CHAPTER 6

EXPERIMENTAL RESULTS AND DISCUSSION
ON THE SELECTED 0.5 wt% Pt/USY CATALYST

To study the individual effects of temperature, pressure and space velocity on the hydroisomerization of n-heptane using the 0.5 wt% Pt/USY zeolite (the selected catalyst), each experimental variable was varied while the remaining were kept constant. In the following, the observed n-heptane conversion and product selectivity are discussed and compared among various experimental conditions.

6.1 Effect of Reaction Temperature

6.1.1 Effect of Reaction Temperature on Total Conversion of n-Heptane

Based on the experimental data, a summary is made as shown in **Table 6-1**. A plot of the total conversion of n-heptane versus temperature is shown in **Figure 6-1**. The obtained results show that at each fixed pressure, the conversion rose as temperature increased by 20 degrees Celcius from 240^{o} to $320^{o}C$. On the other hand, the rate of increase in conversion slowed down as the temperature increased, as evident from the decreasing slope of the curves in **Figure 6-1**. This finding indicated, as expected, that essentially complete conversion was obtained when the temperature was high enough, regardless of pressure.

Table 6-1 Effect of Temperature on the Total Conversion of n-Heptane

Catalyst Type : 0.5 wt% Pt/USY

Space Velocity (LHSV) : 5.5 h^{-1}

Reaction Pressure : 5, 10, 20 and 30 bars

Temperature (°C)	Conversion (%)			
	P = 5 bars	P = 10 bars	P = 20 bars	P = 30 bars
240	25.27	29.05	20.66	15.66
260	64.68	69.46	55.95	43.08
280	84.53	93.10	87.61	83.86
300	95.78	98.15	96.51	98.72
320	99.20	99.77	99.56	99.94

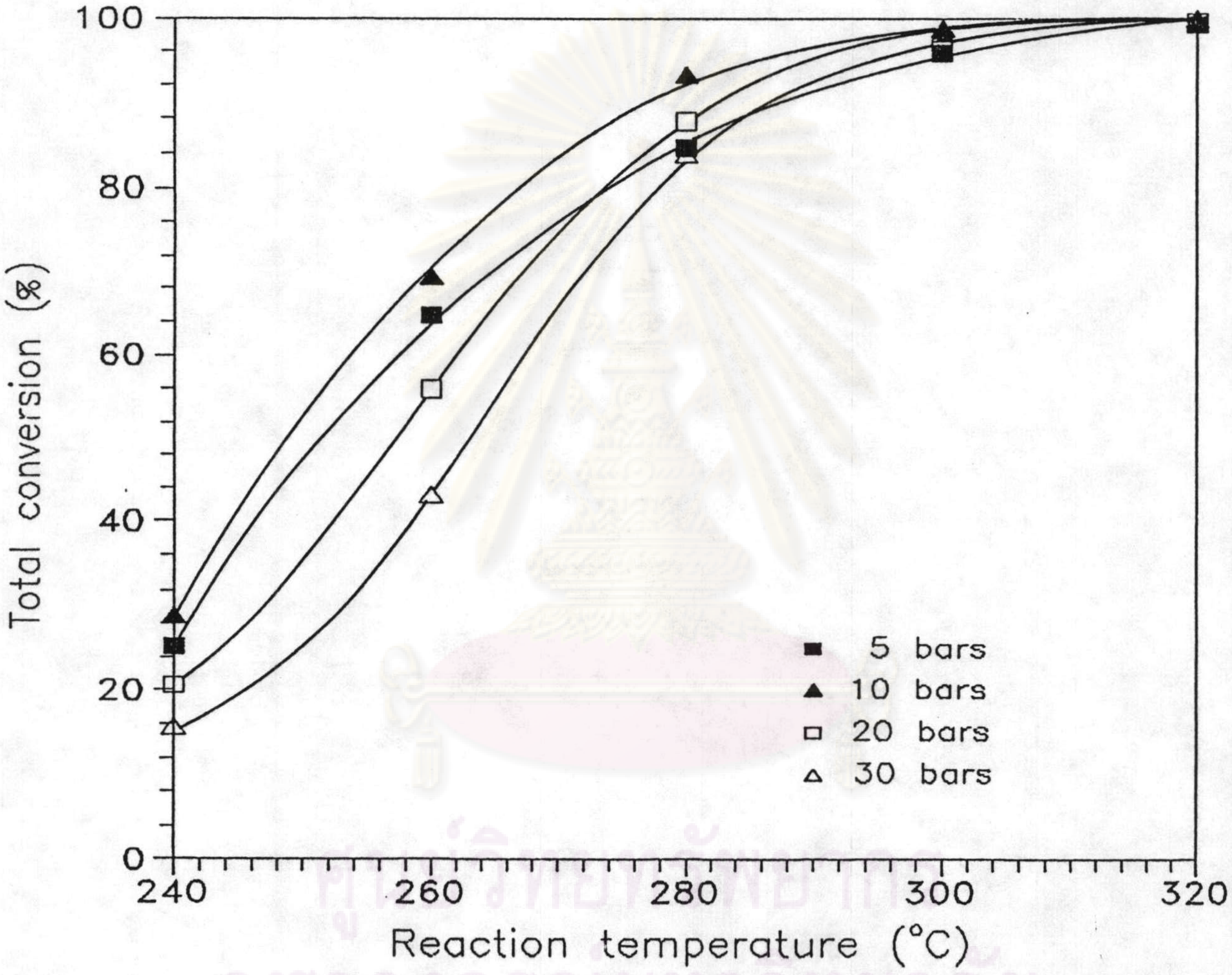


Figure 6-1 n-Heptane Conversion vs. Temperature at P = 5, 10, 20 and 30 bars; LHSV = 5.5 h^{-1} for 0.5 wt% Pt/USY Catalyst

6.1.2 **Effect of Reaction Temperature on iso-Heptane Selectivity**

To illuminate the effect of temperature on iso-heptane selectivity, the observed selectivity at four fixed pressures are summarized in **Table 6-2**, and shown graphically in **Figure 6-2**.

Figures 6-3 to 6-6 show the product distribution as a function of the reaction temperature at a fixed LHSV of 5.5 h^{-1} for the pressures of 5, 10, 20 and 30 bars, respectively.

Since the branched heptyl carbonium ions obtained through protonated cyclopropane intermediates (see pp. 82-84) can undergo two reactions: (1) hydrogenation to iso-heptane, or (2) cracking to light products. So, in discussing the activities of these two reactions, the words "hydrogenation activity" and "cracking activity" were be used, respectively. On the other hand, the word "isomerization" simply means a shift in the configuration of a molecule, without change in the number of atoms present.

It appears that at a low reaction temperature the hydrogenaton activity dominated. As the reaction temperature went up from 260° to 320°C both hydrogenation and cracking activities of the catalyst increased. The highest isomerization/cracking ratio was obtained at 260°C (see **Figure 6-7**). A rise in temperature above 280°C shifted the balance towards more cracking. Iso-heptane yields went down rapidly and cracked products increased remarkably.

Increasing the reaction temperature up to 320°C caused a negligible change in dry gas (C_1 and C_2) yield but a remarkable

Table 6-2 Effect of Temperature on iso-Heptane Selectivity

Catalyst Type : 0.5 wt% Pt/USY

Space Velocity (LHSV) : 5.5 h^{-1}

Reaction Pressure : 5, 10, 20 and 30 bars

Temperature (°C)	iso-Heptane Selectivity (%)			
	P = 5 bars	P = 10 bars	P = 20 bars	P = 30 bars
240	100.00	97.52	99.00	100.00
260	91.61	86.21	92.69	92.51
280	68.67	38.79	66.26	63.91
300	31.31	12.26	24.74	8.49
320	6.29	0.24	1.64	0.07

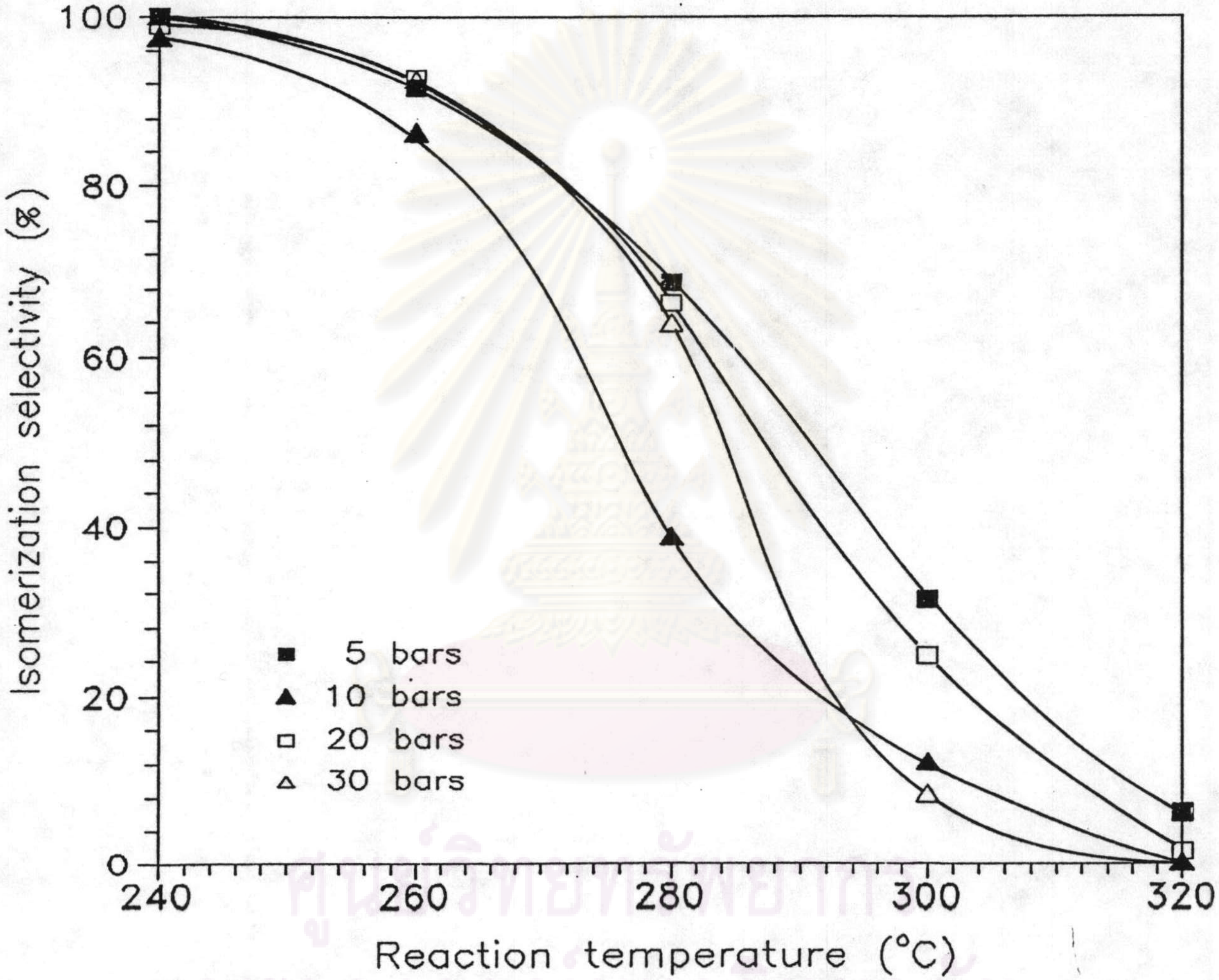


Figure 6-2 iso-C_7 Selectivity vs. Temperature at P = 5, 10, 20 and 30 bars; LHSV = 5.5 h^{-1} for 0.5 wt% Pt/USY Catalyst

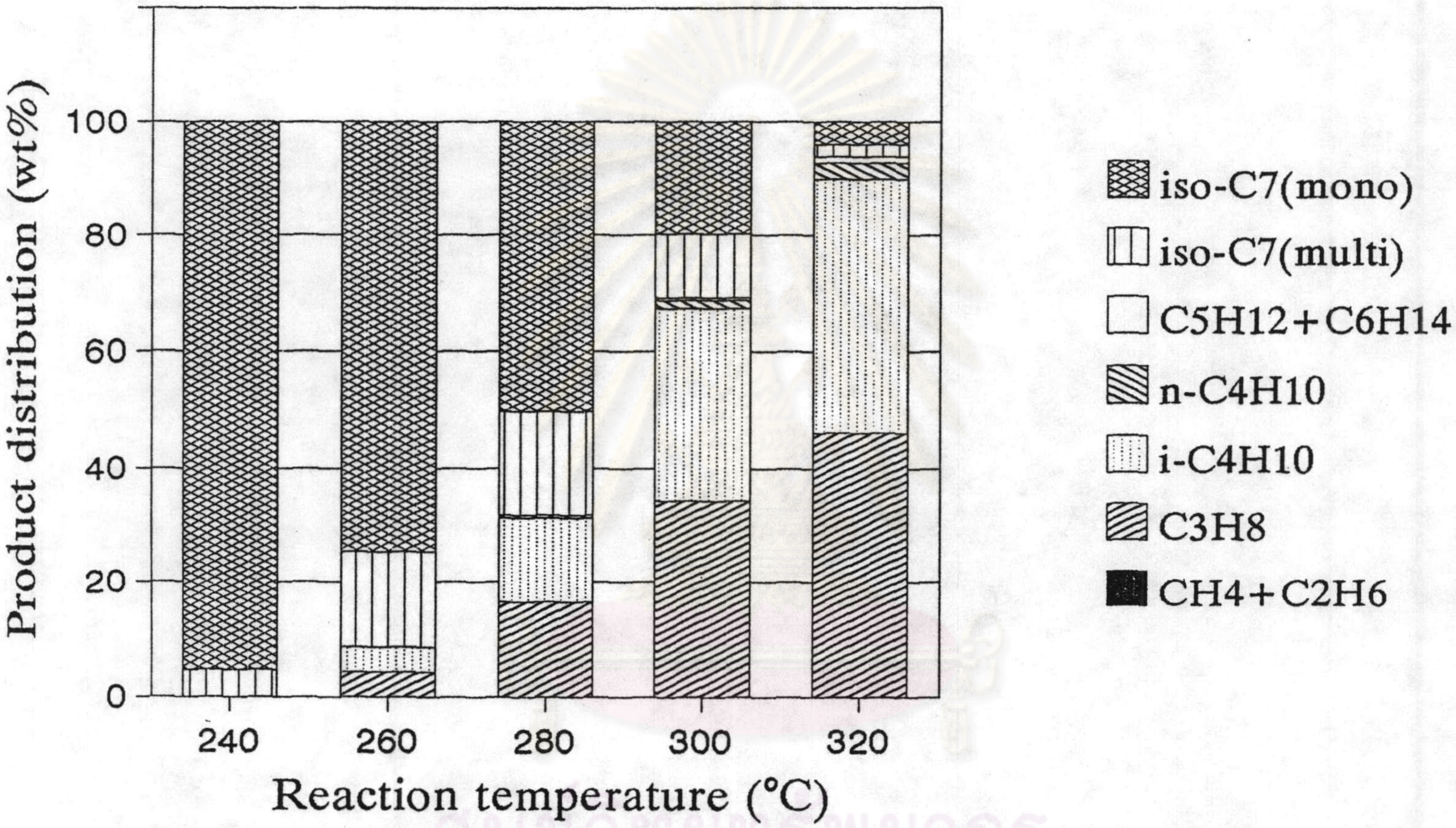


Figure 6-3 Product Distribution vs. Temperature at P = 5 bars; LHSV = 5.5 h^{-1} for 0.5 wt% Pt/USY Catalyst

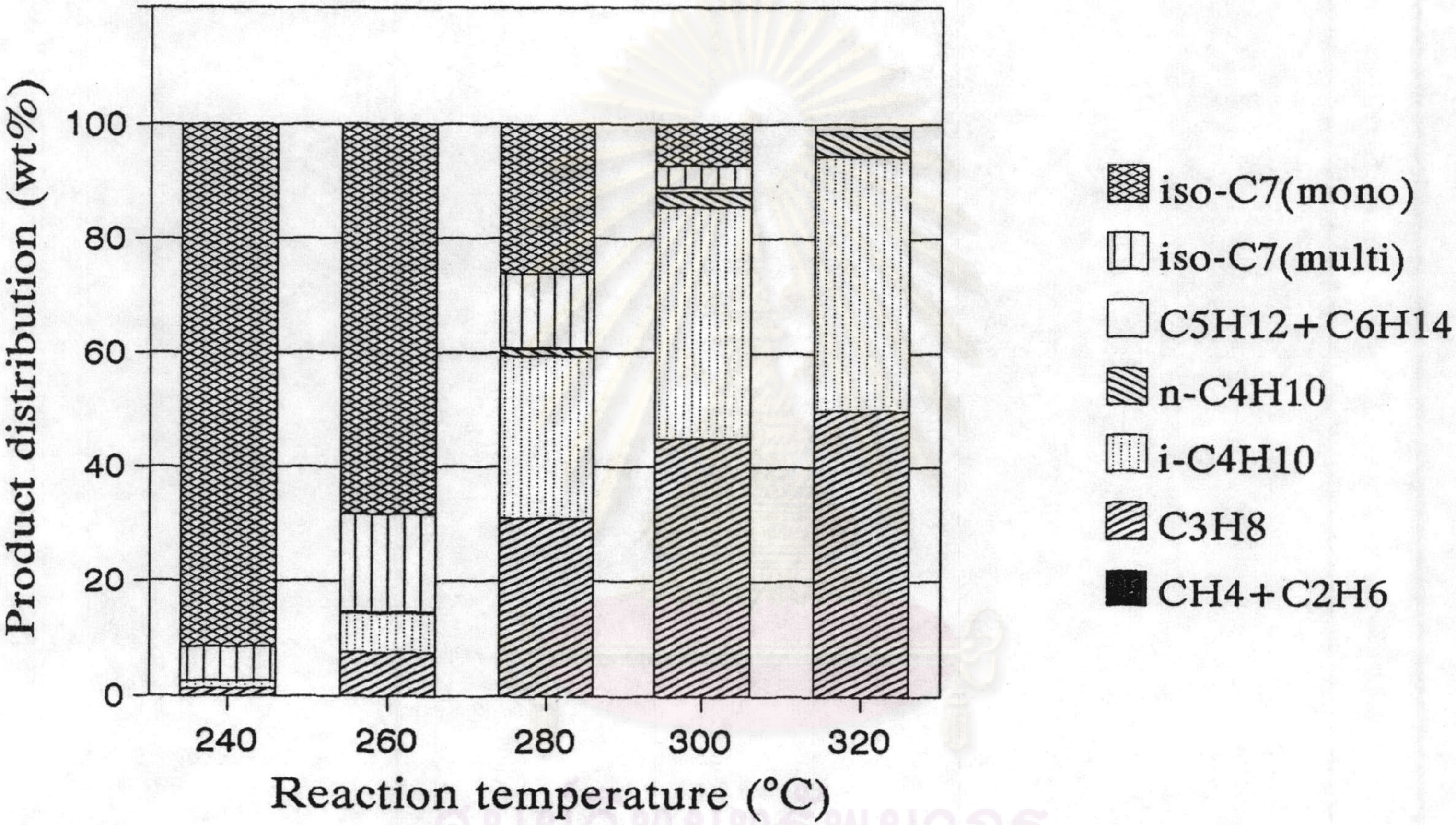


Figure 6-4 Product Distribution vs. Temperature at P = 10 bars; LHSV = 5.5 h^{-1} for 0.5 wt% Pt/USY Catalyst

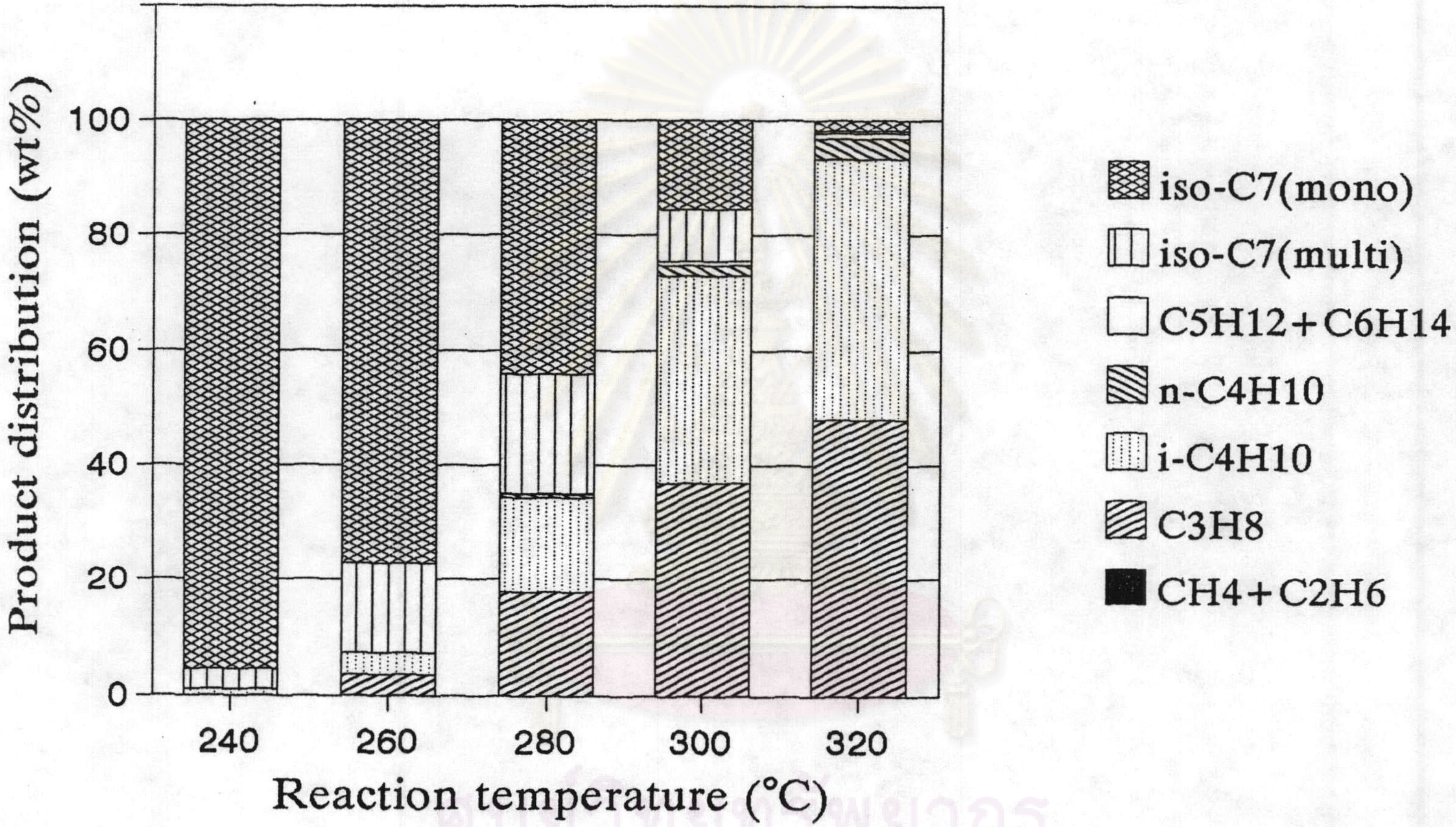


Figure 6-5 Product Distribution vs. Temperature at P = 20 bars; LHSV = 5.5 h^{-1} for 0.5 wt% Pt/USY Catalyst

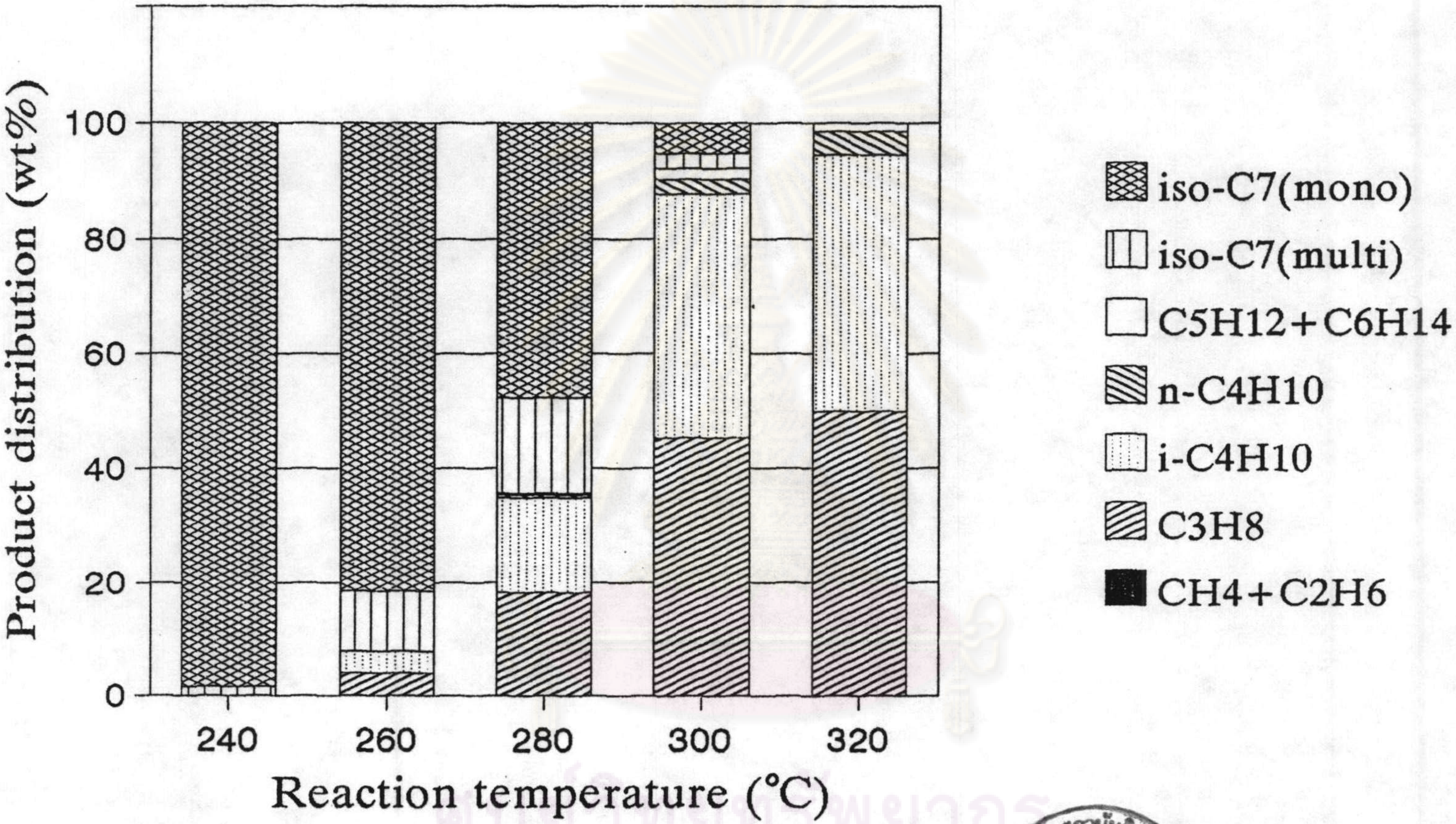


Figure 6-6 Product Distribution vs. Temperature at P = 30 bars; LHSV = 5.5 h^{-1} for 0.5 wt% Pt/USY Catalyst

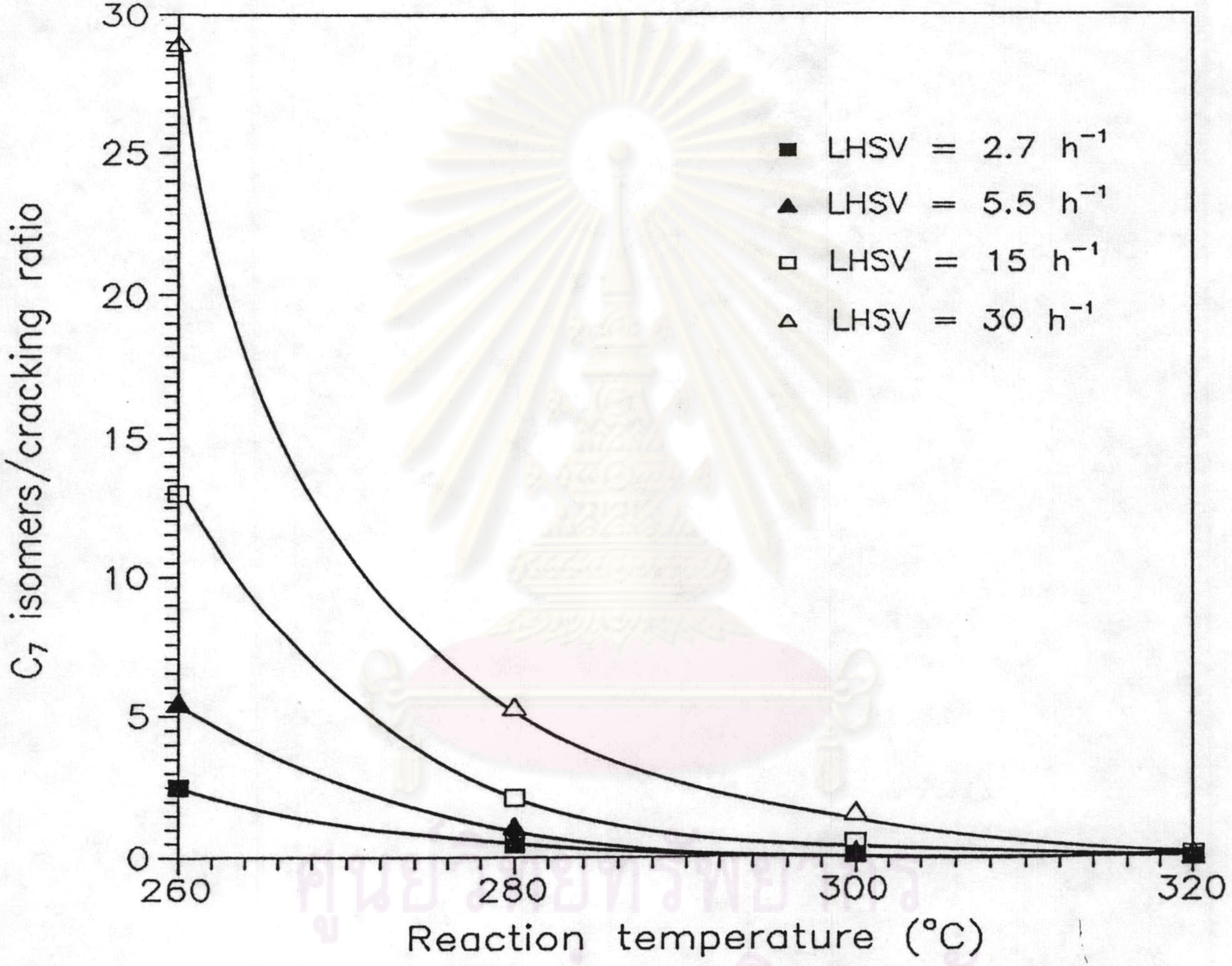


Figure 6-7 **Effect of Reaction Temperature on C_7 Isomers/Cracking Ratio for 0.5 wt% Pt/USY Catalyst**

increase in the yield of liquefied petroleum gas constituents (C_3 and C_4). This increase was more pronounced at temperature above 300°C, where the balance between the cracking and hydrogenation was shifted towards more cracking.

6.1.3 Effect of Reaction Temperature on Space Time Yield

As seen from **Table 6-3** and the corresponding **Figure 6-8**, the isomerization yield increased with temperature and then passed through a maximum beyond which increasingly the isomerized C_7-molecules were cracked. The yield of heptane isomers attained a maximum at 260°-280°C and decreased continuously as the reaction temperature increased. This decrease was noticeable at higher temperatures (320°C) where most of the heptane isomers cracked to lower ones (propane and butanes).

The main heptane isomers were 2- and 3-methylhexane (monobranched isomers). Similar results were also reported by other researchers (Sakai et al., 1975; Giannetto et al., 1986; Mahos et al., 1986).

The reaction temperature accelerated the cracking rate more than the hydrogenation rate. Data in **Figure 6-7** show that the cracking activity of the catalyst increased rapidly as the temperature rose. At temperatures higher than 280°C the isomerization activity of the catalyst started to fall behind. Therefore, the isomerization/cracking ratio decreased. In this research it is clear that, below 280°C the reaction was mainly hydrogenation while above 280°C the balance was shifted towards more cracking reactions.

Table 6-3 Effect of Temperature on the STY of iso-Heptane

Catalyst Type : 0.5 wt% Pt/USY

Space Velocity (LHSV) : 5.5 h^{-1}

Reaction Pressure : 5, 10, 20 and 30 bars

Temperature (^{o}C)	STY of iso-Heptane (g/cm^3-h)			
	P = 5 bars	P = 10 bars	P = 20 bars	P = 30 bars
240	0.95	1.04	0.76	0.58
260	2.23	2.23	1.94	1.50
280	2.18	1.33	2.22	1.98
300	1.13	0.49	0.89	0.25
320	0.23	0.02	0.04	0.00

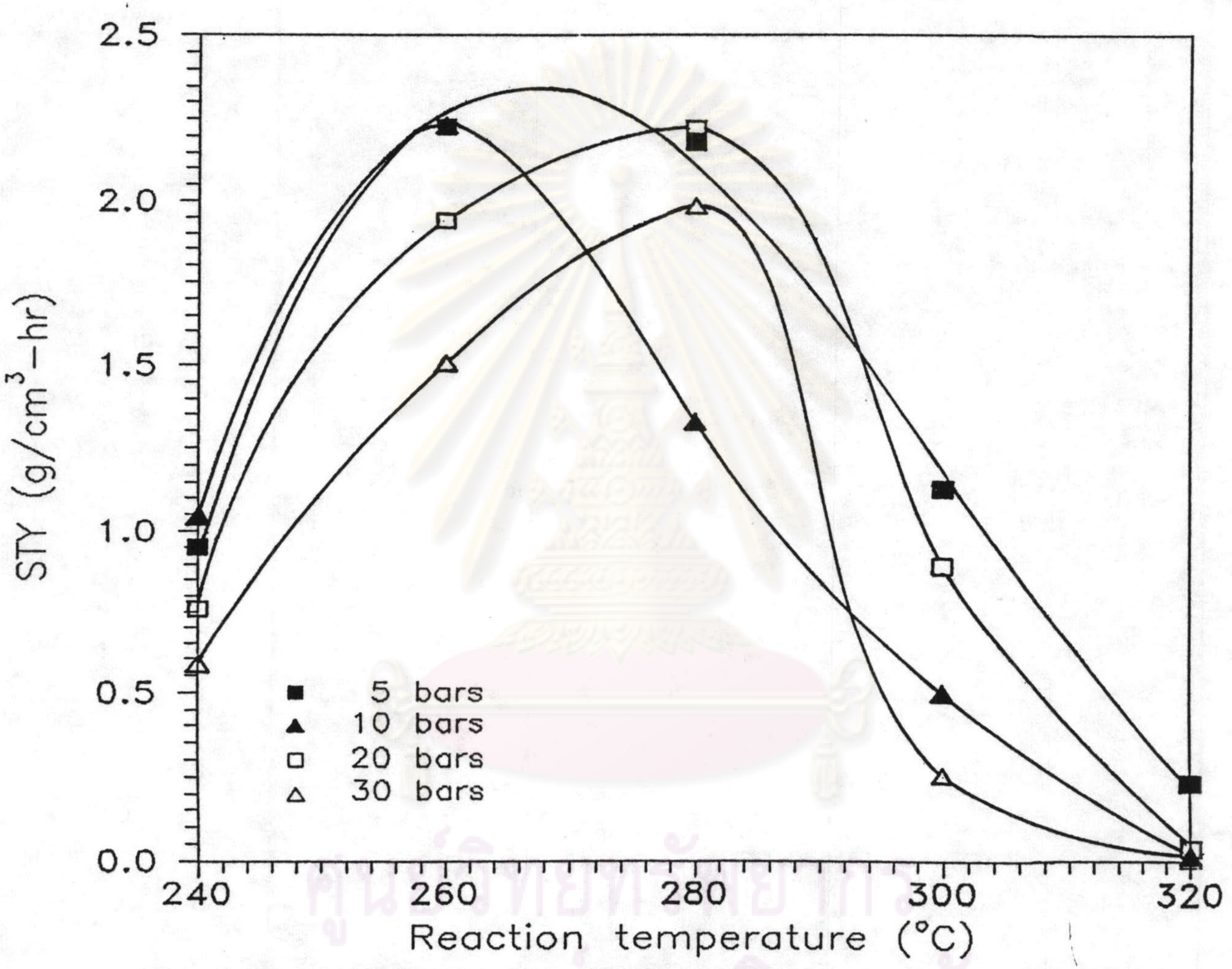


Figure 6-8 STY of i-C_7H_{16} vs. Temperature at P = 5, 10, 20 and 30 bars; LHSV = 5.5 h^{-1} for 0.5 wt% Pt/USY Catalyst

6.2 Effect of Reaction Pressure

6.2.1 Effect of Reaction Pressure on Total Conversion of n-Heptane

The effect of reaction pressure on the conversion of n-heptane in the presence of the 0.5 wt% Pt/USY catalyst was investigated at pressures from 5 to 30 bars and at five reaction temperatures, namely, 240,260,280,300 and 320°C. The data are given in **Table 6-1**. Comparison of the conversion of n-heptane as a function of the reaction pressure is shown in **Figure 6-1**.

At lower temperatures (240°-280°C) the effect of pressure on n-heptane conversion was significant. A lower reaction pressure seemed to give a higher n-heptane conversion than a higher pressure did, but this behavior was not so at higher temperatures, especially at 320°C where the effect of pressure was indistinguishable since almost all n-heptane was converted.

6.2.2 Effect of Reaction Pressure on iso-Heptane Selectivity

As seen from **Table 6-2** and **Figure 6-2**, the iso-heptane selectivity dropped as pressure increased while the reaction temperature ranged from 240 °C to 320 °C. **Figure 6-9** is a plot of the heptane isomers/cracking ratio against the reaction pressure in the range of temperature studied.

Within the reaction temperature range used in this study, the reaction pressure affected both cracking and hydrogenation activities to different extents. Its influence was evidently more

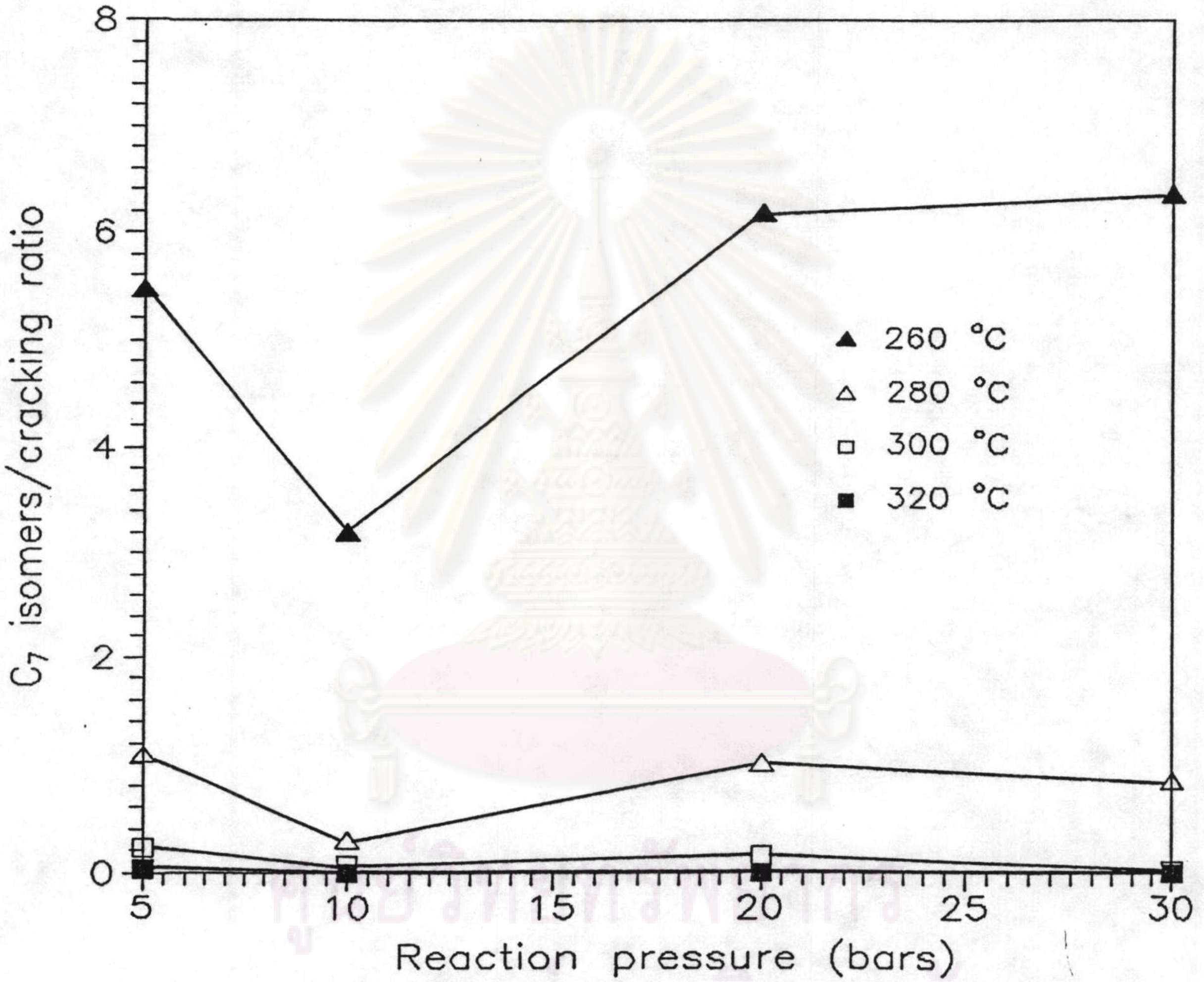


Figure 6-9 Effect of Reaction Pressure on C_7 Isomers/Cracking Ratio for 0.5 wt% Pt/USY Catalyst

significant on the hydrogenation activity at temperature of 260°C. At 260°C, the cracking activity of the catalyst was apparently low as compared with the relatively high hydrogenation activity of the catalyst. This means that the olefinic carbonium ions formed on the hydrogenation-dehydrogenation sites and isomerized on the acid sites were preferably saturated rather than being cracking further. As the reaction temperature went up to 280°C, both the hydrogenation and cracking sites of the catalyst were activated; hence more iso-heptane and cracked products were obtained.

It is obvious from **Figure 6-9** that C_7 isomerization/cracking ratio decreased as pressure increased from 5 to 10 bars, but the obtained results were reversed as pressure increased from 10 to 20 bars. Above 20 bars the effect of pressure was insignificant. The observed decrease in C_7 isomerization/cracking ratio may be due to catalyst deactivation resulting from long time on-stream operation.

In conclusion, it may be postulated that there is little efffect of the total pressure on the selectivity of the isomerization reaction up to conversion of 70 to 80%.

6.2.3 Effect of Reaction Pressure on Space Time Yield (STY)

The optimum STY of iso-heptane was affected by pressure, as revealed in **Table 6-3**. The corresponding results plotted in **Figure 6-8** show the effect of varying the reaction pressure from 5 to 30 bars on the STY of iso-heptane, while maintaining the other variables constant. The maximum value of STY of iso-heptane at 5 bars was essentially the same as those at 10 and 20 bars, but the corresponding optimum temperatures were different,i.e., at a low reaction pressure, the optimum temperature was low and as the pressure increased, the optimum temperature tended to shift to a higher value.

6.3 Effect of Liquid Hourly Space Velocity (LHSV)

6.3.1 Effect of Liquid Hourly Space Velocity on Total Conversion of n-Heptane

The experimental data are summarized in **Table 6-4** in order to illustrate the effect of space velocity on the total conversion of n-heptane.

The results plotted in **Figure 6-10** show the effect of varying the feed rate of n-heptane from 2.7 to 30 volumes per volume of catalyst per hour on the conversion of n-heptane, while maintaining the other variables constant. As the liquid space velocity of the feed increased, the contact time decreased, so the conversion of n-heptane decreased at constant reaction temperature. The magnitude of decrease in conversion against space velocity increase was smaller at the higher reaction temperatures due to the onset of hydrocracking reactions which became dominant when conversion of n-heptane exceeded 70 to 75 mole%. As the reaction temperature increased, hydrocracking reactions were accelerated so that smaller changes in conversion were observed against increase in liquid space velocity at higher temperatures than at lower reaction temperatures where isomerization

Table 6-4 Effect of Space Velocity on Total Conversion of n-Heptane

Catalyst Type : 0.5 wt% Pt/USY

Reaction Pressure : 5 bars

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

Temperature (^{o}C)	Conversion (%)			
	LHSV=2.7 h^{-1}	LHSV=5.5 h^{-1}	LHSV=15 h^{-1}	LHSV=30 h^{-1}
240	42.80	25.27	15.60	4.26
260	79.34	64.68	39.83	16.61
280	93.19	84.53	73.60	42.32
300	98.52	95.78	89.82	69.81
320	100.00	99.20	97.64	88.97

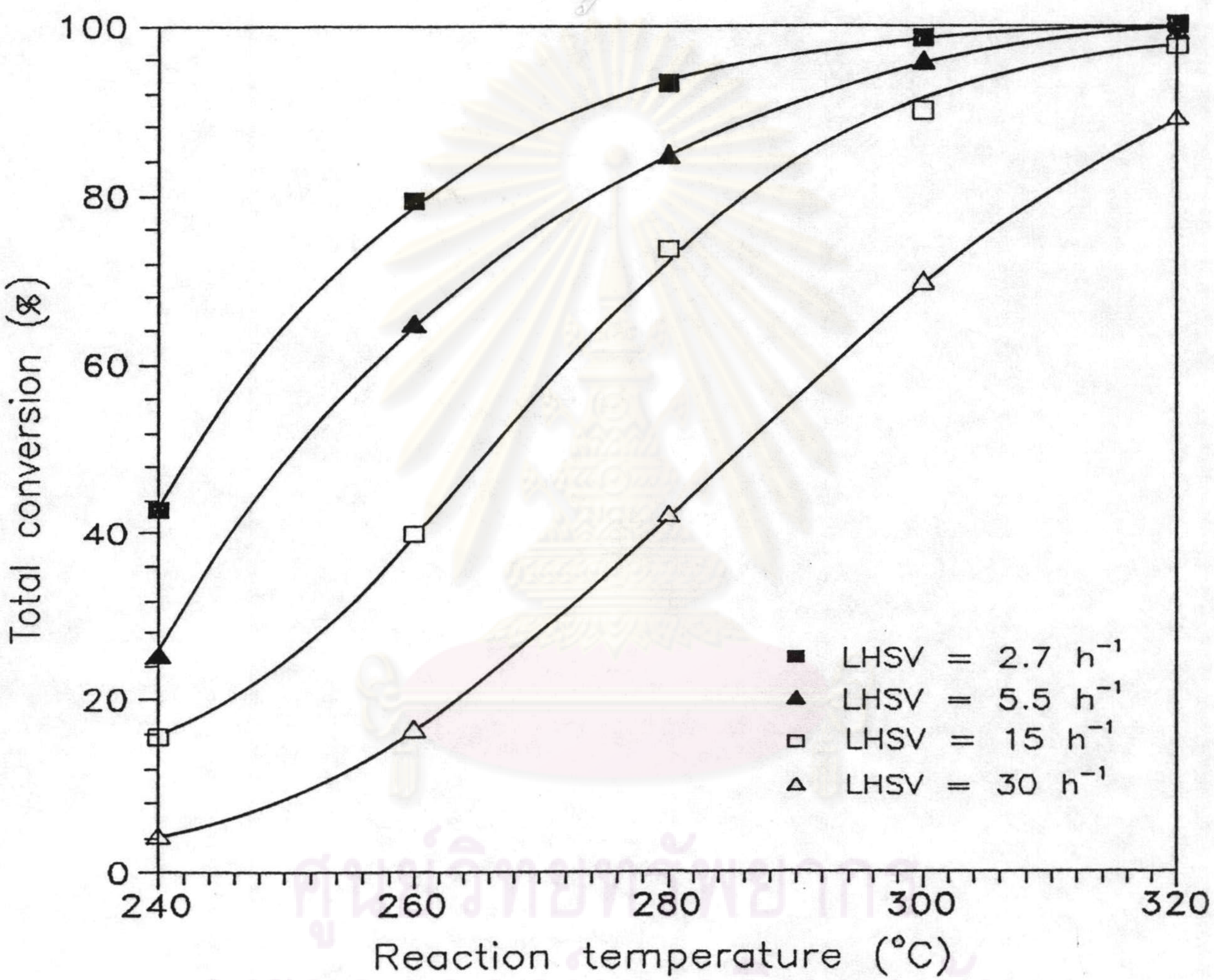


Figure 6-10 n-Heptane Conversion vs. Temperature at LHSV = 2.7, 5.5, 15 and 30 h^{-1}; P = 5 bars for 0.5 wt% Pt/USY Catalyst

to C_7 isomers was the only major reaction. This behavior was similar to that observed by several investigators (El-Kady et al., 1983; Mahos et al., 1986).

6.3.2 Effect of Liquid Hourly Space Velocity on iso-Heptane Selectivity

The effect of LHSV within the range of 2.7-30 v/v h^{-1} on the hydroisomerization of n-heptane was investigated at five reaction temperatures, namely, 240°, 260°, 280°, 300° and 320°C. The experimental data are summarized in **Table 6-5** and shown graphically in **Figure 6-11**. **Figure 6-12, Figure 6-3, Figure 6-13** and **Figure 6-14** show the product distribution as a function of the reaction temperature at fixed pressure of 5 bars for the LHSV of 2.7, 5.5, 15 and 30 h^{-1}, respectively.

Figure 6-7 shows the effect of reaction temperature on the C_7 isomerization/cracking ratio at a fixed pressure of 5 bars with LHSV of 2.7 to 30 h^{-1} as parameter. As the reaction temperature increased, the hydrocracking reaction was accelerated so that a decrease in the C_7 isomerization/cracking ratio was observed at a fixed contact time. On the other hand, as contact time was increased (lower LHSV), the heptyl carbonium species adsorbed at acid sites might further be cracked to light products, thus reducing the isomerization/cracking ratio. At lower reaction temperatures, isomerization to heptane isomers was the major reaction. The results were similar to those observed by other investigators (El-Kady et al., 1983; Mahos et al., 1986).

Table 6-5 Effect of Space Velocity on iso-Heptane Selectivity

Catalyst Type : 0.5 wt% Pt/USY

Reaction Pressure : 5 bars

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

Temperature (^{o}C)	iso-Heptane Selectivity (%)			
	LHSV=2.7 h^{-1}	LHSV=5.5 h^{-1}	LHSV=15 h^{-1}	LHSV=30 h^{-1}
240	97.40	100.00	100.00	100.00
260	83.21	91.61	96.29	98.30
280	49.54	68.67	81.10	91.40
300	12.54	31.31	50.91	76.31
320	0.00	6.29	16.15	30.35

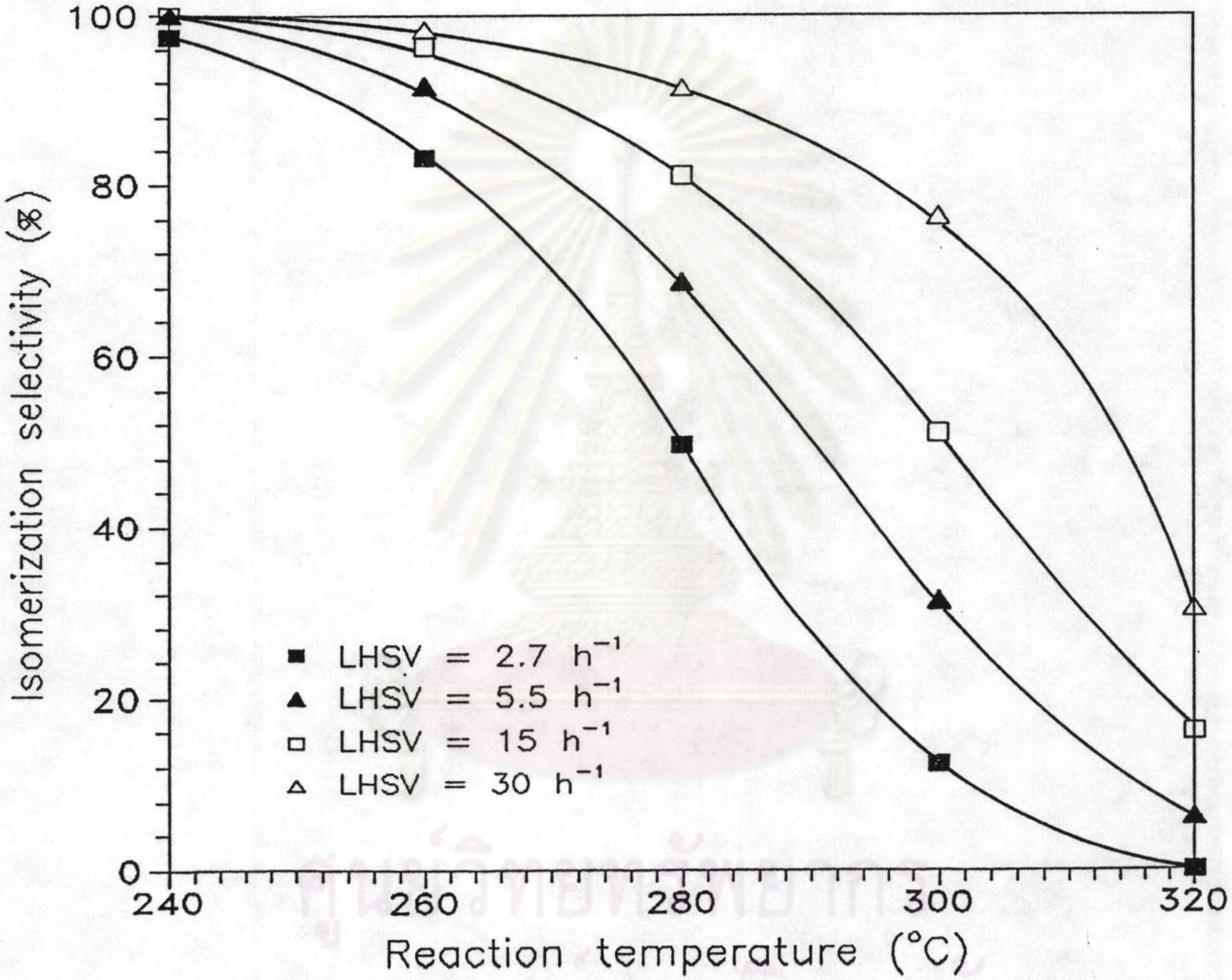


Figure 6-11 iso-C_7 Selectivity vs. Temperature at LHSV = 2.7, 5.5, 15 and 30 h^{-1}; P = 5 bars for 0.5 wt% Pt/USY Catalyst

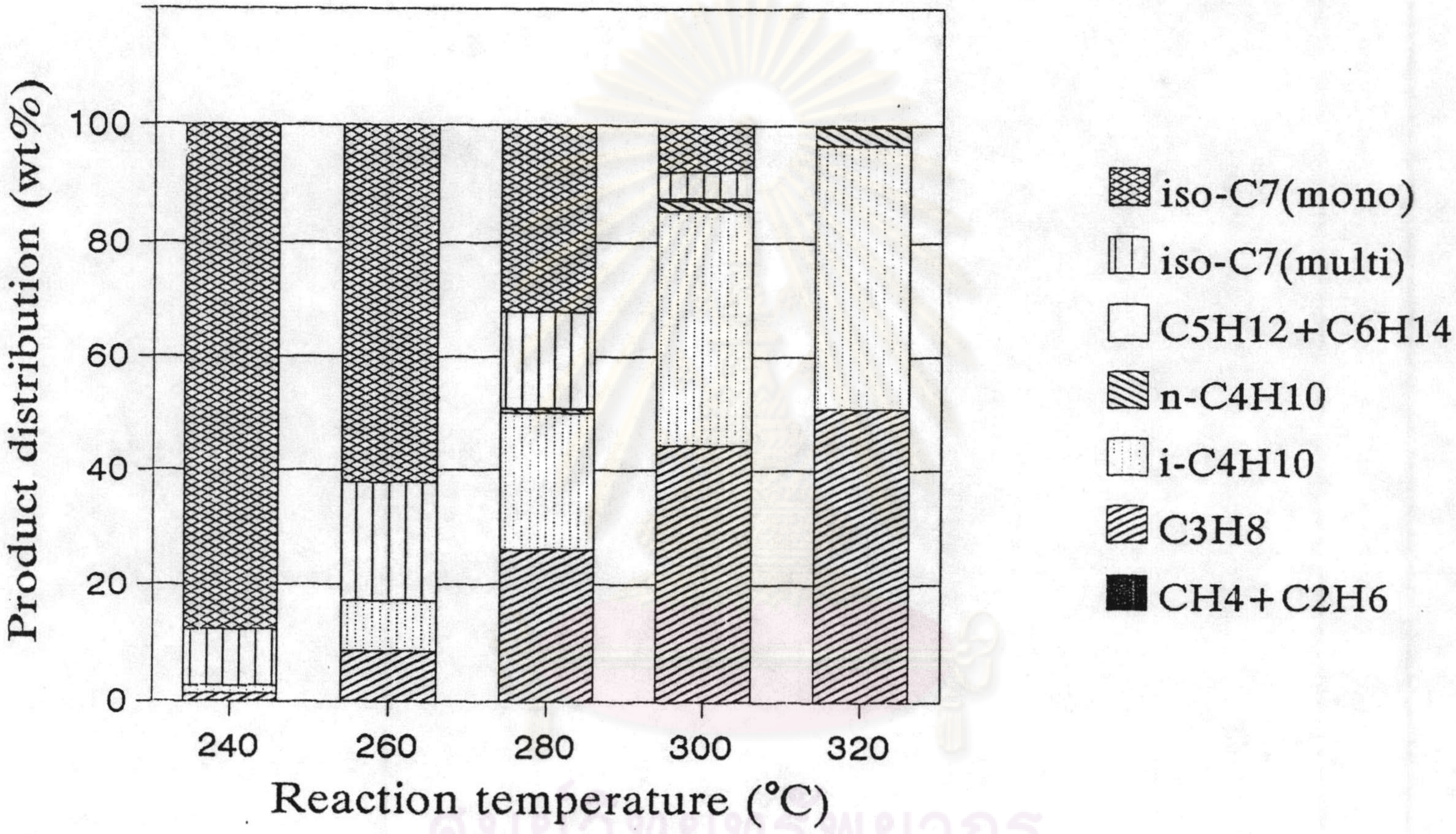


Figure 6-12 Product Distribution vs. Temperature at

P = 5 bars; LHSV = 2.7 h^{-1} for 0.5 wt%

Pt/USY Catalyst

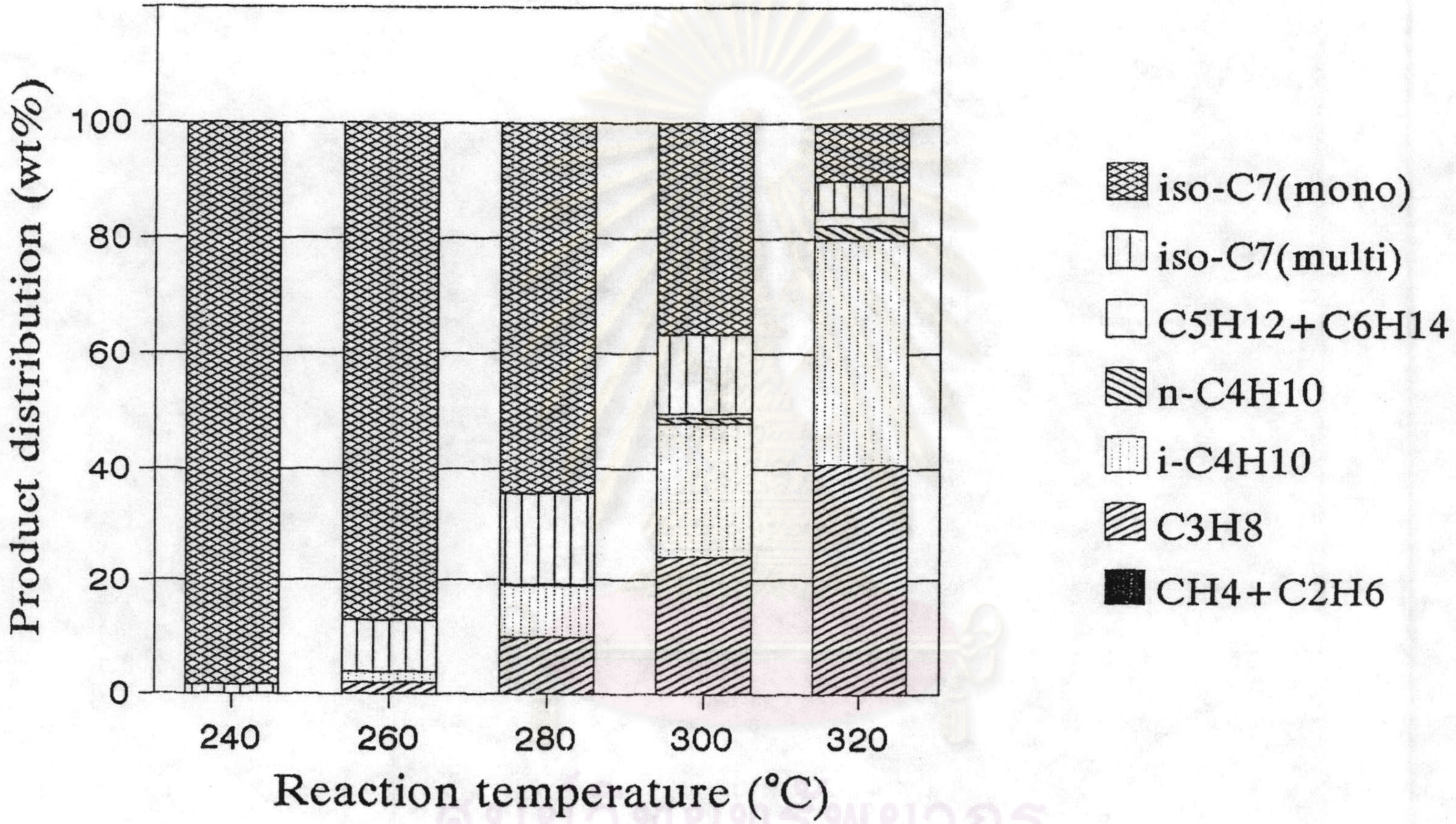


Figure 6-13 Product Distribution vs. Temperature at P = 5 bars; LHSV = 15 h^{-1} for 0.5 wt% Pt/USY Catalyst

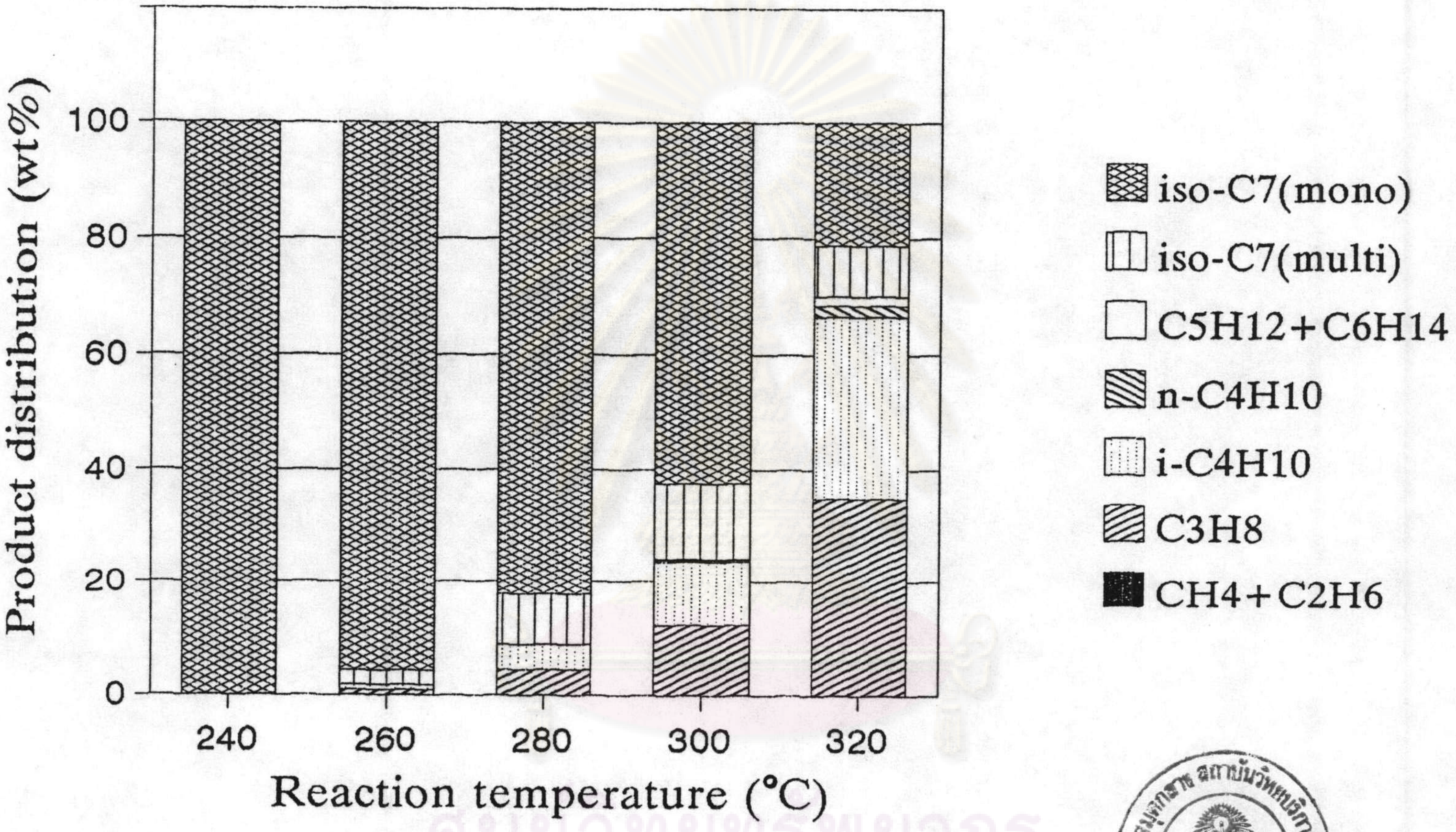


Figure 6-14 Product Distribution vs. Temperature at P = 5 bars; LHSV = 30 h^{-1} for 0.5 wt% Pt/USY Catalyst

At a relatively high LHSV the reaction temperature had a moderate effect on the reaction product distribution (see **Figure 6-14**). At a low LHSV, where the contact time was remarkably high, both the yield and distribution were strongly affected by raising the reaction temperature (see **Figures 6-3 and 6-12**). Analogously, the yield and product distribution were more strongly affected by contact time at higher reaction temperatures (300° and 320°C) than at lower temperatures; at 240°C, the influence of contact time was least (see **Figure 6-3, Figures 6-12 to 6-15**).

In conclusion, significant effect of liquid hourly space velocity was observed on the selectivity of the isomerization reaction.

6.3.3 Effect of Space Velocity on Space Time Yield

The effect of space velocity on the STY of iso-heptane is summarized in **Table 6-6** and shown graphically in **Figure 6-15**. The results clearly reveal that the higher the LHSV, the greater the maximum STY of iso-heptane and the higher the optimum temperature. In fact, the highest observed LHSV gave the global maximum STY of iso-heptane as 11 g/cm^3-h and the optimum temperature was 300°C.

6.4 The Pathway of the Reaction

In view of the type of products obtained, the reaction network involved should include isomerization reactions (to explain the formation of heptane isomers) and cracking reactions (because fractions shorter than C_7 were present in the products). The following

Table 6-6 **Effect of Space Velocity on the STY of iso-Heptane**

Catalyst Type : 0.5 wt% Pt/USY
Reaction Pressure : 5 bars
Space Velocity (LHSV) : 2.7, 5.5, 15 and 30 h^{-1}

Temperature (^oC)	STY of iso-Heptane (g/cm^3-h)			
	LHSV=2.7 h^{-1}	LHSV=5.5 h^{-1}	LHSV=15 h^{-1}	LHSV=30 h^{-1}
240	0.77	0.95	1.60	0.87
260	1.22	2.23	3.94	3.35
280	0.85	2.18	6.12	7.94
300	0.23	1.13	4.69	10.93
320	0.00	0.23	1.62	5.54

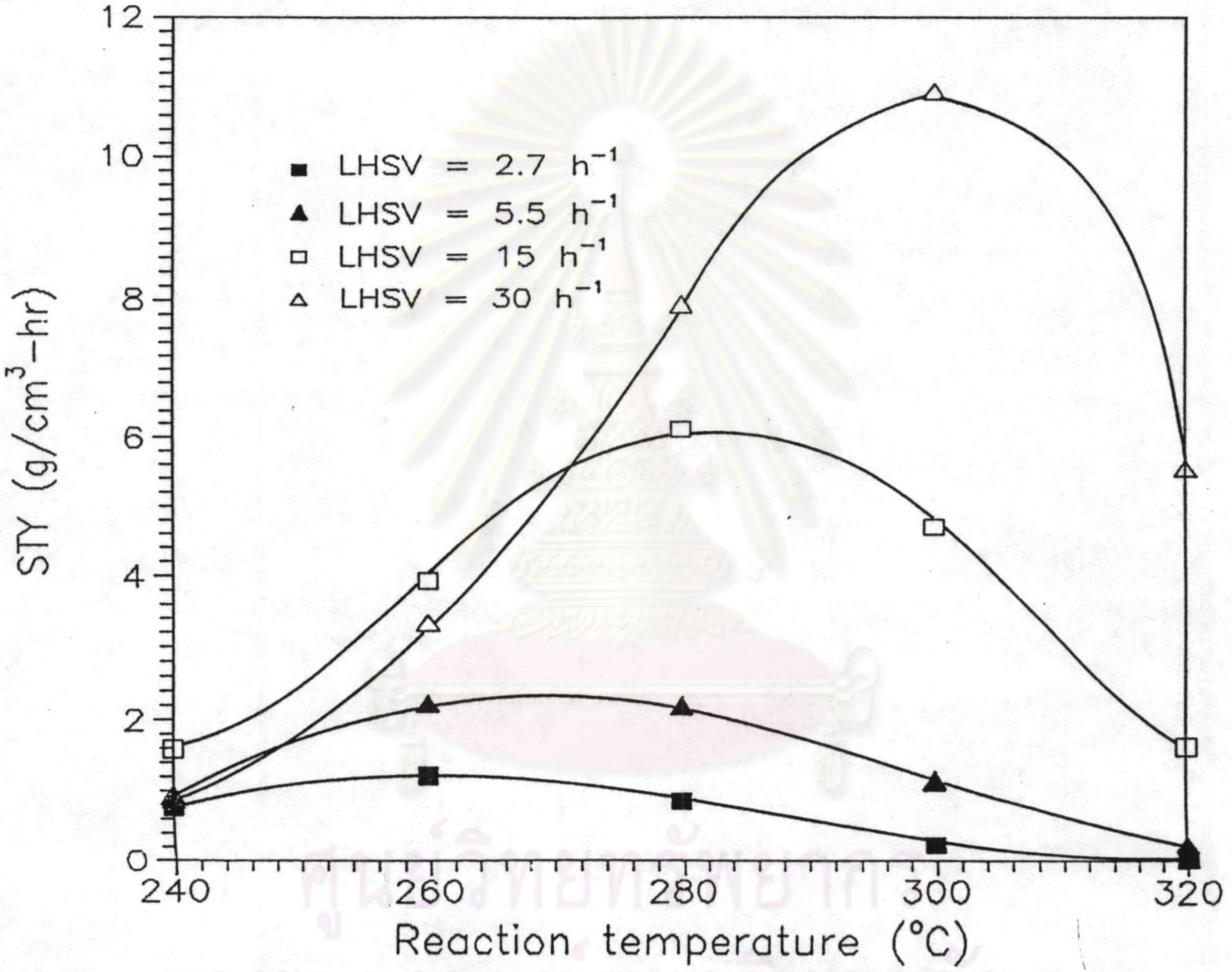
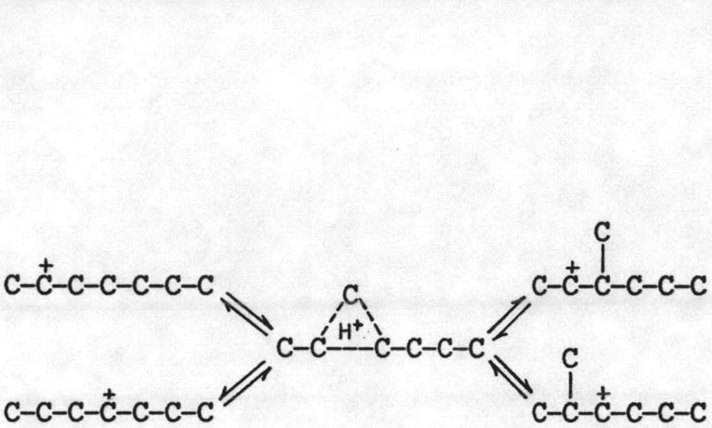


Figure 6-15 STY of i-C_7H_{16} vs. Temperature at LHSV = 2.7, 5.5, 15 and 30 h^{-1}; P = 5 bars for 0.5 wt% Pt/USY Catalyst

mechanisms were suggested by considering previous mechanisms proposed by several investigators as guidance (Sakai et al., 1975; Weitkamp, 1982; El-Kady et al., 1983; Giannetto et al., 1986).

6.4.1 Isomerization Reactions

It is generally accepted that the branching (isomerization) of olefins occurs through protonated cyclopropane intermediates (Chevalier et al., 1977): this is the mechanism for the isomerization of n-heptenes into methylhexenes (reactions 1 and 2), for that of methylhexenes into dimethylpentenes (reactions 3 and 5), and for that of dimethylpentenes into trimethylbutenes (reaction 6). The isomerization of n-heptenes into ethylpentenes, however, cannot directly be explained only by these intermediates. Since ethylpentane is an observed major product of n-heptane conversion, a new reaction intermediate, for example, cyclobutanic or, more likely, a rapid rearrangement by ethyl shift (reaction 7) should be considered to explain its formation. It is indeed well-known that rearrangements by alkyl shifts are much more rapid than those which occur through protonated cyclopropanes (5-30 times faster (Chevalier et al., 1977, cited by Giannetto et al., 1986)). The n-heptenes (resulting from n-heptane dehydrogenation) should have undergone two consecutive reactions before hydrogenation on metallic sites: first through protonated cyclopropane intermediates (reactions 1 and 2), then by ethyl shift (reaction 7).



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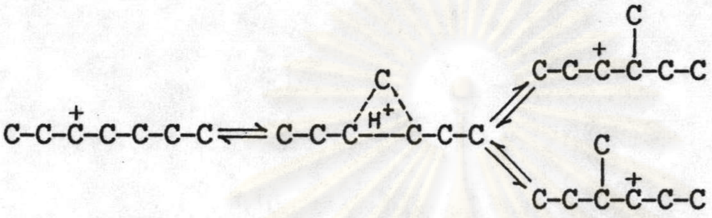

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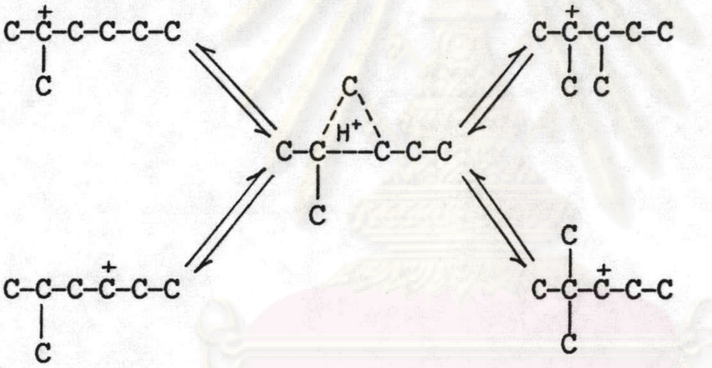

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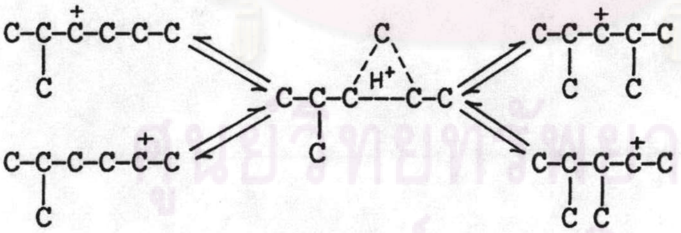

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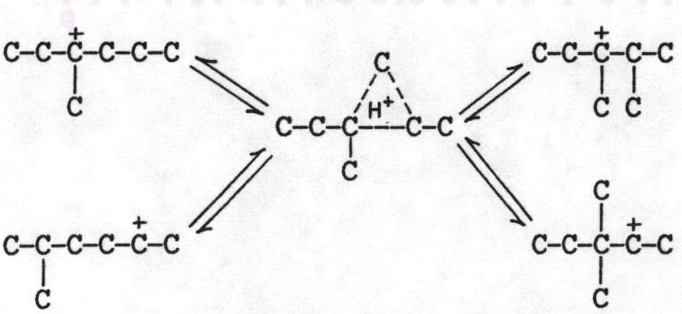

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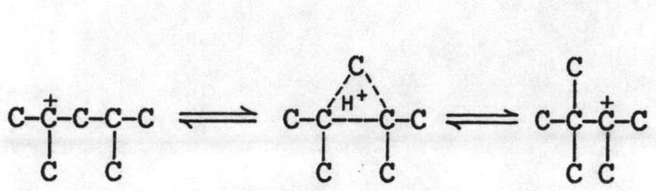
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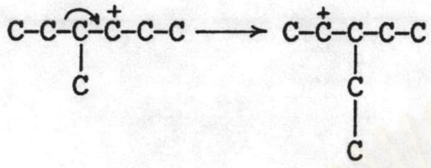
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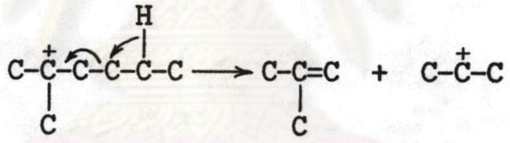
6.4.2 Cracking Reactions

On all the investigated catalysts the cracked products comprise essentially propane and isobutane in equimolar quantities. Isobutane can be formed by cracking of tertiary 2-methylhexanic or 2,2- and 2,4-dimethylpentanic carbonium ions.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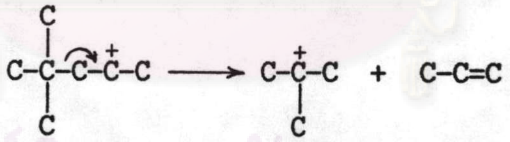
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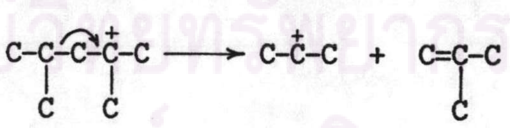
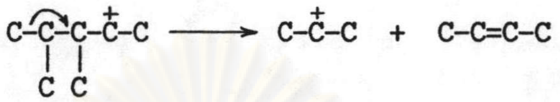
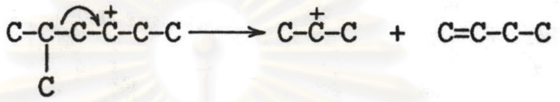

(10)

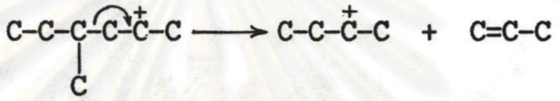
Moreover, the small quantity of n-butane formed indicates the cracking of carbonium ions that have a 2,3-dimethylpentanic skeleton (reaction 11). n-Butane can also be the result of the scission of 2-methylhexanic or 3-methylhexanic carbonium ions (reactions 12 and 13). These reactions, which like reaction 11 involve two secondary carbonium ions, probably occur at a slow rate, i.e., much more slowly than reactions 8, 9 and 10.



$$\mathrm{C\text{-}\underset{\underset{C}{|}}{C}\text{-}\underset{\underset{C}{|}}{C}\text{-}\overset{+}{C}\text{-}C \longrightarrow C\text{-}\overset{+}{C}\text{-}C + C\text{-}C{=}C\text{-}C} \quad (11)$$



$$\mathrm{C\text{-}\underset{\underset{C}{|}}{C}\text{-}C\text{-}\overset{+}{C}\text{-}C\text{-}C \longrightarrow C\text{-}\overset{+}{C}\text{-}C + C{=}C\text{-}C\text{-}C} \quad (12)$$



$$\mathrm{C\text{-}C\text{-}\underset{\underset{C}{|}}{C}\text{-}C\text{-}\overset{+}{C}\text{-}C \longrightarrow C\text{-}C\text{-}\overset{+}{C}\text{-}C + C{=}C\text{-}C} \quad (13)$$

Next it could be postulated that C_6 is formed through the interaction of propylene with propyl carbonium ion. However, a similar explanation could not fully account for the formation of C_5, i.e., through the interaction of propyl carbonium ion with ethylene, because of the small amounts of C_2 present in the product. It appears, thus, that the more likely mechanism for the formation of C_5 and particularly C_6 is through the intermediate propylene and butyl carbonium ion (reaction 13), or butylene and propyl carbonium ion (reactions 11 and 12). These intermediates can then react either with heptane or with heptyl carbonium ion to produce C_{10} or C_{11} carbonium ions, with subsequent hydrocracking to produce C_5 and C_6 hydrocarbons.