

of methanol, Chang and Silvestri. (1977). In that study the liquid product increased until about 623 to 673 K where the production slightly decreased. This drop in liquid production was probably due to the heightened cracking effect of the catalyst. However this trend may have been reversible at even higher temperatures, i.e. temperatures high enough to cause small normal paraffins to react. This shifting in the smaller products did however give an insight in how a chosen fraction of a given liquid could be more selectively chosen. Since this was consistent throughout most of the experiments the temperature effects could perhaps be used to roughly estimate the needed reaction temperature in order to obtain high selectivities of selected compounds.

Space Velocity Effects

The effect of the space velocity was shown to be of a lesser importance than some of the other process variables studied.

The effect of the space velocity was studied again in two ways. The first method arose from the design of the factorial experiments. The second method was to pick a compound, n-heptane, and at increasingly higher flow rates obtain the product distributions. These distributions would possibly show any trend in the effect of the space velocity. The space velocity calculated took into account the entire catalyst, including the binder.

The first method compared the product distributions of several feeds over both the nickel and zinc ZSM-5. In Figures 19 and 20 the product distributions for differing space times for passing n-heptane over Ni-ZSM-5 are shown. The aromatic fraction increased with decreasing space time. In both cases most of the aromatic differences were found in the propane content. However, the differences were only about 5 to 7 weight percent; not a large difference.

More comparisons using the factorial design experiments were shown in Figure 21. Figure 21 shows again a switching from the aromatic yield to propane yield of 4 weight percent over the Zn-ZSM-5 when using the Fischer-Tropsch liquid. This amount is very small. Figure 22 shows the same behavior when the Fischer-Tropsch liquid was reacted at the different velocities over the Ni-ZSM-5, where there are only slight changes.

Figure 23 showed the effect of changing space velocity over a constant temperature. The feed of n-heptane and H_2 was passed over the Zn-ZSM-5. As the space velocity increased the aromatic yield decreased. The decrease in aromatic yield was reflected in an increase in the C_5+ oils yield. The butane and propane yields were fairly constant. The olefin content, though not specifically shown, also was constant. This seemed to lead to the conclusion that as the weight hourly space velocity increased the final steps of the mechanism did not have time to occur, and the

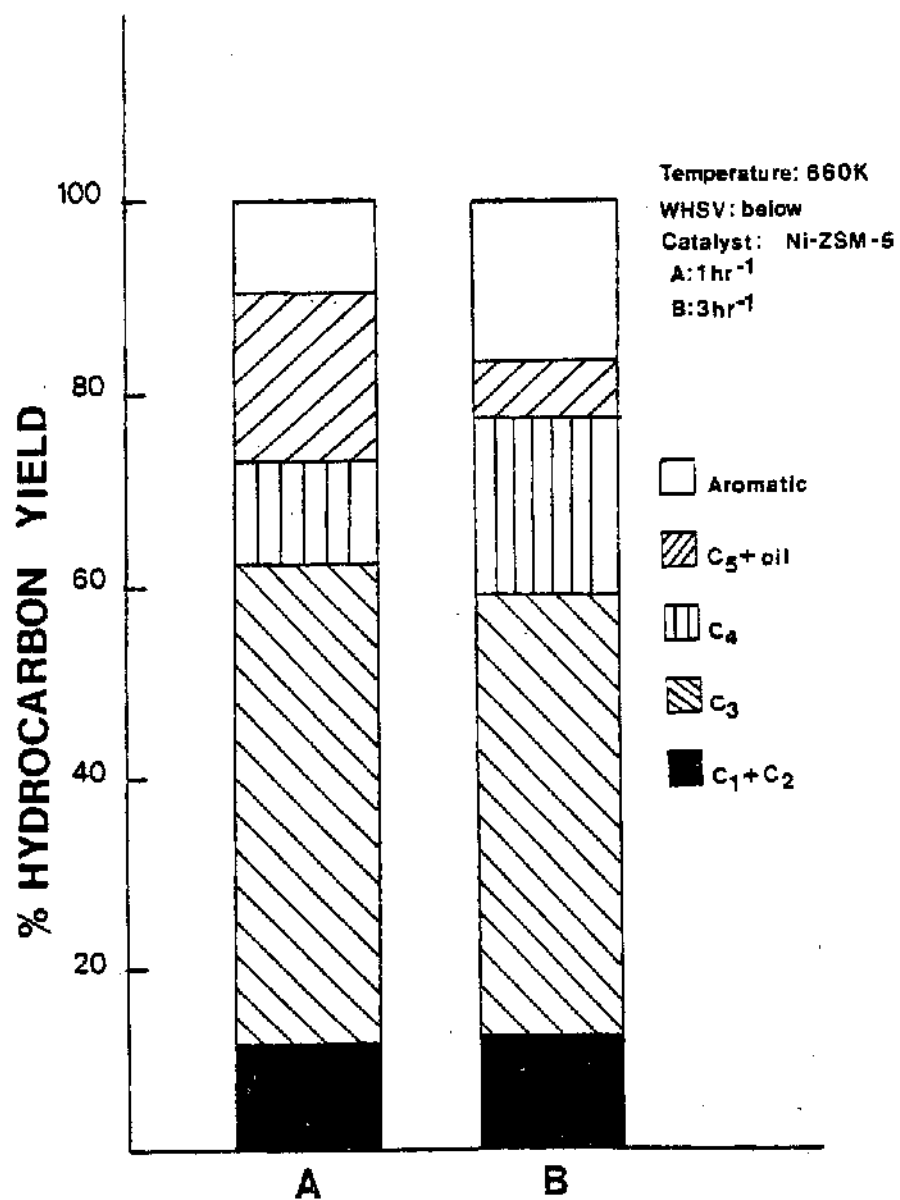


Figure 19. Space Velocity Effect on n-heptane at 660 K over Zn-ZSM-5. ($H_2/HC = 2$)

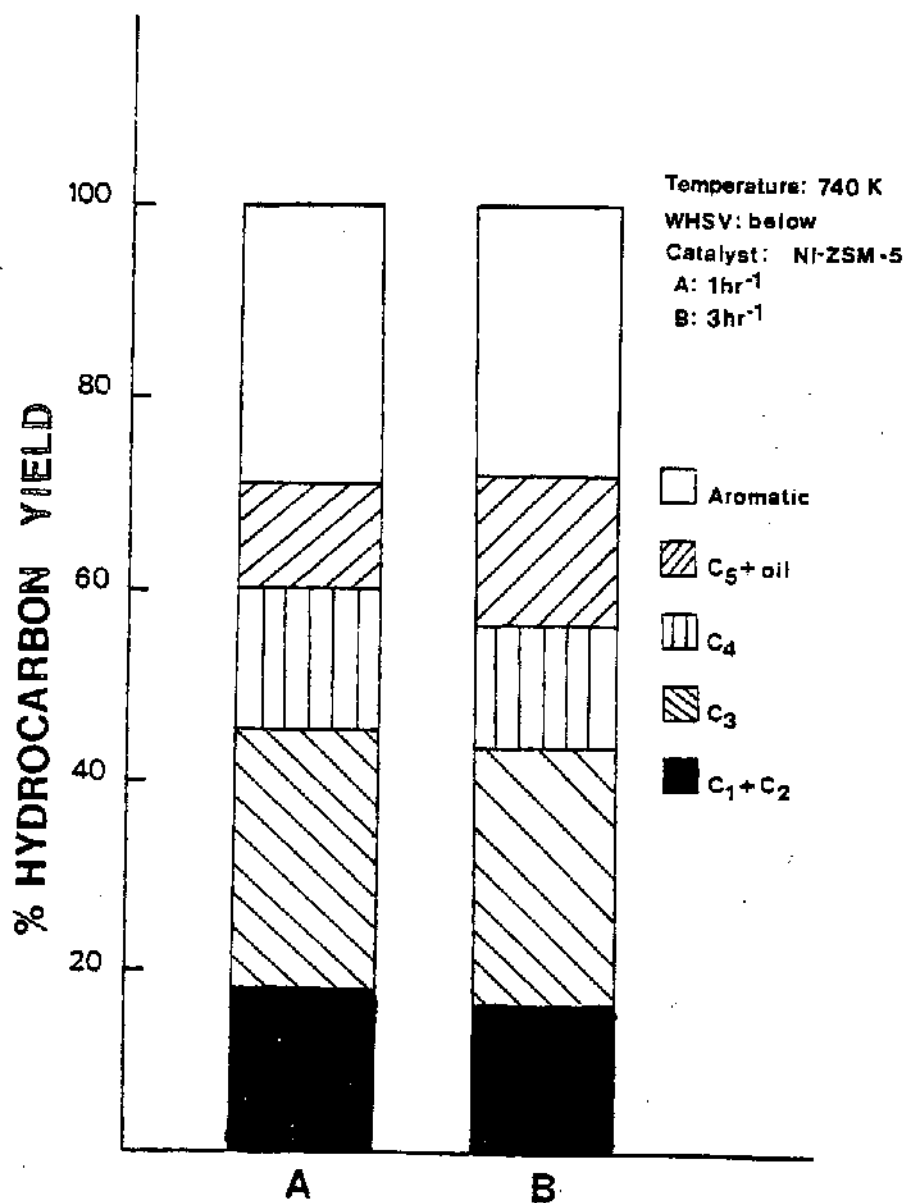


Figure 20. Product Distribution of n-heptane at 740 K with WHSV of 1 and 3 hr⁻¹. ($H_2/HC = 2$)

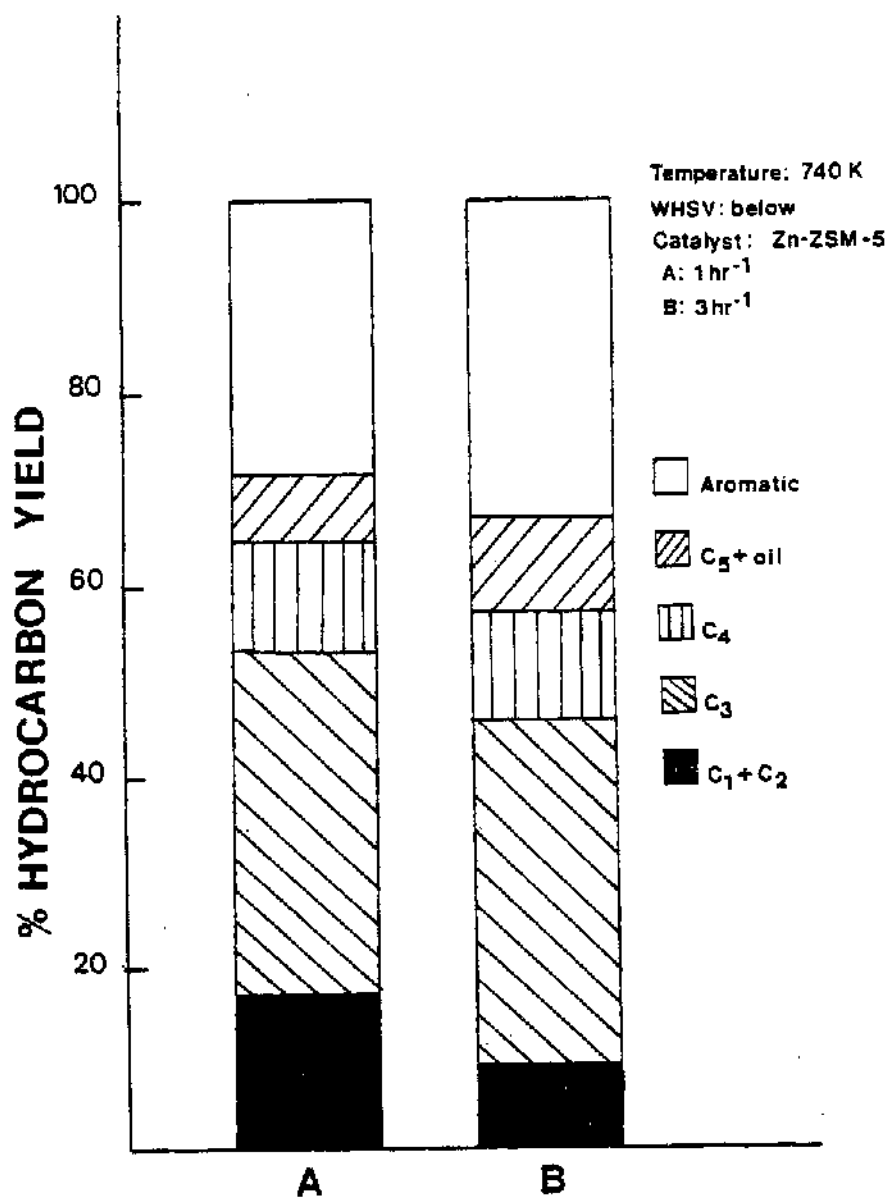


Figure 21. Product Distribution of F-T liquid at WHSV of 1 and 3 hr⁻¹. ($H_2/HC = 2$)

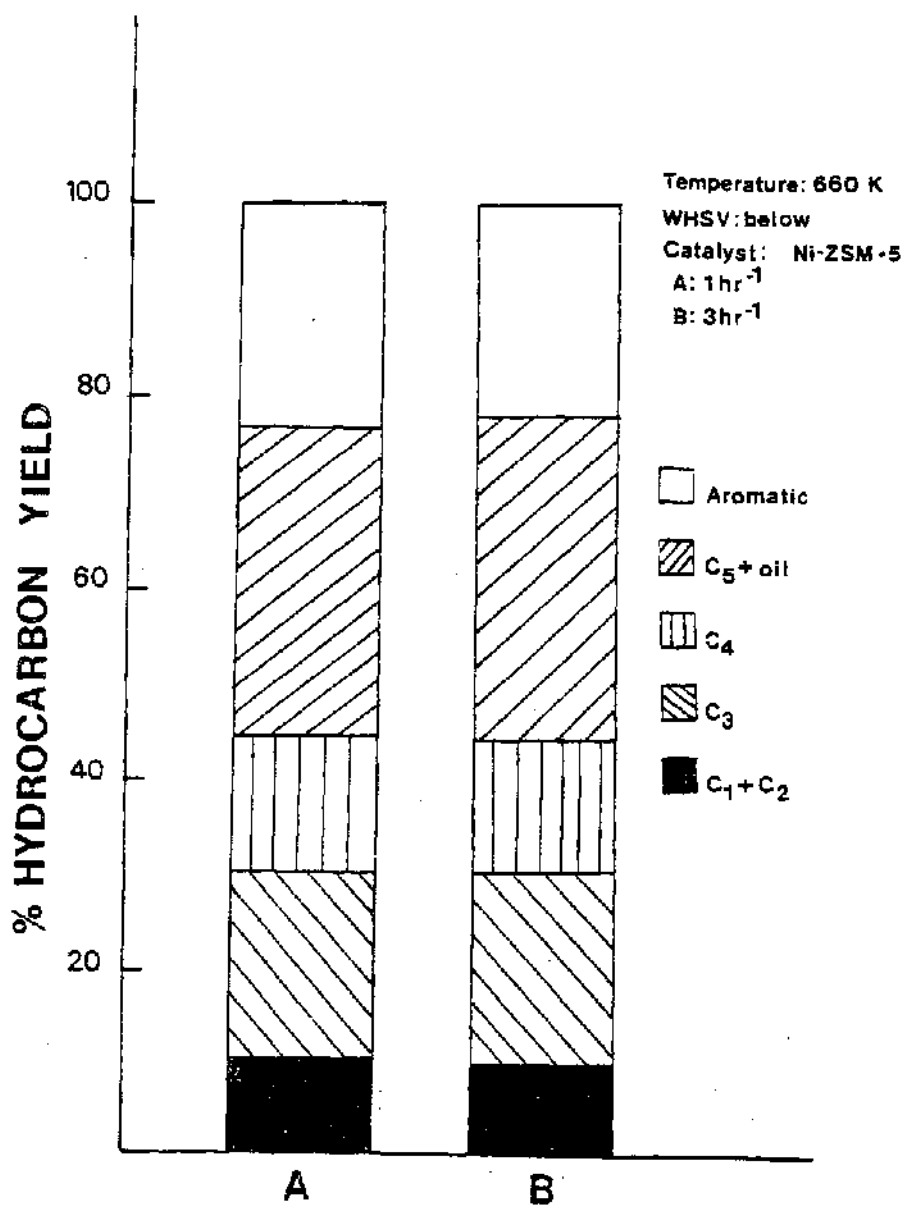


Figure 22. Product Distribution of F-T liquid over Ni-ZSM-5 at WHSV of 1 and 3 hr⁻¹. ($H_2/HC = 2$)

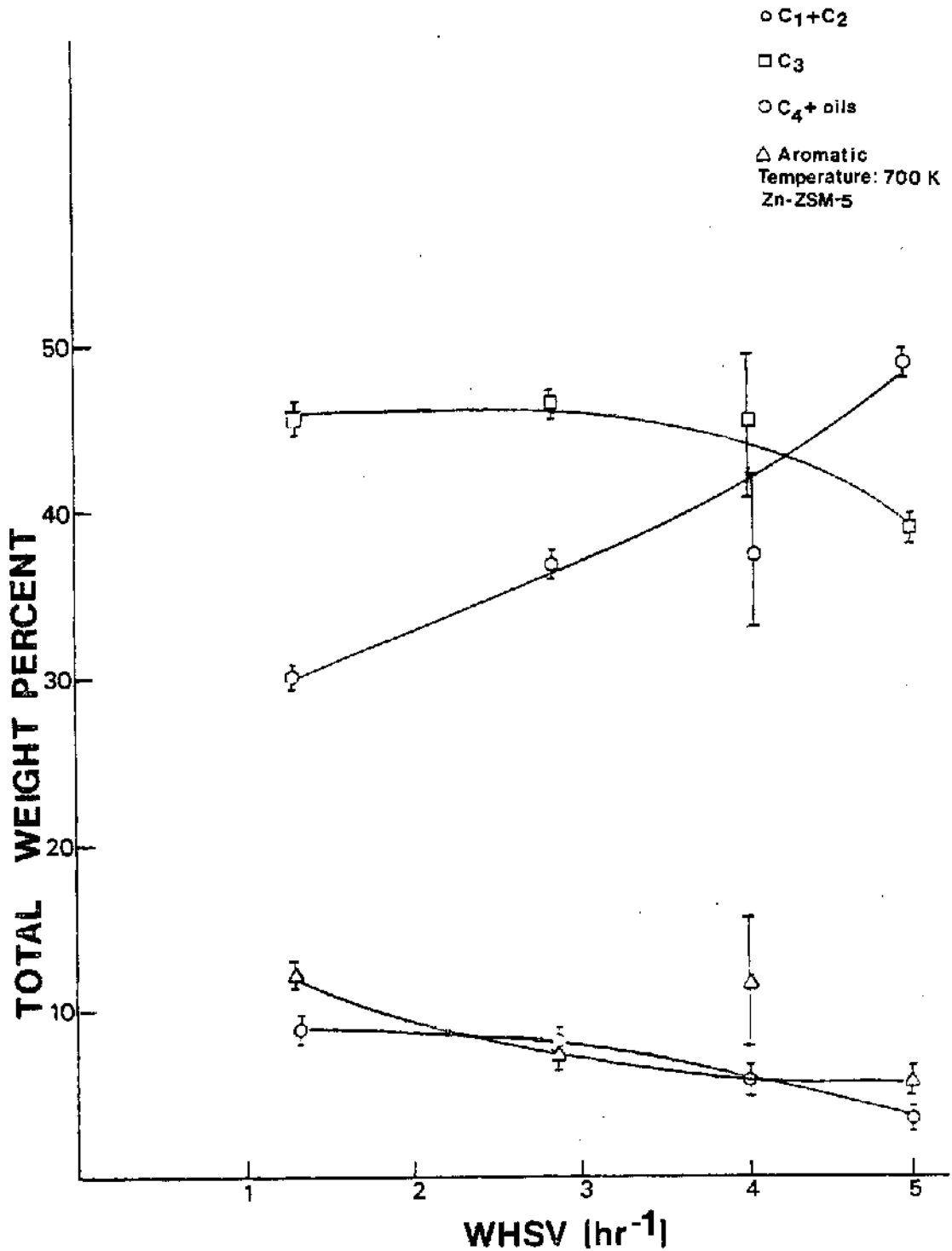


Figure 23. Effect of Space Velocity on Product Distribution of n-heptane over Zn-ZSM-5 (700 K, H₂/HC = 2)

intermediate steps increased. This result is expected with a series mechanism. If the cyclization and subsequent formation of aromatics were the final steps of a mechanism these steps would not have had an opportunity to occur because of the decrease in the space velocity.

The effect of space velocity was shown to decrease the aromatic yield as the space velocity increased over the total range studied. However this decrease was not significant, especially within the range of the factorial design. Even at the highest weight hourly space velocity the feed conversion was greater than 99 percent.

Pressure Effects

An increase in pressure seemed to cause a decrease in selectivity towards aromatics, when compared to similar runs at lower pressures. The aromatic product was shown to be decreased for both the synthetic mixture and the n-heptane.

For the n-heptane, along with the aromatic change, changes occurred in most of the individual paraffin yields. In Figure 24, the aromatic yield dropped from 13.42 to 3.29 weight percent. The paraffin yields showed a 4.70 percent increase for methane, 4.33 percent increase for ethane, and a 17.4/ weight percent increase for the C₅+ oils. The propane was the exception to the rule, dropping 22.02 weight percent.

The mix exhibited the same general characteristics, Figure 25. Again the aromatic yield dropped to 4.47 weight

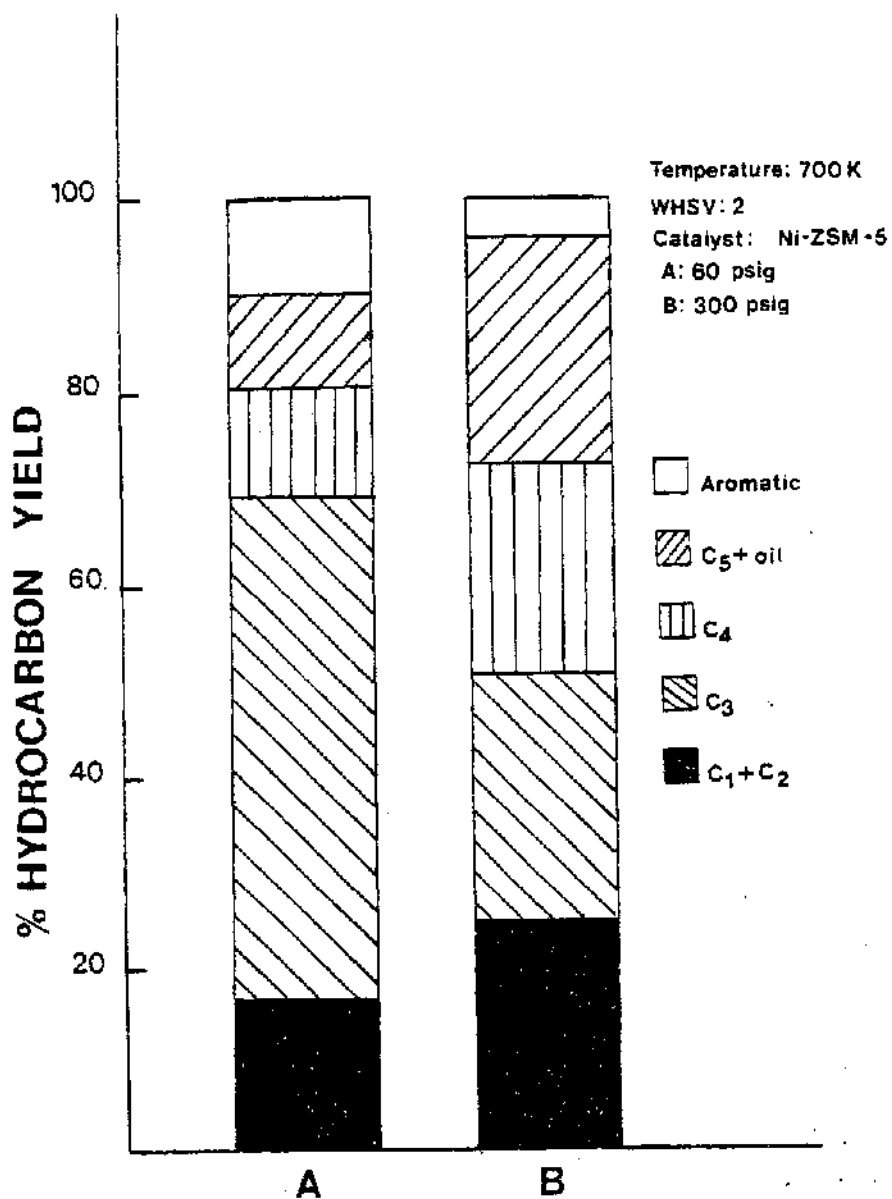


Figure 24. Effect of Pressure on Conversion of n-heptane over Ni-ZSM-5

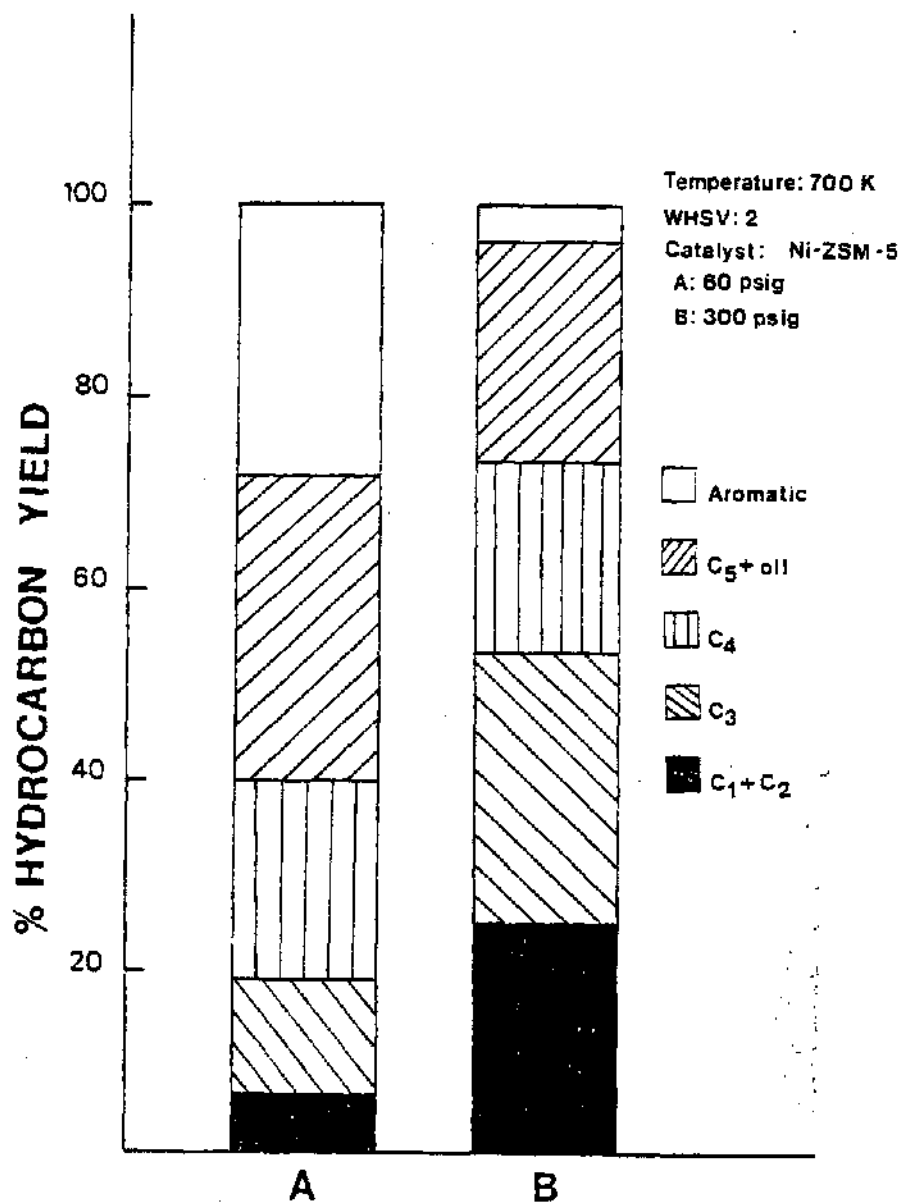


Figure 25. Product Distribution of Synthetic Mixture at 60 and 300 psig.

percent. This was a much larger drop than for the n-heptane. The paraffin yields also increased. However, the propane yield increased instead of dropping, as in the case of the n-heptane. In both cases the butane yield was virtually unchanged.

In trying to explain these yields both product distribution should be compared, Figure 26. The distributions are almost identical. This is a vast difference from the comparison of the product distributions of the synthetic mixture and n-heptane at lower pressures, see Figure 11. The reason for the lowered aromatic yield was due probably to the increased hydrogen partial pressure. In studies using a hydrogen over-pressure, Cattanaach, (1973) found that hydrogen in substantial amounts resulted in a decline in the aromatic yield. This was in disagreement with Chang et al. (1979), where methanol reacted under pressure formed highly methyl substituted aromatics in high yields. However this studies was not conducted with a hydrogen over-pressure.

The increased partial pressure would have tended to cause hydrogen to occupy more sites than at lower pressures. This would have left fewer spaces for the conversion of the hydrocarbons. The resulting loss in sites would have tended to drive the catalyst to the hydrogenation of the products formed from the cracking reaction. These would tend to inhibit the cyclization reactions, thus the yields of two

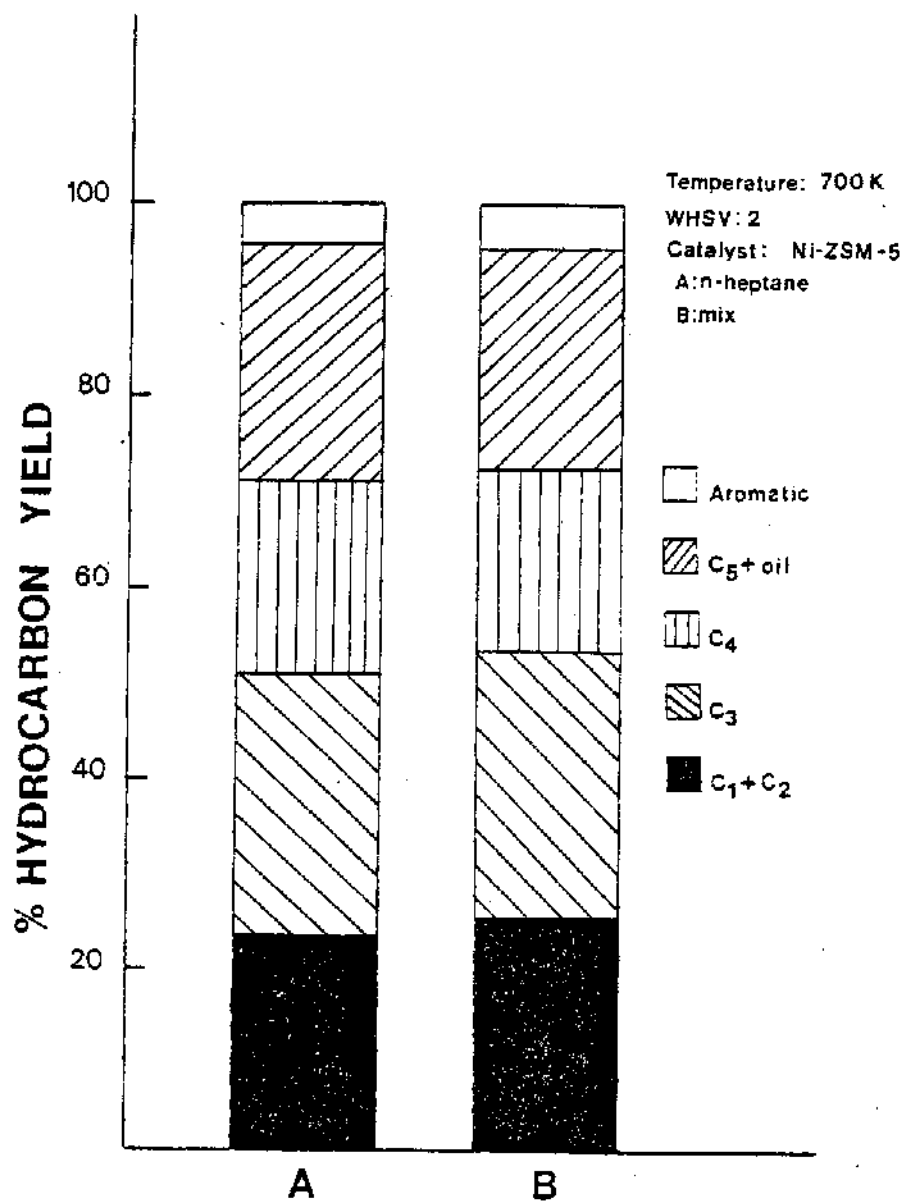


Figure 26. Comparison of Results of Increased Pressure Experiments. (Pressure = 300 psig)

different compounds or mixtures may well have resulted in similar distributions.

Water Effect

The effect of added water showed mixed results. Shown in Figures 27 and 28, were comparisons of runs involving n-heptane and Fischer-Tropsch liquid with and without water. The runs not involving water were runs which included the 2:1 molar ratio of added hydrogen to hydrocarbon.

In the runs involving n-heptane and water, Figure 27, a decrease in selectivity for the aromatics, ethane, methane, and propane was observed. The higher paraffins, butanes and C₅+ oils, showed a substantially increased selectivity. This product distribution, showed an increased C₄ and liquid product. This was a change from the run not including water.

The runs involving the Fischer-Tropsch liquid and water, Figure 28, showed again a decrease of aromatics and propane. Also, the selectivity of the butanes and C₅+ oils increased. However these runs showed a decrease in the C₅+ fraction, from 54.29 to 48.84 weight percent, Table 5. But when the C₄ fraction was included the C₄ plus total liquid amounts were nearly equal.

This perhaps can be explained by the ability of water to shift the acidity of certain sites. First, Singh, (1980) reported that water aids in the formation of ethylene from methanol, and van den Berg et al. (1981) reported that water

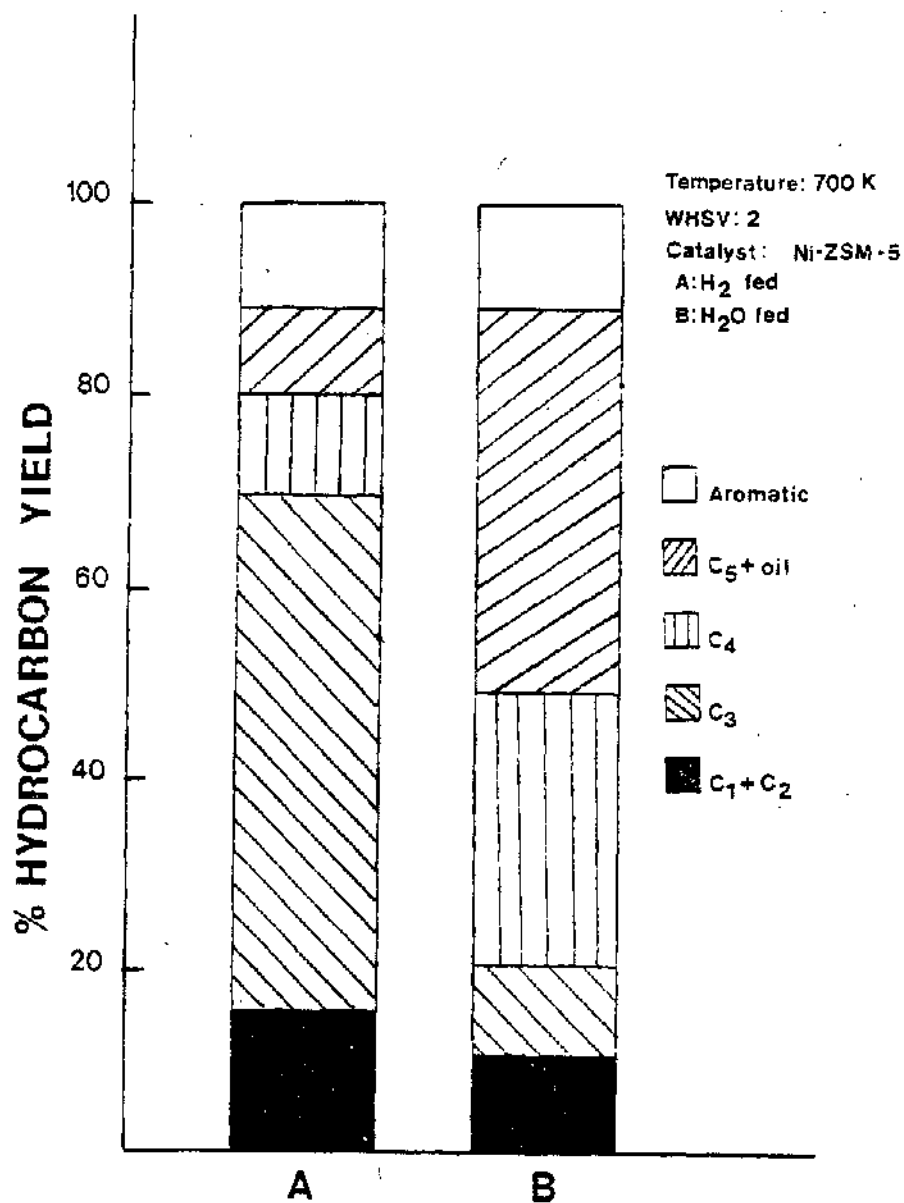


Figure 27. Effect of Added H₂O on Product Distribution of n-heptane

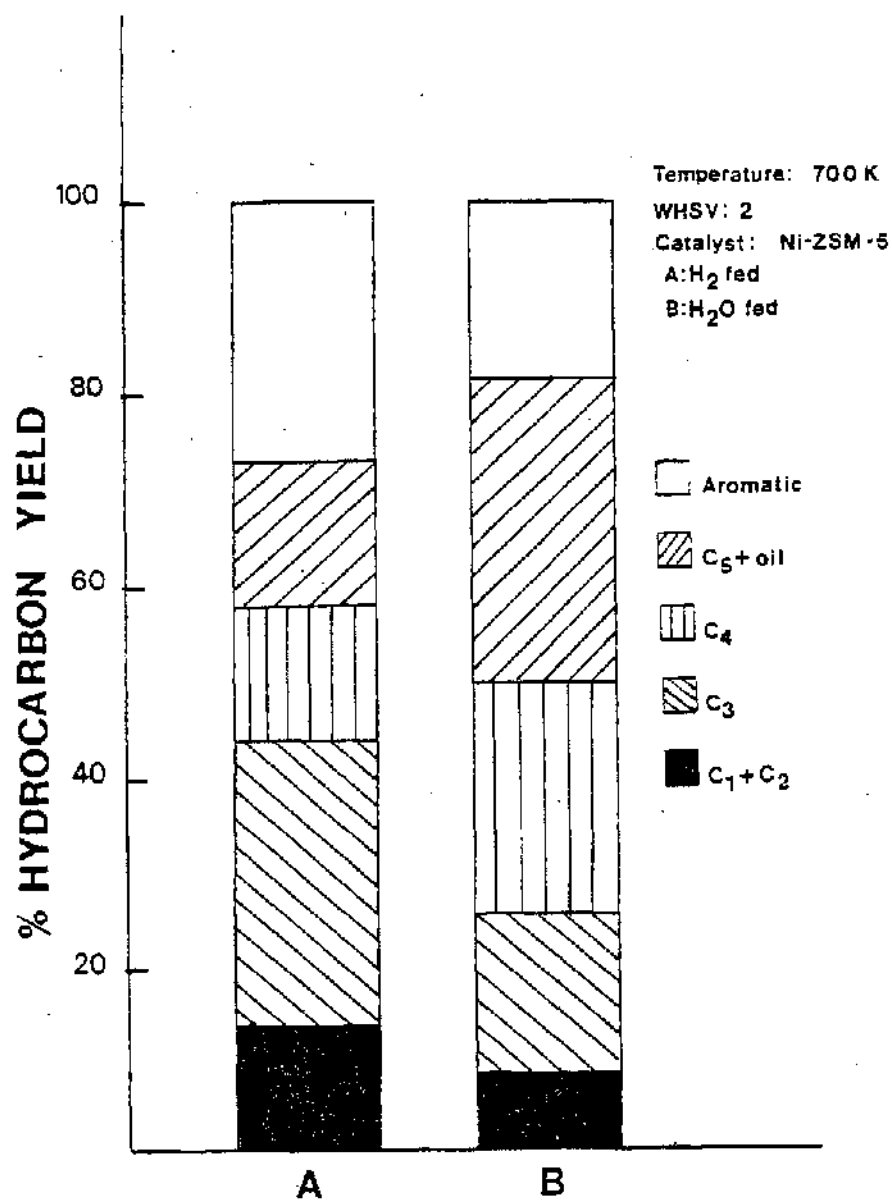


Figure 28. Effect of Added H₂O on Product Distribution of F-T liquid

increased the selectivity of aromatics from ethylene. The increased aromatic selectivity was explained by the water shifting the Lewis acid sites that are present at temperatures over 573 K to Bronsted sites. This reduced the coking inherent in the Lewis sites, Hall et al. (1964). However this increase in selectivity towards aromatics was not evident in this study. This may be due to the amount of water fed during the reaction. In van den Berg's work the highest H_2O/HC ratio was 1.23. In this work the H_2O/HC ratio was 2.20. The possibility then exists that somewhere between the H_2O/HC ratios of 0.74 and 1.60 the aromatic selectivity reaches a maximum and then declines. This decline in aromatics would probably explain the increased C_4 and C_5 selectivities.

Hydrogen Effects

Figures 29 through 34 showed the comparison of the product distributions for the zinc and nickel exchanged catalysts. All runs were performed at base conditions. Up to this point, with the exception of the runs which included water, all runs have included a 2:1 molar ratio of H_2 to hydrocarbon.

Figure 29 shows the absence of hydrogen on the Zn-ZSM-5 with n-heptane as the feed. There seemed to be little difference in the aromatic or butane yield whether or not hydrogen was added. The propane and C_5+ oils seemed to have traded off about 10 weight percent. In the case of

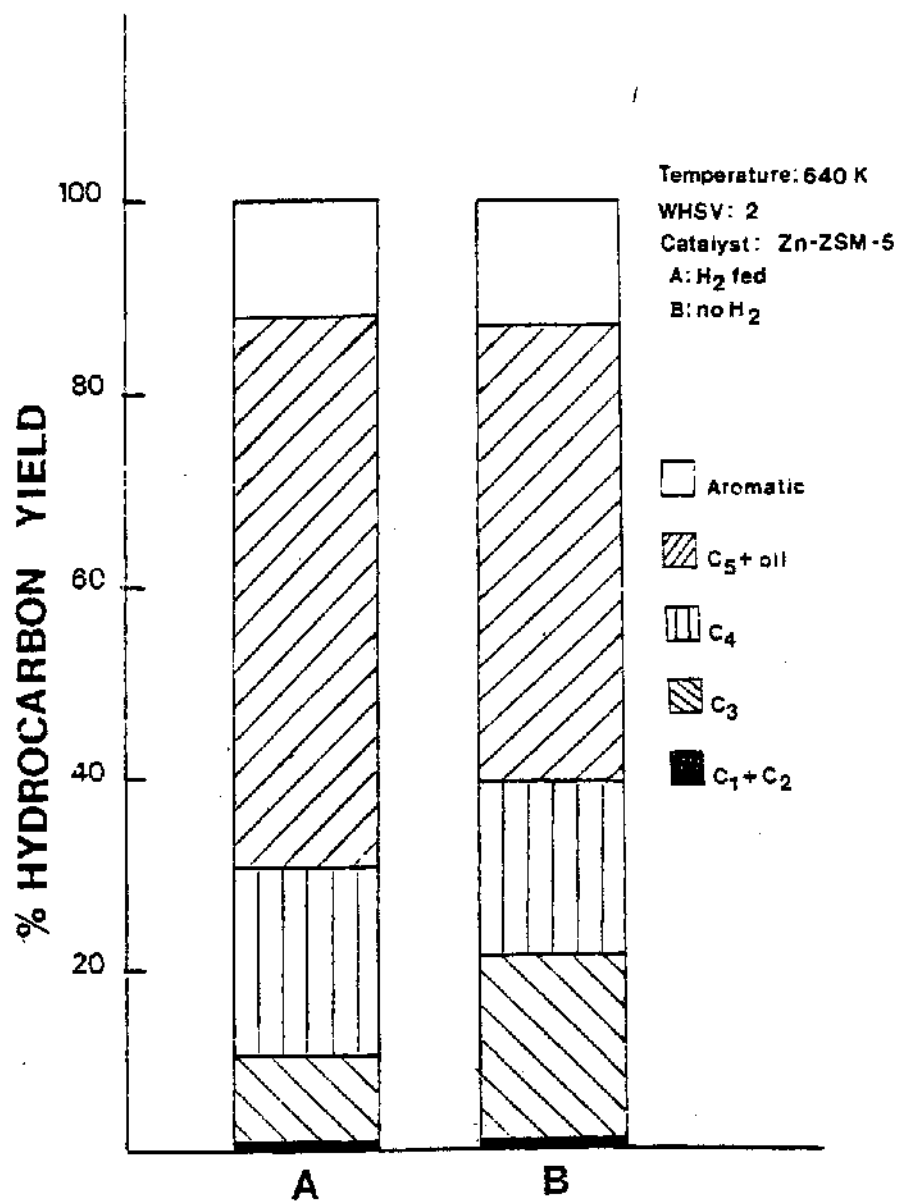


Figure 29. Comparison of Results With and Without H₂ for n-heptane over Zn-ZSM-5

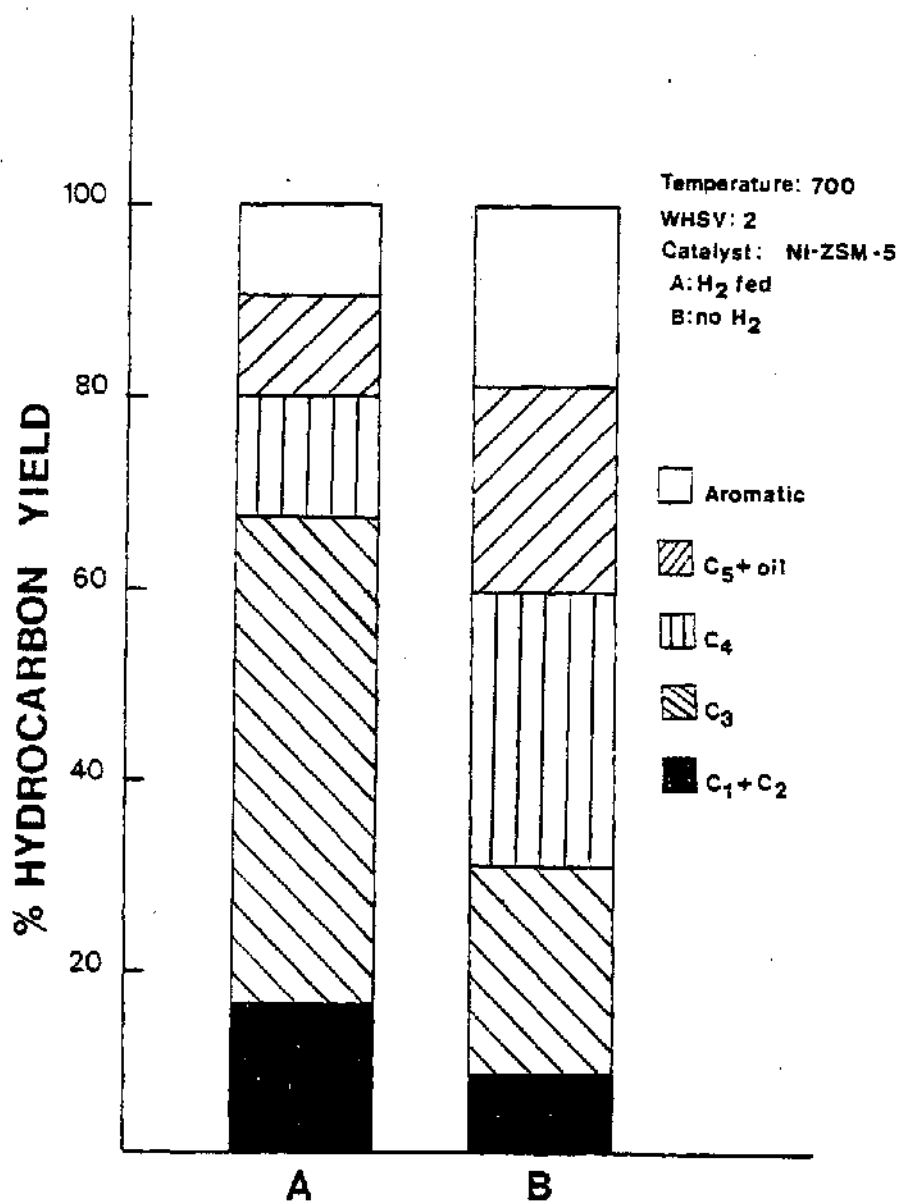


Figure 30. Comparison of Results With and Without H₂ for n-heptane over Ni-ZSM-5

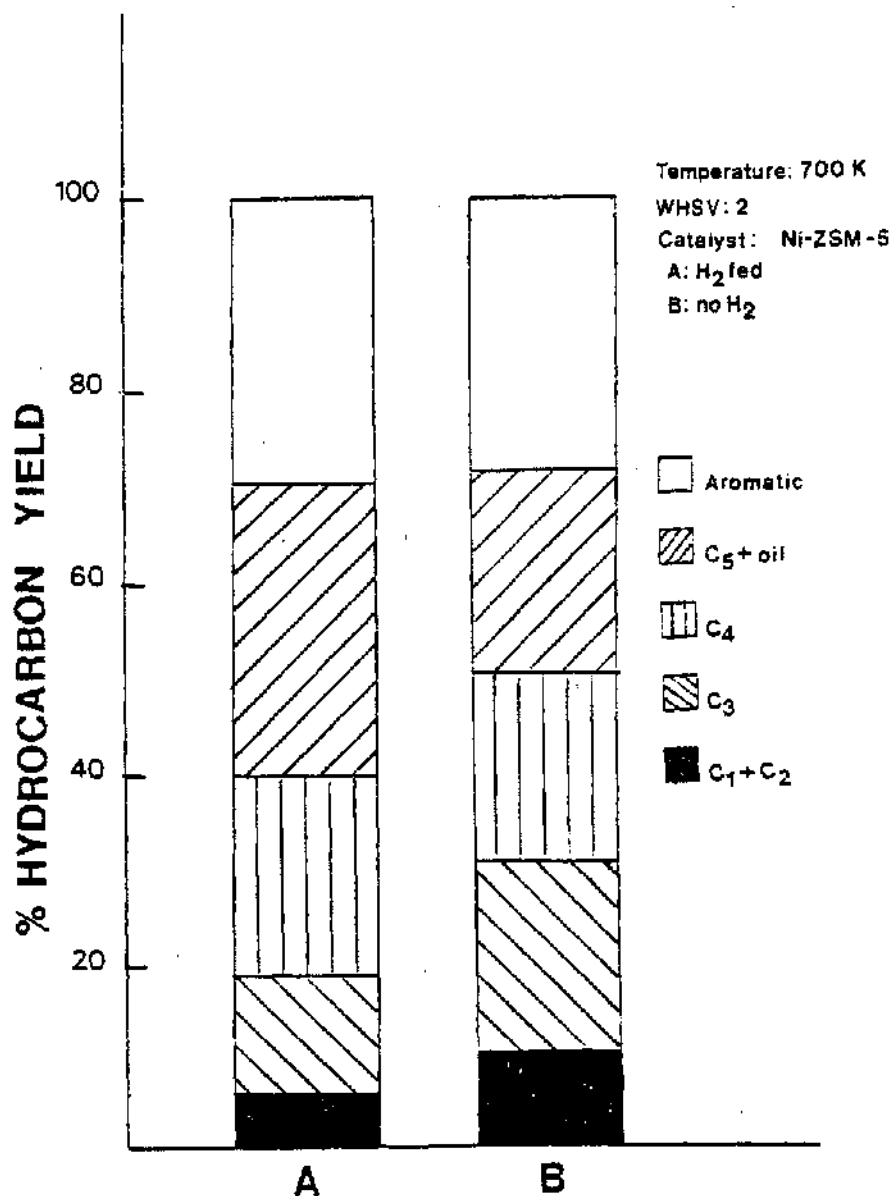


Figure 31. Effect of the Absence of Added H₂ on the conversion of Synthetic Mixture over Ni-ZSM-5

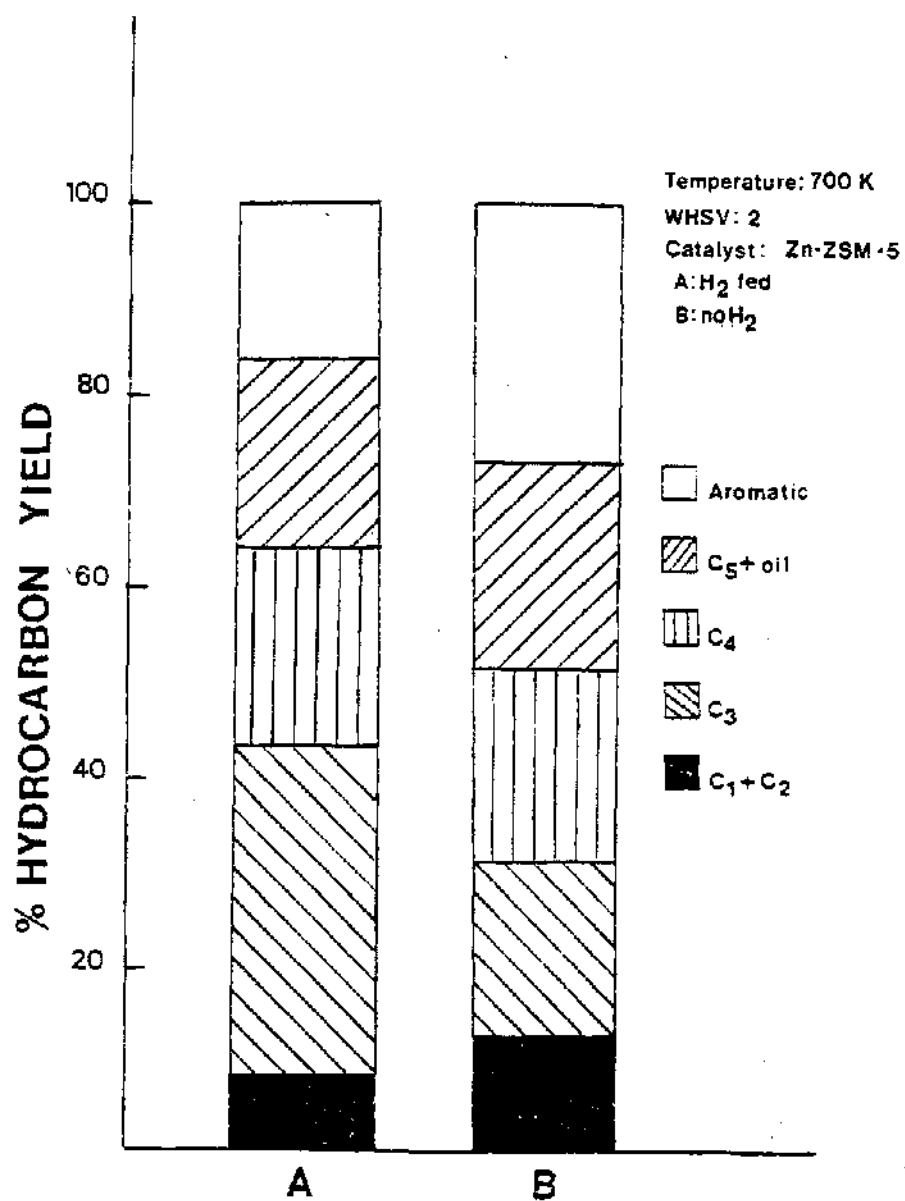


Figure 32. Effect of the Absence of Added H₂ on the conversion of Synthetic Mixture over Zn-ZSM-5

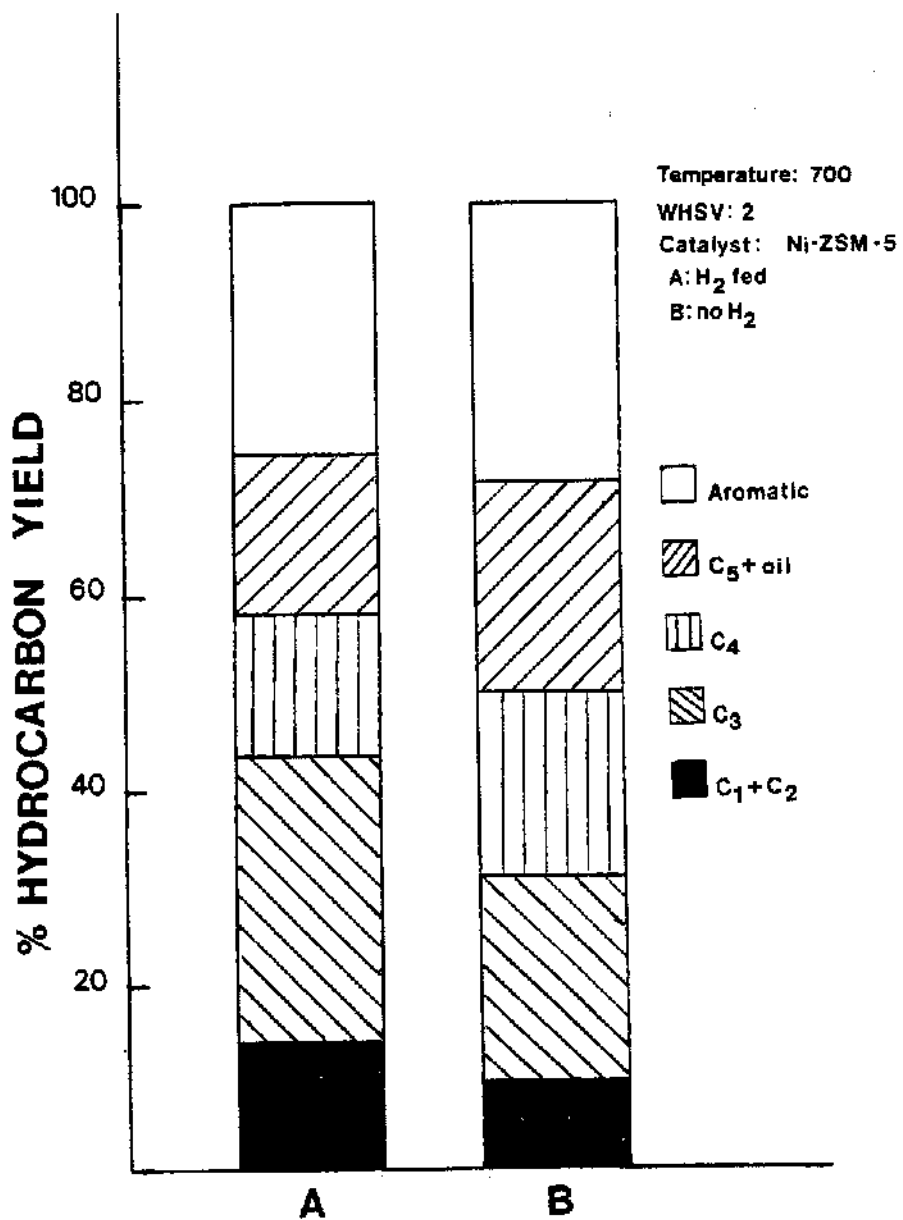


Figure 33. Comparison of Results With and Without Added H₂ on the conversion of F-T liquid over Ni-ZSM-5

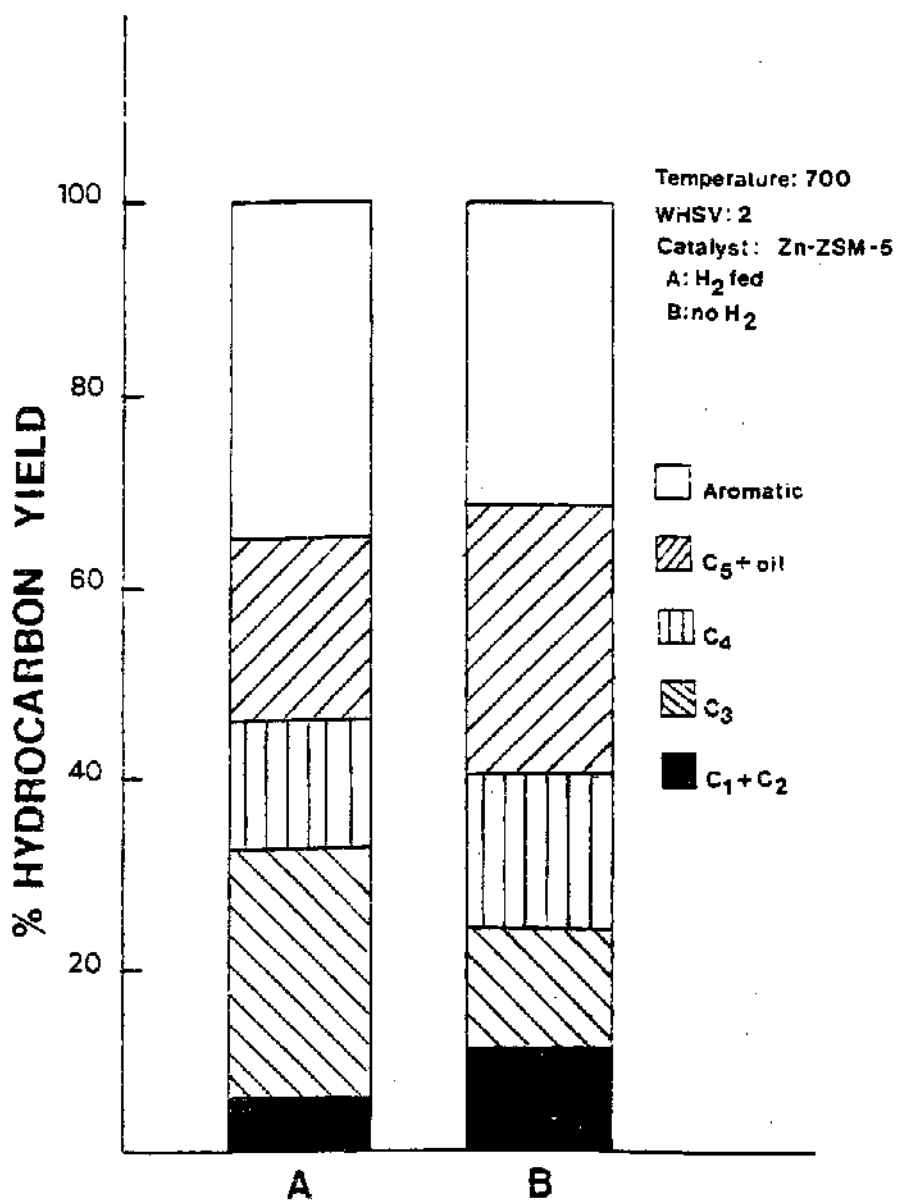


Figure 34. Comparison of Results With and Without Added H₂ on the conversion of F-T liquid over Zn-ZSM-5.

Ni-ZSM-5, Figure 30, again with n-heptane as the feed the aromatic content had risen from 12.83 to 18.93 weight percent, while the propane yield had dropped from 54.01 to 23.56 weight percent. The butanes and C₅+oils increased, from a combined total of 10.94 to 47.72 weight percent. The selectivity of the methane and ethane dropped, along with propane. The distribution of the aromatics also changed. In the case of the added hydrogen the benzene/toluene ratio was 0.17, and without hydrogen the benzene/toluene ratio was unchanged. However the xylene/toluene ratio for the runs with and without hydrogen were 0.66, and 0.88. This showed a shift in the aromatics towards the larger aromatics.

The results for the synthetic mix were shown in Figures 31 and 32. In Figure 31, the absence of added hydrogen had little effect on the aromatic yield for the Ni-ZSM-5. But this was not the case for the Zn-ZSM-5. In Figure 32, the aromatic yield rose by 12 weight percent, while the light gases and propane dropped by nearly 15 percent. The butanes and C₅+ oils were relatively unchanged. The benzene/toluene and xylene/toluene ratios stayed constant at 0.26 and 0.77 respectively.

The final runs involved the Fischer-Tropsch liquid. Shown in Figures 33 and 34 were the distributions for the Zn-ZSM-5 and the Ni-ZSM-5. In Figure 33, the absence of added hydrogen showed only a slight effect. The propane dropped from 24 to 20 weight percent, while the aromatics

rose by only 2 weight percent. All else stayed the same. The results for the Zn-ZSM-5 again shows the same results, Figure 34. The aromatic yield dropped about 3 weight percent, while the light gases and propane yields dropped by 11 percent. The changes were absorbed by increases in the butane and C₅+ oils yields.

In most of the above experiments the results showed an increased aromatic yield and a decreased light gas content, notably propane. The butane and pentane yields fluctuated from run to run. The ion-exchange effects were also shown, in that the zinc exchanged catalyst exhibited, with the exception of the n-heptane feed, a greater aromatic selectivity in the absence of hydrogen in the feed, while often the selectivity of the Ni-ZSM-5 was unchanged or just slightly changed. The probable explanation for the increased yields of higher molecular weight products lay in the fact that the catalyst surface had a finite number of sites available at any one time for reaction. The number of sites for H-ZSM-5 was about 4.7 Bronsted sites per unit cell, Auroux et al. (1979). Without hydrogen all possible sites were available for the feed and subsequent products. With the addition of hydrogen there was an increased competition for those sites. This probably was the reason for the drop in aromatic production. One item which seemed to aid in this postulation was the consistent jump in propane yields when hydrogen was added.

These results also support the earlier postulation that an increase in hydrogen over-pressure results in a decline in aromatic selectivity. However hydrogen was used to retard coking in the catalyst. So there could very easily be a point at which the hydrogen over-pressure could be reduced such that the aromatic selectivity would not decrease, and the coking formation would be retarded.

Ion Exchange Effects

The results of metal-exchange showed results that differed from feed to feed. Figures 35 through 39 shows the comparisons of results of both nickel and zinc exchange, along with the unexchanged H-ZSM-5 at base conditions. These runs were all conducted in the presence of a 2:1 molar hydrogen over-pressure. In Figure 35, the comparison of the product distributions using n-heptane showed a difference in the propane, C₅+ oils, and light gas contents. The propane content for the nickel was 51 percent, for the zinc 32 percent and for the H-ZSM-5 19.75 weight percent. The differences in these yields were spread mainly throughout the C₅+ oils and butanes. The aromatic content was fairly similar in overall yields. However the ratio of individual aromatic specie yields differed only slightly from catalyst to catalyst. The benzene/toluene and xylene/toluene ratios for the H-ZSM-5 and Ni-ZSM-5 were close at 0.23 and 0.29. The Zn-ZSM-5 shifted more towards a methyl substitution with ratios of 0.16 and 1.27. However these results show very

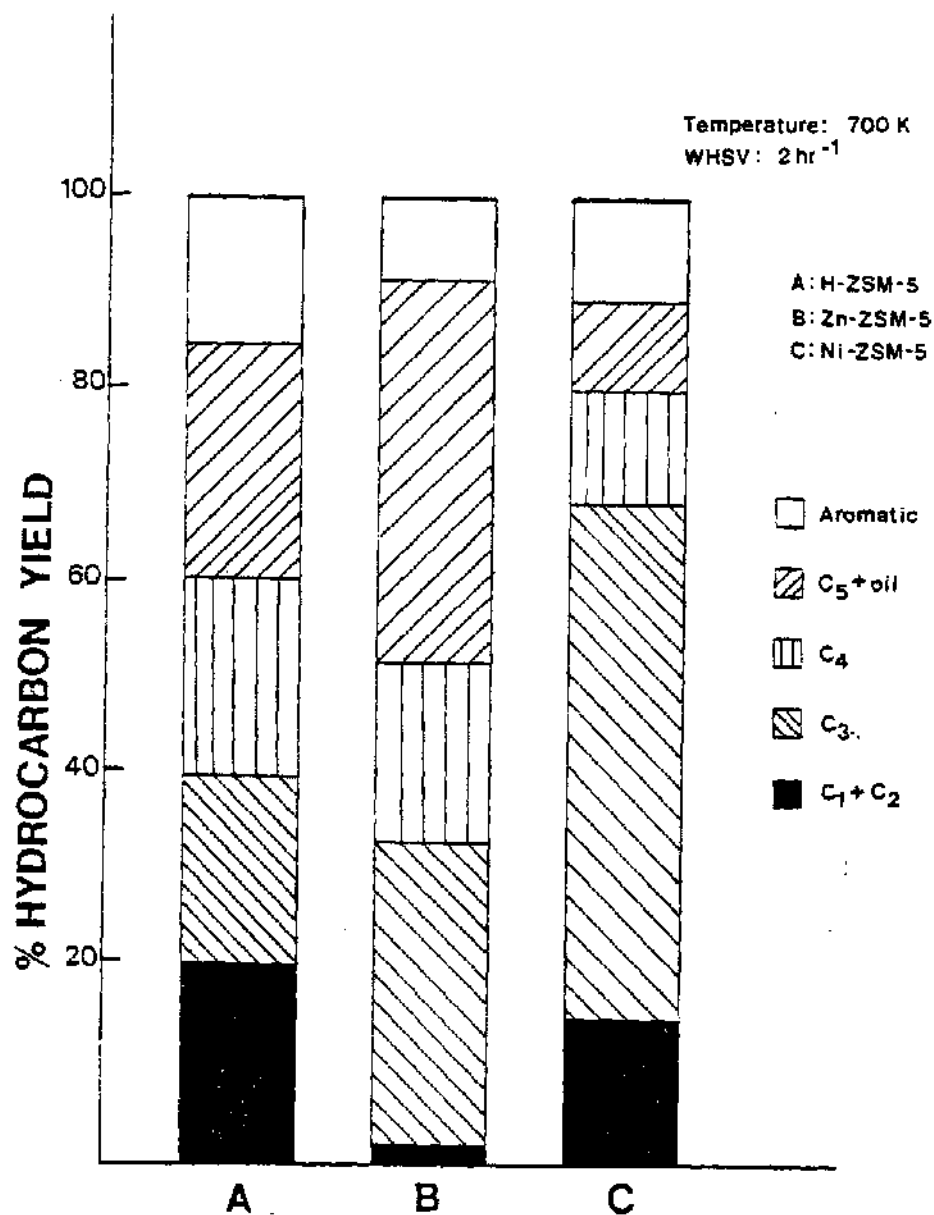


Figure 35. Effect of Ion Exchange on the Product Distribution using n-heptane

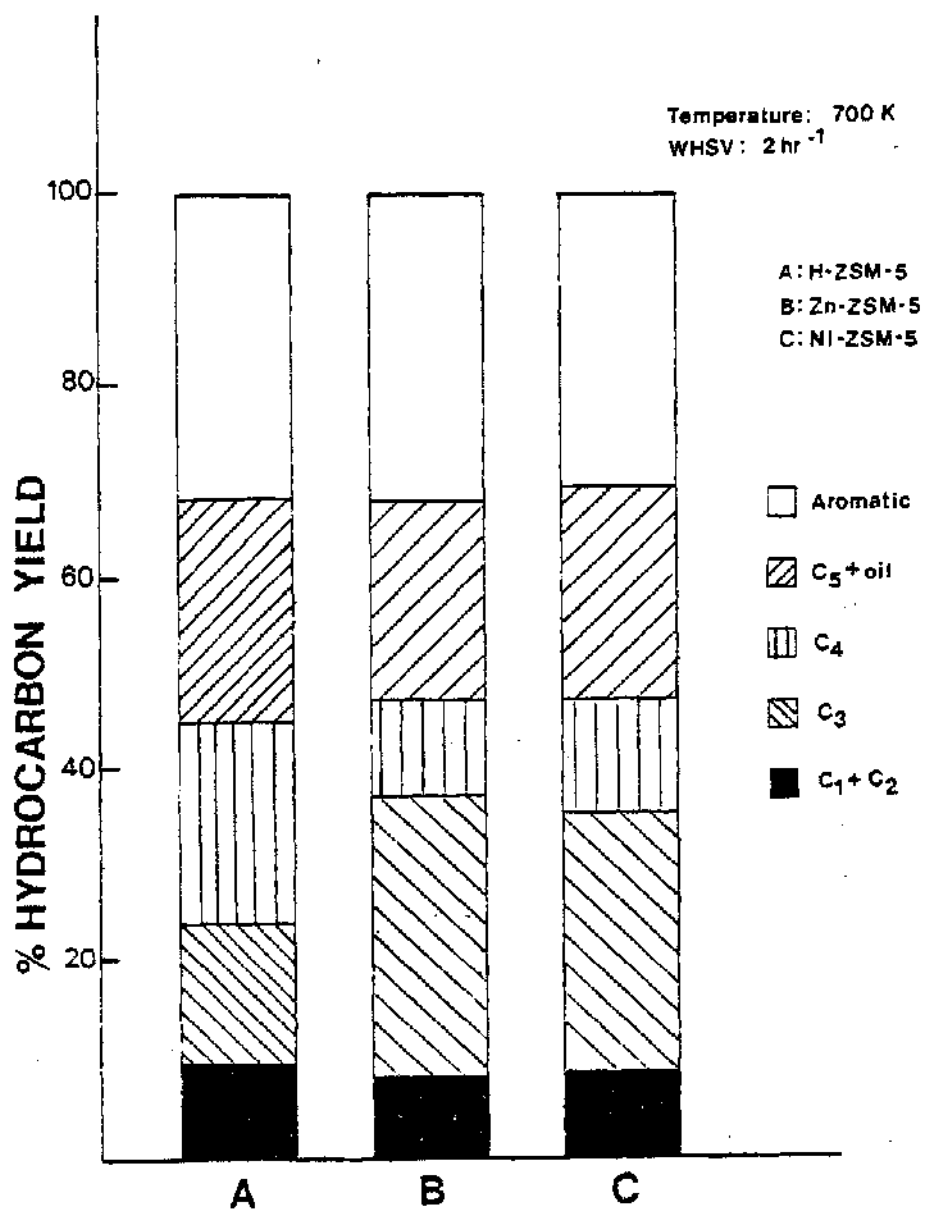


Figure 36. Effect of Ion Exchange on the Product Distribution using n-decanol

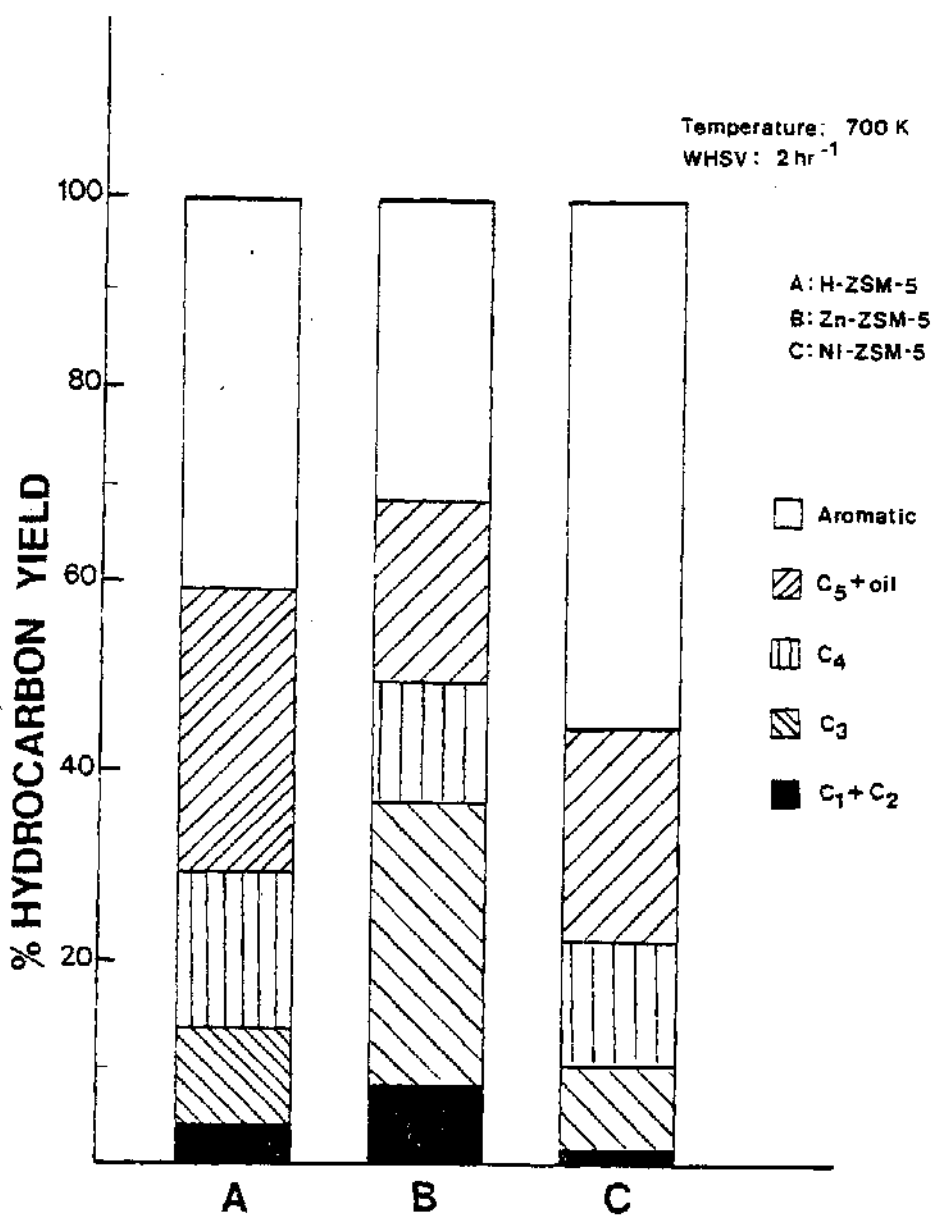


Figure 37. Effect of Ion Exchange on the Product Distribution using n-decanal

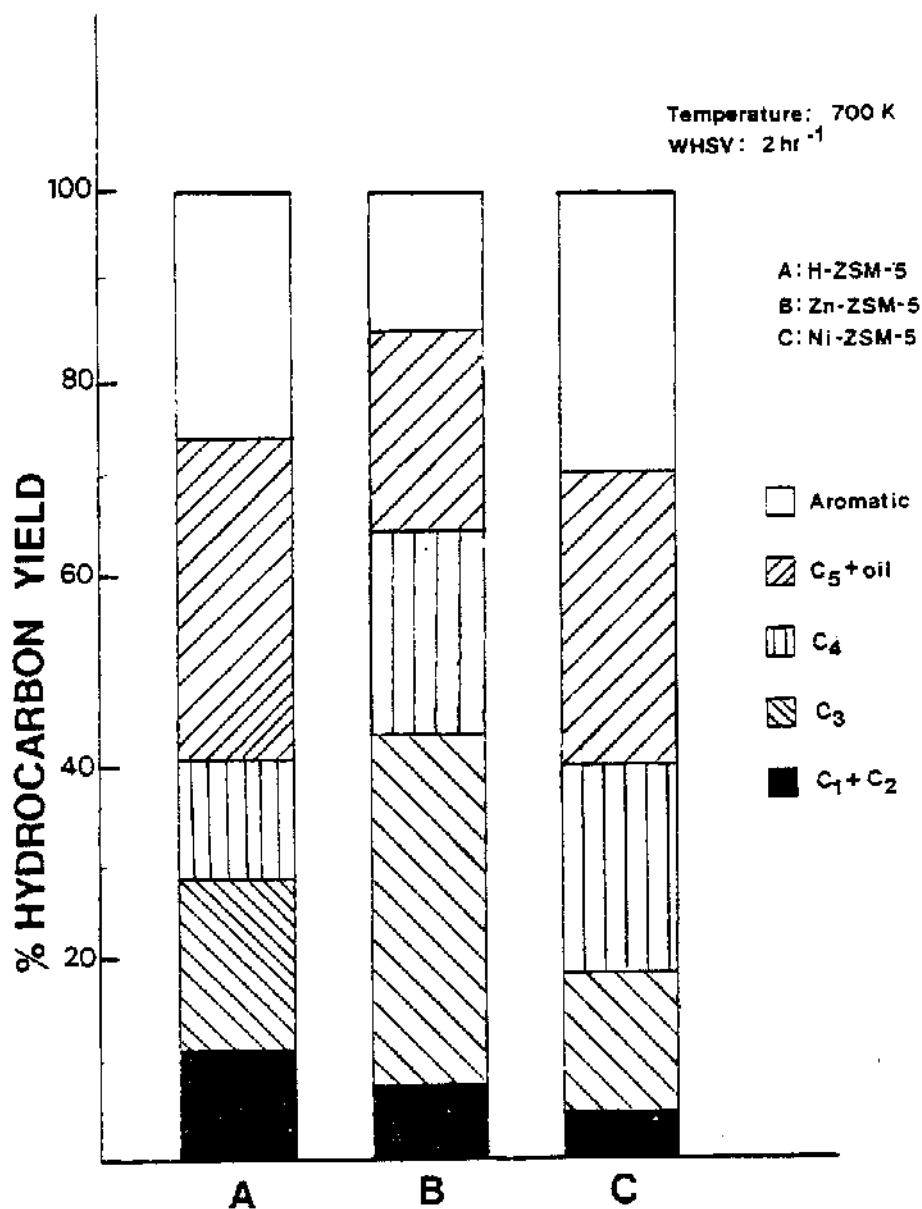


Figure 38. Effect of Ion Exchange on the Product Distribution using the Synthetic Mixture

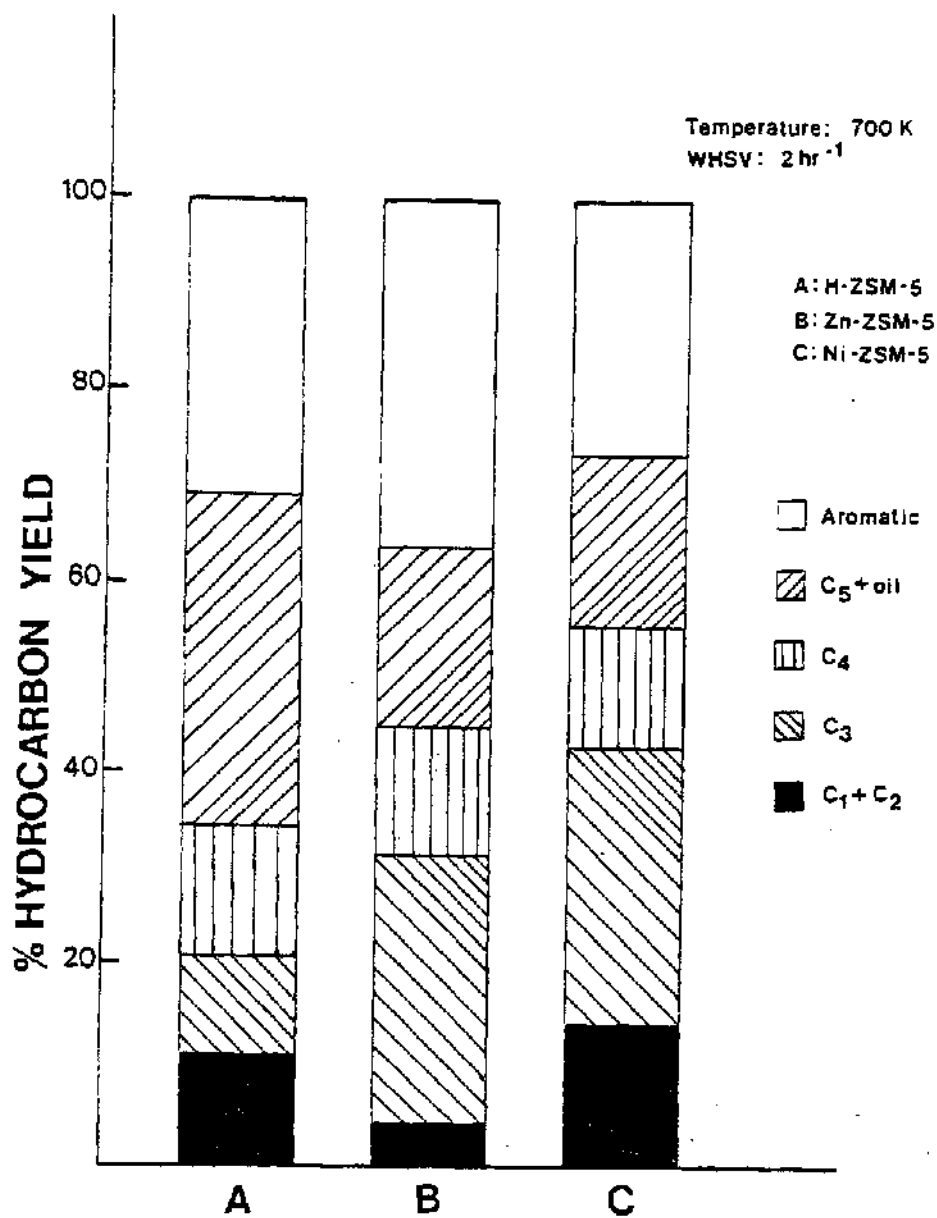


Figure 39. Effect of Ion Exchange on the Product Distribution using the F-T liquid

little evidence for any conclusions about the increased upgrading activity obtained through ion exchange.

The next feed compared was the n-decanol. Figure 36 showed the comparison of the three catalysts. The results showed very similar results, with the propane again showing the major difference. The ion-exchange increased the propane content by about 14 weight percent in both cases. The butane yields in both cases were decreased by about 5 weight percent, and the C₅+ Oils also dropped about 10 weight percent. The olefin content was essentially constant. The aromatic yields were again fairly similar with the individual aromatic ratios being very similar from catalyst to catalyst.

The n-decanal was then passed over the catalyst, Figure 37. These results show a vast difference between ion exchanges. The aromatic content for the H-ZSM-5 was 41 weight percent while the aromatic content for the nickel and zinc ZSM-5 were 36 and 51 weight percent. The light gases were fairly similar. However the propane yield for the three catalysts were 10, 7.7, and 32 percent. The butane content varied only about 5 percent. But the C₅+ Oils varied from 7 percent for the Zn-ZSM-5 to 23 percent for the H-ZSM-5. The ratio of aromatics also changed. The H-ZSM-5 yielded benzene/toluene and xylene/toluene ratios of 0.23 and 1.02, while the Zn-ZSM-5 had ratios of 0.29 and 0.85. The Ni-ZSM-5 showed a very different set of ratios, those

being 0.52 for the benzene/toluene ratio and 1.37 for the xylene/toluene ratio. This showed a possible flexibility in the choosing of a catalyst for production of specific aromatic distributions.

The variation of product distributions continued with the synthetic mixtures. In Figure 38, the results of the runs performed over the varied catalysts were shown. The aromatic yields fluctuated with ion exchange, from a base of 21 weight percent for the H-ZSM-5 to 14.7 and 27.96 for the Zn-ZSM-5 and Ni-ZSM-5. The individual ratios also differed. The benzene/toluene ratio and the xylene/toluene ratio for the H-ZSM-5 were 0.10 and 0.51 while the same ratios for the Zn-ZSM-5 and Ni-ZSM-5 were 0.26, 0.77, 0.30, and 0.80 respectively. The light gases decreased with ion exchange while the propane content fluctuated. Only a small change was observed with the Ni-ZSM-5, while the propane yield increased 23 weight percent for the Zn-ZSM-5. The butane yield seemed to stay fairly constant. The isopentane content stayed fairly constant with ion exchange, Appendix 5.

Finally the Fischer-Tropsch results were shown in Figure 39. These results showed that the aromatic yield of the ion-exchanged catalysts fell on either side of the yield of the unexchanged catalyst. Also significant was that the aromatic ratios for the ion-exchanged forms, while similar to each other, were different from the ratios for the

H-ZSM-5. These ratios were the benzene/toluene and xylene/toluene ratios, which were 0.3 and 0.8 for the exchanged catalysts and 0.18 and 1.28 for the H-ZSM-5. The paraffin yields showed an increase in propane, a decrease in the pentanes, and the butanes and light gases stayed constant.

The above yields and ratios, tabulated in Table 4, showed a wide range of selectivities. However there was too much fluctuation to accurately predict whether or not ion-exchange is better. The determining factor tested on what specific products were desired. For instance with the Fischer-Tropsch liquid, if total liquids were desired the obvious choice would have been the H-ZSM-5. However if the maximum aromatic yield was desired, the Zn-ZSM-5 would have been the choice. This fluctuation manifested itself throughout all feeds. However, with the exception of a few experiments, the ion-exchanged catalysts caused the butane and pentane contents to drop, while the aromatics yields stayed constant or increased. But in all cases the propane content was seen to increase significantly. This probably due to the increased hydrogenation ability of the catalyst, thus terminating the propyl species before the cyclization step.

Coking Effects and Catalyst Activity

The final process variable studied was the coking effect, and any deactivation of the catalyst after time on

Table 4: Selected Selectivities and Ratios for H-ZSM-5
Zn-ZSM-5 and Ni-ZSM-5

	H-ZSM-5	Zn-ZSM-5	Ni-ZSM-5 ¹
n-heptane			
Light Gases	16.22	1.52	14.68
Propane	19.75	32.14	51.12
Butane	21.13	17.11	11.48
Pentane	21.52	28.74	7.89
Total Liquids	59.82	53.90	32.20
Aromatics	15.36	8.05	12.83
B/T	0.23	0.16	0.18
X/T	0.90	1.27	1.00
n-decanol			
Light Gases	7.93	6.88	6.91
Propane	11.68	29.29	25.06
Butane	19.92	18.19	14.71
Pentane	20.15	10.59	10.00
Total Liquids	77.70	48.48	63.92
Aromatics	33.38	26.42	32.18
B/T	0.25	0.19	0.17
X/T	0.93	0.84	1.00
n-decanal			
Light Gases	2.88	3.60	2.60
Propane	10.10	25.34	7.68
Butane	15.82	15.70	11.90
Pentane	23.18	14.72	10.43
Total Liquids	84.71	68.35	85.63
Aromatics	41.05	35.81	51.37
B/T	0.23	0.29	0.52
X/T	1.02	0.85	1.37

stream. The methods used to study these effects was an extended run to study the effect of coke deposition on the product distribution, and x-ray diffraction on the catalysts before and after use.

The extended run, whose results were shown as a function of time in Figure 40, are the results of running the process for a total of 18 hours. The feed was the Fischer-Tropsch liquid and hydrogen over the Ni-ZSM-5. As can be seen there is not much change in the distribution until the last when the olefin content jumps. Also discovered was that the xylene content surpassed the toluene content for the first time in any of the previous runs. When the catalyst was regenerated, the CO_2 given off during the regeneration reaction was collected by the use of ascarite. This amount collected corresponded to a carbon deposition of 5 weight percent of the total catalyst weight. The only major effect of this deposition was to raise the olefin content and rearrange the aromatic selectivity. The total aromatic yield was only slightly affected, while the paraffins seemed to shift to olefins.

In order to see if there had been any deactivation of the catalysts due to crystal destruction, samples of the catalysts both before and after use were submitted for x-ray diffraction. The side by side comparisons of all three catalysts were shown in Figures 41 through 43. All figures show no change in phase with no evidence of sintering or

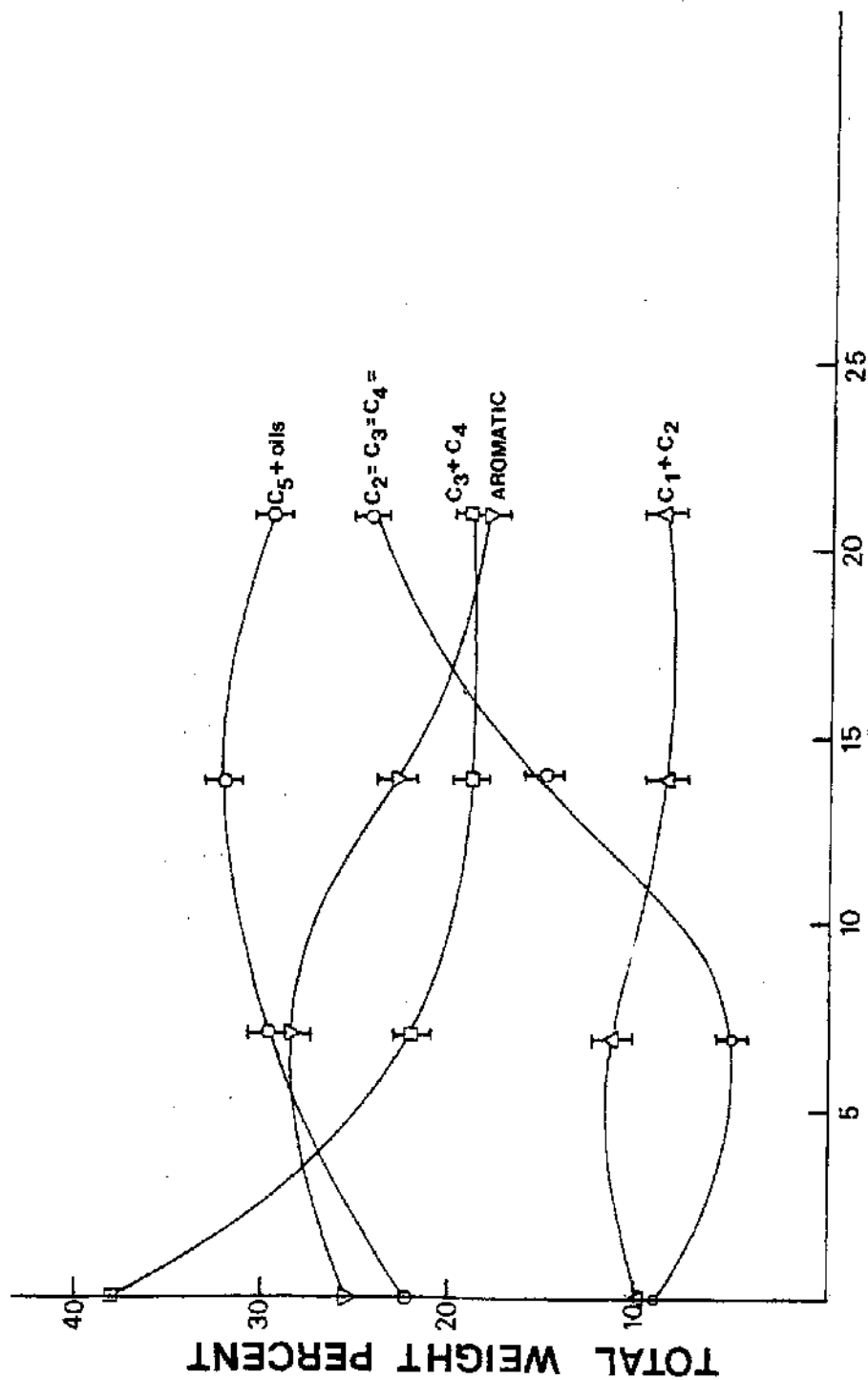


Figure 40. Effect of Coking on the Product Yields Using the F-T liquid over Ni-ZSM-5
(WHSV = 2 hr⁻¹, T = 700 K, H₂/HC = 2)

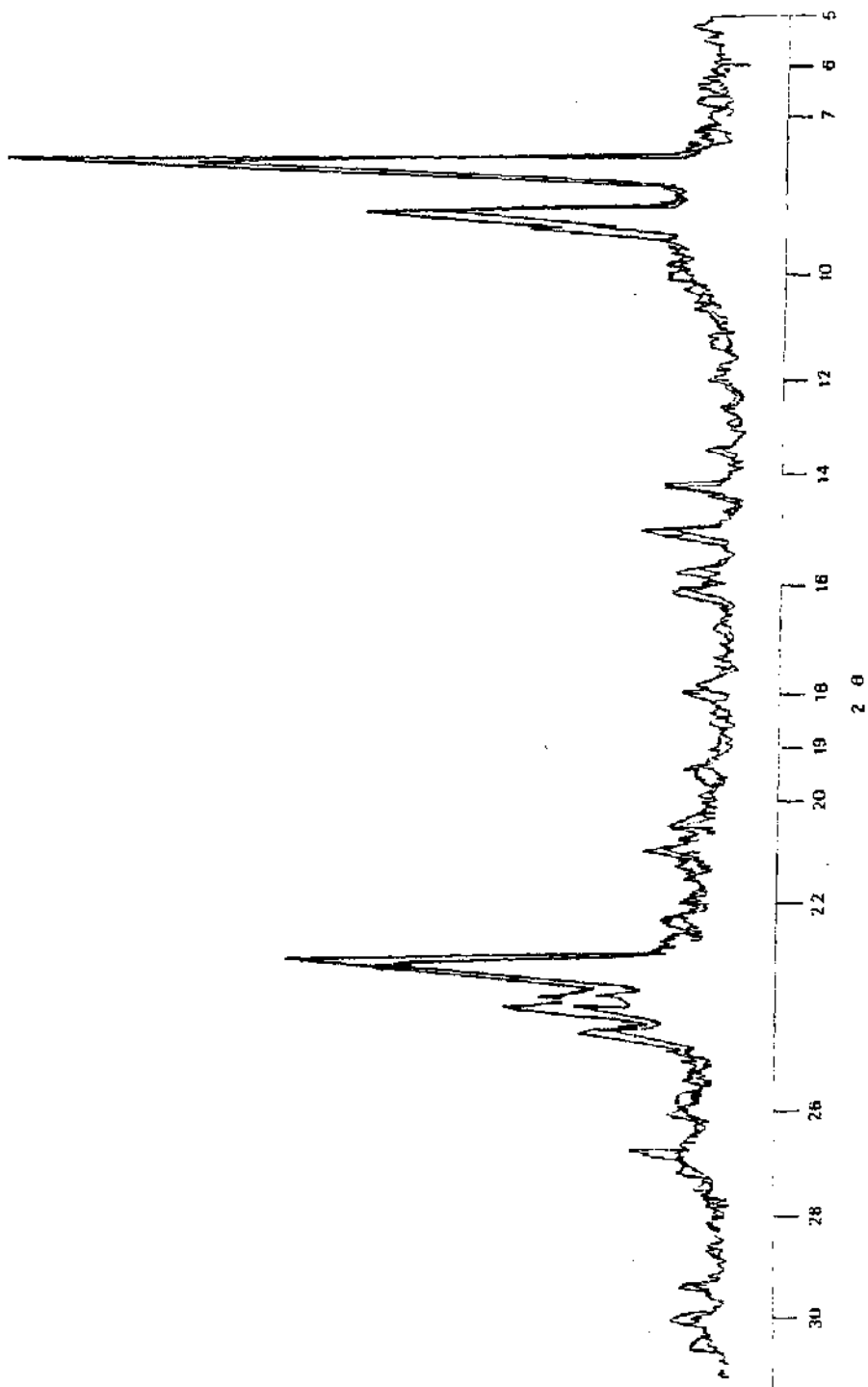


Figure 41. X-ray Pattern of H-ZSM-5 Before and After Use

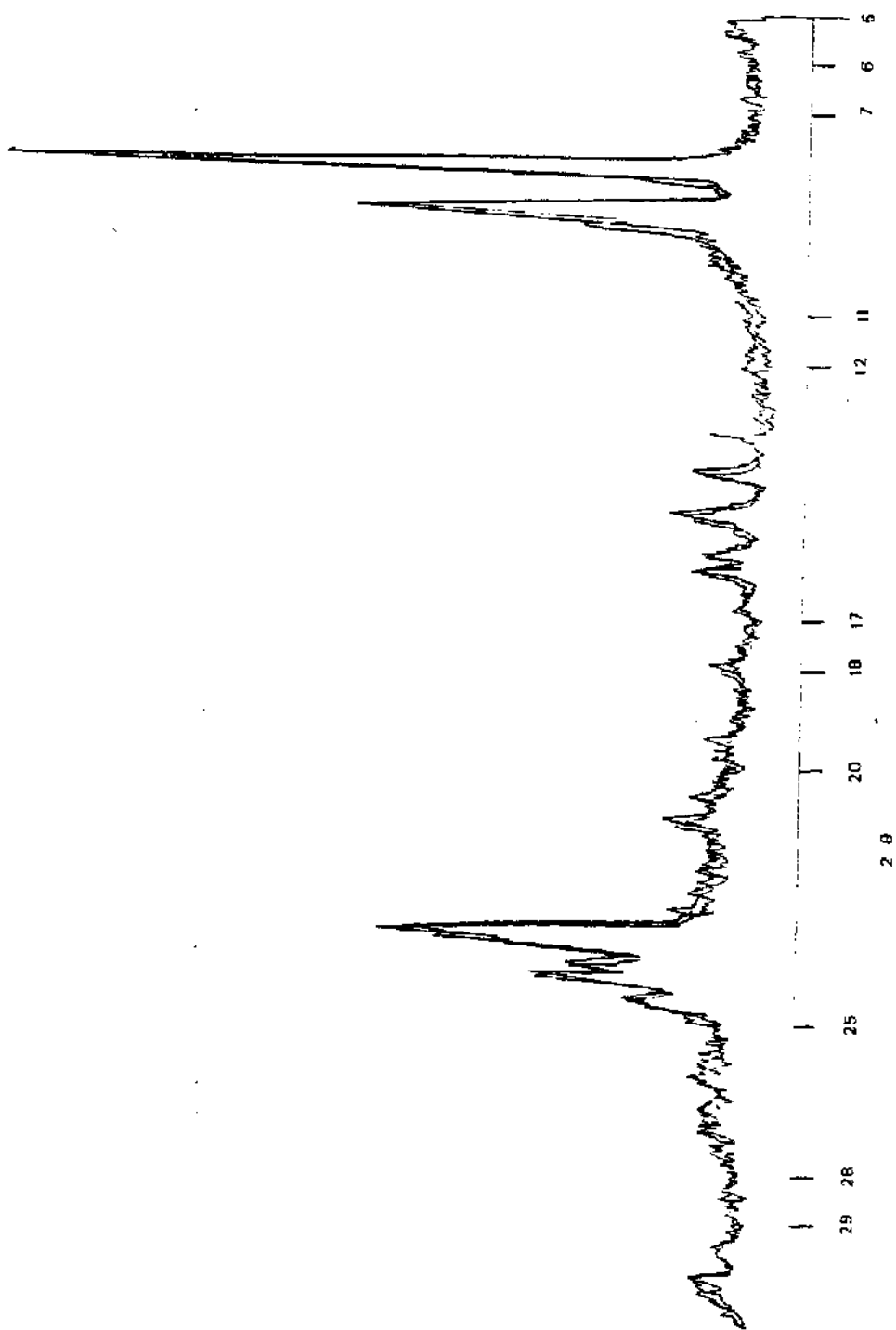


Figure 42. X-ray Pattern of Ni-ZSM-5 Before and After Use

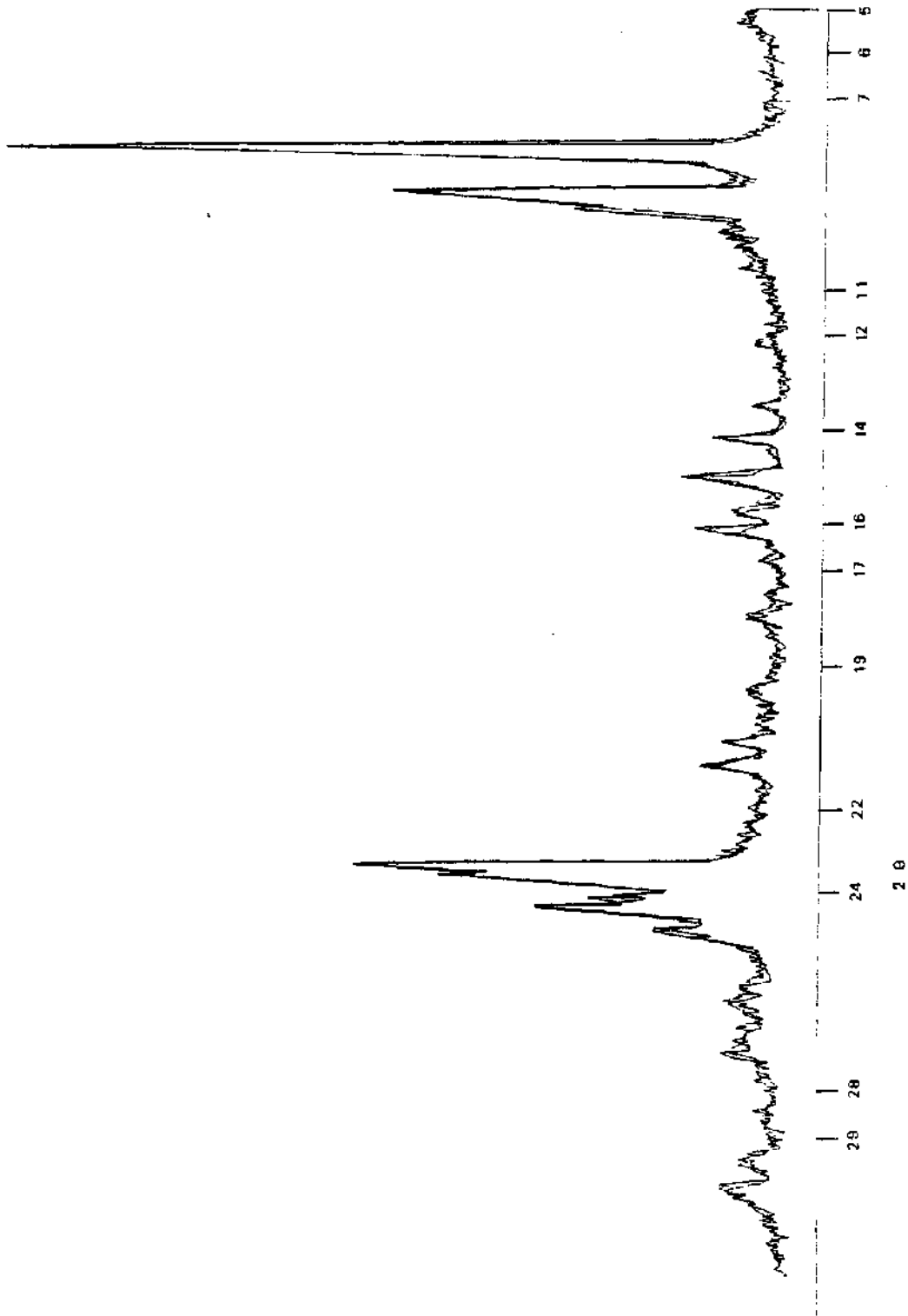


Figure 43. X-ray Pattern of Zn-ZSM-5 Before and After Use