CHAPTER 5

EXPERIMENTAL SCREENING OF MODIFIED ZEOLITE TYPE CATALYSTS

The activities of the six modified zeolite type catalysts were screened using the hydroisomerization of n-heptane as a test reaction in order to search the most suitable one for further study in details. The experimental conditions used to screen these catalysts were: temperature 200-400^{o}C, pressure 5 and 20 bars, molar ratio of H_2/n-heptane = 10, and a liquid hourly space velocity of 5.5 v/v h^{-1}. All the runs were made at relatively high ratios of H_2/n-heptane in order to prevent coking.

5.1 Results and Discussion

Of the six catalysts tested, only two, 0.5 wt% Pt/USY and 0.5 wt% Pt/HM, were found to merit interest and discussion. The remaining either were hardly active (0.5 wt% Pd/HY, 0.5 wt% Pt/HY, and 0.5 wt% Pd/USY) or had too much cracking activity (0.5 wt% Pd/HM) thus clearly inferior to the above two. The BET surface area of the Pt/HM and Pt/USY catalysts were measured using a Micromeritics surface area analyzer (model ASAP 2000) and found to be 233 and 495 m^2/g, respectively.

5.1.1 Effect of Reaction Temperature

The total conversion of n-heptane on 0.5 wt% Pt/USY and 0.5 wt% Pt/HM was plotted as a function of reaction temperature in

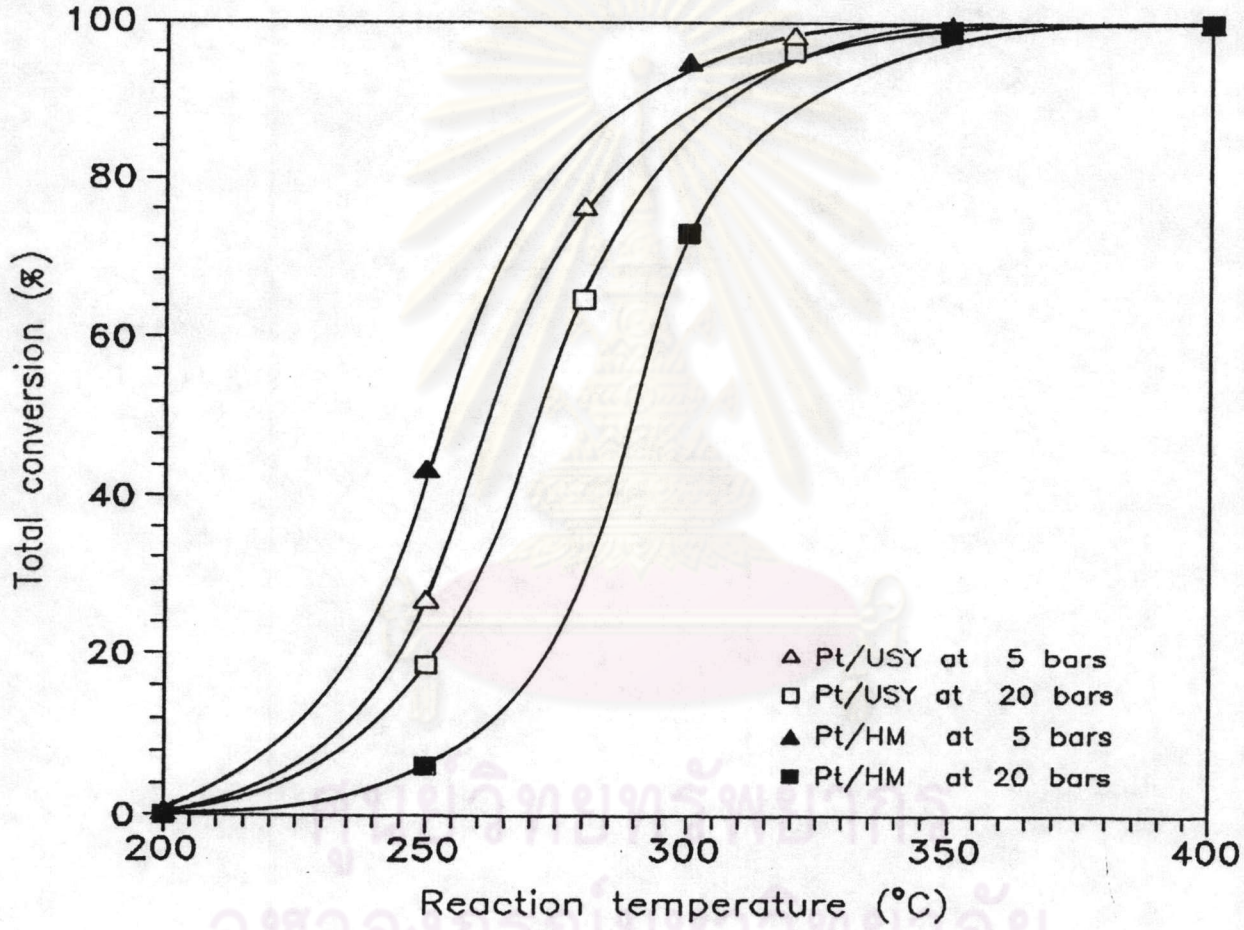

Figure 5-1 n-Heptane Conversion vs. Temperature at P = 5 and 20 bars for 0.5 wt% Pt/USY and 0.5 wt% Pt/HM Catalysts

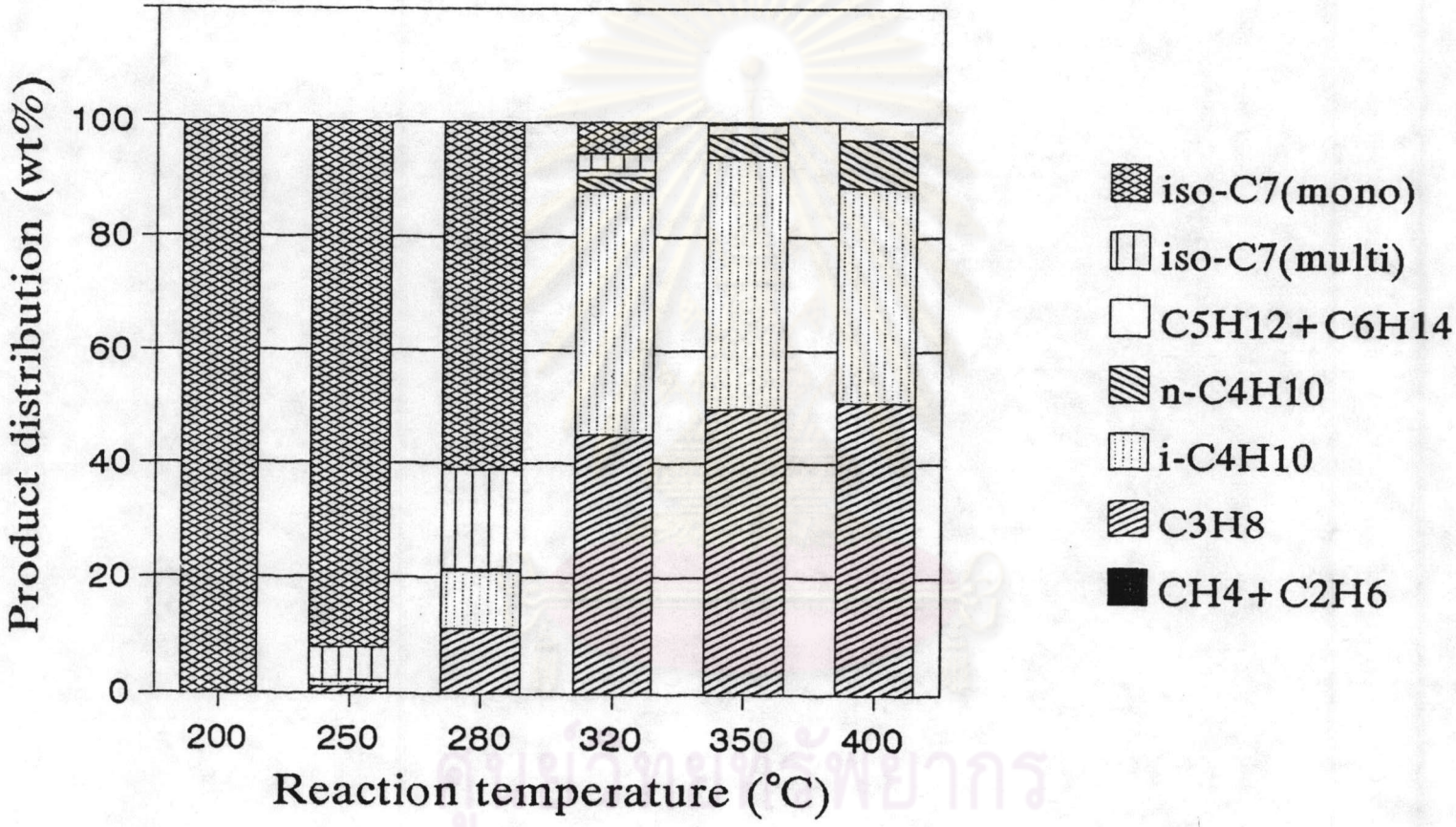

Figure 5-2 Product Distribution vs. Temperature at P = 5 bars for 0.5 wt% Pt/USY Catalyst

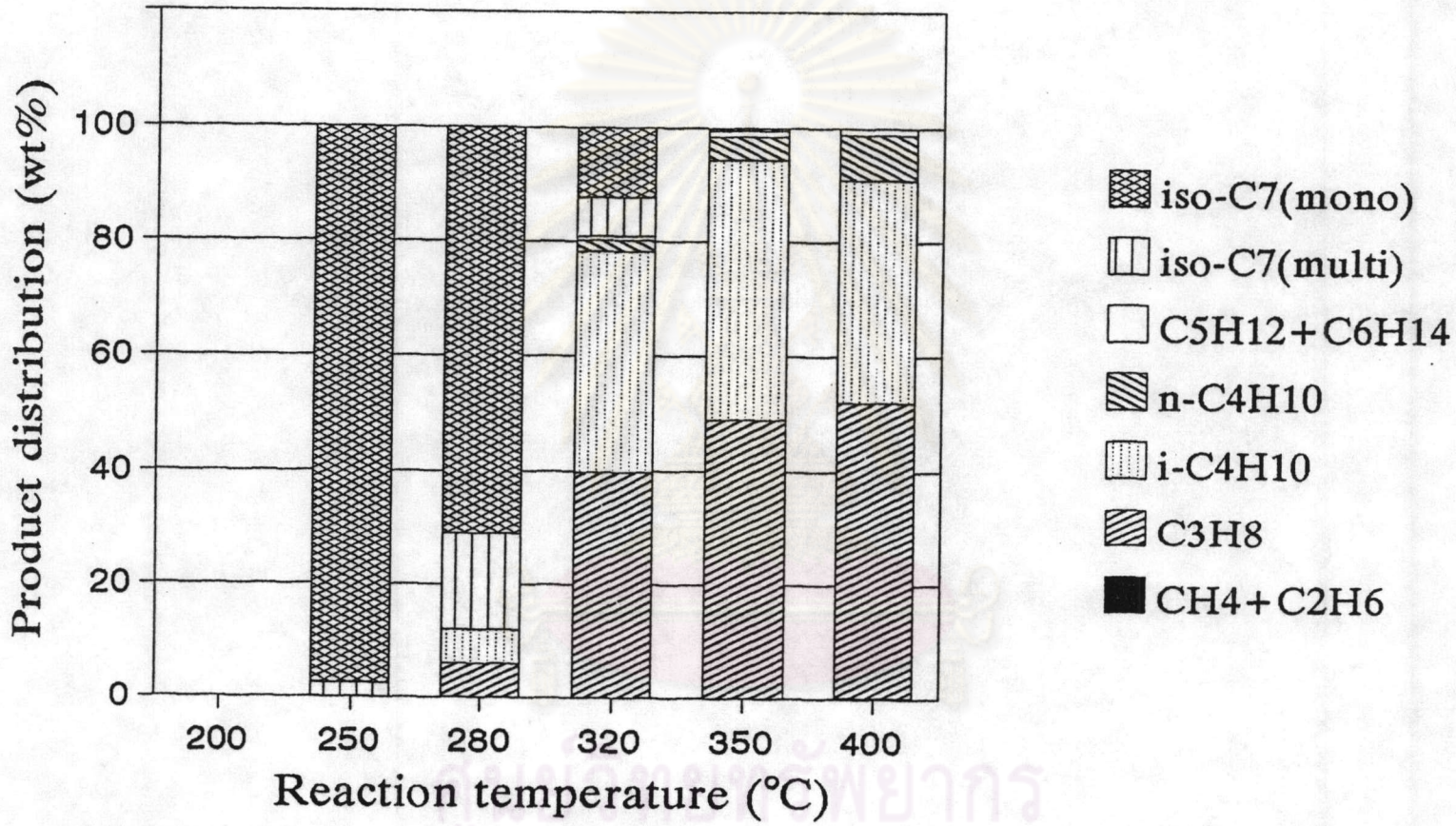

Figure 5-3 Product Distribution vs. Temperature at P = 20 bars for 0.5 wt% Pt/USY Catalyst

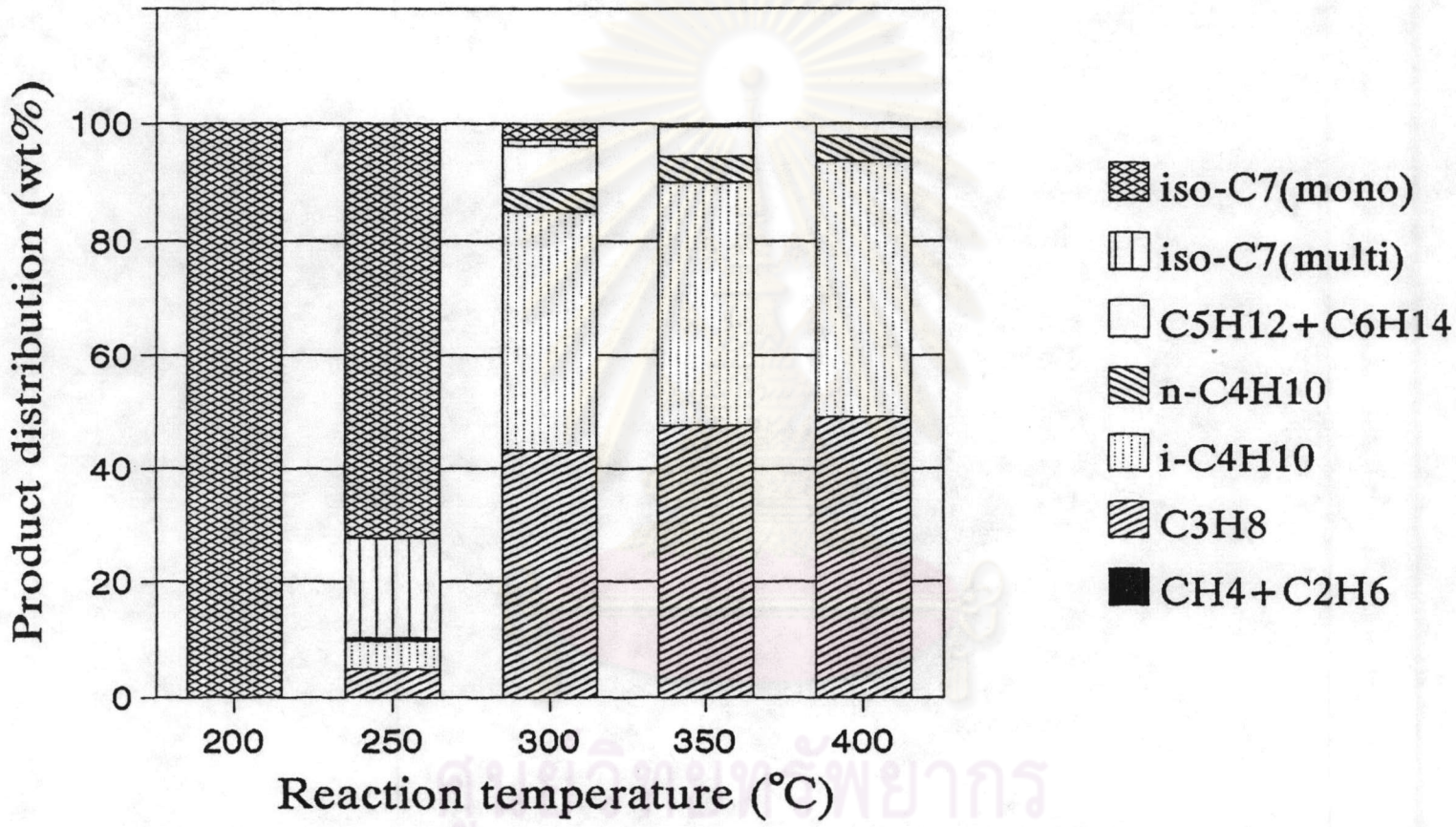

Figure 5-4 Product Distribution vs. Temperature at P = 5 bars for 0.5 wt% Pt/HM Catalyst

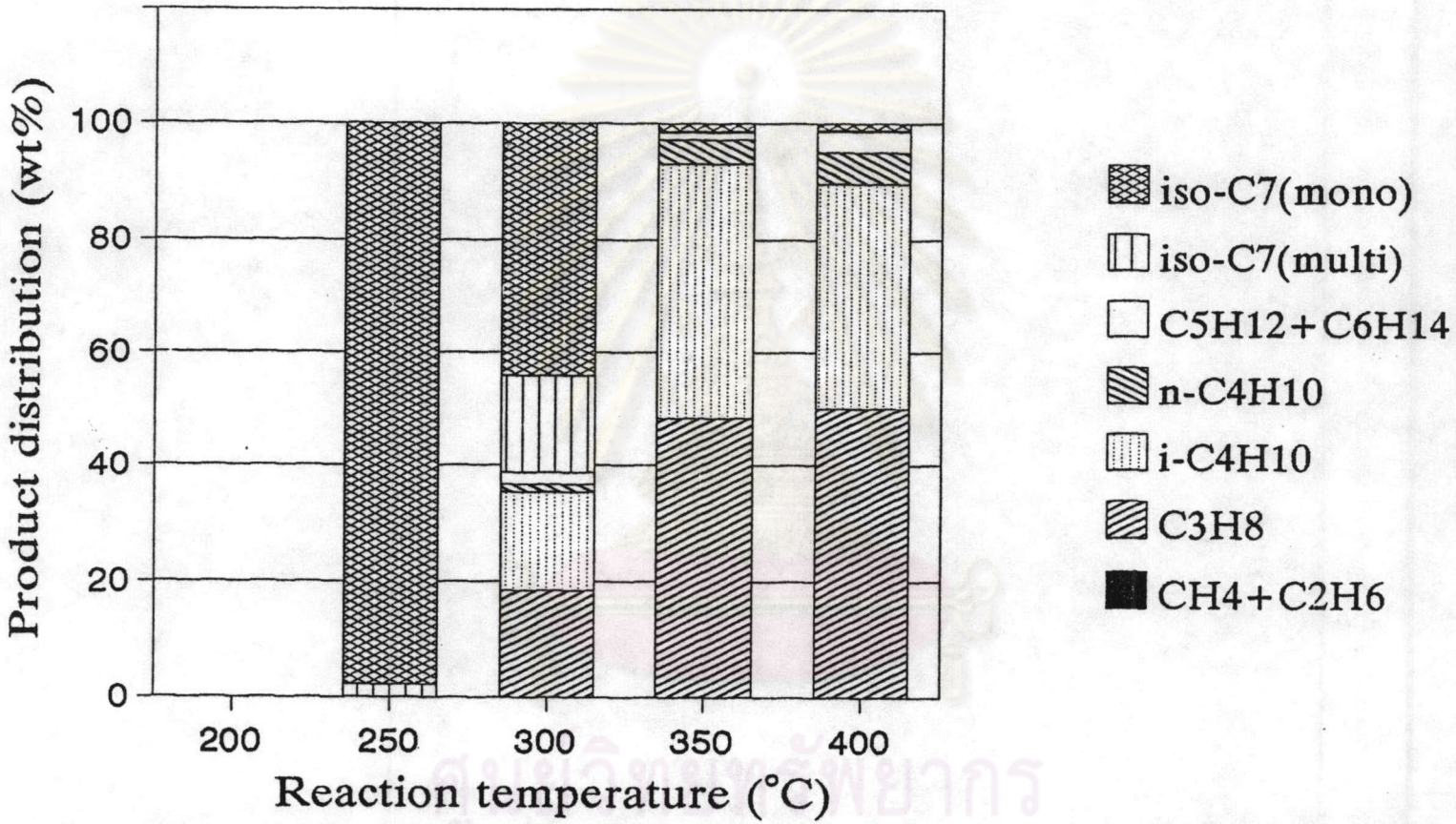

Figure 5-5 Product Distribution vs. Temperature at P = 20 bars for 0.5 wt% Pt/HM Catalyst

Figure 5-1. At each fixed pressure, the conversion rose as temperature increased from 200° to 400°C. Complete (100%) conversion was found at temperature above 350°C in all cases.

Figures 5-2 and **5-3** showed the observed product distribution vs. reaction temperature for Pt/USY catalyst at 5 and 20 bars, while **Figures 5-4** and **5-5** showed the same results for Pt/HM catalyst. As isomerization proceeded, the relative content of dibranched C_7 isomers increased, but in all cases the monobranched C_7 isomers were predominant in the C_7 fraction. Similar results were also reported by other researchers (Sakai et al., 1975; Giannetto et al., 1986; Mahos et al., 1986). Hydrocarbons higher in molecular weight than n-heptane were not formed on any of the catalysts investigated. The maximum total isomer content was 57% at temperature 280°C, pressure 20 bars for the Pt/USY catalyst. As for the Pt/HM catalyst the maximum isomer content was 43% at temperature 300°C, pressure 20 bars.

Above 70 % n-heptane conversion, hydrocracking reactions became predominant. The major constituents of the cracked products were propane and butanes, which seemed to indicate that the hydrocracking of n-heptane occurred preferentially near the center of the molecule rather than near its terminals. The higher ratio of isobutane to n-butane in the cracked products implied that isomerization preceded cracking. The results were similar to those observed by other investigators (Ciapetta and Hunter,1953; El-Kady et al., 1983; Mahos et al., 1986; Aboul-Gheit et al.,1987).

The C_7 isomer selectivity on the Pt/USY and Pt/HM was plotted as a function of reaction temperature in **Figure 5-6.** The results

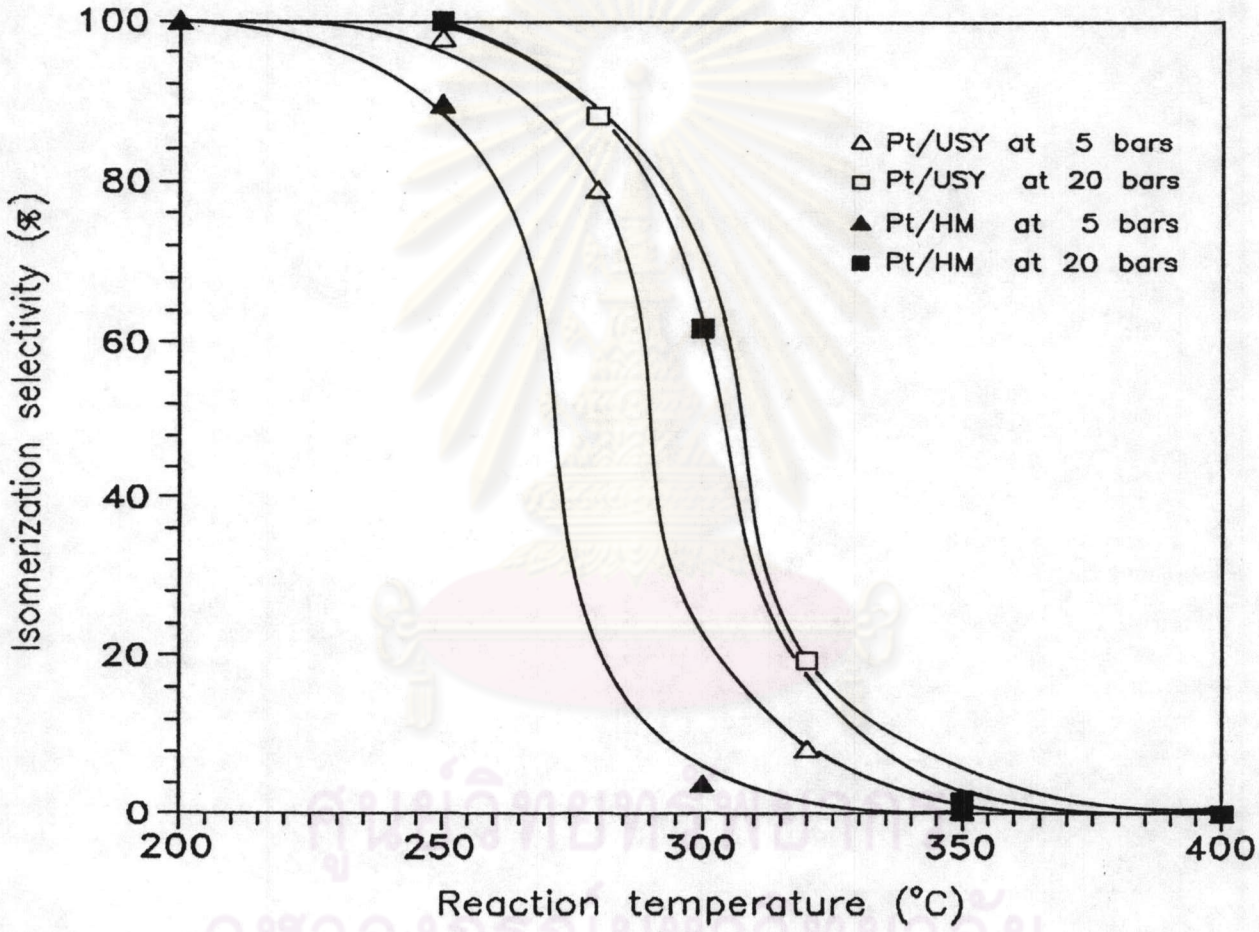

Figure 5-6 iso-C_7 Selectivity vs. Temperature at P = 5 and 20 bars for 0.5 wt% Pt/USY and 0.5 wt% Pt/HM Catalysts

showed that at each fixed pressure, this selectivity dropped drastically at temperatures above 250-260^{o}C because of cracking.

5.1.2. Effect of Reaction Pressure

The effect of pressure on the total conversion of n-heptane was shown in **Figure 5-1**. When the other conditions were the same, the effect of pressure on n-heptane conversion was noticeable between 250^{o}C and 300^{o}C. Above 320^{o}C, especially at 350^{o}C, the conversion was essentially complete. As evident from **Figures 5-2** to **5-5**, the selectivity for C_7 isomers was enhanced by pressure in the temperature range of 250^{o}C to 320^{o}C. According to Le Chatelier's law, cracking reactions are suppressed by high pressures, while isomerization is not affected either way by pressure.

5.2 Conclusions

It must be borne in mind that carefully selected catalysts are required for isomerization of long-chain alkane such as n-heptane. Otherwise hydrocracking is predominant even at low conversions. The situation encountered on the 0.5 wt% Pt/USY zeolite is a most favorable one for isomerization of n-heptane.

It can be concluded that, the 0.5 wt% platinum impregnated ultrastable Y zeolite is the most suitable among the 6 catalysts for n-heptane isomerization, so it is chosen for further experimental studies. The experimental conditions to be investigated in the hydroisomerization of n-heptane are summarized as follows:

Catalyst Type : 0.5 wt% Pt/USY

Temperature : 240°, 260°, 280°, 300° and 320°C

Pressure : 5, 10, 20 and 30 bars

Space Velocity : 2.7, 5.5, 15 and 30 h^{-1}