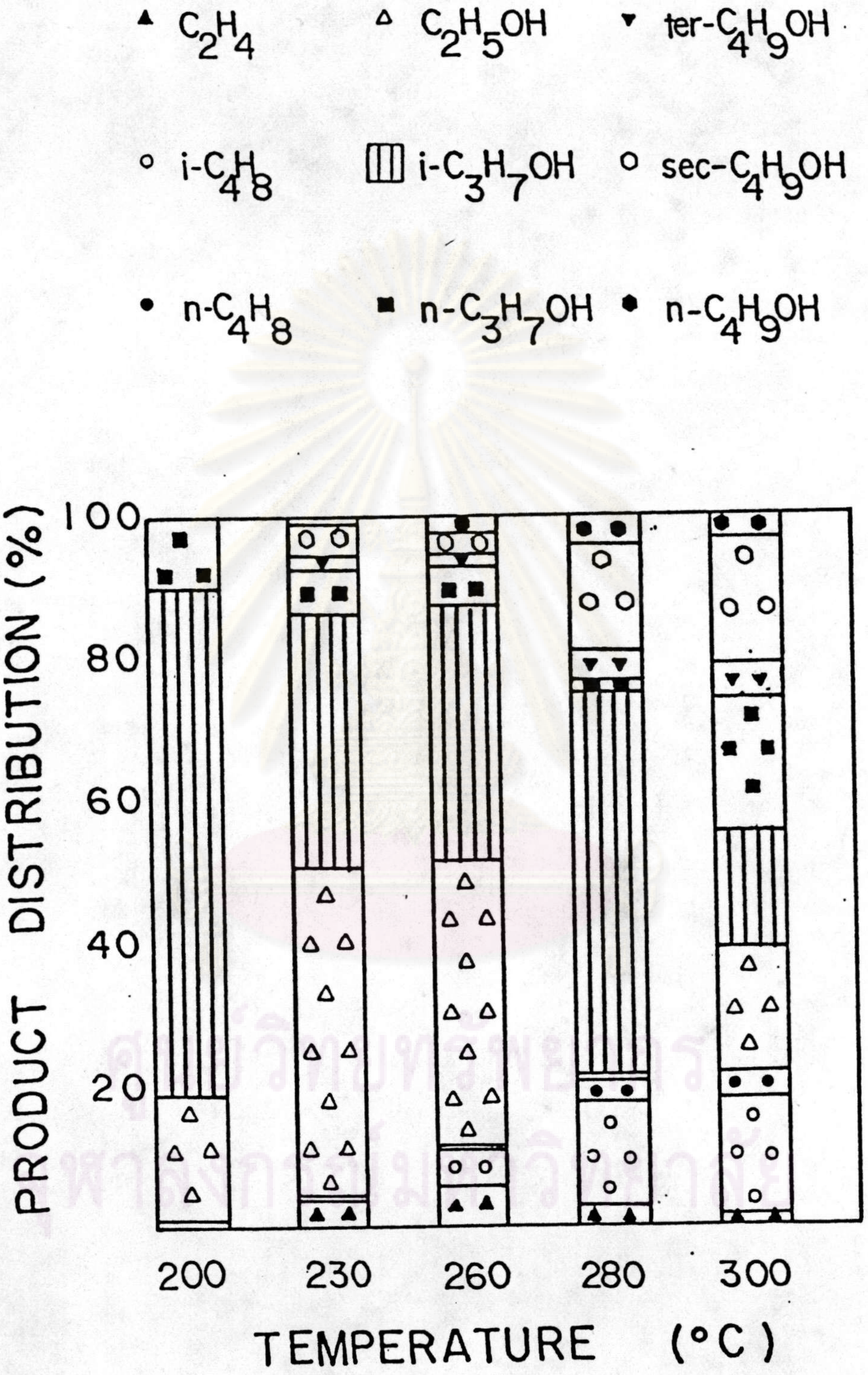

Figure 6.61 Effect of Temperature (200-300 °C) on Product Distribution (at 105 psig, 2000 hr^{-1}) for Catalyst no.3

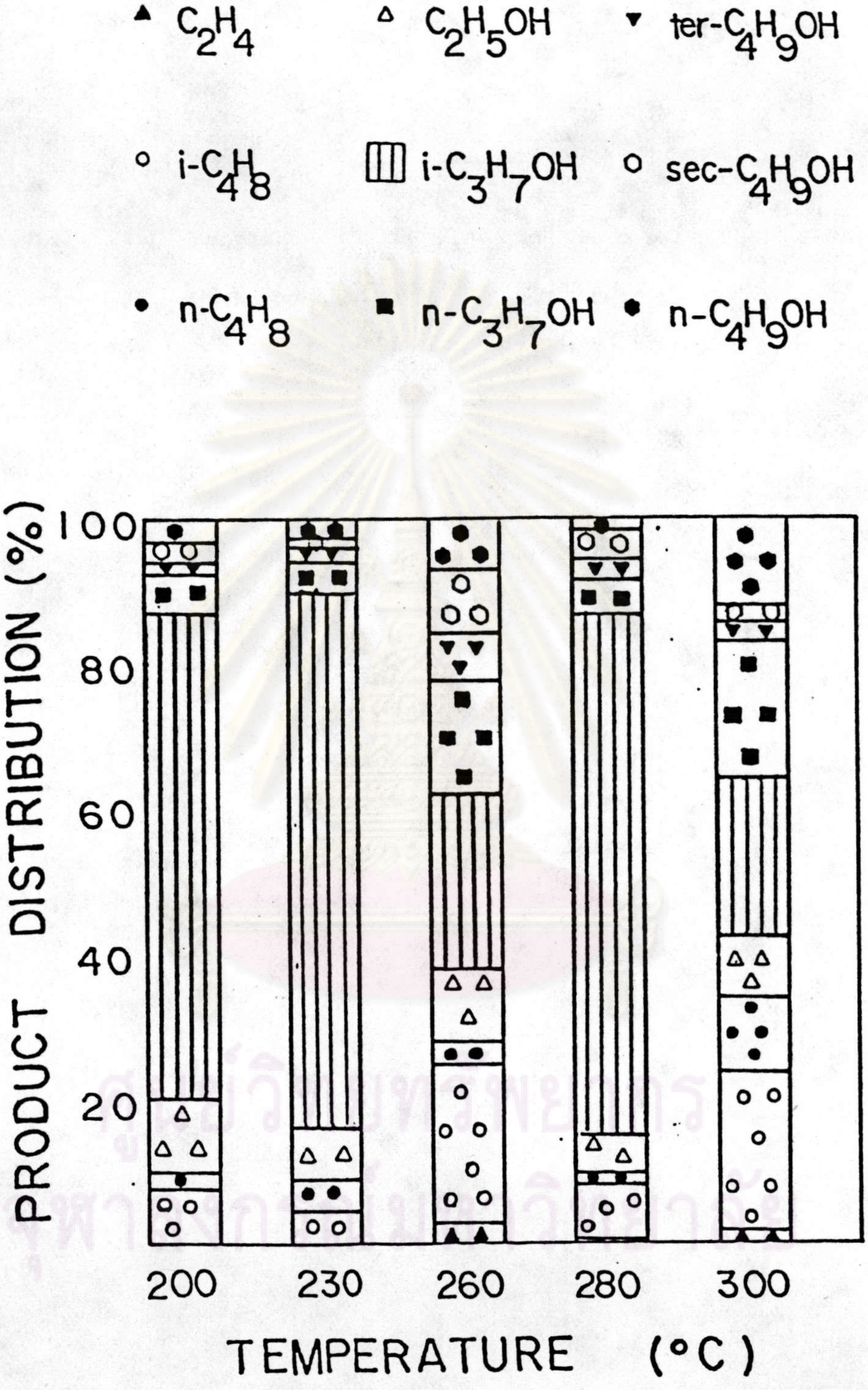

Figure 6.62 Effect of Temperature (200-300 °C) on Product Distribution (at 105 psig, 5000 hr^{-1}) for Catalyst no.3

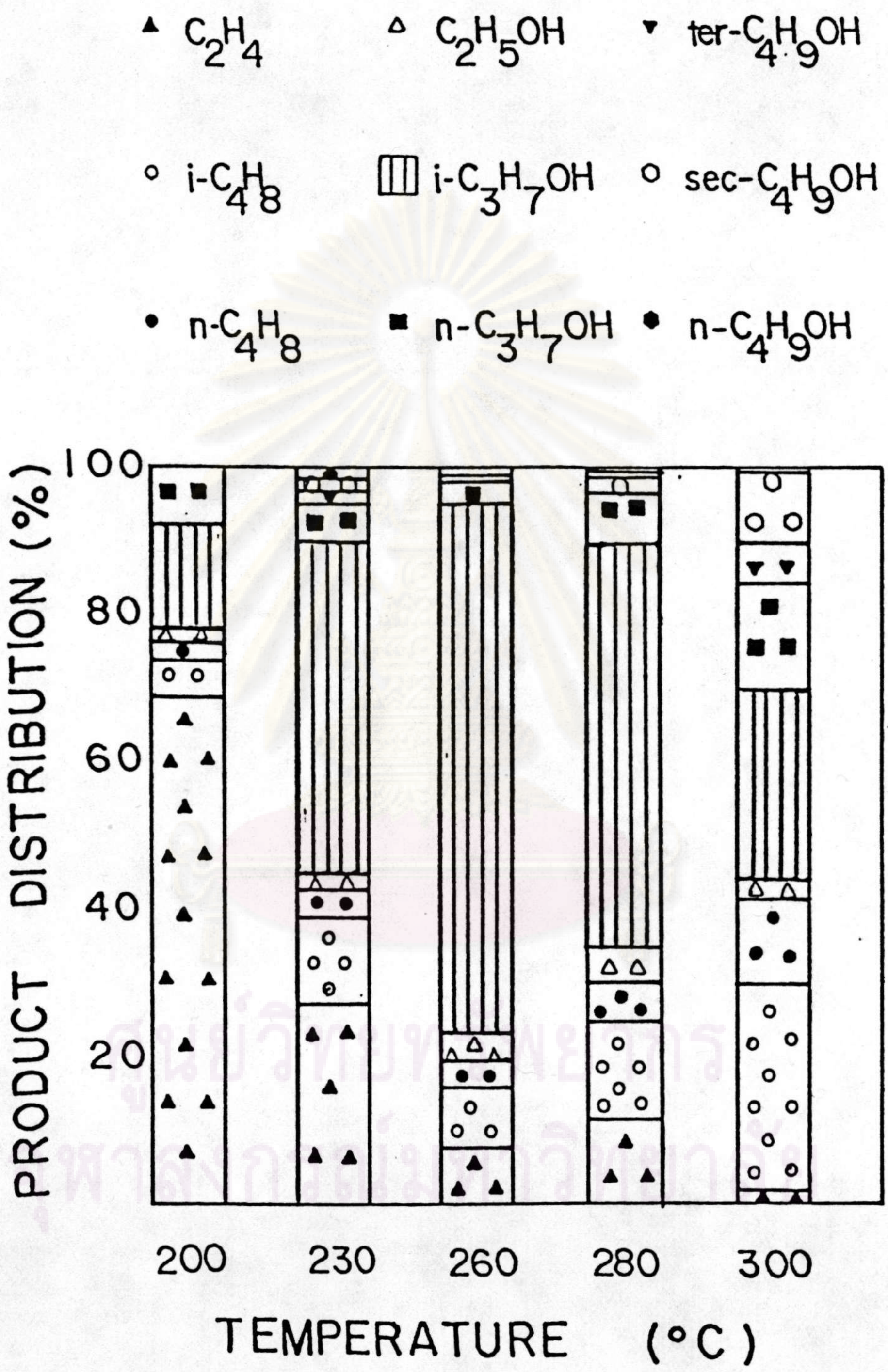

Figure 6.63 Effect of Temperature (200-300°C) on Product Distribution (at 105 psig, 8000 hr^{-1}) for Catalyst no.3

Comparison of Isopropanol Synthesis Performance between Present Catalyst and Industrial Catalyst

The isopropanol synthesis industry typically used a series of 2-10 reactors, in which strong acid cation exchanged resins are packed. The reported performance at 120-200 °C, 60-200 bar is 99.6 % propylene conversion and 99.4 % isopropanol selectivity. On the other hand the present work used a single differential reactor, in which a cation exchanged zeolite catalyst was passed. At the present low pressure of only 45 psig, 230 °C and SV 2000 hr^{-1}, it was found that the H-Y catalyst give 11.09 % propylene conversion and 95 % isopropanol selectivity. To make the comparison, we assume that a series of 10 reactors are packed with the H-Y catalyst, and that all products are removed between each pair of reactors. Then we have the following results.

no. of reactors	% conversion	%selectivity
1.	11.09	95
2.	20.95	94.79
3.	29.71	94.85
4.	37.50	94.88
5.	44.42	94.91
6.	50.58	94.91
7.	56.05	94.91
8.	60.91	94.92
9.	65.23	94.93
10.	69.07	94.94

Thus the above salsulation showed that the industrial catalyst is still quite superior to our own catalysts. Thus there is still room for further improvement before industrial application may be considered.