HYDROISOMERIZATION OF N-HEXANE USING 0.5 WT% Pt/USY CATALYST

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ABSTRACT

A 0.5 wt% Pt/USY catalyst, which had been found active for hydroisomerization of n-heptane, was investigated here for isomerization of n-hexane. The reaction conditions used were similar to those of n-heptane, except the pressure was fixed here at 5 bars. As expected, the experimental results revealed that the initial products formed in the isomerization of n-hexane as well as n-heptane were monobranched isomers, while some multibranched isomers and cracked products were formed by consecutive reactions. At the fixed pressure of 5 bars, the maximum space-time yield (STY) of both iso-hexane and iso-heptane occurred at a highest liquid hourly space velocity (LHSV) of 30 v/v h^{-1}, though the corresponding optimum temperatures were different. The optimum temperature for n-hexane isomerization at 320 °C was 20 °C higher than that for n-heptane.

1. INTRODUCTION

In a previous paper (1), it has been revealed that a 0.5 wt% platinum impregnated ultrastable Y zeolite (USY) is quite active and selective for the isomerization of n-heptane in the presence of hydrogen. Here, the activity of the 0.5 wt% Pt/USY catalyst was further investigated for the isomerization of n-hexane.

2. EXPERIMENTAL METHOD

The experimental apparatus, procedure and methods of analysis were previously described in the isomerization of n-heptane (2). The reactants used were n-hexane (Merck, 99% purity) and hydrogen gas (99.999% purity). The reactants were fed at the desired pressure to a tubular through-flow reactor without any further purification.

In the present investigation the reaction pressure and the hydrogen-to-hydrocarbon molar ratio were maintained constant at 5 bars and 10:1, respectively. The reaction temperature and space velocity was varied within the range of 240°-320°C and 2.7-30 v/v h^{-1}, respectively.

3. RESULTS AND DISCUSSION

3.1 Effect of Reaction Temperature

The effects of temperature and space velocity on the conversion of n-hexane and on the space-time yield of C_6 isomerized products are summarized in Tables 1 and 2, respectively. The molar conversion of n-hexane based on the feed is plotted as a function of the reaction temperature in Figure 1. The data show that under the conditions investigated the conversion of n-hexane commenced at 240° to 250°C and increased remarkably as temperature increased. The effect of reaction temperature on the total conversion was most notable in the temperature range of 280°-300°C.

The isomerization selectivity of n-hexane was quite independent of the total conversion of n-hexane. The isomerization selectivity was close to 100% at low conversion levels (see Figure 2 and Table 3). This indicates the absence of direct cracking of n-hexane.

Figures 3 to 6 show the product distribution as a function of the reaction temperature at 5 bars for the space velocities of 2.7, 5.5, 15 and 30 h^{-1}, respectively. As revealed in these figures, the major products formed in the presence of this catalyst, up to the level of 60 to 75% conversion of n-hexane, were primarily hexane isomers. The main hexane isomers were monobranched isomers. Multibranched isomers and cracked products were formed via consecutive reactions. The product distribution of the iso-hexanes was markedly dependent on the degree of conversion. At low conversions iso-hexanes with a single branching, i.e., 2-methylpentane and 3-methylpentane were predominant. At higher conversions the content of multibranched hexane isomers increased.

At n-hexane conversion above 65%, hydrocracking reactions became prominent. As shown in Figures 3 to 6, demethylation to form methane and iso- and n-pentanes occurred together with central cracking of n-hexane to form two molecules of propane. As the hydrocracking became more severe, demethylation of pentanes also occurred to yield iso- and n-butanes, propane and ethane. Products having a carbon number exceeding that of the feed were not detected throughout this study.

According to Ciapetta and Hunter (3), there was little or no effect of the molar ratio of hydrogen to hydrocarbon on the isomer yield at the same conversion level of n-hexane. Thus, provided hydrocracking be negligible, and since hydrogen was not consumed during the isomerization reaction, this catalyst should show a high selectivity for the isomerization of n-hexane even at low molar ratios of hydrogen to hydrocarbons.

As seen from Table 2 and the corresponding Figure 7, the space-time yield (STY) of hexane isomers increased with temperature but there existed some maximum temperature above which the isomerized C_6-molecules were increasingly cracked. At low space velocities (2.7 and 5.5 h^{-1}), STY of hexane isomers attained a maximum around 300°C and decreased as the reaction temperature further increased due to the onset of hydrocracking reactions which became prominent at high temperatures. At high space velocities (15 and 30 h^{-1}), STY of the C_6 isomerized products increased as temperature increased up to 320°C. This may be explained that the C_6 isomerized products occurred had not enough time to undergo other consecutive reactions such as hydrocracking. However, it was expected that if reaction temperature was further raised, say above 400°C, the observed trend should be similar to the case of low LHSV.

3.2 Effect of Liquid Hourly Space Velocity (LHSV)

Table 1 also reveals the effect of space velocity on the total conversion of n-hexane. The corresponding Figure 1 shows the effect on the conversion of n-hexane of varying the space velocity of n-hexane from 2.7 to 30 liquid volumes per volume of catalyst per hour, while maintaining the other variables constant. As the liquid hourly space velocity (LHSV) of the feed increased, the contact time inversely decreased, so the conversion of n-hexane decreased at a constant reaction temperature, namely, 240°, 260°, 280°, 300° and 320°C. At a very high LHSV, the reaction temperature had less effect on the reaction product distribution (see Figure 6). At a low LHSV, where the contact time was remarkably high, the product distribution was moderately affected by the reaction temperature (see Figures 3 to 5).

The effect of LHSV on the STY of iso-hexane is summarized in Table 2 and shown graphically in Figure 7. The results clearly reveal that the higher the LHSV, the greater the maximum STY of iso-hexane and the higher the optimum temperature. Within the range of the experimental conditions studied, the highest LHSV (30 h^{-1}) gave a global maximum STY of iso-hexane as 11.53 g/cm^3-h and the optimum temperature was 320°C at 5 bars.

3.3 Hydroisomerization of n-Hexane vs. n-Heptane

Under the reaction conditions studied, the 0.5 wt% Pt/USY catalyst was found to be quite active and highly selective for the isomerization of both n-hexane and n-heptane.

It was found that, as the carbon number increased, the temperature required to obtain the same conversion level decreased remarkably. For example, at 50 mole% conversion, the required temperatures were 279°C for n-hexane and 251°C for n-heptane (LHSV = 5.5 h^{-1}), which is approximately 30°C lower. The increase in reactivity with an increase in the carbon number was similar to that observed for the catalytic cracking of these n-paraffins in the presence of a cracking catalyst (3).

Experimental data presented previously on-n-heptane (1) and on n-hexane here (Figures 3 to 6) reveal that the initial products formed in the isomerization of n-hexane and n-heptane are the methyl isomers, with n-hexane isomerizing to 2- and 3-methylpentanes, and n-heptane to 2- and 3-methylhexanes. These results substantiate the conclusion of Evering and Waugh (4) that the isomerization reaction occurs in a stepwise manner.

At the fixed pressure of 5 bars, the maximum STY of both iso-hexane and iso-heptane occurred at the same highest LHSV of 30 h^{-1}, but the corresponding optimum temperatures were different. The optimum temperature at 320°C for n-hexane isomerization was 20°C higher than that for n-heptane.

4. CONCLUSIONS

It may be concluded that, 0.5 wt% platinum on ultrastable Y zeolite was active and highly selective for hydroisomerization of n-hexane. The experimental results revealed that the initial products formed in the isomerization of n-hexane was monobranched isomers. At 5 bars, the maximum STY of iso-hexane (11.53 g/cm^3-h) occurred at the highest LHSV of 30 v/v h^{-1}. The optimum temperature for n-hexane isomerization was 320°C.

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Table 1 Effects of Temperature and Space Velocity on Total Conversion of n-Hexane (P = 5 bars)

Temperature (°C)	Conversion (%)			
	LHSV = 2.7 h^{-1}	LHSV = 5.5 h^{-1}	LHSV = 15 h^{-1}	LHSV = 30 h^{-1}
240	9.48	6.41	3.19	1.61
260	31.08	23.40	10.62	5.27
280	55.46	52.37	25.64	16.28
300	78.25	74.57	45.64	40.49
320	80.97	80.09	59.66	60.47

Table 2 Effects of Temperature and Space Velocity on the STY of iso-Hexane (P = 5 bars)

Temperature (°C)	STY of iso-Hexane (g/cm^3-h)			
	LHSV = 2.7 h^{-1}	LHSV = 5.5 h^{-1}	LHSV = 15 h^{-1}	LHSV = 30 h^{-1}
240	0.17	0.23	0.32	0.32
260	0.55	0.85	1.05	1.04
280	0.99	1.90	2.53	3.22
300	1.36	2.63	4.41	8.00
320	1.32	2.44	4.84	11.53

Table 3 Effects of Temperature and Space Velocity on iso-Hexane Selectivity (P = 5 bars)

Temperature (°C)	iso-Hexane Selectivity (%)			
	LHSV = 2.7 h^{-1}	LHSV = 5.5 h^{-1}	LHSV = 15 h^{-1}	LHSV = 30 h^{-1}
240	100.00	100.00	100.00	100.00
260	100.00	100.00	100.00	100.00
280	100.00	100.00	100.00	100.00
300	97.99	97.47	97.82	100.00
320	91.71	84.23	82.16	96.47

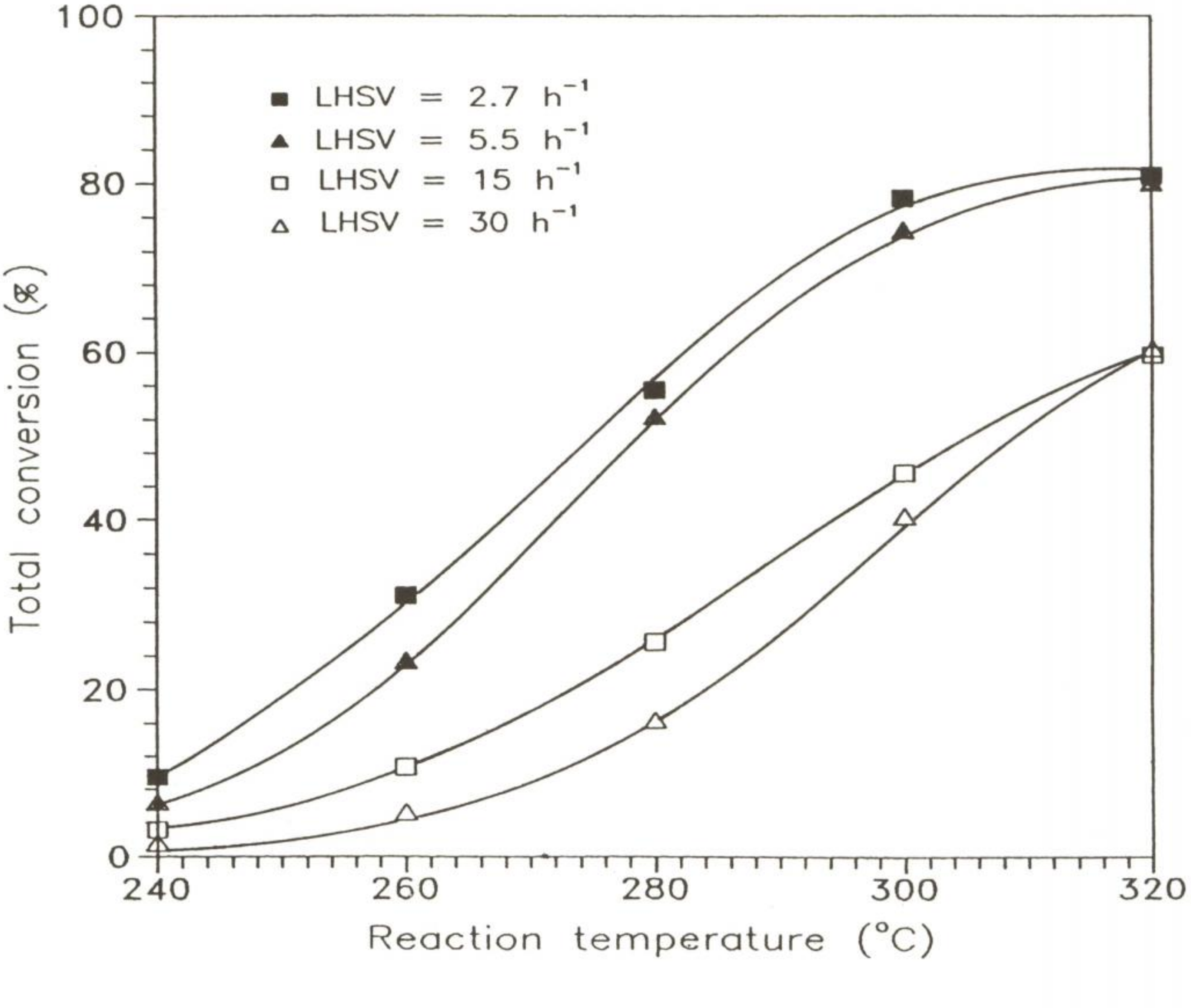

Figure 1 n-Hexane Conversion vs. Temperature at LHSV = 2.7, 5.5, 15 and 30 h^{-1}; P = 5 bars for 0.5 wt% Pt/USY Catalyst

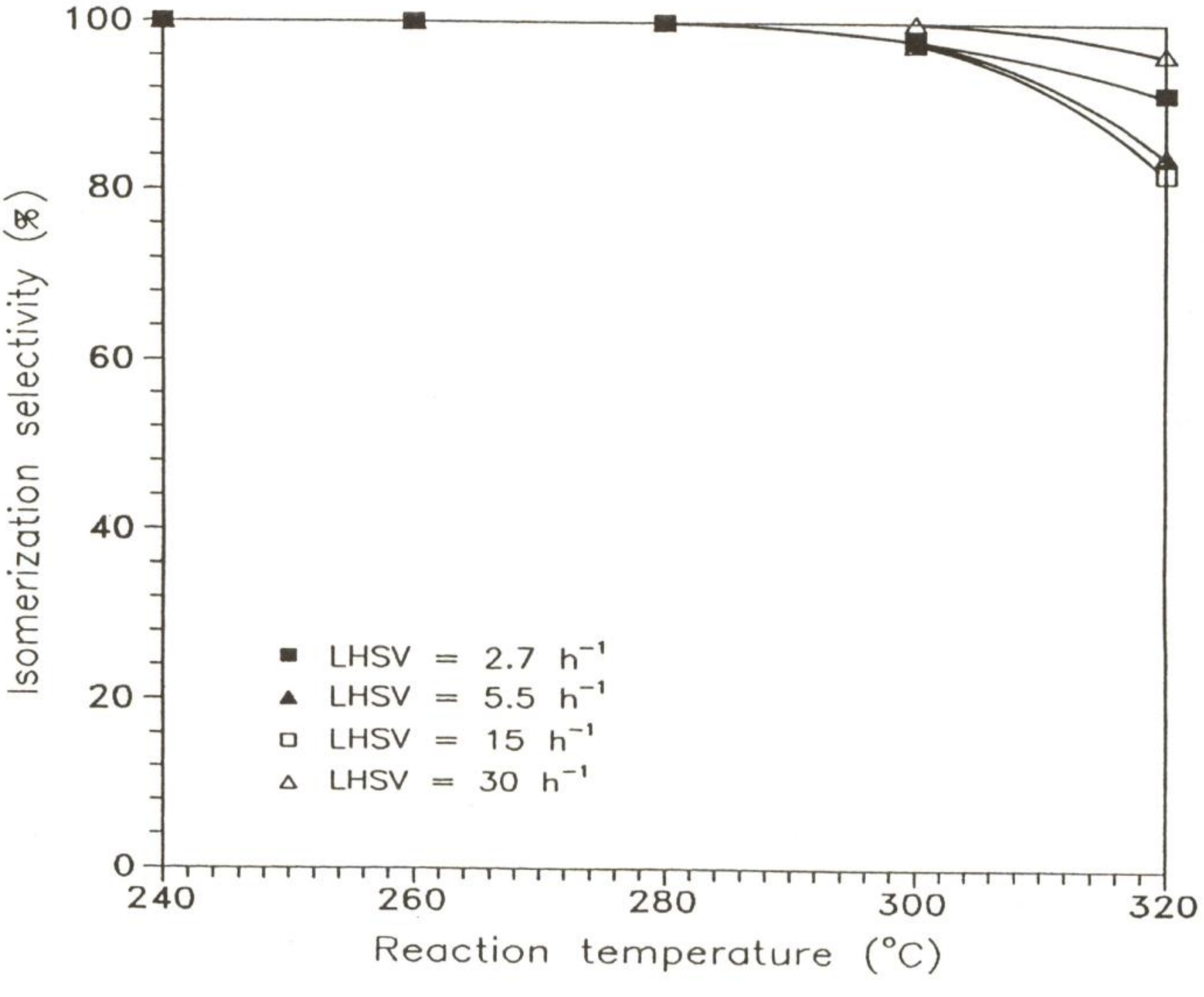

Figure 2 iso-C_6 Selectivity vs. Temperature at LHSV = 2.7, 5.5, 15 and 30 h^{-1}; P = 5 bars for 0.5 wt% Pt/USY Catalyst

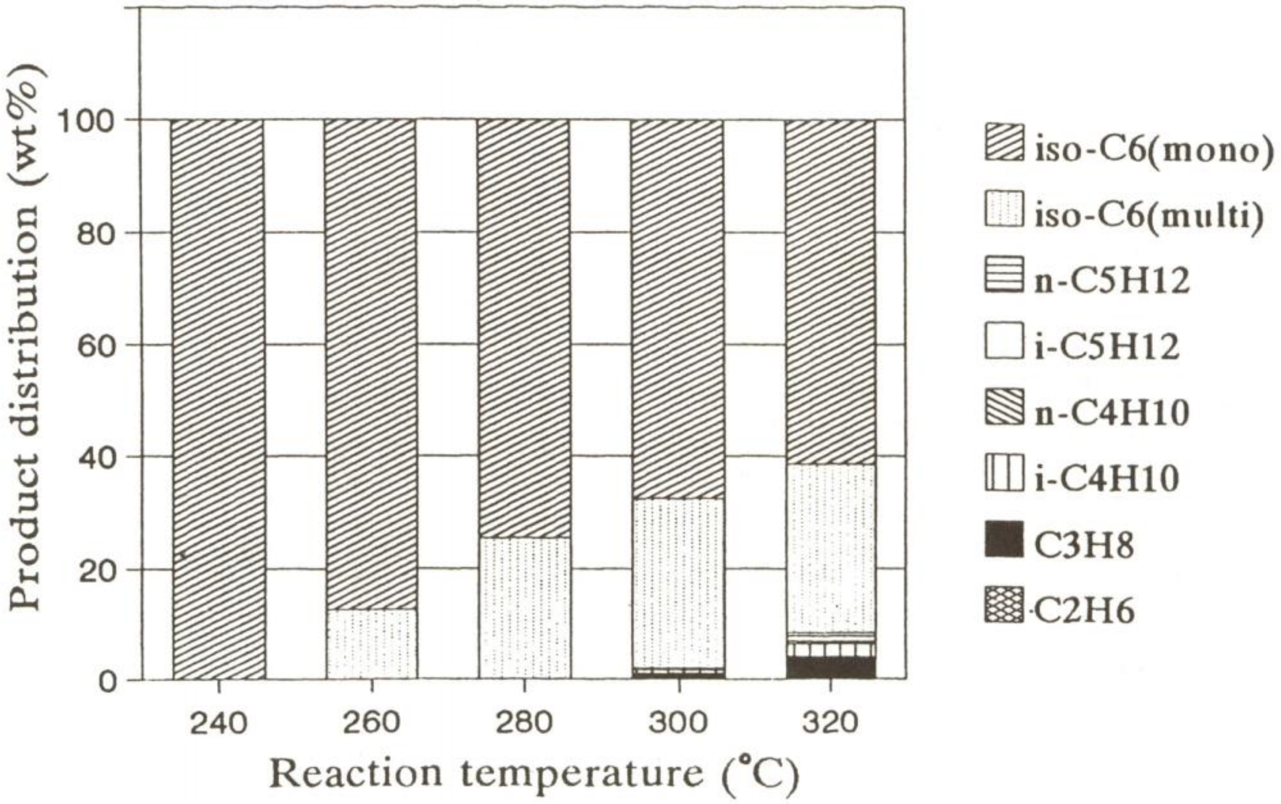

Figure 3 Product Distribution vs. Temperature at P = 5 bars; LHSV = 2.7 h^{-1} for 0.5 wt% Pt/USY Catalyst (n-Hexane as a feedstock)

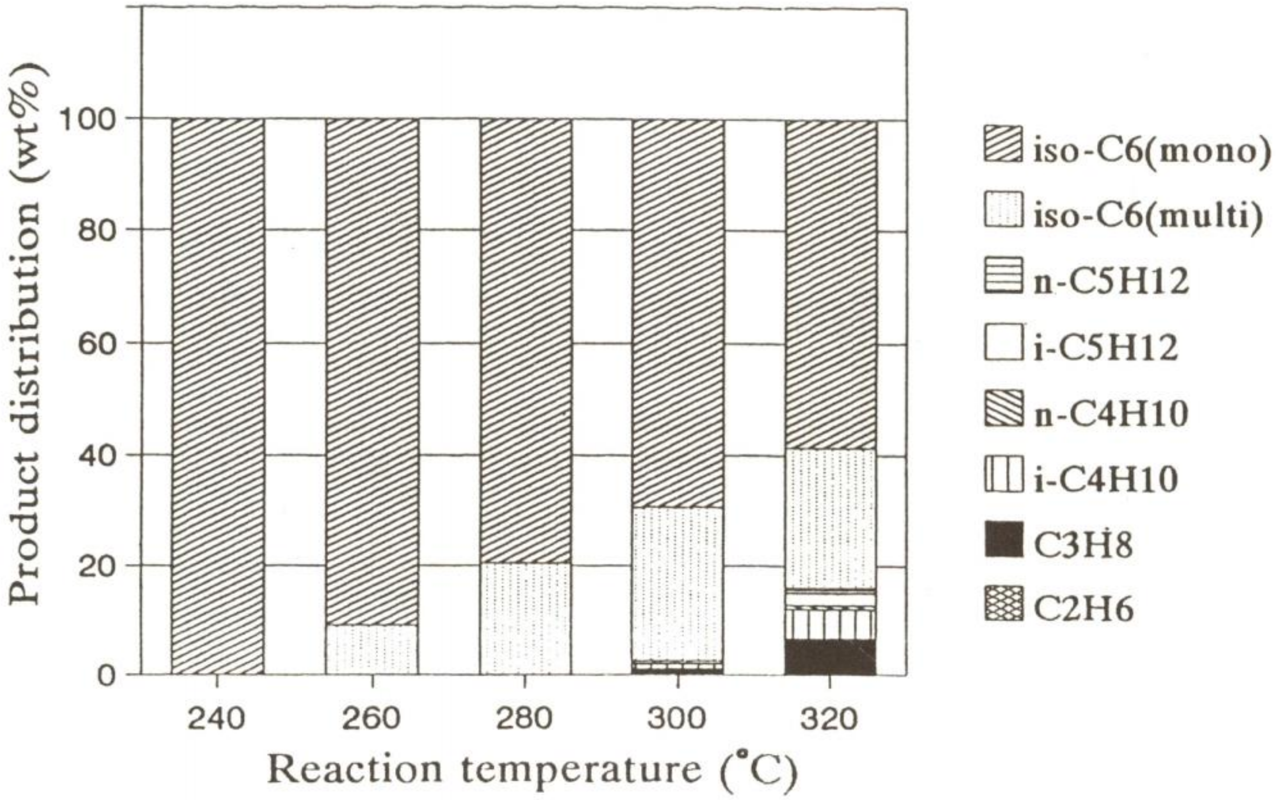

Figure 4 Product Distribution vs. Temperature at P = 5 bars; LHSV = 5.5 h^{-1} for 0.5 wt% Pt/USY Catalyst (n-Hexane as a feedstock)

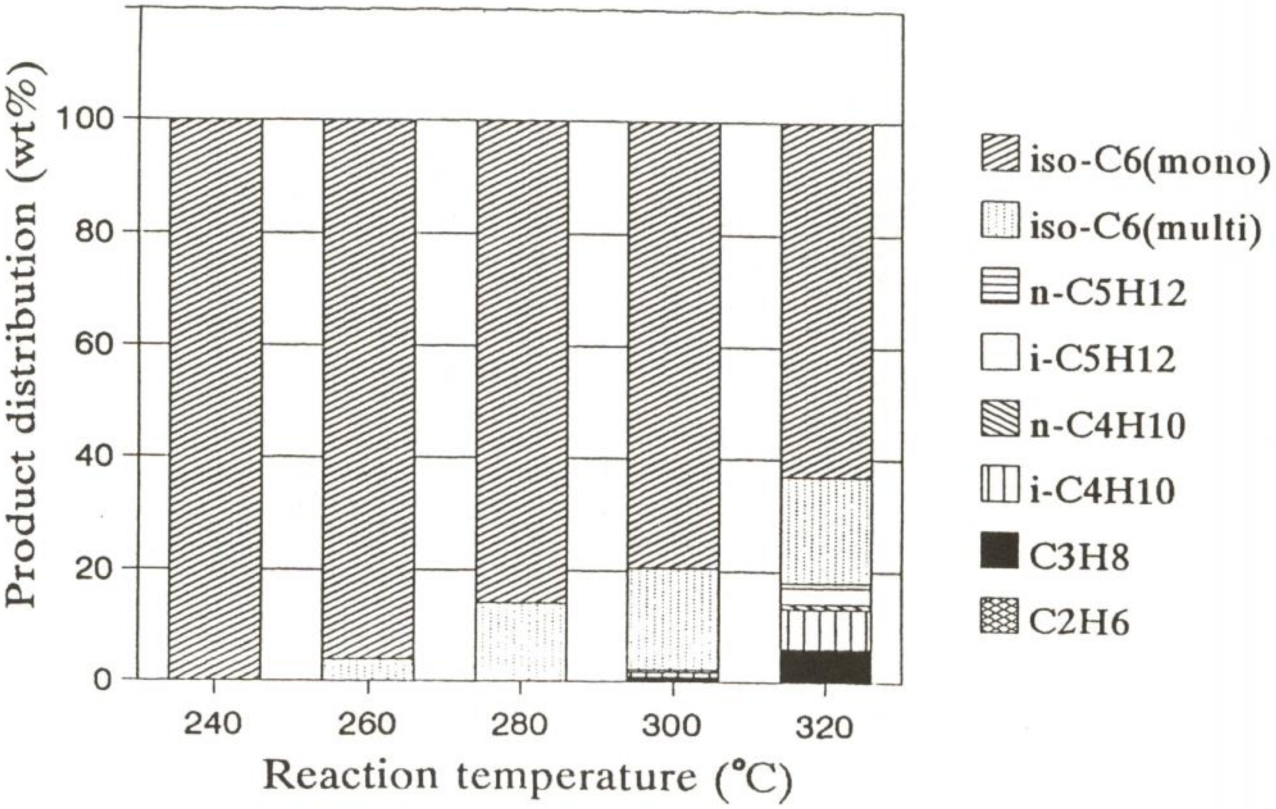

Figure 5 Product Distribution vs. Temperature at P = 5 bars; LHSV = 15 h^{-1} for 0.5 wt% Pt/USY Catalyst (n-Hexane as a feedstock)

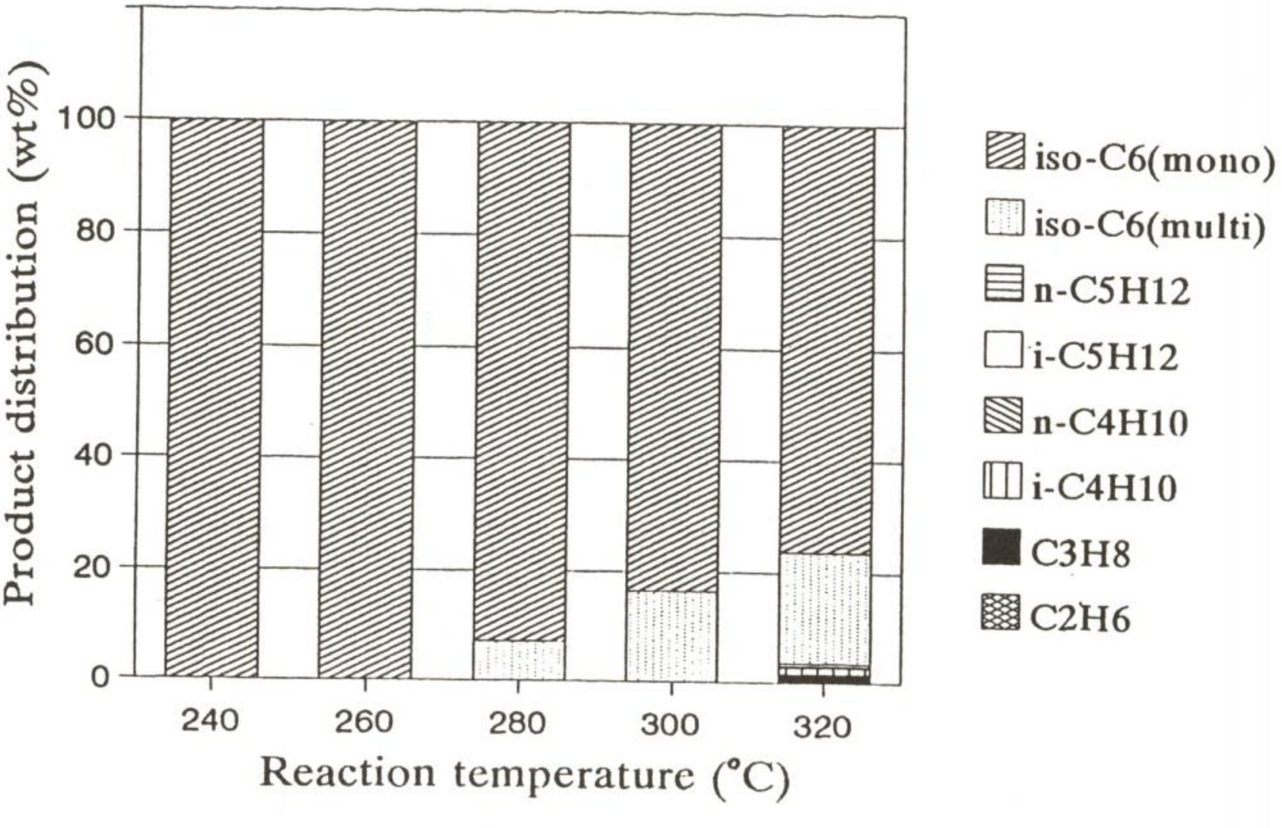

Figure 6 Product Distribution vs. Temperature at P = 5 bars; LHSV = 30 h^{-1} for 0.5 wt% Pt/USY Catalyst (n-Hexane as a feedstock)

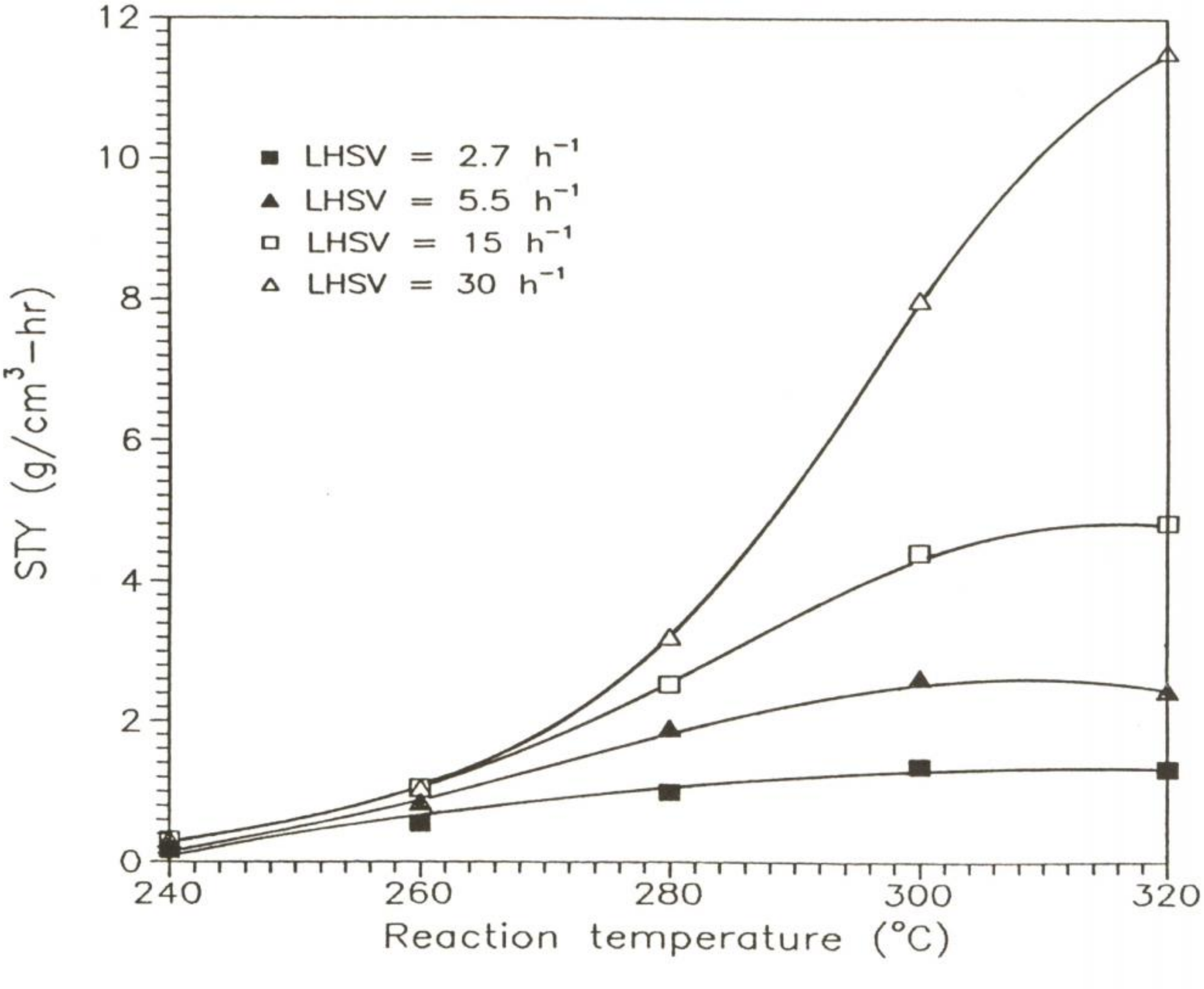

Figure 7 STY of i-C_6H_{14} vs. Temperature at LHSV = 2.7, 5.5, 15 and 30 h^{-1}; P = 5 bars for 0.5 wt% Pt/USY Catalyst