

grain growth. This lack of change in the diffraction patterns showed that for the ion-exchanged catalysts, there was no discernable change even after over 100 hours on stream. Due to the low amount of metal exchange, the zinc or nickel was not observed on the patterns. When the catalysts were recovered from their reactor tubes the catalysts were examined. The color of the catalysts had changed from a chalky white to a charcoal color. Also a darkening of the catalyst was observed when going from the top of the catalyst bed down. However this probable coke was not present in sufficient enough quantity to be detected in the x-ray diffraction.

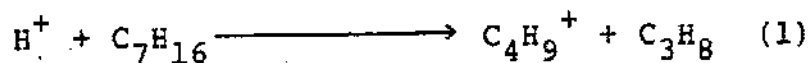
These two separate studies showed the catalyst's durability and resistance to coking. However it should be noted that even at the end of the extended run the conversion had not dropped below 99+ percent. The change in the product distribution however was significant. It was then postulated that the product distribution for a given catalyst can possibly be selectively shifted by deliberate coking. However this could not be proven at this time.

Reaction Mechanism

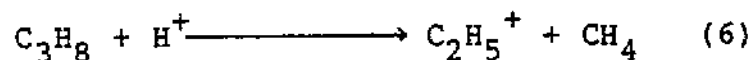
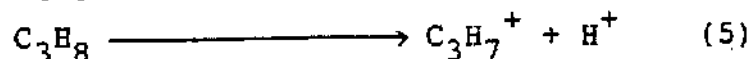
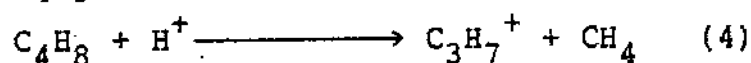
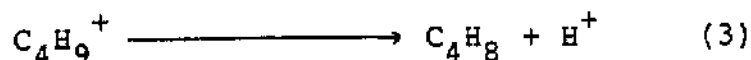
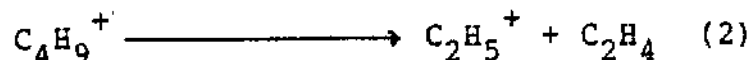
The reaction mechanism is of interest for the possible prediction of formation of compounds. The possible mechanism for the conversion of n-heptane was discussed due to the simplicity of the molecule, i.e. no oxygen.

The first step in the reaction was an obvious step, the

cracking of the n-heptane molecule, Katzer et al. (1980).



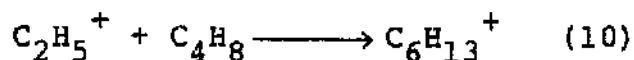
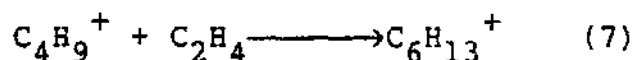
This would have been the most common of the cracking products. This step would then have proceeded in several possible ways.



It was in two steps, (5) and (6) that one possible rate controlling step was occurring. This reasoning was due to the large difference in propane yields obtained when comparing n-heptane reactions over Ni-ZSM-5 with and without hydrogen. If the hypothesis about the competition of the hydrocarbons and the hydrogen were true, then a slower step would have been the most affected. The addition of hydrogen caused a large rise in the propane yield, with a corresponding change in the higher molecular weight products. Though not specifically shown, most of these reactions are probably reversible. Also during this time isomerization will occur giving branched species. The butanes will go from the normal form to an isoform, and there will migration on the carbonium ions to more stable arrangements. Most likely these reactions were to shift the charge to the midpoint of the normal ion, which was more

stable.

The next step was the formation of the higher paraffins and olefins. This area was postulated to contain at least one more rate controlling step because of the fluctuation of the C₅ - C₇ compounds. Most likely the rate controlling step involved the C₅ compounds.

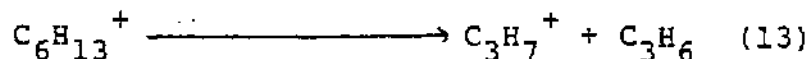
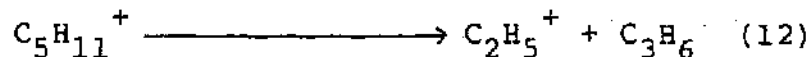


These steps are probably rapid in relation to the hydrogenation of the individual ions. This was supported by the normally constant butane yields. The probable rate controlling step in this area was, as indicated previously, occurred in steps 8 or 9. After the above reactions occurred, there was probably a high competition for the C₅.



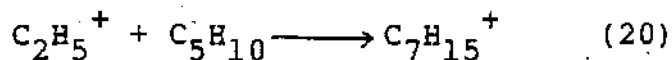
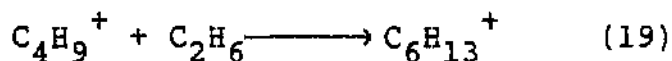
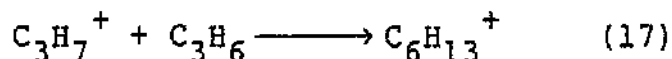
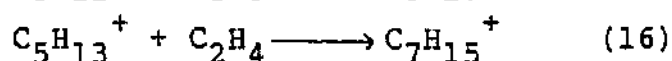
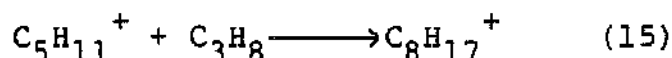
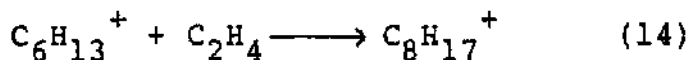
Again isomerization would be occurring. These reactions would now take a larger part in the mechanism.

Now with larger molecules being formed, secondary cracking reactions began occurring. These reactions constituted cracking of the olefinic products, and could have constituted the formation of more smaller olefins and paraffins.

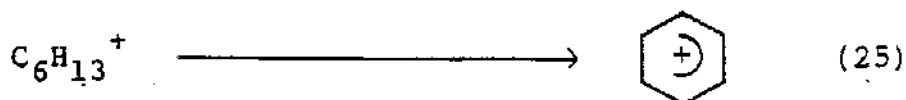
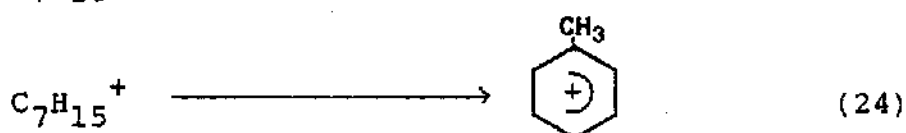
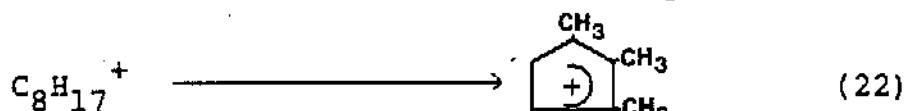
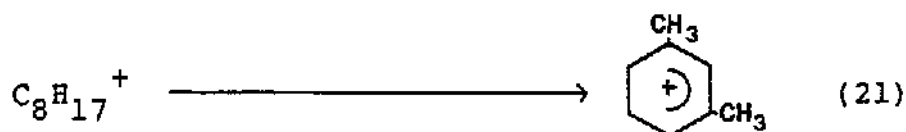


This could have been the basis for an increased olefin concentration for use in the overall reaction.

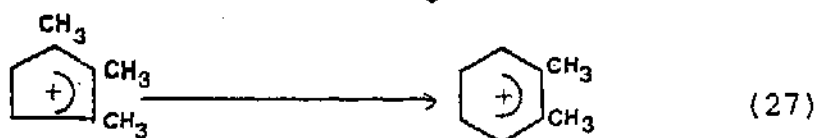
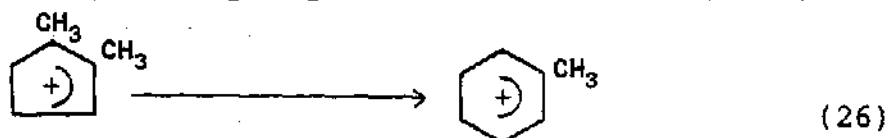
With the addition of secondary reactions adding olefins to the overall reaction, further oligomerization and aromatization can occur



At this point the molecules probably started becoming too bulky, and condensation occurred. The compounds cyclized into the smaller cyclopentyl and cyclonexyl species.



The cyclopentyl species could then rearrange its structure into a stable cyclonexyl species, Deno et al. (1963).

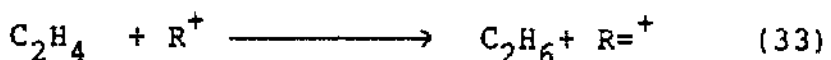
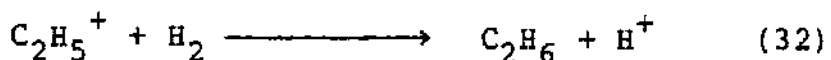
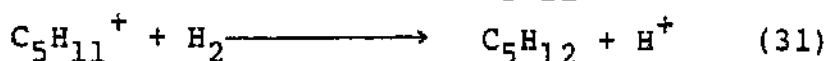
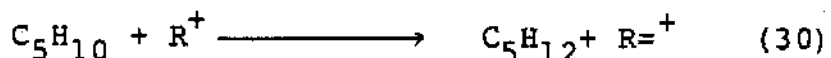
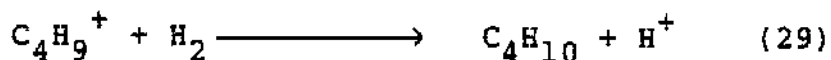
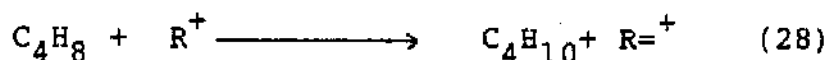


These cyclonexyl species would then have donated several H^+ to form aromatic species of predominately $\text{C}_6 - \text{C}_8$ range. The higher range aromatics could have come from methyl or ethyl substitution of the benzene ring. This mechanism was taken in part from Vadrine et al. (1980), who postulated the steps 18 and 26 in the production of benzene from methanol. However, the above mechanism shows the formation of the predominate toluene and xylene without the predominant methyl substitution found in the conversion of methanol.

The peak identification in Figure 12 seemed to coincide with this mechanism. The large number of cyclopentyl species were shown to be highly methyl substituted ions with several highly branched paraffins. Since there were few olefins present in Figure 12, the rate at which the higher olefins cyclized must have been fast.

To explain the yield of paraffins the comparison of the paraffins contents in the runs made with and without hydrogen were used. These runs showed that though the paraffin yield is less when the hydrogen was not fed, there

was still a significant amount of paraffins present. This was easily explained by the fact that when aromatization occurred, hydrogen was given off. This excess hydrogen and any additional hydrogen fed could have caused the following reactions



R = carbonium ion

The propane was discussed earlier. The methane occurred from secondary cracking. These reactions, though shown as reversible were probably unable to return to the olefinic form and the only possible way to re-enter into the reactions was through the cracking of the chain. This was supported by the fact that at higher temperatures there was a decrease in butanes and pentanes.

This mechanism, though postulated using n-heptane, was probably applicable to the other feeds, including the Fischer-Tropsch liquid. The main difference was in the addition of an oxygen component. This oxygen, as long as it was in the alpha position, probably aided in the reaction by weakening the carbon-carbon bond adjacent to the

carbon-oxygen bond. This weakening of the bond probably lowered the initial activation energy and eased the initial cracking. The severed carbon with the oxygen attached then completed the reaction through a mechanism similar to the proposed methanol mechanism (Vedrine et al. 1980, Anderson et al. 1980). However it was possible there was some difference in the dissociation of the oxygen bond, whether or not water, CO or CO₂ was favored. In most cases it was shown the formation of water was favored.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The objective of this research was to gather catalytic and kinetic data on model compounds and Fischer-Tropsch liquid. These data were to be used to categorize the possible behavior exhibited by compounds similar in scope to Fischer-Tropsch liquids. Two separate metal-exchanged ZSM-5 catalysts were used, along with the hydrogen form.

Catalytic testing results showed a wide range of product distributions with n-decanal producing the highest liquid and aromatic yield. The n-heptane produced the lowest of both aromatics and liquids. The Fischer-Tropsch liquid fell between these two types. The temperature effect showed the ability to vary the total liquid product of a reactant. The aromatic yield however, stayed somewhat consistent. This same behavior was also exhibited in the Fischer-Tropsch liquid. This ability to vary the yield of general products enables one to choose what products are to be produced without extensive trial and error.

The space velocity effect was shown to be of only slight importance in the range studied. This does not mean the space velocity was not of importance at much higher velocities. Literature studies showed that if the space velocity was greatly increased, the yields changed. However this was not the case for these experiments.

The effect of water and additional pressure proved to

be detrimental to the upgrading of the reactants. Water however increased the total liquids product, while lowering the aromatic content. But in a large scale operation the energy required to vaporize the water would probably outweigh the economic benefit of production of the extra liquid product.

In a result opposite to the result incurred from the addition of the hydrogen over-pressure the absence of hydrogen proved to aid in the yield of total liquid products. The reason for this was postulated to be the lessening of competition for reaction sites incurred by the absence of hydrogen.

Coking and ion-exchange studies showed a strong catalyst which resisted breakdown of crystallinity over a period of time, approx. 100 hours. The catalyst shows a high resistance to coking. Studies using x-ray diffraction showed no change of phase whatsoever. The ion-exchange showed another method in which to vary the product distributions, while usually upgrading the entire product.

The above results showed that through the combination of ion-exchange and variation of process variables the yields of a hydrocarbon mixture such as the Fischer-Tropsch liquid could be qualitatively predicted. A simple example of the choosing of the process variables to start a reaction in the general vicinity of the desired product can shown.

For a mixture similiar to the synthetic mixture used

herein, a gasoline type mixture with maximum liquid and C_4 yields could be produced using a form of ZSM-5. In study, the Ni-ZSM-5 consistently gave the higher liquids content along with a high aromatic content. Hydrogen should be added, not because of a increased yield, but to aid in reducing coking. In fact there is little difference in the total liquids content when the synthetic mixture is reacted with or without hydrogen. This was one of the exceptions which showed little change in the absence of hydrogen. The pressure should obviously be kept at atmospheric due to both the cost and the loss of liquid yield at higher pressures. The space velocity can be varied to fit the need, but the best initial start should be a WHSV of 1. Finally the temperature offers a large leeway in the production distribution. At both 700 and 740 K the liquid content is essentially the same. However the selectivity to aromatics differs vastly. At 700 K the aromatic content was 27.96 weight percent, while at 740 K the aromatic content was 46.90 percent. If a higher octane gasoline mixture was desired the higher temperature should be used. However if the gasoline is to be blended to make jet fuel the aromatic content should be lowered to meet the requirement for aromatics. This simple example showed the ability to predict selectivities which would enable the user to be able to quickly reach the desired point of maximum production of a chosen product with little trial and error.

Based on this study and the literature review the following recommendations were suggested for further study.

1. A factorial series of experiments which includes temperatures in the range of 780 to 840 K. This would be to find the maximum yield of aromatics.
2. In a separate series of experiments an increase of space velocity would be needed to explore the outer limits of aromatic and liquid production.
3. The study of whether or not increased amounts of exchanged metals significantly changes product yields should be studied.
4. Other metals such as magnesium should also be tried. This would show more variation caused by the metal exchange.
5. Another possible method was to study to effect of selective coking on the catalyst on changes of product yield.

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APPENDIX A
Factorial Design

The factorial design, as discussed in the experimental procedure was coded as follows:

Code:	-1	0	+1
Temperature K:	580	640	700
WHSV hr ⁻¹	1	2	3

This coding resulted in a total of five separate experiments. The mid-point of the design was repeated for the determination of experimental error.

This design was later modified because of the temperature being too low to obtain the desired results. The modified design was coded as follows:

Code	-1	0	+1
Temperature K:	660	700	740
WHSV hr ⁻¹ :	1	2	3

The design for the mixture required a different approach. The design was as follows:

Code	-1	0	+1
Temperature K:	660	700	740
WHSV hr ¹ :	1	2	3
n-decanol wt. %:	10	15	20

This design would then implicitly hold the n-heptane at 70 weight percent and the n-decanol at 70 - (% n-decanol). The actual experimental procedure was to be a half

replicate, but was discontinued when little change in product yields were detected.

APPENDIX B

Catalyst Preparation

The H-ZSM-5 was ion-exchanged in accordance with U.S. Patent 3960978 (Givens et al. 1976). The following are the ion-exchange procedures used in this thesis for the Ni and Zn-ZSM-5. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was 30.

Zinc Exchange

1. A slurry of 6 gm. H-ZSM-5, 52 ml 0.5 N ZnCl_2 , and 18 ml 0.5 N NH_4Cl was mixed in a three-neck flask.
2. The slurry was heated to 189-192 °F.
3. At the above temperature the slurry was refluxed, while stirring for 4 hours.
4. After reflux the slurry was filtered and washed with 600 ml distilled, de-ionized water.
5. The cake was then dried at 230 °F for 75 hours.
6. The catalyst was mixed with 32 weight percent alumina. The alumina was prepared by cofeeding a solution of 2.5 % Al_2O_3 and 5.0 % sodium aluminate at 343 - 348 K and a pH of 7.5. The Al_2O_3 solution was then aged at temperature for 30 minutes. Then the solution was filtered, washed, and dried. The alumina was then mixed with the catalyst and sufficient water added to form a thick slurry. The resulting slurry was then pelletized into 1/16" (0.159 cm) diameter pellets.
7. The catalyst was calcined in air for 10 hours at

1000 °F.

8. The catalyst was then crushed into 100 micron particles.

Nickel Exchange

1. A slurry of 6 gm H-ZSM-5 and 59 ml of 0.5 N $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was prepared in a three-neck flask.

2. The slurry was heated to 190 °F.

3. After heating to 190 °F, the slurry was refluxed, while stirring for 4 hours.

4. After refluxing the slurry was filtered and washed for 2 hours to remove any excess Ni.

5. The catalyst was dried for 18 hours at 230 °F.

6. The dried catalyst was mixed with 35 weight percent Ludox AS-40 and pelletized to 1/16" pellets.

7. The resulting catalyst was calcined in air for 10 hours at 1000 °F.

8. The catalyst was then crushed to 100 micron particles.

H-ZSM-5

1. The H-ZSM-5 was mixed with 35 weight percent Ludox AS-40

2. The slurry was pelletized to 1/16" (0.159 cm) and calcined in air for 10 hours at 1000 °F.

APPENDIX C
Calculations

The following calculations were used in the tabulations of distributions and results found in the body of this thesis. The product distribution used two different methods, tailored to each chromatograph. The response factors used in the calculation of the liquid products were found in Dietz (1967). The pertinent notation was shown below.

Notation:

P = log mean pressure using reactor bed entrance and exit, atm

n = molar flow rate, mol/s

R = gas constant

T = temperature K

B = molar expansion factor

k_c = rate constant, sec^{-1}

m_i = mole fraction of component i found in Carle gas chromatograph analysis

MW_i = molecular weight of component i , g

y_i = weight fraction of component i

Wt_j = weight collected in individual collector, g, j = gas, CO_2 , liquid

R_i = response factor for liquid component i

ρ_{ho} = density of component i , g/cc

V_{ol} = volume displaced in the water displacement
bottle, ml.

M_{in} = mass of feed in as figured by the difference in
buret readings taken at the beginning and end of each sample
collection, g.

M_{out} = cumulative total of mass collected in sample
collectors and the water displacement bottle, g.

v_0 = volumetric flow rate at reaction entrance
temperature and log mean pressure ml/s

W = weight of catalyst, g.

X = conversion

Product Distribution:

1. Weight of Product Collected in Water Displacement Bottle:

$$Wt = (y_i \text{ gas } \rho_{o_i}) \text{ Vol}$$

2. Carle Gas Chromatograph:

$$Y_i \text{ gas, CO}_2 = (m_i \text{ MW}) / \sum (m_i \text{ MW})$$

3. Varian Gas Chromatograph:

$$Y_i \text{ liquid} = (A_i/R_i) / \sum (A_i/R_i)$$

4. Total Percent Product Distribution:

$$Y_i \text{ total} = [(y_{i,j} Wt_j) / Wt_{\text{total}}] \times 100.$$

5. Mass Balance:

$$[1 - ((M_{\text{in}} - M_{\text{out}}) / M_{\text{in}})] 100.$$

6. Inlet Feed Rate:

$$P (v_o) = n (R T)$$

$$v_o = (n R T) / P$$

7. Molar Expansion Factor:

$$b = \sum Y_i / MW_i$$

This assumed that the conversion was high enough to ignore any unreacted feed in the effluent from the reactor.

8. Rate Constant:

$$-by_a^o \ln(1-X) - (y_a^o b - 1) X = k_c (W/v_o) y_a^o$$

APPENDIX D

Representative Gas Chromatographic Analyses:

The representative analyses were picked to show the analysis of the three products. The liquid analysis was in Figure 44, the CO₂ analysis in Figure 45, and the water displacement in Figure 46.

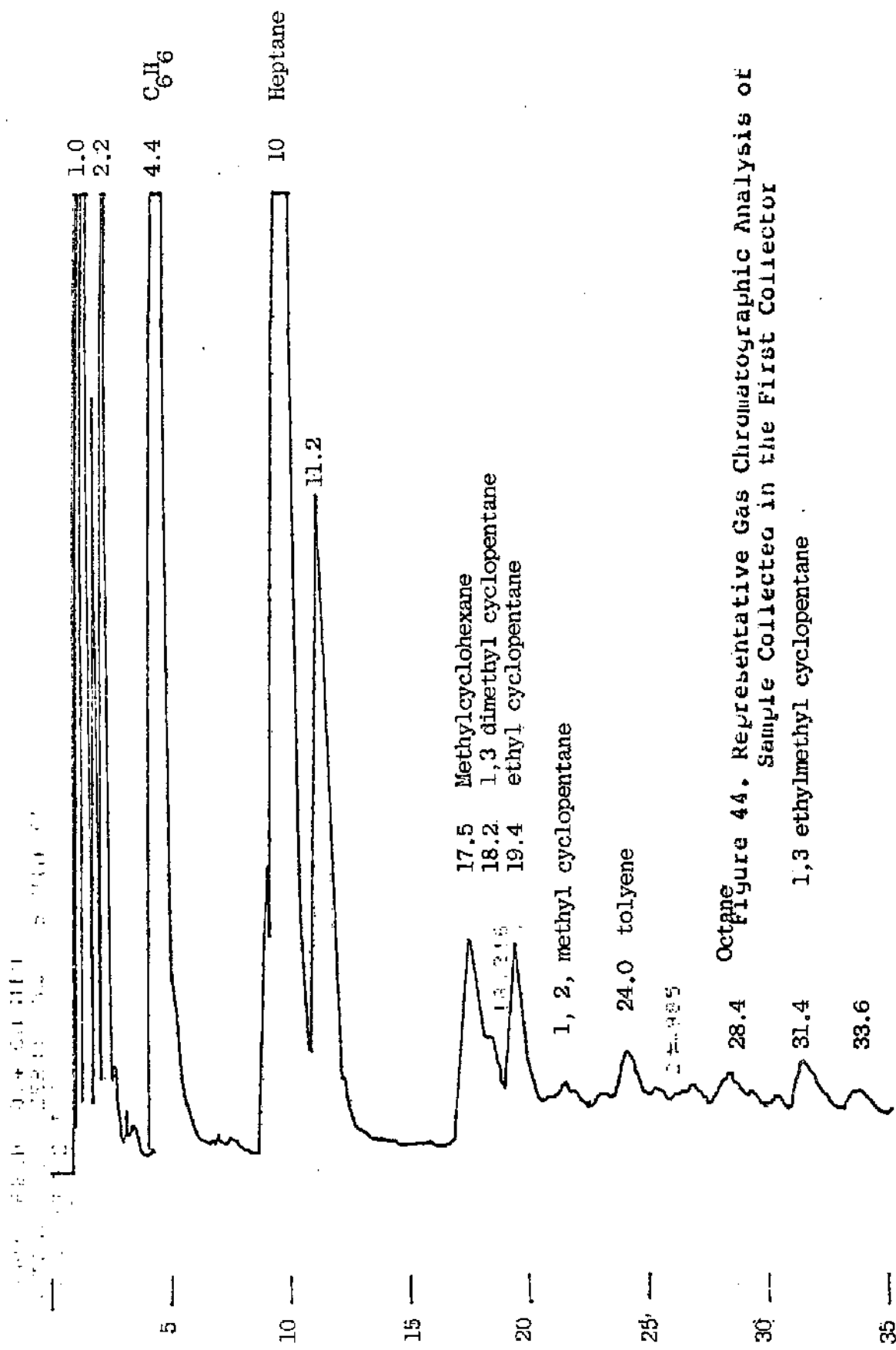


Figure 44. Representative Gas Chromatographic Analysis of Sample Collected in the First Collector

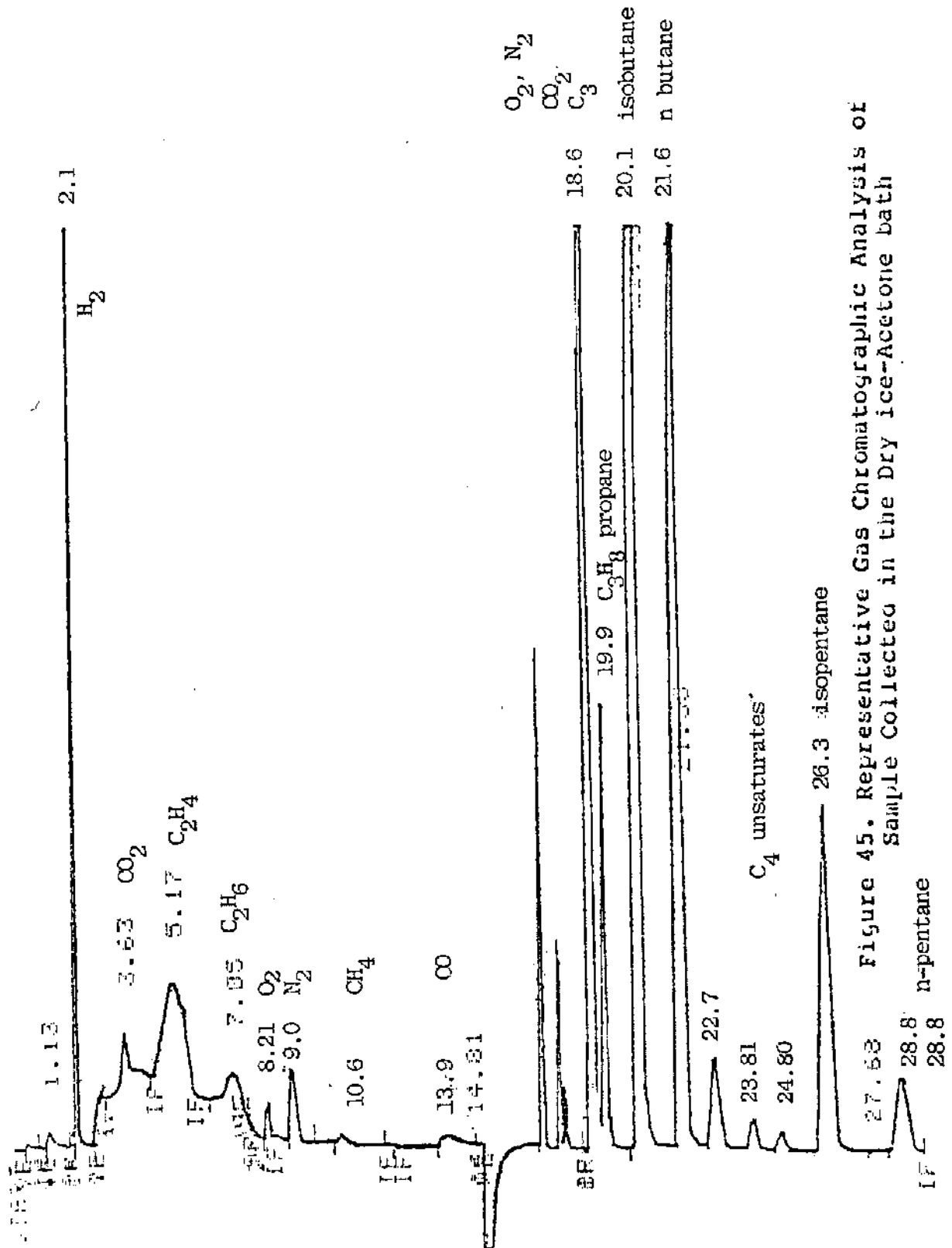


Figure 45. Representative Gas Chromatographic Analysis of Sample Collected in the Dry ice-Acetone bath

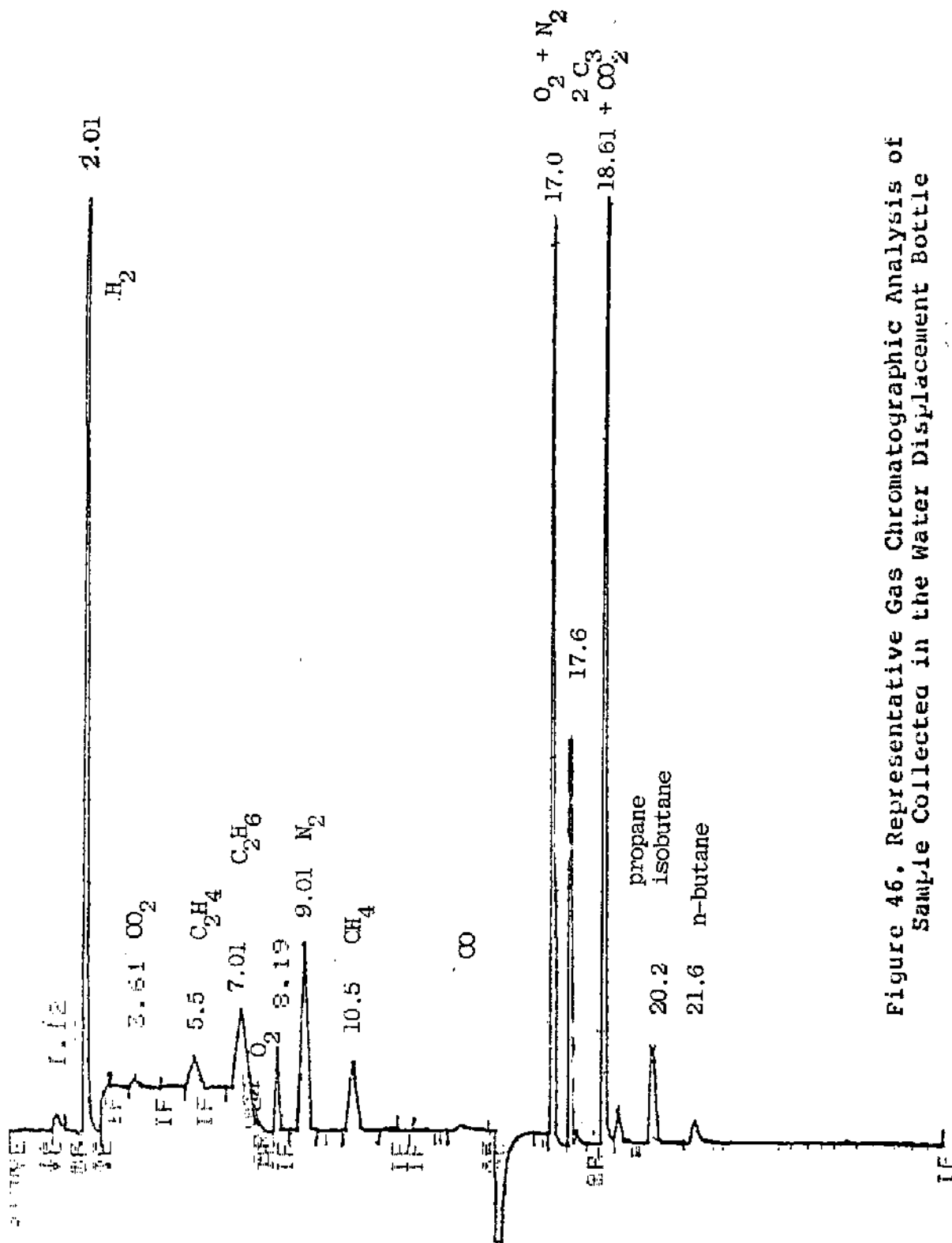


Figure 46. Representative Gas Chromatographic Analysis of Sample Collected in the Water Displacement Bottle

APPENDIX E

Product Distributions

The product distributions obtained in this thesis are presented in the following table, Table 5. The run conditions and catalyst used have been included. The product distributions are the hydrocarbon fractions obtained. The amounts of CO and CO₂ are also included, where needed.

TABLE 5. CALCULATED PRODUCT DISTRIBUTIONS OF EXPERIMENTS.

CATALYST: M1-ZSM-5		1	2	3	4	5	6
FEED N-HEPTANE		700	740	740	700	660	660
RUN NO							
TEMPERATURE (K)		1.60	2.35	0.84	1.43	2.93	0.81
WHSV		2:1	2:1	2:1	2:1	2:1	2:1
HYDROGEN		89	105	40	80	90	40
INLET PRESSURE (PSIG)		99.89	98.47	95.41	97.62	95.15	88.89
MASS BALANCE CLOSURE %							
HYDROCARBON DISTRIBUTION							
CH4		3.50	5.77	8.23	4.03	2.96	3.50
C2H6		11.10	15.43	23.67	12.51	7.66	6.36
C2H4		0.93	0.95	1.21	1.29	1.14	1.17
C3H8		51.12	54.01	43.83	51.86	49.38	46.88
C3H6		1.73	2.21	1.03	0.76	1.00	0.96
I-C4H10		6.85	4.10	12.31	4.52	7.73	6.03
N-C4H10		4.63	2.86	1.71	2.96	5.00	5.20
C4H8		0.18	1.20	0.50	0.80	0.08	0.70
I-C5H12 + C5H10		6.29	2.75	0.97	3.81	8.09	7.16
N-C5H12		1.60	0.78	0.14	0.79	4.09	3.61
C6		0.60	0.15	0.17	1.38	0.73	0.19
C7 + OILS		--	0.02	0.06	0.67	0.73	0.02
AROMATIC TOTAL		12.83	11.15	18.11	13.42	10.23	15.23
BENZENE		0.91	0.90	1.37	0.00	0.65	1.06
TOLUENE		5.19	5.91	9.37	5.42	4.39	6.78
ETHYLBENZENE		0.19	0.12	0.20	0.38	0.21	0.19
META + PARA - XYLENE		3.32	2.92	5.03	4.11	3.16	3.98
ORTHO - XYLENE		1.26	0.85	1.47	1.10	0.92	1.30
C9 AROMATICS		1.05	0.16	0.29	1.35	0.67	1.00
C10 + AROMATICS		0.31	0.21	0.30	0.18	0.23	0.12
REGENERATION OCCURRED BETWEEN RUNS 4 AND 5							

TABLE 5. CONT.

CATALYST: ZN-ZSM-5		F-T	DECANDL	MIXT	C7H16
FEED:		780	780	700	640
TEMPERATURE (K)					
WHSV		2.04	2.56	2.56	2.50
HYDROGEN					
INLET PRESSURE (PSIG)		140	120	120	
MASS BALANCE CLOSURE %		95.54	99.00	99.15	90.63
HYDROCARBON DISTRIBUTION					
CH4		2.04	2.56	2.58	0.04
C2H6		2.73	0.86	4.30	0.57
C2H4		0.80	0.03	1.71	0.15
C3H8		14.63	8.30	10.31	19.88
C3H6		0.25	0.14	0.21	0.45
1-C4H10		9.25	8.14	9.92	9.20
N-C4H10		7.28	6.35	9.92	9.11
C4H8		0.63	0.47	0.70	0.30
1-C5H12 + C5H10		16.74	22.77	16.74	46.33
N-C5H12		3.11	4.12	4.20	COMBINED WITH
C6		4.20	5.05	3.70	1-C5H12
C7 + OILS		2.48	0.11	0.05	+C5H10
AROMATIC TOTAL		34.35	41.14	27.11	13.11
BENZENE		3.63	4.97	2.50	0.72
TOLUENE		13.88	15.37	10.08	3.99
ETHYLBENZENE		0.79	0.90	0.51	1.20
META + PARA - XYLENE		9.16	10.09	7.72	4.34
ORTHO - XYLENE		2.04	3.36	2.27	1.27
C9 AROMATICS		3.97	4.94	2.29	1.50
C10 + AROMATICS		0.60	0.90	2.24	WITH C9

CO AND CO2 (% OF TOTAL)

CO2

CO

0.50

REGENERATION OCCURRED BEFORE THE FISCHER-TROPSCH LIQUID AND BEFORE THE N-HEPTANE. THE N-HEPTANE WAS RUN AS ONE OF THE INITIAL RUNS. THE OTHERS WERE THE FINAL RUNS INVOLVING THE ZN-ZSM-5

TABLE 5. CONT.

CATALYST: NI-ZSM-5		FEED: FISCHER-TROPSCH LIQUID				
RUN NO.	1	2	3	4	5	
TEMPERATURE (K)	700	740	740	660	660	
WHSV	2.20	3.07	0.99	2.57	0.99	
HYDROGEN	2:1	2:1	2:1	2:1	2:1	
INLET PRESSURE (PSIG)	90	85	60	120	90	
MASS BALANCE CLOSURE %	96.23	96.63	97.07	90.91	97.62	

	HYDROCARBON DISTRIBUTION				
	1	2	3	4	5
CH4	3.99	6.95	8.37	2.39	3.51
C2H6	5.96	0.49	5.64	5.99	5.96
C2H4	3.05	2.30	1.06	1.20	1.19
C3H8	24.23	25.76	27.99	18.52	17.44
C3H6	5.78	0.65	0.56	0.17	0.23
I-C4H10	7.76	0.32	7.23	0.33	9.51
N-C4H10	5.69	6.06	5.60	5.50	6.03
C4H8	0.59	0.57	0.67	0.43	0.35
I-C5H12 + C5H10	13.82	7.61	10.65	21.00	18.12
N-C5H12	2.05	1.14	1.76	5.07	3.93
C6	1.63	1.46	1.90	5.37	5.38
C7 + OILS	0.02	0.01	0.03	1.44	1.76
AROMATIC TOTAL	25.07	33.40	27.23	21.62	24.25
BENZENE	3.40	4.30	3.57	1.48	1.70
TOLUENE	10.59	12.35	11.17	7.73	8.07
ETHYLBENZENE	0.42	0.37	0.40	0.96	1.10
META + PARA - XYLENE	6.38	12.36	7.16	5.73	6.57
ORTHO - XYLENE	2.85	2.30	2.33	1.55	1.70
C9 AROMATICS	1.40	1.35	1.73	3.09	3.00
C10 + AROMATICS	0.71	0.44	0.87	1.07	1.23

	CO AND CO2 (% TOTAL WEIGHT)				
CO	----	1.15	1.04	1.19	1.17
CO2	----	----	----	----	----

REGENERATION OCCURRED BETWEEN RUNS 3 AND 4

TABLE 5. CONT.

CATALYST: NI-ZSM-5	FEED: FISCHER-TROPSCH LIQUID	TIME ON STREAM (HR)	TEMPERATURE (K)	WHSV	HYDROGEN	INLET PRESSURE (PSIG)	MASS BALANCE CLOSURE %	7 HR	14 HR	21 HR
		700	700	2.16	1.97	1.98	1.84	700	700	700
		2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1
		80	100	96.63	91.67	90.74	91.30	100	100	100

HYDROCARBON DISTRIBUTION

CH4	3.99	4.32	2.84	3.01
C2H6	5.93	6.92	5.72	6.01
C2H4	3.05	2.59	6.64	9.03
C3H8	24.28	10.17	10.55	10.28
C3H6	5.08	1.96	6.55	11.77
I-C4H10	7.76	6.99	5.89	5.54
N-C4H10	5.698	3.352	3.261	3.261
C4H8	0.59	0.87	2.03	3.23
I-C5H12 + C5H10	13.02	15.78	11.86	12.09
N-C5H12	2.05	4.26	3.86	3.91
C6	1.63	8.47	11.55	9.93
C7 + OILS	0.02	2.29	5.56	3.02
AROMATIC TOTAL	25.07	28.50	23.97	18.04
BENZENE	3.49	1.70	1.35	1.31
TOLUENE	10.59	9.61	6.61	4.64
ETHYLBENZENE	0.42	1.12	1.04	---
META + PARA - XYLENE	6.38	9.37	7.76	6.67
ORTHO - XYLENE	2.05	2.47	1.61	0.30
C9 AROMATICS	1.43	4.16	5.60	4.04
C10 + AROMATICS	0.71	---	---	---

CO AND CO2 (% OF TOTAL)

CO2	---	0.86	---	---
CO	---	---	---	---

TABLE 5. CONT.

CATALYST: NI-ZSM-5
 FEED: N-DECANAL
 TEMPERATURE (K) 700 740 660
 2:1 2:1 2:1
 HYDROGEN
 INLET PRESSURE (PSIG) 80 95 95
 MASS BALANCE CLOSURE % 96.91 99.99 99.99

HYDROCARBON DISTRIBUTION			
CH4	1.29	3.27	0.98
C2H6	1.31	4.40	3.00
C2H4	--	1.090	0.914
C3H8	7.60	15.26	6.39
C3H6	0.22	0.25	0.83
1-C4H10	7.37	6.11	15.75
N-C4H10	4.53	3.74	3.08
C4H0	0.49	0.36	10.15
1-C5H12 + C5H10	9.15	6.89	5.13
N-C5H12	1.28	1.02	1.99
C6	11.26	4.39	5.94
C7 + OILS	0.67	0.11	0.11
AROMATIC TOTAL	51.37	50.06	44.20
BENZENE	7.40	6.63	6.61
TOLUENE	14.10	21.49	16.43
ETHYLBENZENE	2.94	1.10	1.09
META + PARA - XYLENE	17.71	12.43	12.40
ORTHO - XYLENE	1.54	3.87	3.06
C9 AROMATICS	5.66	3.44	3.12
C10 + AROMATICS	2.02	1.10	0.69

CO AND CO2 (% TOTAL WEIGHT)

CO2	----	1.09	----
CO	1.28	1.10	3.23

TABLE 5. CONT.

CATALYST: ZN-ZSM-5	1	2	3	4	5	6
FEED: N-DECAHOL						
RUN NO	700	710	740	700	660	660
TEMPERATURE (K)	2.27	3.70	0.97	1.96	3.58	0.92
WHSV	160	185	110	140	190	95
INLET (PSIG)	2:1	2:1	2:1	2:1	2:1	2:1
HYDROGEN	98.10	98.97	99.33	98.39	93.08	92.66
MASS BALANCE CLOSURE %						

HYDROCARBON DISTRIBUTION

CH4	2.83	3.70	8.36	4.40	2.29	2.32
C2H6	4.05	4.51	6.49	4.40	2.35	1.21
C2H4	1.06	1.63	1.08	2.03	3.06	1.25
C3H8	29.29	37.01	30.12	29.54	12.91	17.58
C3H6	0.29	0.80	0.64	1.00	0.43	0.53
I-C4H10	10.41	7.63	7.14	10.36	11.82	13.84
N-C4H10	7.70	4.16	4.49	7.87	7.02	8.30
C4H8	0.27	0.71	0.08	1.01	0.54	0.56
I-C5H12 + C5H10	10.593	16.262	5.261	11.004	23.700	24.549
N-C5H12	WITH	1-C5H12				
C6	0.86	0.71	0.21	0.35	4.01	1.98
C7 + OILS	0.02	----	----	0.03	1.16	0.50
AROMATIC TOTAL	26.42	27.56	26.57	21.60	20.90	27.39
BENZENE	2.16	2.86	3.00	1.79	1.94	1.48
TOLUENE	11.18	11.25	11.51	9.02	8.20	8.63
ETHYLBENZENE	0.35	0.30	0.33	0.38	0.71	0.67
META + PARA - XYLENE	7.12	7.27	5.74	5.98	6.32	7.15
ORTHO - XYLENE	2.21	2.45	1.87	0.79	1.88	2.16
C9 AROMATICS	2.38	2.13	2.04	1.87	4.70	4.06
C10 + AROMATICS	1.02	1.29	2.23	1.77	3.64	3.25

CO AND CO2 (% TOTAL WEIGHT)

CO2	0.05	2.44	3.61	----	1.53	----
CO	----	----	----	----	----	----
REGENERATION OCCURRED BETWEEN RUNS 3 AND 4						

TABLE 5. CONT.

CATALYST: ZN-ZSM-5 FEED: N-DECANAL		RUN NO					
		1	2	3	4	5	6
TEMPERATURE (K)		700	740	700	700	660	660
WHSV		1.95	3.58	2.16	2.22	3.28	0.84
HYDROGEN		2:1	2:1	2:1	2:1	2:1	2:1
MASS BALANCE CLOSURE %		98.10	99.33	98.97	95.00	99.90	99.93
HYDROCARBON DISTRIBUTION							
C14		3.29	3.85	2.30	2.41	1.35	2.55
C2H6		2.39	2.96	1.36	2.49	1.39	1.21
C2H4		1.32	1.35	0.04	1.35	1.51	1.31
C3H8		20.79	31.57	25.34	29.60	10.18	16.60
C3H6		0.72	0.97	0.72	1.10	1.07	1.01
I-C4H10		0.62	0.60	0.96	0.43	11.24	9.94
M-C4H10		4.86	3.59	5.74	3.94	6.40	7.06
C4H8		0.60	0.64	0.71	0.81	1.00	1.15
I-C5H12 + C5H10		14.63	7.91	14.72	11.24	15.30	16.89
N-C5H12	WITH	2.65	2.37	1-C5H12	1.53	2.00	1.72
C6		0.953	0.836	2.09	4.40	5.50	2.64
C7 + OILS		35.81	37.05	0.036	1.325	2.486	1.266
AROMATIC TOTAL		1.72	4.99	3.82	26.11	29.92	36.55
BENZENE		9.96	15.57	12.98	1.86	1.55	2.04
TOLUENE		0.96	0.67	0.66	9.22	7.67	11.43
ETHYLBENZENE		7.93	9.06	8.45	1.66	1.52	1.57
META + PARA - XYLENE		2.30	1.51	2.60	7.00	7.81	9.21
ORTHO - XYLENE		4.67	2.78	4.07	1.85	1.32	2.42
C9 AROMATICS		3.28	2.46	3.23	1.14	7.17	6.06
C10 + AROMATICS					2.58	2.89	3.02
CO AND CO2 (% TOTAL WEIGHT)							
CO2		0.34	1.15	1.27	1.41	1.46	2.63
CO		---	---	---	0.52	1.32	---
REGENERATION OCCURRED BETWEEN RUNS 3 AND 4 AND BEFORE 1							

TABLE 5. CONT.

CATALYST: H-ZSM-5		1		2		3		4		5	
RUN NO.	C7H14	C10ALC	CIBALD	MIX	F-T	700	700	700	700	700	700
FEED:	700	700	700	700	700	700	700	700	700	700	700
TEMPERATURE (K)	1.79	2.59	2.33	2.07	2.42	2.59	2.33	2.07	2.42	2.59	2.42
WHSV	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1
HYDROGEN	60	75	70	60	60	60	70	60	60	60	60
INLET PRESSURE (PSIG)	90.00	90.00	93.28	94.23	94.78	90.00	93.28	94.23	94.78	90.00	94.78
MASS BALANCE CLOSURE %	90.00	90.00	93.28	94.23	94.78	90.00	93.28	94.23	94.78	90.00	94.78

HYDROCARBON DISTRIBUTION

CH4	5.07	2.53	0.96	2.87	1.76
C2H6	11.15	15.30	11.92	4.78	4.78
C2H4	3.04	1.76	0.96	3.82	5.26
C3H8	19.75	11.60	10.10	12.68	9.31
C3H6	0.26	1.93	0.20	0.24	0.23
I-C4H10	10.96	12.45	6.19	7.87	7.44
N-C4H10	10.17	7.47	9.63	8.03	5.83
C4H8	0.08	0.67	1.26	1.09	1.25
I-C5H12 + C5H10	17.35	17.59	15.32	17.93	17.80
N-C5H12	4.17	2.50	7.06	6.80	5.11
C6	1.74	4.20	4.19	3.74	8.29
C7 + OILS	0.07	0.05	0.47	3.45	2.66
AROMATIC TOTAL	15.36	33.30	41.05	21.16	30.24
BENZENE	1.39	3.00	3.70	1.72	1.70
TOLUENE	6.08	12.09	16.15	7.65	9.54
ETHYLBENZENE	0.35	0.78	1.53	0.70	1.28
META + PARA - XYLENE	4.19	8.54	12.72	7.06	9.88
ORTHO - XYLENE	1.30	2.72	3.69	1.58	2.33
C9 AROMATICS	1.25	4.37	1.11	2.43	4.35
C10 + AROMATICS	0.60	1.81	2.15	0.48	1.17

CO AND CO2 (%TOTAL PRODUCT)

CO	-----	1.90	1.93
CO2	-----	1.90	2.06

REGENERATION OCCURRED BETWEEN RUNS 3 AND 4.

TABLE 5. CONT.

RUN NO.	1	2	3	4	5	6
CATALYST: NI-ZSM-5						
FEED: N-DECANOL						
TEMPERATURE (K)	700	740	740	700	660	660
WHSV	1.29	2.49	1.24	1.34	1.72	1.37
HYDROGEN	2:1	2:1	2:1	2:1	2:1	2:1
INLET PRESSURE (PSIG)	60	75	45	60	70	60
MASS BALANCE CLOSURE %	98.82	98.73	98.75	97.70	88.10	99.93

HYDROCARBON DISTRIBUTION

CH4	2.66	6.52	8.51	2.67	2.38	1.36
C2H6	4.25	12.54	13.60	3.89	3.80	2.92
C2H4	1.34	1.00	2.14	1.26	2.38	1.37
C3H8	25.36	34.11	29.84	21.98	17.14	11.57
C3H6	0.49	0.63	1.30	0.40	0.43	2.81
1-C4H10	9.54	5.62	15.03	10.86	11.67	9.48
N-C4H10	5.17	3.59	3.84	6.62	5.33	4.49
C4H8	0.70	0.52	0.65	0.85	0.67	0.50
1-C5H12 + C5H10	0.75	3.60	2.00	9.67	16.30	10.30
N-C5H12	1.25	0.52	0.10	1.53	2.80	1.72
C6	5.78	0.56	1.10	4.93	6.83	5.40
C7 + OILS	1.53	0.06	0.04	1.75	2.26	1.46
AROMATIC TOTAL	32.18	32.33	31.47	31.84	25.29	25.29
BENZENE	1.99	4.25	4.15	2.44	1.77	1.42
TOLUENE	11.59	14.03	14.77	13.57	9.71	9.76
ETHYLBENZENE	1.24	0.35	0.36	0.83	1.54	1.04
META + PARA - XYLENE	9.09	7.35	2.82	8.83	7.16	7.53
ORTHO - XYLENE	2.52	2.31	1.86	2.67	3.50	2.15
C9 AROMATICS	5.18	1.68	1.26	2.59	6.15	3.78
C10 + AROMATICS	0.57	1.75	1.18	1.01	0.90	0.61

CO AND CO2 (% TOTAL WEIGHT)

CO2	1.25	4.48	5.67	1.25	0.04	1.31
CO	-----	0.00	1.42	1.25	-----	-----

REGENERATION OCCURRED BETWEEN RUNS 3 AND 4

TABLE 5. CONT.

CATALYST: NI-ZSM-5			
FEED:	MIX	C7C16	F-T
TEMPERATURE (K)	700	700	700
WHSV	2.00	2.77	1.84
HYDROGEN			
INLET PRESSURE (PSIG)	00	80	50
MASS BALANCE CLOSURE %	90.00	93.20	90.00

HYDROCARBON DISTRIBUTION

CH4	3.22	2.96	3.06
C2H6	4.41	4.03	4.33
C2H4	1.09	0.97	1.05
C3H8	17.19	23.56	20.72
C3H6	0.25	0.43	0.44
I-C4H10	9.47	14.06	10.09
N-C4H10	9.253	12.484	7.700
C4H8	0.67	0.88	0.74
I-C5H12 + C5H10	18.59	17.20	16.27
N-C5H12	4.33	3.90	2.00
C6	3.06	0.39	3.96
C7 + OILS	0.77	0.19	0.70
AROMATIC TOTAL	26.86	18.93	27.23
BENZENE	2.64	1.26	2.71
TOLUENE	10.50	7.45	10.79
ETHYLBENZENE	0.61	0.43	0.62
META + PARA - XYLENE	7.55	6.12	7.75
ORTHO - XYLENE	2.44	1.93	2.50
C9 AROMATICS	2.16	1.36	2.21
C10 + AROMATICS	0.65	0.30	0.66

CO AND CO2 (% OF TOTAL)

CO2: 0.21
 REGENERATION OCCURRED BEFORE THE RUN USING THE SYNTHETIC MIXTURE

TABLE 5. CDNT.

CATALYST: ZN-ZSM-5
 FEED: FISCHER-TROPSCH LIQUID

RUN NO.	1	2	3	4	5
TEMPERATURE (K)	700	740	740	740	740
WHSV	1.98	2.90	0.98	2.30	1.06
HYDROGEN	2:1	2:1	2:1	2:1	2:1
INLET PRESSURE (PSIG)	85	100	70	100	100
MASS BALANCE CLOSURE %	70.00	95.40	95.12	81.94	86.35

HYDROCARBON DISTRIBUTION

CH4	2.38	3.31	7.50	2.23	1.41	2.02
C2H6	2.47	3.86	7.57	2.24	1.41	2.07
C2H4	0.02	1.14	1.26	1.11	0.69	1.01
C3H8	27.61	37.93	36.20	26.34	13.75	13.96
C3H6	0.24	0.57	1.07	0.19	0.30	1.23
I-C4H10	7.05	4.98	6.16	10.07	13.41	8.51
N-C4H10	5.49	4.85	4.56	9.10	9.30	6.14
C4H8	0.91	0.60	0.65	0.55	0.72	0.40
I-C5H12 + C5H10	13.02	6.11	4.01	14.08	21.26	10.60
N-C5H12	2.57	2.10	1.64	3.03	5.00	4.84
C6	2.44	1.93	1.20	4.29	6.06	9.14
C7 + OILS	0.08	0.02	0.01	0.07	0.57	0.19
AROMATIC TOTAL	36.18	32.40	28.09	24.52	21.91	32.09
BENZENE	4.00	3.98	4.30	2.84	1.42	3.61
TOLUENE	14.76	12.42	13.27	10.01	7.29	12.42
ETHYLBENZENE	0.76	2.99	0.32	0.54	1.07	1.09
META + PARA - XYLENE	9.11	7.42	6.30	6.24	6.08	8.83
ORTHO - XYLENE	2.00	2.99	2.02	1.91	1.72	2.61
C9 AROMATICS	3.24	2.30	1.42	2.69	4.33	3.45
C10 + AROMATICS	1.52	0.29	0.39	0.30	---	0.68

CO AND CO2 (% TOTAL WEIGHT)

CO	---	0.02	---	---	---	---
CO2	---	---	---	---	---	0.02

REGENERATION OCCURRED BETWEEN RUNS 3 AND 4

TABLE 5. CONT.

CATALYST: ZN-ZSM-5			
FEED: SYNTHETIC MIXTURE			
TEMPERATURE (K)	700	740	
WHSV	2.20	2.88	
HYDROGEN	2:1	2:1	
INLET PRESSURE (PSIG)	140	160	
MASS BALANCE CLOSURE X	98.98	98.46	
HYDROCARBON DISTRIBUTION			
CH4	2.10	3.98	
C2H6	3.16	3.92	
C2H4	1.12	1.66	
C3H8	35.63	42.03	
C3H6	0.86	1.40	
I-C4H10	11.06	9.31	
N-C4H10	6.17	6.97	
C4H8	0.91	0.56	
I-C5H12 + C5H10	19.89	10.76	
N-C5H12			INCLUDED WITH I-C5H12
C6	0.62	0.52	
C7 + OILS	0.97	0.01	
AROMATIC TOTAL	14.78	15.31	
BENZENE	1.59	1.45	
TOLUENE	6.17	5.07	
ETHYLBENZENE	0.26	0.19	
META + PARA - XYLENE	3.63	3.32	
ORTHO - XYLENE	1.13	1.04	
C9 AROMATICS	1.21	1.21	
C10 + AROMATICS	0.70	1.39	
CO AND CO2 (% TOTAL WEIGHT)			
CO	1.09	0.79	
		0.79	

TABLE 6. CONT.

	1	2	3	4	5	6	7	8	9
CATALYST: ZN-ZSM-5	580	580	640	640	700	700	700	700	700
FEED: N-HEPTANE	1.30	4.00	2.50	2.54	1.33	1.37	4.04	9.50	5.85
TEMPERATURE (K)	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1
WHSV	97.93	92.68	90.65	67.35	93.58	97.88	99.20	63.63	93.21
HYDROGEN									
MASS BALANCE CLOSURE %									

HYDROCARBON DISTRIBUTION

CH4	0.21	--	0.68	0.57	2.72	1.86	1.22	4.48	1.42
C2H6	0.02	0.02	0.84	0.56	5.36	4.24	2.39	3.00	1.42
C2H4	0.02	0.02	0.73	--	0.60	0.61	0.43	0.65	0.79
C3H8	12.99	12.05	32.14	30.29	44.33	44.11	45.03	46.04	39.66
C3H6	1.00	1.43	0.27	0.18	0.41	0.33		0.98	1.08
1-C4H10	10.25	11.15	11.08	7.41	8.98	8.62	8.20	11.26	10.61
N-C4H10	10.06	11.53	9.03	6.91	6.67	6.40	7.23	9.37	11.09
C4H8	2.22	4.41	0.27	0.14	0.27	0.25	0.24	0.10	0.52
1-C5H12 + C5H10	61.82	58.22	18.54	14.43	13.03	12.51	20.15	15.80	19.20
N-C5H12			14.20	13.01				0.55	6.06
C6		ABOVE	3.17	3.69	1.44	0.34	1.76	0.32	0.96
C7 + OILS		ABOVE	1.50	2.36	0.13	0.05	0.51	0.12	0.42
AROMATIC TOTAL	1.21	1.08	8.05	20.25	20.82	16.74	12.40	7.69	6.95
BENZENE	0.77	0.76	0.49	0.92	0.93	0.63	0.50	0.54	0.48
TOLUENE	0.44	0.32	3.15	6.66	6.62	9.62	4.13	2.89	2.68
ETHYLBENZENE			0.32	0.62	0.23	0.19	0.28	0.15	0.16
META + PARA - XYLENE			3.09	6.09	5.05	6.94	4.18	2.13	2.04
ORTHO - XYLENE			0.90	1.77	1.31	1.41	1.31	0.66	0.65
C9 AROMATICS			2.24	3.39	1.39	1.64	1.73	1.11	---
C10 + AROMATICS			0.54	0.00	0.72	0.90	0.32	0.21	---

REGENERATION OCCURRED BETWEEN RUNS 6 AND 7, AND BEFORE RUNS 8 AND 9
 RUN 6 WAS TO CHECK THE EFFECT OF COKING IN A SHORT PERIOD OF TIME
 THE ORDER OF THE FIRST RUNS WERE 5,3,4,6, THEN 7,1,2. THE RUNS 8 AND 9 WERE MADE AT A LATER DATE

TABLE 5. CONT.

CATALYST: NI-ZSM-5
 FEED: THE FIRST PAIR ARE SYNTHETIC MIXTURE, THE THIRD IS H₂O + HEPTANE,
 FOURTH H₂O + F-T; FIFTH MIX PRESSURE, SIXTH HEPTANE PRESSURE

RUN NO.	1	2	3	4	5	6
TEMPERATURE (K)	700	560	700	700	700	700
WHSV	2.38	3.50	1.82	1.92	1.78	1.98
HYDROGEN	2:1	2:1	0	0	2:1	2:1
INLET PRESSURE (PSIG)	75	80	200	200	300	300
MASS BALANCE CLOSURE %	99.90	93.94	99.41	93.44	99.09	99.30

HYDROCARBON DISTRIBUTION

CH ₄	1.64	2.34	2.20	2.63	6.57	8.20
C ₂ H ₆	2.51	6.23	2.24	2.67	17.90	15.51
C ₂ H ₄	0.31	1.57	2.21	2.63	---	0.01
C ₃ H ₈	12.89	3.41	14.42	14.74	29.10	26.37
C ₃ H ₆	0.75	0.27	0.55	1.80	0.14	0.16
I-C ₄ H ₁₀	10.73	6.33	17.02	14.88	9.52	9.15
N-C ₄ H ₁₀	1.92	0.76	9.24	8.07	9.25	11.29
C ₄ H ₈	1.92	0.76	1.29	1.13	0.19	0.47
I-C ₅ H ₁₂ + C ₅ H ₁₀	20.49	10.91	27.65	24.17	19.47	19.78
N-C ₅ H ₁₂	4.46	5.23	5.60	4.90	3.11	5.58
C ₆	3.12	3.05	2.66	3.29	0.20	0.10
C ₇ + OILS	0.04	0.04	1.06	0.60	---	---
AROMATIC TOTAL	27.96	46.90	10.66	15.80	4.47	3.29
BENZENE	3.49	6.79	0.66	1.12	0.43	0.24
TOLUENE	11.51	19.67	3.95	5.86	1.80	1.10
ETHYLBENZENE	0.54	0.76	0.29	0.44	0.06	0.06
META + PARA - XYLENE	7.05	11.77	3.56	4.80	1.39	1.01
ORTHO - XYLENE	2.21	3.85	1.09	1.51	0.44	0.34
C ₉ AROMATICS	1.94	3.13	0.90	1.64	0.35	0.54
C ₁₀ + AROMATICS	1.22	0.93	0.87	0.43	---	---

CO AND CO₂ (% TOTAL WEIGHT)

CO	0.82	0.01	---	1.32	---	---
CO ₂	0.60	0.00	---	1.32	---	---

REGENERATION OCCURRED BEFORE RUNS 1, 3, AND 5.