CHAPTER III

EXPERIMENTAL APPARATUS

The experimental apparatus used in this study was a low flow, microreactor system. The apparatus consisted of four integral parts, the feed system, microreactor, sample collection trains, isothermal bath and control. A schematic drawing of the apparatus is shown in Figure 6.

Feed System

The feed system consisted of two parts, the liquid and gas feeds. The system could be operated with either feed by itself or combined. The liquid was drawn from a buret, filtered through an Eldex 2 micron filter, and subsequently fed to, and metered by an Eldex model A-30-S high pressure pump. The outlet from the pump then passed through a Nupro model SS-4C-50 variable check valve and pressure gauge. These were placed at the outlet to provide a back-pressure for the pump, and to measure the outlet pressure, respectively. The liquid feed then passed into the reactor preheat through 1/16" (0.159 cm) O.D. 316 stainless steel tubing.

The gas feed was drawn from any of several cylinders, and then passed through a Brooks model 5815-1Z1B mass flow sensor and controller. The gas was first purified of any small particles by passing through a Nupro model SS-2F-2 2 micron filter immediately before the mass flow meter. The

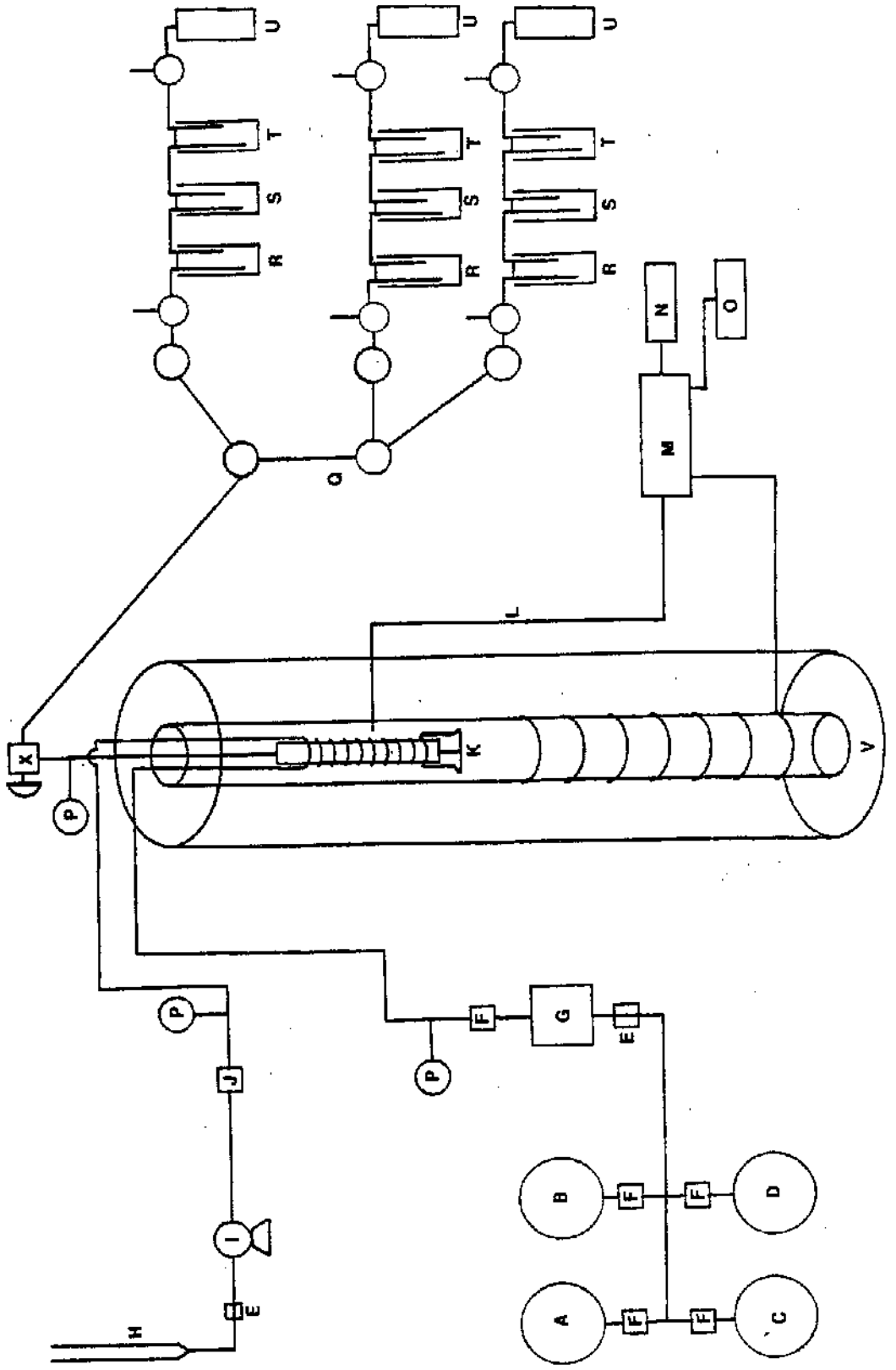

Figure 6. Experimental Apparatus

Table 3. Key to Experimental Apparatus

A.	Oxygen cylinder plus regulator
B.	Hydrogen cylinder plus regulator
C.	Air cylinder plus regulator
D.	Helium cylinder plus regulator
E.	Filter
F.	Check valve
G.	Mass flow meter
H.	Buret
I.	Pump
J.	Adjustable check valve
K.	Microreactor
L.	Thermocouple
M.	Temperature controller
N.	Temperature indicator
O.	Millivoltage input
P.	Pressure gauge
Q.	Switching network
R.	1st. collector
S.	2nd. collector
T.	3rd. collector
U.	Water displacement bottle
V.	Isothermal salt bath
X.	Back pressure regulator

metered gas then passed into the reactor preheat section, after flowing through a check valve which prevented gas back-up. The tubing from the cylinders to the flow meter, and to the reactor preheat section was 1/8" (0.318 cm) O.D. 316 stainless steel tubing.

Microreactor

The microreactor system, shown in Figure 7, consisted of three sections. The first section, the preheat section, was two coils of 1/16" (0.159 cm) O.D. 316 stainless steel tubing, 45 inches (114.30 cm) long. One coil was for the liquid feed and the other for gas feed. The two preheat coils met below the reactor at a mixing tee. At this tee the two feeds were mixed and were introduced into the reactor.

The microreactor was constructed of 1/4" (0.635 cm) O.D., 0.01" (0.025 cm) I.D. 321 stainless steel, 6.25 inches (15.88 cm) long. The catalyst was packed into the tubing with glass wool packing at each end to insure no catalyst was lost.

At this point the products and any unreacted feed entered the reactor exit section. This section was to direct the product out of the reactor and salt bath into the glass collection unit. The exit section consisted of 1/8" (0.318 cm) O.D. 316 stainless steel tubing, 13 inches (23.04 cm) long. A pressure gauge and high pressure Autoclave Engineers model VRM-10 metering valve were included to

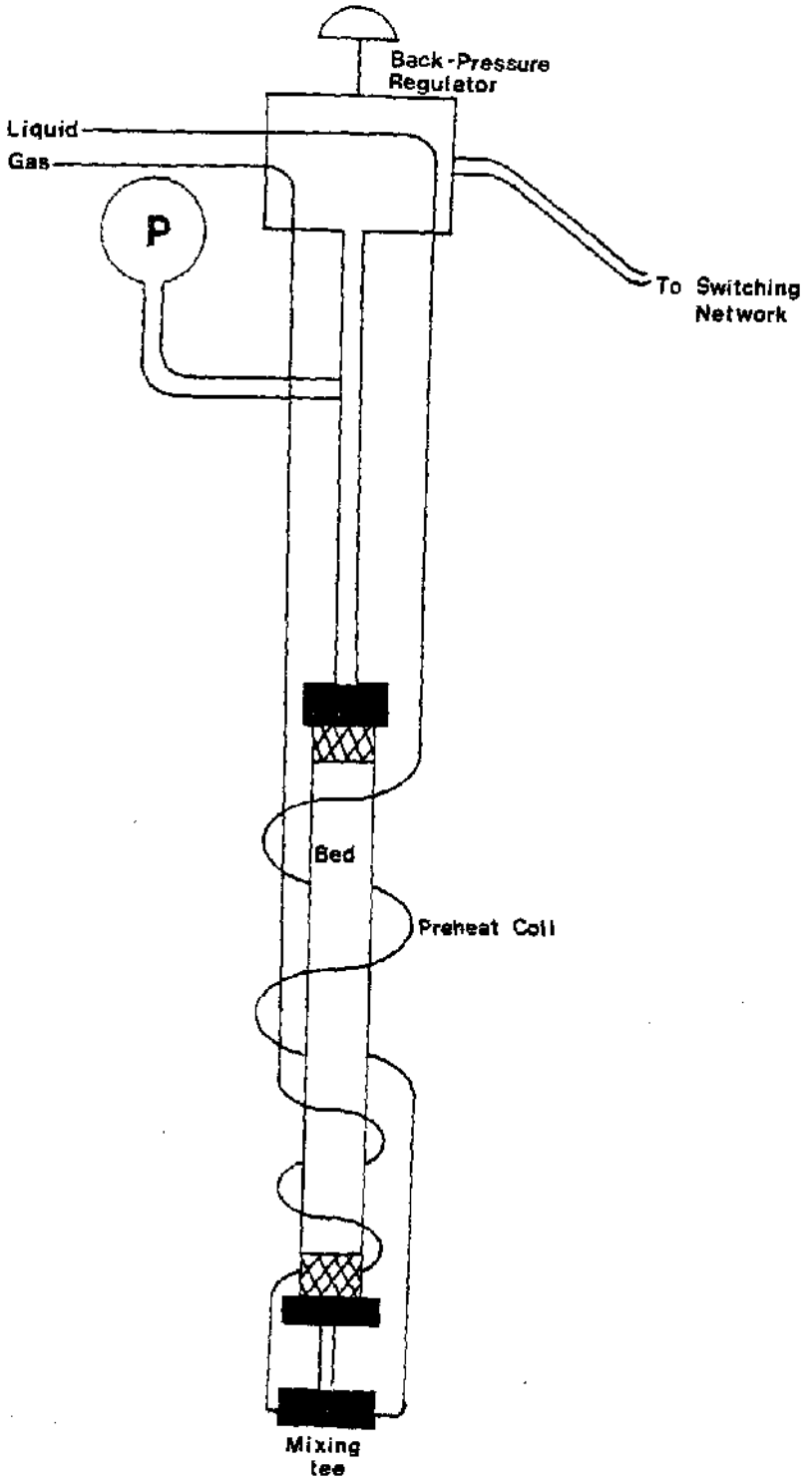

Figure 7. Microreactor System

measure back pressure, or pressure drop, and to regulate back pressure respectively.

Sample Collection

After the effluent from the reactor passed through the reactor exit section it passed through a stainless to glass transition tube into the collection network. The effluent then passed through a switching network, shown in Figure 8, which channeled the flow into any one of three identical collection units. The channel network and the transition region were all placed on a downnill slope to aid in the flow of any condensed product. The collection network, transition region, and the metering valve were all heated by electrical tape, and wrapped in insulating tape to prevent premature condensation.

The collection units were composed of three sample collectors clamped in series, and a water displacement bottle. The sample collectors, designed especially for this experiment, are similiar in form to dust impingers. As shown in Figure 9, the gas entered through a 5 mm o-ring joint. The gas continued through the inner glass tubing to the 1/32" (0.0o0 cm) dropper outlet. Here the condensed liquid separated from any remaining gas and fell to the botton. The non-condensed gas continued up and through the other outlet. This outlet, as the first, was constructed using a 5mm o-ring joint. The outer body of the collector was constructed from 8 mm I.D. glass tubing. The top of the

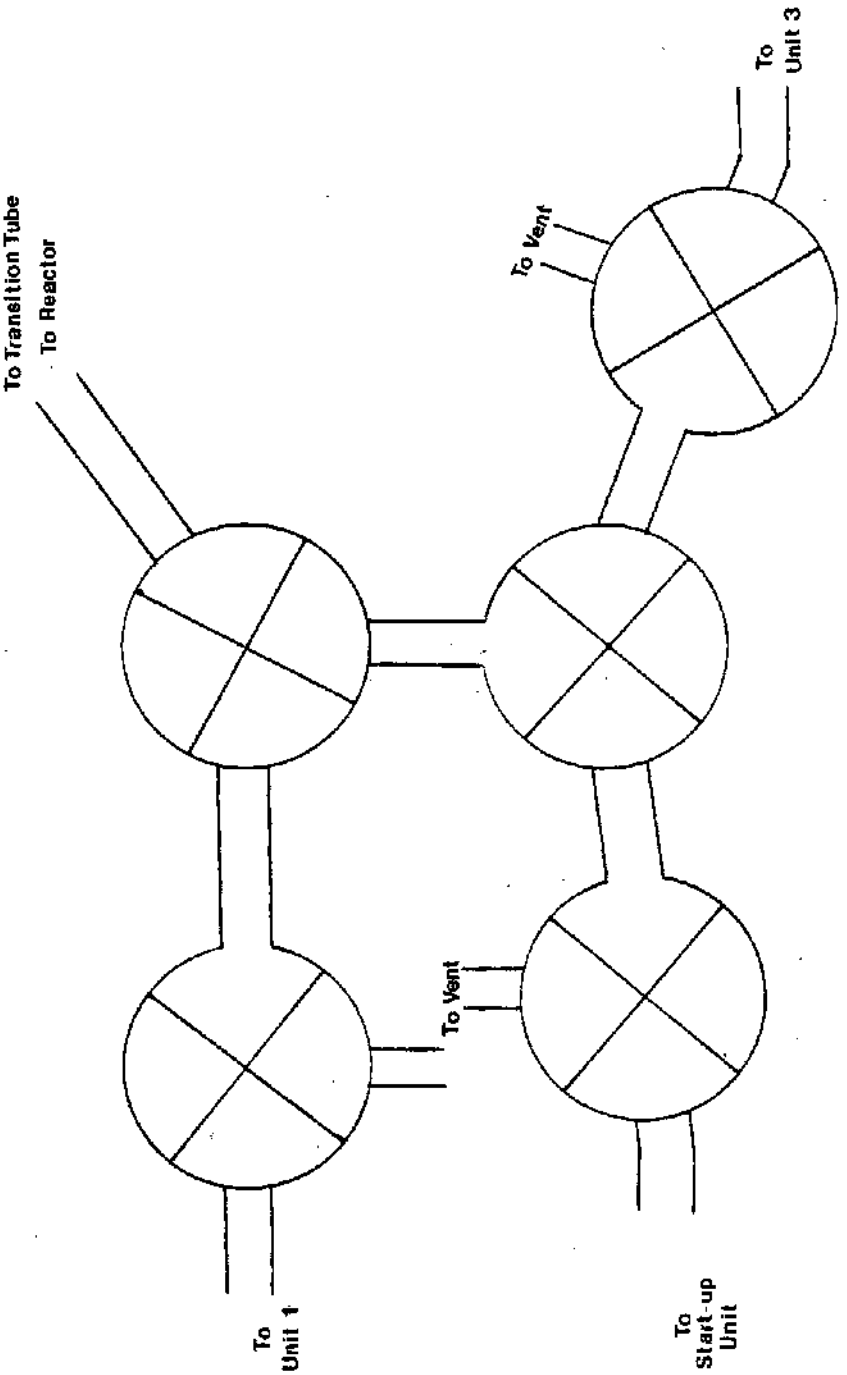

Figure 8. Sample Switching Network

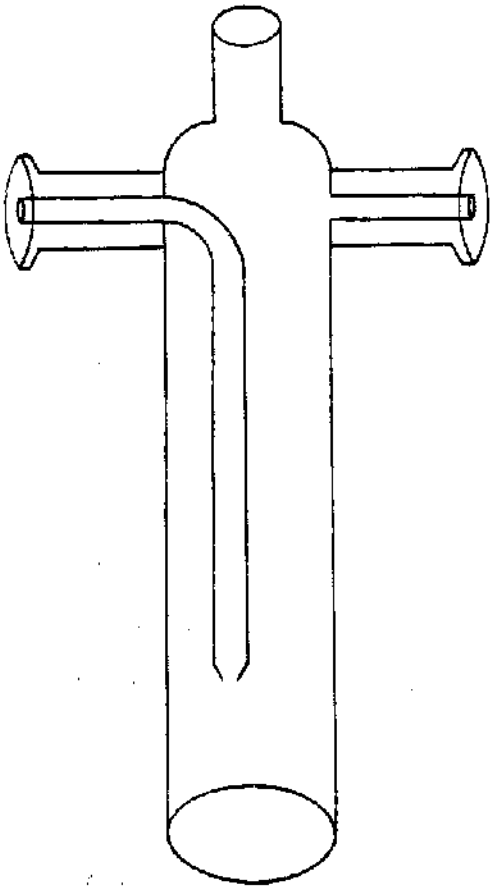

Figure 9. Sample Collector

collector was constrained into a shoulder and 1/4" (0.635 cm) O.D. throat arrangement. This allowed the placement of a rubber septum over the opening. This allowed the sample to be taken without any chance of contamination or chance of spillage. All collectors, along with the glass switching network were fabricated by the Texas A&M University Department of Chemistry glass shop.

The three collectors were cooled to three differing temperatures to catch three separate cuts of the product. The first was held at the freezing point of water, the second at a point approximately 253 K, and the third collector was cooled to approximately 233 K by a dry ice-acetone bath. The water displacement bottle, which contained calcium hydroxide to lower gas solubility, trapped any non-condensibles. A three-way valve was placed between the third collector and the water displacement bottle to provide an emergency release to the vent, if needed.

Isothermal Bath and Temperature Control

The isothermal salt bath and control loop was shown in Figure 10. The bath itself was constructed of a 4 foot (1.21 m) piece of 2 inch (5.08 cm) I.D. carbon steel pipe with the bottom capped and welded to prevent leaks. At the top of the bath a trough was placed to catch any spillage of molten salt. The heater load was provided by wrapping the bath with two Marsh beaded heaters. One heater, an 800 watt heater, provided any needed base heat input. This heater

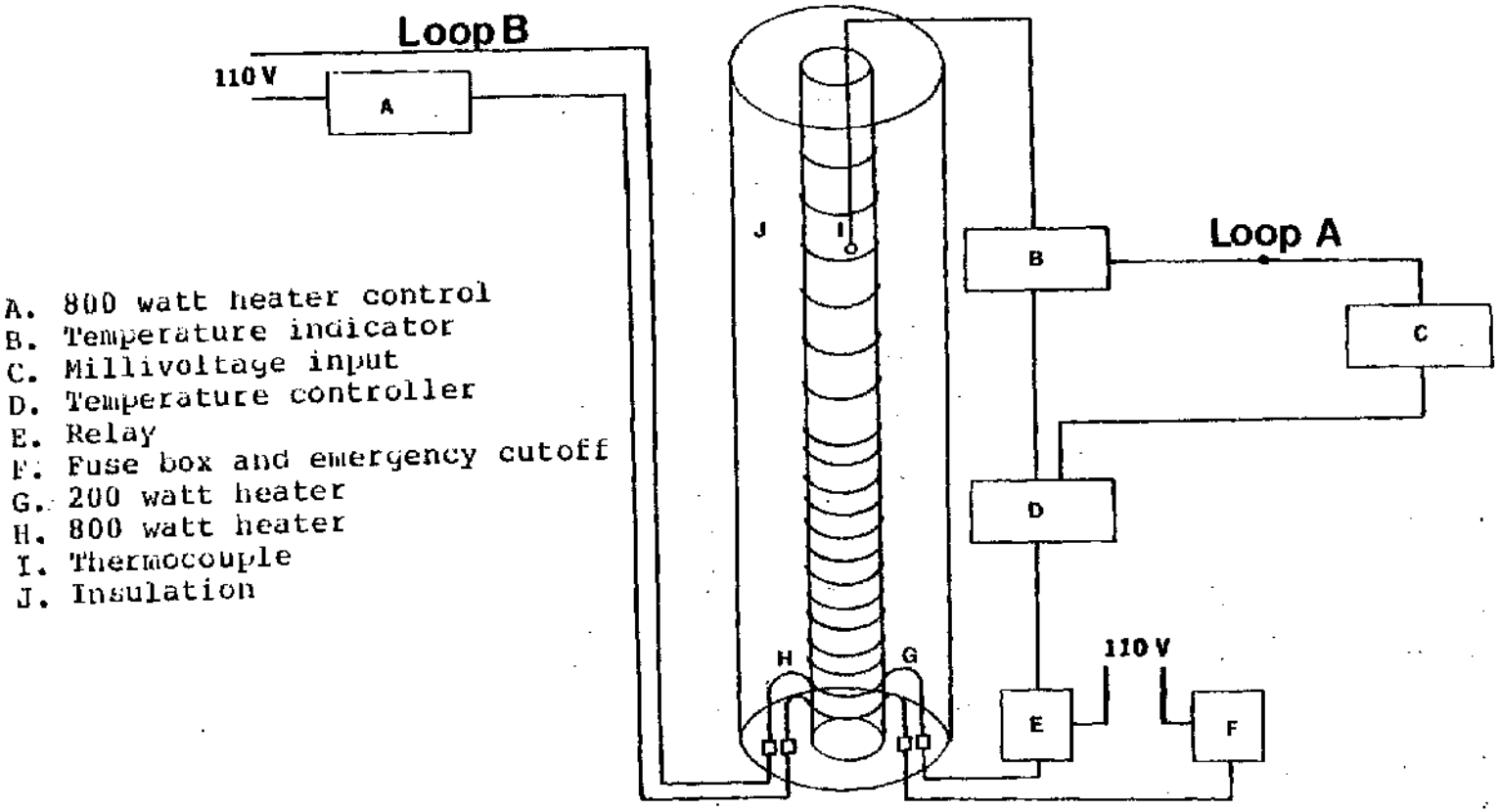

Figure 10. Isothermal Bath and Temperature Control System

loop is loop A in Figure 10. The controlling heater, a 200 watt heater, was connected as shown in loop B. The controlling heater was triggered by a solid state relay, Thermo Electric model 32807-33, which in turn was connected to a Thermo Electric model 32109-00 proportional temperature controller. The input to the controller consisted of an Omega CASS-140-14 type K thermocouple next to the reactor, and a constant millivoltage source. The millivoltage source provided a constant voltage in the same range as a type K thermocouple. The controller sensed any differences in voltage inputs and operated the relay accordingly. An Omega model 175 temperature indicator was placed in series between the bath thermocouple and the controller to provide a digital reading of the temperature. After the heater loops were completed the salt bath was wrapped with three layers of 1 in 6 lb Johns Manville "Cerablanket" to reduce heat loss.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Experimental Design

In order to have the most efficient experimental procedure, a classical factorial arrangement as shown by Himmelblau, (1970) was utilized. For the individual model compounds and the Fischer-Tropsch liquid a two-level, two-dimensional factorial design was employed, see Appendix A. The independent variables, temperature and space velocity, were chosen because these were the main points of study. Pressure was not included because it was to be the focal point of seperate independent experiments.

In order to observe the greatest change in the design the four corners of the design were obviously chosen to be the outer limits of the two independent variables. The outer limits of the temperature were first chosen to be 580 and 700 K. Later these temperatures were changed to 660 and 740 K due to experimental findings. Several experiments utilizing a higher space velocity were made in order to obtain kinetic data.

The experiments involving mixtures required a different approach. In order to hold the numbers of experiments to a minimum, the n-heptane was held constant at 70 weight percent. This component was held constant on the assumption that the Fischer-Tropsch liquid would be about 70% paraffinic hydrocarbons. This assumption was made on the basis of

the very wide range of Fischer-Tropsch liquids possible, ranging from less than one percent to more than 80 weight percent oxygenates, Groggin, (1958). This assumption accounted for one extra independent variable and added one dependent variable, these being the amounts of decanol and decanal in the mixture. This extra independent variable, along with temperature and space velocity required a two-level, three-dimensional factorial design, see also Appendix A. The outer limits of this design corresponded in part with the design for the individual model components. The extra variable, the amount of decanol added to the mixture, had limits ranging from 10 to 20 weight percent of the mixture.

In order to study special effects above and beyond the scope of a factorial experiment, "base case" experiments were used. The special effect experiments dealt with the effect of pressure, absence of added hydrogen, added water, and the effect of ion exchange. To study the effect of ion exchange the hydrogen form of ZSM-5 was utilized. In all cases the "base case" corresponded to the zero point of the factorial experiments for the individual model compounds.

Reagents

The n-heptane, reagent grade, was obtained from Aldrich Chemicals. The n-decanol and n-decanal, both grade one, 99 mole percent pure were obtained from Sigma Chemical Co. The Fischer-Tropsch liquid was obtained from the Pittsburgh

Energy Technology Center under
DOE contract DE-AC22-81PC41264.

Catalysts

The hydrogen form of the ZSM-5, H-ZSM-5, was obtained from the Pittsburgh Energy Technology Center under the above DOE contract. The ion-exchange and binding techniques are given in Appendix B.

Procedure

The procedure for the different catalyst types consisted of the initial startup, the individual experiments, product analysis and regeneration of the catalyst.

Initial Startup

After 3 grams of catalyst was placed in the reactor tube, and pressure tested to 400 psig, the reactor was placed in the salt bath and purged with helium. Then air was passed through the system at a flow rate of approximately 3 ml/min. After the air was introduced, the bath temperature was slowly raised from 600 to 810 K over a period of about 3 hours. Also during this time the air flow rate was increased to about 30 to 35 ml/min. When the final temperature was reached it was held for 1 hour. Then the temperature was slowly reduced to the desired reaction temperature. This procedure was performed on each new catalyst to burn off any water or stray carbon, and to activate the catalyst.

Individual Experiments

All individual experiments were conducted in the same manner. After the entire system was purged with helium the feed liquid and gas flow rates were calibrated to the desired rates. The collection network and reactor exit heater was then turned on and the systems then allowed to warm up to prevent condensation. When reaction temperature was attained, the liquid pump was started and the liquid was introduced to the system. At this point the time, buret reading, and pressure were noted. The feeds were allowed to mix and travel through the catalyst bed. This initial product stream was collected in a separate sample train.

After the initial product was detected in the startup train, and the feed rates stabilized, the product stream was directed into the second sample train. Again the time, buret reading, and pressure was noted. After a specified period of time, usually dictated by the capacity of the water displacement bottle, the product stream was directed to the third sample collection train. The same readings as before were taken. After the same period of time as the previous sample train the product stream was directed back to the startup train. The time, buret reading, and pressure were taken a final time, and the liquid feed was shut off. The gas feed was continued to purge the liquid from the reactor system. The individual collectors were weighed and recorded, along with the volume of water displaced. After

several minutes the gas feed was shut off and helium introduced to purge the system. The network heater was then shut off and any changes in the bath temperature were then made.

The product obtained in the collectors of the second and third sample trains, and the corresponding displacement bottles were analyzed in two separate ways. The liquid obtained in the first collectors, and any liquid product in the second also, was analyzed in a Varian Vista 44 gas chromatograph system. This system utilized a automated gas chromatograph Model 4600, Vista Model 410 chromatograph Data System (250 K bytes), and autosampler Model 8000. The gas chromatagraph utilized a flame ionization detector, and analyzed components in the C_5 and larger range. The column used was a 30 meter capillary with a SE-54 coating. The sample for injection was prepared by injecting 10 microliters into a vial containing 1 ml of carbon disulfide. An injection portion of 0.1 microliter was then used for analysis in the Vista 44.

The products obtained in the third collector and the displacement bottle were analyzed in a Carle model 157 gas chromatograph. This gas chromatograph utilized a complex series of columns in which the flow and temperature were controlled by a Hewlett-Packard 3385 automation system. This system was described in detail by Philip et al. (1978). This gas chromatograph utilized thermistors as the detector.

The C_1 - C_5 hydrocarbons were separated by a system of four columns, and CO, CO_2, H_2, and air by another column system. Representative gas chromatographic analyses are shown in Appendix D. However, before the product in collector three could be analyzed for the product distribution the condensed gases had to expanded so the sample would be a true representation of the products contained. This was accomplished by slipping a latex rubber balloon over one end, the other end plugged and the gas expanded into the balloon. After complete gas expansion the sample was taken.

Regeneration

After a series of three experiments the catalyst was regenerated. This frequent rate of regeneration was to insure that each experiment was seeing as fresh a catalyst as possible. After the third experiment and the system was throughly flushed with helium at a flow rate of 1 ml/min, air was slowly introduced, keeping the overall flow rate constant. When the air had replaced the helium, the flow rate was held constant for half an hour. The air flow was then slowly increased up to a flow rate of 40 ml/min at a rate of 1 ml/min, and simultaneously the air flow was increased to 40 ml/min the temperature was also raised from the previous reaction temperature to 815 K at a rate of 1 K/min.

When the regeneration temperature was reached, it was held for 30 minutes. The temperature was then slowly

reduced back to the initial temperature. During this time the flow rate of the air was reduced to about 5 ml/min. At this point helium was slowly re-introduced until the air flow rate was about 1 ml/min. The air flow was then shut off.

CHAPTER V

DISCUSSION OF RESULTS

General Discussion

In a general review of all experiments the product distribution varied greatly from reactant to reactant. For complete product distributions, see Appendix 5. However, due to the shape selectivitive nature of the catalyst similar behavior occurred in all experiments. In all experiments the cutoff for products occurred in the C_9 to C_{10} range, with no compounds larger than C_{11} detected. In most runs a low selectivity for methane was exhibited. The major products in most cases were C_3 to C_5 paraffins and aromatics. With the exception of one case, n-decanal at 660 K, few olefins were produced. In comparing the product distributions for the feeds, Figure 11 showed that the n-decanal had the highest aromatic yield, while n-heptane had the lowest yield. The Fischer-Tropsch liquid was shown to fall in an intermediate area. This was to be expected because of the varied hydrocarbon nature of the liquid, see Table 1. In all cases, unless otherwise reported, hydrogen was fed along with the hydrocarbon feed to help retard any coking that might be occurring.

In obtaining the breakdown of products several samples were analyzed by using GC/MS, located at the Texas A&M University Center for Trace Characterization. These results are shown in Figures 12 and 13. These results show two

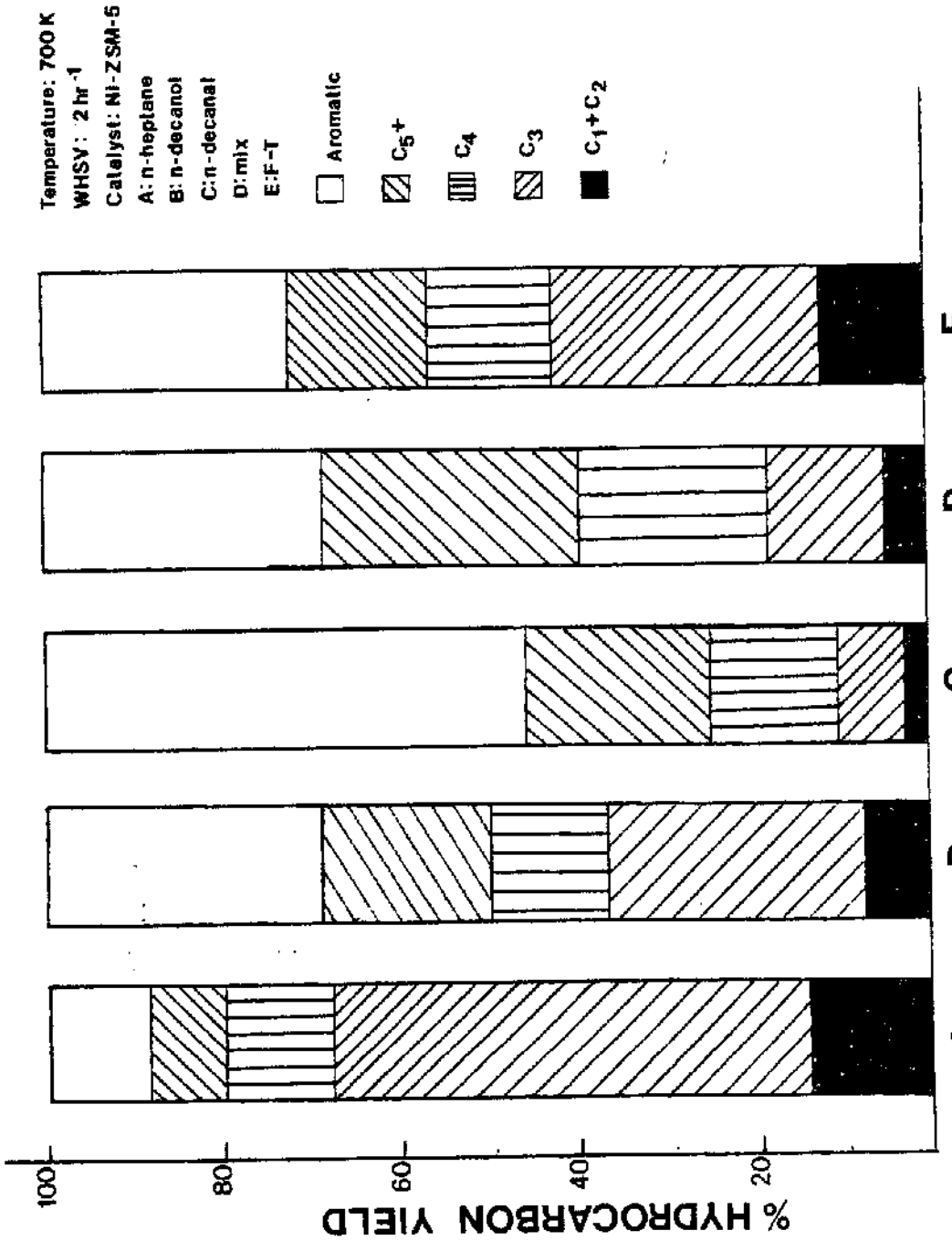

Figure 11. Product Distribution of the Different Feeds with H_2 Fed.

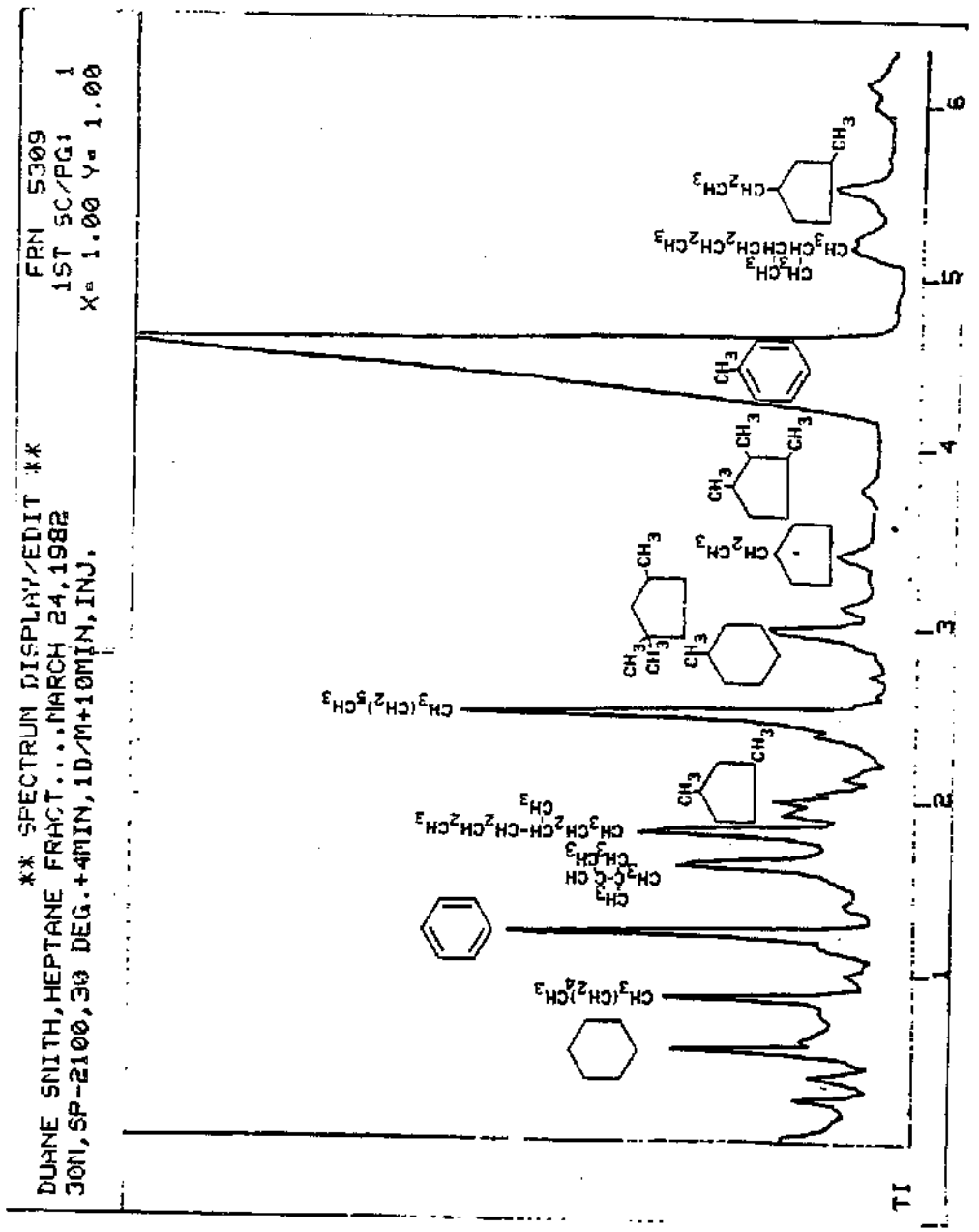

Figure 12. GC/MS Analysis of C_6 through C_8 Hydrocarbons

30 M, SP-2100 Capillary column; Temperature 30 C for 4 min, 1 C/min for 10 min, 4 C/min for 20 min, 10 C/min to 250 C.

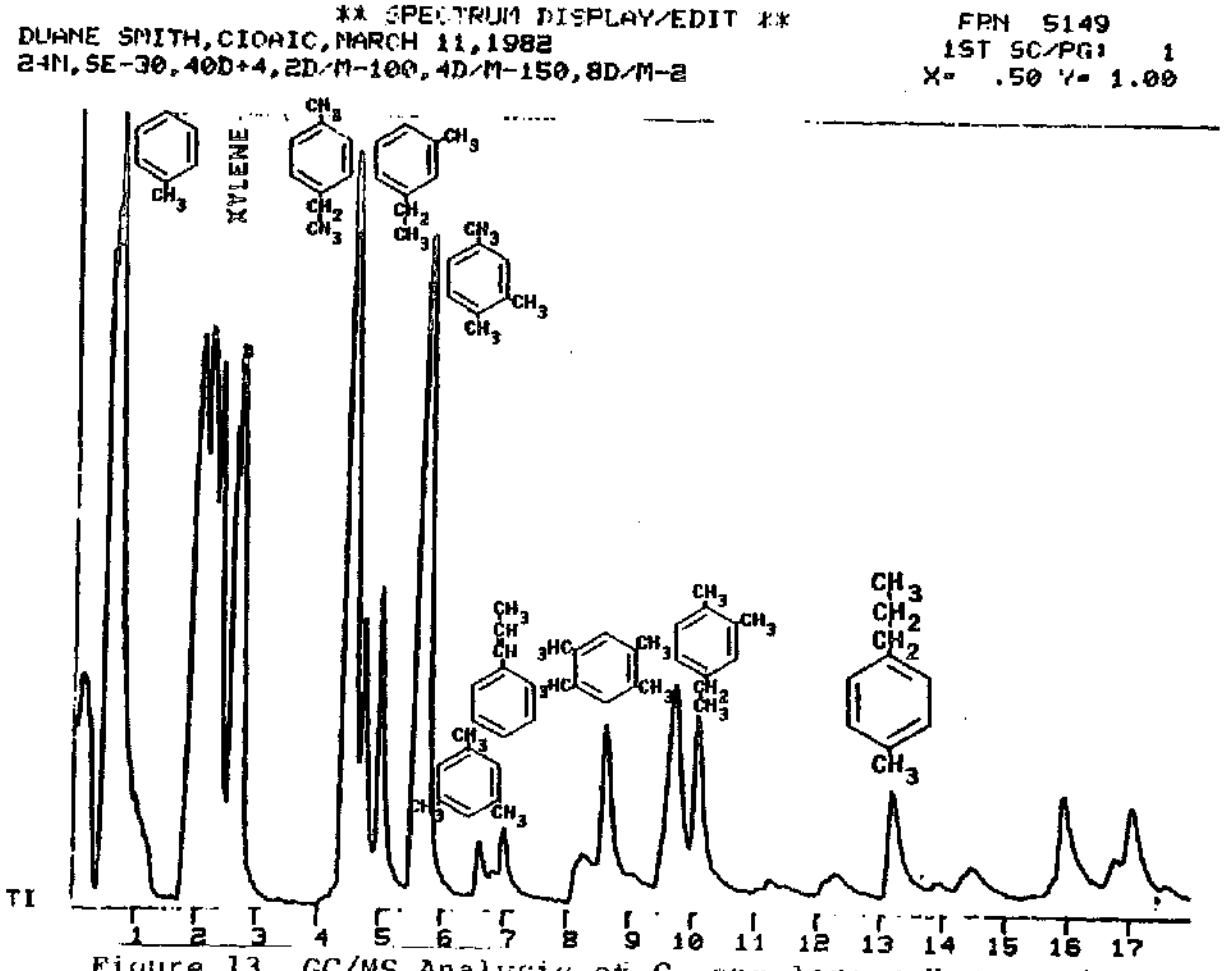

Figure 13. GC/MS Analysis of C_7 and larger Hydrocarbons

30 M, SP-2100 Capillary column, Temperature 30 C for 4 min, 1 C/min for 10 min, 4 C/min for 20 min, 10 C/min to 250 C.

different sample analyses performed using di-ethyl ether as the solvent in the first analysis, and n-octane as the solvent in the second. In the C_6 - C_8 range the compounds are either aromatic and/or methyl substituted cyclic compounds. There were few C_6 or larger olefins or paraffins.

To aid in the verification of the experimental accuracy of these runs mass balances were calculated for all runs. As shown in Appendix 5, almost all runs have a 90 or greater percent closure. Most discrepancies found in the results were normally traced to runs having less than satisfactory mass balances. In using elemental balances, only the carbon balance on selected runs was made. This was because the oxygen balance was used determine the amount of water collected in the liquid product, and since hydrogen was a feed this balance was neglected. However in all cases on which the elemental carbon balance was performed the resulting closure was very similar to the mass balance closure. For this reason only the mass balance closure was reported.

The reproducibility or the experiments was, most cases, very good. In all of the factorial designed experiments the midpoint of the design was run at varying times. The results of these experiments, shown in Appendix 5, showed only slight differences in the product yields. These results were independent of whether or not the runs were

performed on the same day, or whether or not regeneration had occurred between the runs. This slight difference in yields, along with the mass balance closures being on the average, greater than 90% provided the basis for the assumption that the experimental error was very close to the average value of the mass not accounted for in the mass balances. This was logical in that the runs which exhibited different behavior were the runs which had a lower mass balance closure.

The conversion for all reactants, except n-heptane, was found to be 100 percent. This included the Fischer-Tropsch liquid. The n-heptane, though having a conversion of 98+ percent, provided a basis for calculating a possible activation energy. To do this a first order decomposition was assumed and a molar expansion term was calculated. Then a rate constant was determined (Holland and Anthony, 1979). The WHSV used in the calculations was based on the total catalyst including the binder. When the rate constant was plotted on an Arrhenius type plot the resulting activation energy was 11.7 kcal/mole, Figure 14. The corresponding rate constant for the Zn-ZSM-5 was found to be 7.4 kcal mole. These were of the same magnitude as an activation energy of 12 kcal/mole found by Leiderman et al. (1978), for the decomposition of methanol.

Temperature Effects

The temperature effect was shown to be one of the most

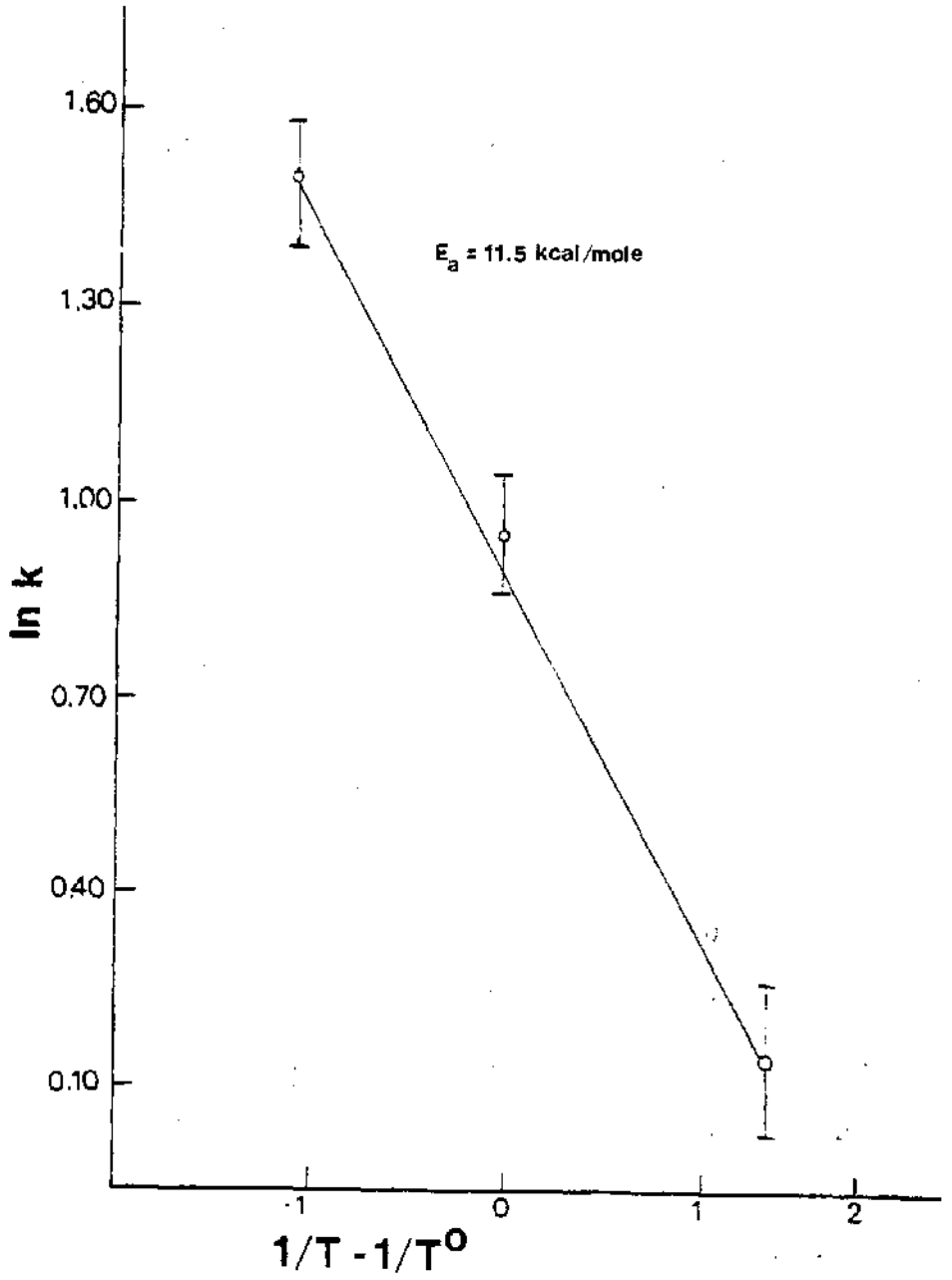

Figure 14. Determination of Activation Energy for n-heptane over Zn-ZSM-5. $H_2/HC = 2.0$

important process variables in the study. To show the temperature effect two seperate methods were used.

The first method utilized the factorial experiments as the experiments were intended. The conversion of n-decanol over Ni-ZSM-5 at two different temperatures and nearly constant space velocities was shown in Figure 15. The aromatic yield only increased slightly, from 15.23 to 18.11 weight percent. However the light gases (methane and ethane) increased almost by a factor of 4. The C_5+ oils (non-aromatic compounds C_5 and larger) and butanes decreased by almost 10 weight percent. The individual aromatic ratios of benzene/toluene and xylene/toluene stayed fairly constant.

The same result was shown for the n-decanol when reacted over the Zn-ZSM-5, Figure 16. With the increase in temperature the yield of aromatics rose 7 weight percent, while the propane content rose nearly 17 weight percent. The butanes and C_5+ oils again dropped by a cumulative total of nearly 23 weight percent. The light gas content rose by a total of 13.88 weight percent. The phenomena was reproduced in almost every run including the Fischer-Tropsch liquids. The behavior extended from catalyst to catalyst. The behavior was on that each series that the aromatics would increase, along with methane through propane. The butanes and C_5+ oils would then decrease. The one major exception to this behavior was the n-decanal at the lower

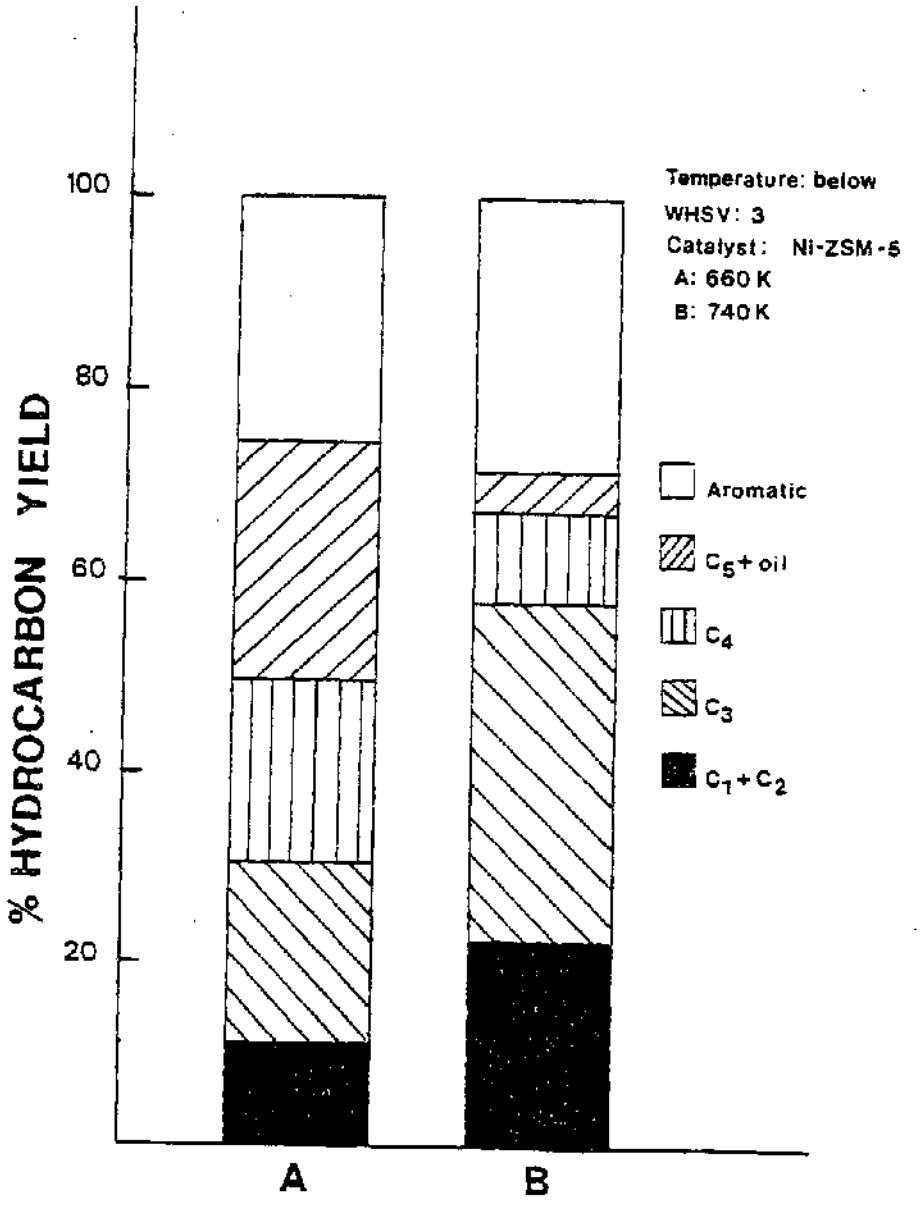

Figure 15. Product Distributions for n-decanol over Ni-ZSM-5 at 660 and 740 K. $H_2/HC = 2$

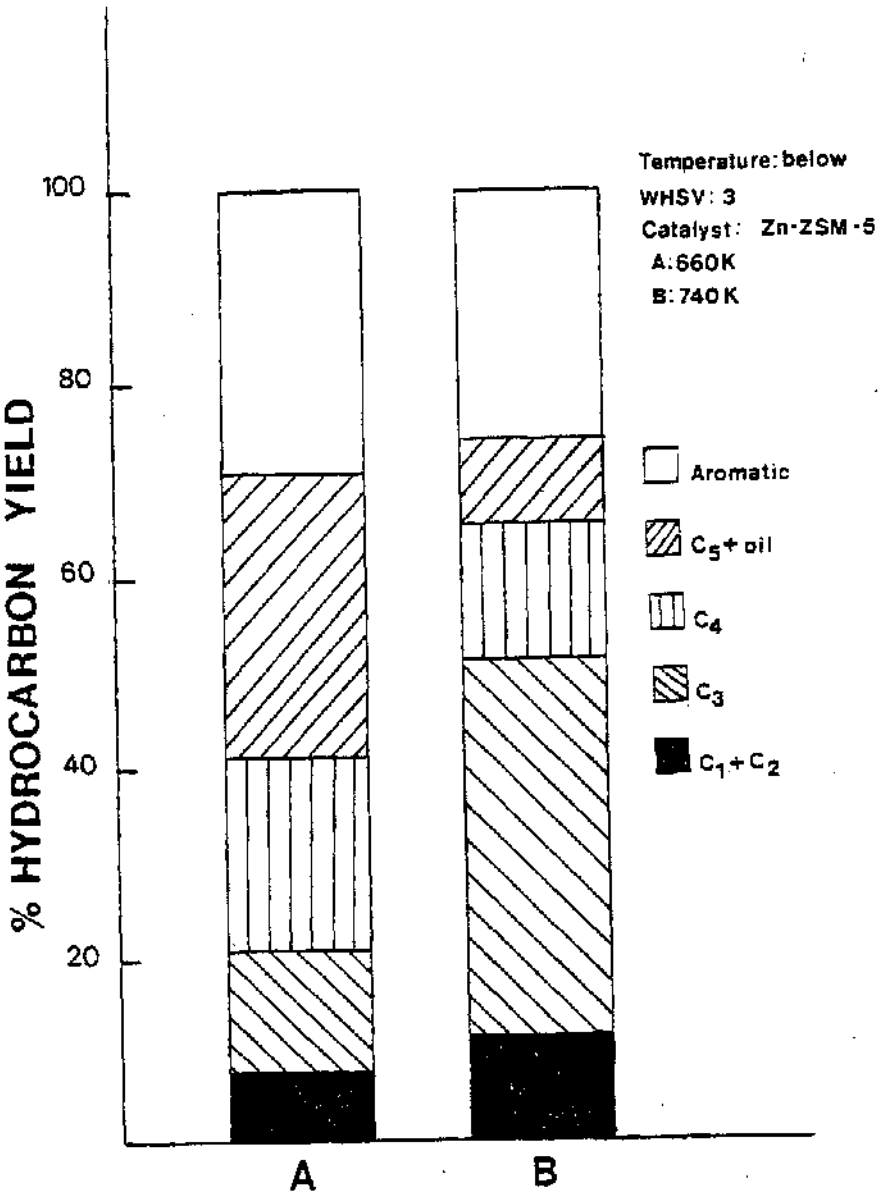

Figure 16. Product Distributions for n-decanol over Zn-ZSM-5 at 660 and 740 K. $H_2/HC = 2$

temperature. Figure 17 compared the n-decanal distribution with the n-decanol. The olefin content of the n-decanal greatly exceeded the n-decanol. This was most likely due to a temperature too low to have completely initiated the aromatization reactions.

The second method utilized the results from the initial n-heptane runs over the Zn-ZSM-5. As stated earlier these runs were made at a lower temperature. The low aromatic yields caused the temperature parameters to be increased for further experiments. However these results can be used to show the temperature effects. In Figure 18, the aromatic yield was plotted as a function of temperature. The final point at 773 K was from Cattanach, (1973). The aromatic yield started at about 5 weight percent and increased to 32 weight percent. Aromatic production increased as the temperature was increased.

In both methods, that as the temperature was increased, the aromatics, light gases, and propane increased, while the butanes and C_5+ oils decreased. At first glance this increase in temperature seemed to bring about an enhanced product. But this was not as true as it seemed. All product yields were closely examined and though the aromatic yield increased as the temperature increased, the total liquid (butanes and higher) content decreased. This meant the product, though higher in aromatics, was dropping in gasoline content. This was also the case in the conversion

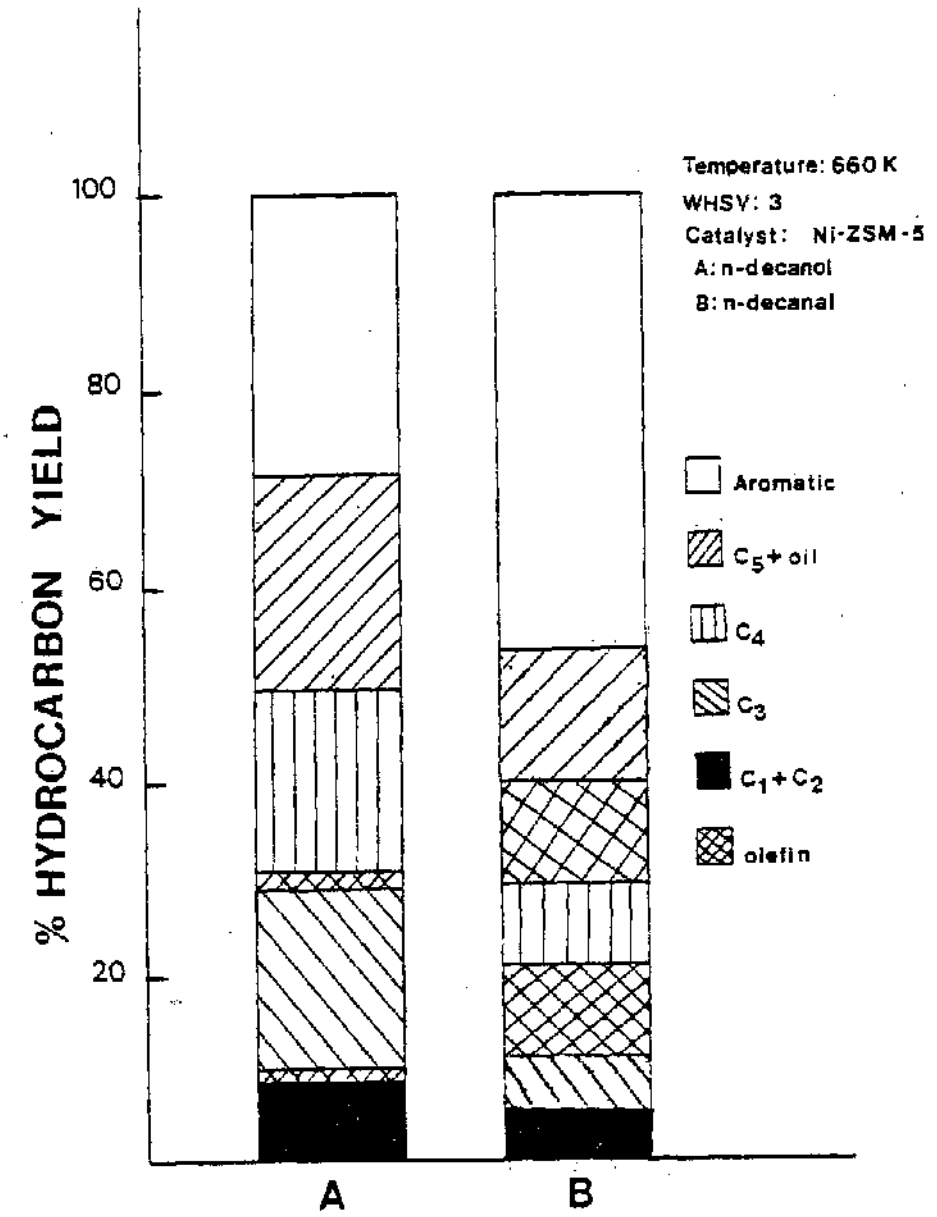

Figure 17. Olefinic Content Comparison at 660 K for n-decanol and n-decanal

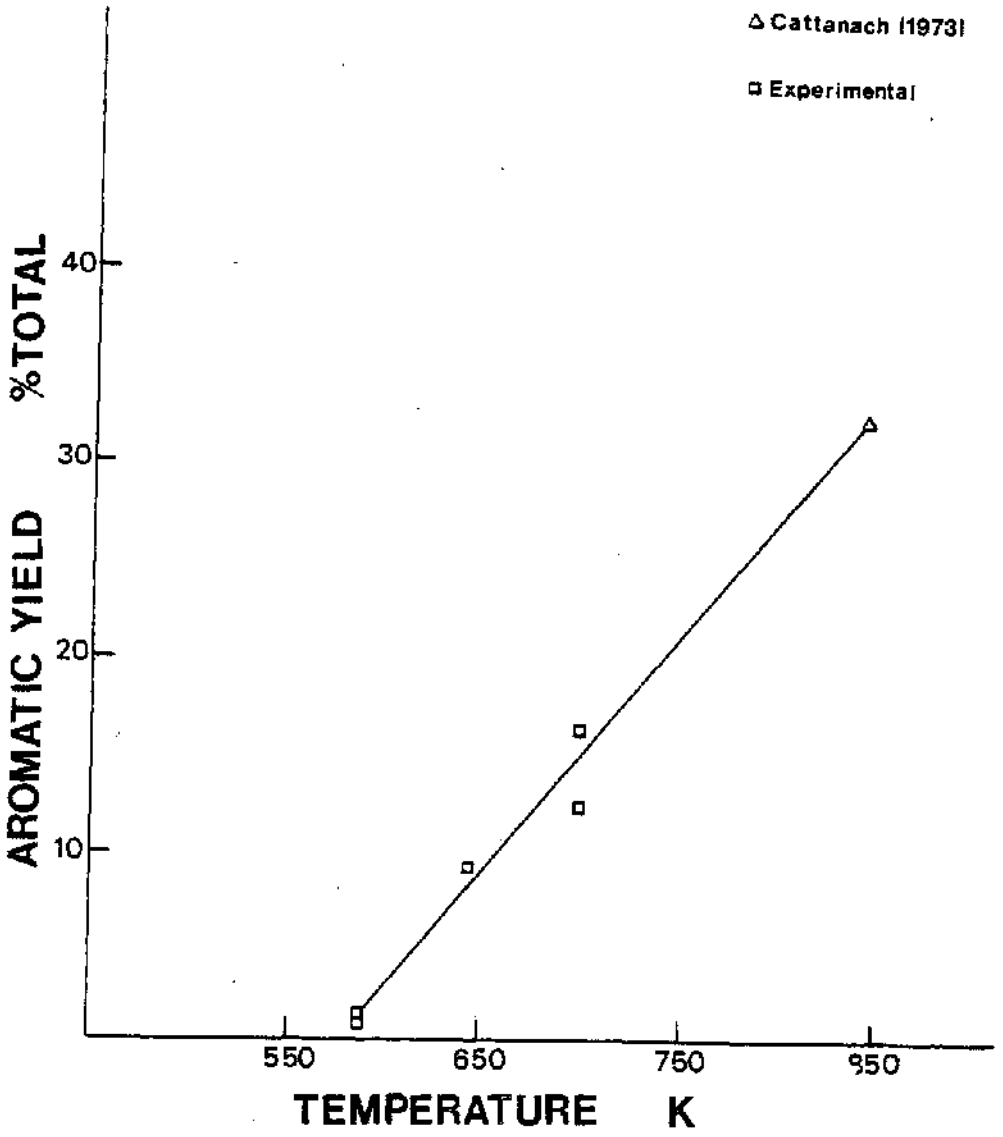

Figure 18. Effect of Temperature on Aromatic Formation for n-heptane over Zn-ZSM-5. $H_2/HC = 2$