selectivities were from catalyst differences rather than feedstock differences. The HZSM-5 produced the highest yield of propylene, regardless of feedstock. The HZSM-5 and the beta zeolite catalysts had higher yields of isobutylene than the USY catalyst with both wax feedstocks. The higher light gas yields for the HZSM-5 and beta catalysts occurred at the expense of the naphtha (Figure 62) and distillate (Figure 63) yields. The 650°F+ cycle oil yields (Figures 64 and 65) did not vary significantly with wax feedstock or catalyst. Figure 66 shows that the RON of the naphtha products from the LaPorte wax feedstock were 1-2 octane numbers higher than the naphtha products from the Sasol wax. This may be another effect of the dehydrogenation activity of the iron F-T catalyst fines.

4.3 UOP Fischer-Tropsch Naphtha Feedstock

Reaction temperatures of 880 and 970°F were used with the following four catalysts: clay diluent only and a 6.3% blend of the Y, beta and HZSM-5 zeolite catalysts and diluent. The catalytic cracking of F-T naphtha gave low conversions, low light olefin yields, and resulted in high yields of water due to dehydration of oxygenates present in the naphtha. These results show that catalytic cracking is not a reasonable processing route for F-T naphtha.

The catalytic cracking runs at 880 and 970°F are summarized in Tables XVI and XVII, respectively. These tables show the distributions of the C_1 through C_5 hydrocarbons plus C_6+, which is the lumped total of products having carbon numbers of 6 and higher. The term "C5- conversion" used in Figures 67-69 is the sum of the C1-C5 hydrocarbon products (100 minus C_6+) in Tables XVI and XVII. Figure 67 shows that naphtha conversion to C_5- products was highest with the HZSM-5 catalyst. Figures 68 and 69, respectively, show that there were no selectivity differences between these USY, beta, and HZSM-5 catalysts for the production of either isobutylene or isoamylenes. The HZSM-5 catalyst gave the highest yields of isobutylene and isoamylenes products, but these increased yields of the desired olefins by the HZSM-5 catalyst were a function of its higher conversion rather than improved selectivity.

The liquid product consisted of two phases, water (and soluble, unconverted oxygenates) and hydrocarbons. The water originated from dehydration of the alcohols and aldehydes. The low water quantities in these MYU tests (~0.2 g) made quantitative analyses difficult. The detailed catalytic cracking behavior of this F-T gasoline is complex. Several of the important reactions are:

1. Dehydration of oxygenates to olefins and water.
2. Isomerization of 1-olefins to 2- or 3-olefins.
3. Cracking of olefins.
4. Cracking of normal paraffins.

5.0 PILOT PLANT TESTS (TASK 4)

Eleven catalytic cracking runs with the Sasol wax feedstock were made in the AU-2L pilot plant using a variety of catalysts and process conditions. The results of those runs are summarized in Table XVIII. Runs 939-1, 939-2, 939-4, and 945-2 used an equilibrium USY zeolite catalyst taken from one of Amoco's commercial FCC units. Run 939-5 used equilibrium USY zeolite catalyst that had been steamed to reduce its activity. Runs 940-1 and 940-2 used steamed 40% beta zeolite catalyst. Run 941-1 used a blend of 75% steamed equilibrium USY zeolite catalyst with 25% steamed HZSM-5 zeolite catalyst. Run 942-2 used a blend of 50% equilibrium USY zeolite catalyst with 50% diluent. Run 943-1 used steamed 10% USY zeolite catalyst. Run 944-2 used steamed 10% beta zeolite catalyst.

TABLE XVI

MYU TESTS: UOP F-T NAPHTHA FEEDSTOCK AT 880°F

Catalyst Type	Diluent Only	Zeolite Y	Zeolite Beta	Zeolite HZSM-5
Run No.	063	057	059	061
C/O	3.0	0.2	0.2	0.2
Product Yields, Wt%:				
Hydrocarbon	86	82	84	80
H_2O	14	18	16	20
Product Yields, HC Only, Wt%:				
H_2	0.01	0.01	0.01	0.01
C_1	0.07	0.04	0.04	0.03
$C_2^=$	0.7	2.8	2.7	4.3
C_2^o	0.31	0.2	0.2	0.1
$C_3^=$	1.1	2.8	3.8	8.1
C_3^o	0.13	0.1	0.1	0.1
$C_4^=$	1.7	3.0	5.4	8.9
C_4^o	0.3	0.1	0.3	0.2
$C_5^=$	3.5	4.9	7.9	8.4
C_5^o	0.4	0.4	0.5	0.4
C_6+	91.7	85.5	79.0	69.4
Coke	0.2	0.2	0.1	0.1
Isobutylene	0.58	0.50	1.6	3.0
Isoamylenes	0.24	1.23	2.9	4.5

WJR/ml/94156
4/11/94

TABLE XVII

MYU TESTS: UOP F-T NAPHTHA FEEDSTOCK AT 970°F

Catalyst Type	Zeolite Y		Zeolite Beta	Zeolite HZSM-5	
Run No.	068	069	070	071	072
Cat/Oil Ratio	0.2	0.2	0.2	0.2	0.1
Product Yields, Wt%:					
Hydrocarbon	85	83	85	84	86
Water	15	17	15	16	14
Product Yields, Hydrocarbon Only, Wt%:					
H_2	0.02	0.03	0.04	0.03	0.04
C_1^-	0.18	0.17	0.16	0.14	0.14
C_2^-	4.76	4.41	4.66	5.55	4.74
C_2°	0.43	0.43	0.46	0.28	0.36
C_3^-	4.28	4.13	6.44	11.75	8.80
C_3°	0.12	0.12	0.13	0.11	0.1
C_4^-	5.88	6.33	9.06	14.02	11.92
C_4°	0.25	0.26	0.28	0.14	0.25
C_5^-	8.81	9.54	12.13	14.91	14.06
C_5°	0.72	0.76	0.87	0.74	0.75
C_6^+	74.6	73.8	65.8	52.3	58.8
Coke	0.2	0.23	0.18	0.12	0.19
Isobutylene	1.22	1.31	3.15	5.61	3.93
Isoamylenes	3.04	3.32	5.84	8.93	7.63
RON	76.2	--	74.6	75.9	74.4
MON	69.0	70.3	68.3	69.4	68.6

WJR/lkv/94156
4/11/94

FIGURE 67

UOP F-T NAPHTHA MYU DATA:
EFFECT OF TEMPERATURE ON C5- CONVERSION

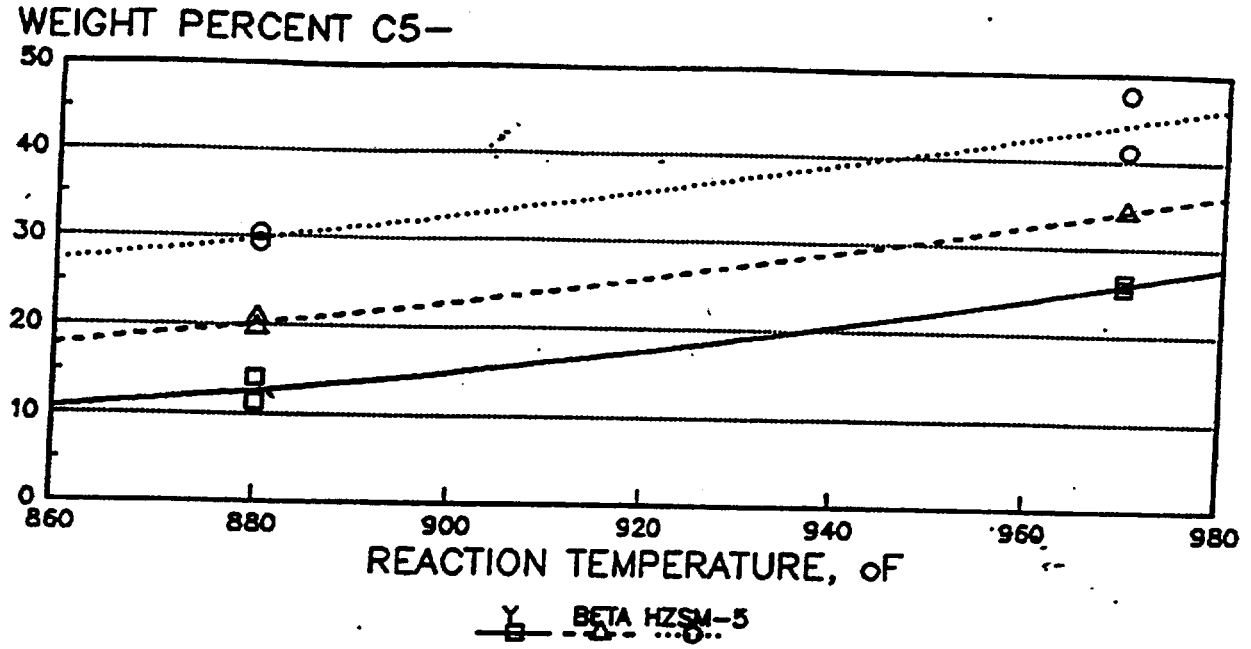


FIGURE 68

UOP F-T NAPHTHA MYU DATA: EFFECT OF C5- CONVERSION ON ISOBUTYLENE YIELD

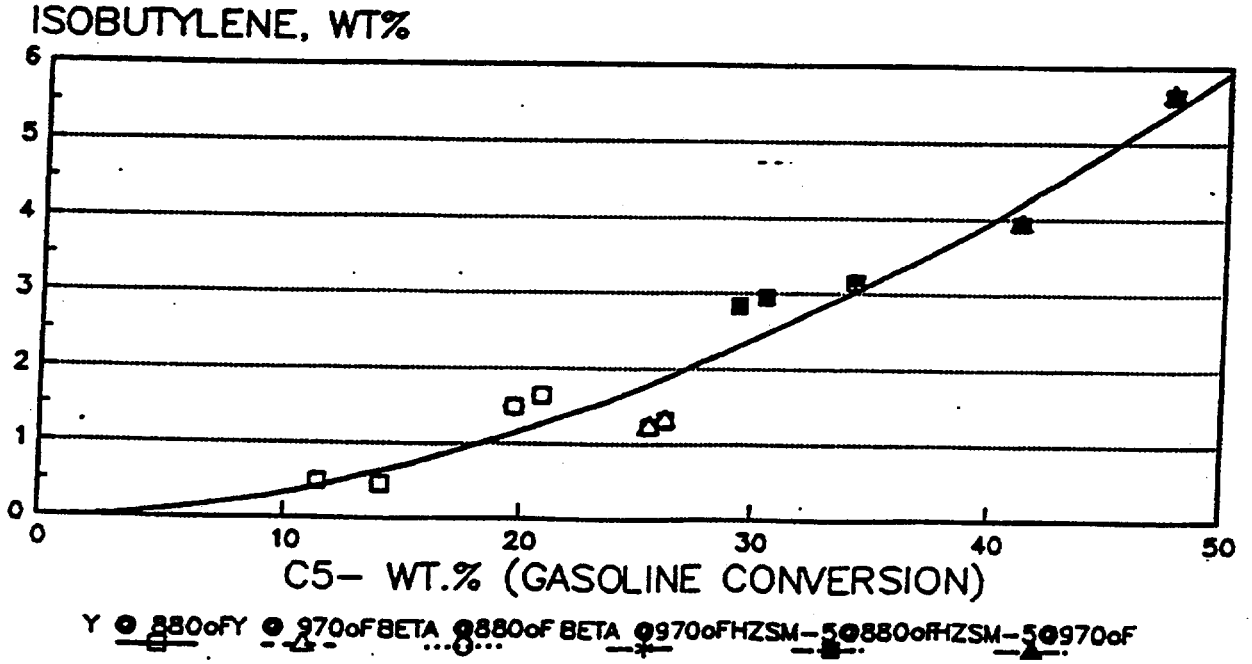


FIGURE 69

UOP F-T NAPHTHA MYU DATA: EFFECT OF C5- CONVERSION ON ISOAMYLENES YIELD

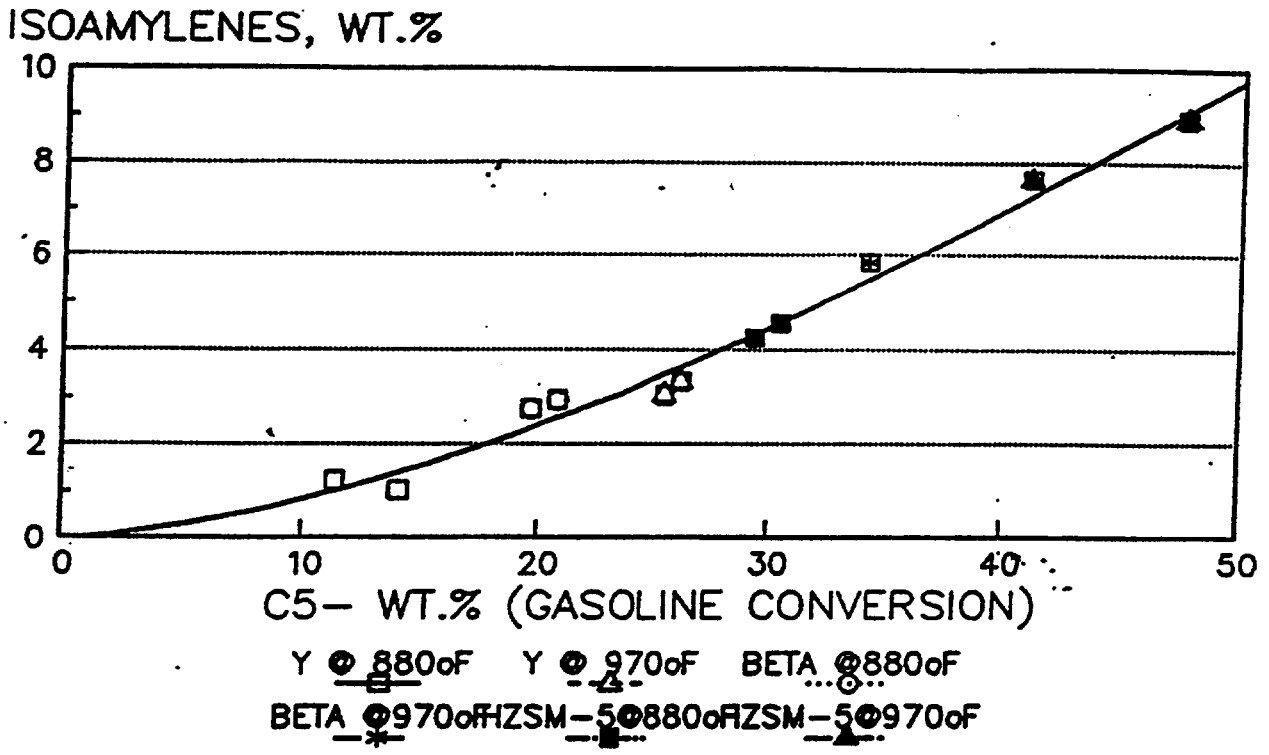


TABLE XVIII

FCC PILOT PLANT RUN DATA

Run No.	939-1	939-2	939-4	939-5	940-1	940-2	941-1	942-2	943-1	944-2	945-2
Run Conditions:											
Reaction Temp., F	944	932	882	879	934	910	965	937	890	897	888
c/o Ratio	5.16	4.06	2.29	2.25	5.08	3.35	2.84	1.57	3.08	3	2.57
WHSV, 1/hr	21	20.4	38.2	42.2	43.8	61.5	54.6	33.5	35.8	31.5	34.2
Catalyst	Eq. USY	Eq. USY	Eq. USY	Stm Eq. USY	Stm Beta	Stm Beta	75% Stm Eq USY 25% Stm HZSM-5	50% Eq USY 50% Diluent	Stm 10% USY	Stm 10% Beta	Eq. USY
Recovery, wt %	98.6	100.7	88.2	92.7	87.7	83.1	82.3	85.9	93.9	55.2	63
Conversion, vol %	93.5	93.7	83	85	96.6	96.5	89	90	89.3	89.7	84.9
Product Yields, wt %											
Hydrogen	0.04	0.04	0.03	0.02	0.02	0.01	0.02	0.02	0.01	0.01	0.03
Methane	0.36	0.33	0.18	0.14	0.1	0.07	0.09	0.16	0.11	0.13	0.23
Ethylene	0.48	0.42	0.26	0.21	0.66	0.5	1.01	0.34	0.22	0.31	0.33
Ethane	0.26	0.23	0.16	0.14	0.11	0.08	0.1	0.15	0.11	0.16	0.2
Propylene	9.26	8.2	7.28	6.28	13.93	13.68	16.03	8.94	6.63	10.94	8.57
Propane	1.86	1.67	1.07	0.9	2.11	1.81	2.47	1.25	0.93	1.27	1.48
Isobutane	7.93	7.23	4.15	3.4	9.04	7.66	3.4	5.02	3.97	4.14	5.59
n-Butane	2.08	1.84	1.21	0.99	2.58	2.09	1.92	1.3	0.99	1.16	1.17
i-Butene+1-Butene	7.38	6.7	7.68	6.75	12.46	12.99	12.95	7.67	6.25	9.62	5.18
t-2-Butene	4.19	3.74	3.69	3.19	5.65	5.44	5.33	3.72	2.27	3.5	2.92
c-2-Butene	3.12	2.77	2.67	2.31	4.16	3.98	3.76	2.68	2.04	2.44	2.14
Isopentane	8.49	8.65	3.38	3.35	5.11	3.73	2.16	3.97	3.66	1.93	3.18
n-Pentane	1.25	1.42	0.77	0.96	1.73	1.51	1.4	0.85	1.56	1.11	0.54
Pentenes	7.37	9.5	6.3	10.54	10.15	10.24	12.47	7.27	11.45	9.65	4.83
C6-430 F Naphtha	37.11	38.98	46.89	46.08	27.34	31.53	24.81	45.36	48.53	43.59	47.15
430+ F Cycle Oils	6.47	6.27	16.69	14.06	3.59	3.67	11.6	10.42	10.12	9.63	14.65
Coke	2.34	2.01	0.61	0.68	1.2	1	0.47	0.88	0.55	0.43	1.81

5.1 Conversion and Selectivity

Changes in the process variables of reaction temperature, catalyst to oil weight ratio, feed rate (WHSV), zeolite type, and catalyst activity had small effects on conversion. High conversions (83-97%) were always obtained. The activities of the USY zeolite catalysts were measured in relative microactivity tests (RMA), which is a standard measurement of FCC catalyst activity. The activities of the equilibrium USY catalyst, steamed equilibrium USY catalyst, and steamed 10% USY catalyst were 120, 85, and 77, respectively. The RMA test uses high sulfur heavy gas oil feedstock, and the value obtained with a beta zeolite catalyst cannot be compared with that of a USY zeolite catalyst. Beta zeolite catalysts have low RMAs but are very active with F-T wax feedstocks. Zeolite type and catalyst activity had a significant effect on product selectivity. Zeolites beta and HZSM-5 gave the higher yields of the target butenes and pentenes than zeolite Y. Zeolites beta and HZSM-5 also gave higher propylene but lower C_6-430°F naphtha yields than zeolite Y. Lowering the catalyst activity by steaming increased pentene and lowered coke yields. The steamed 10% beta zeolite catalyst with mild cracking conditions gave an excellent combination of olefin and naphtha yields.

Product recovery on this pilot plant is consistently over 98% with gas oil feedstock. In contrast, the product recoveries were between 55 and 101% with all the runs that were made with the wax feedstock. Feed rates with the wax were 23-25 g/m versus a standard gas oil feed rate of 13-15 g/m. The combination of wax feedstock and high feed rate flooded the condensing column, which caused the erratic, generally low recoveries in these runs. The cause of the low recoveries was not diagnosed until almost the end of the program. Elimination of this problem would have required a major revamp of the pilot plant which was not possible under the time limitations of this program. We believe that the low mass balances did not affect the conversion and selectivity data; the total liquid products that were recovered were representative of the process conditions and catalyst that were used.

The initial runs with equilibrium USY catalyst (runs 939-1 and 939-2) used process conditions similar to those normally used with petroleum gas oil feedstocks. The wax conversion level was about 94% with those conditions, confirming the high conversions that were observed in the small scale experiments. Lowering the severity of the process conditions (run 939-4) lowered the conversion to 83%, but additionally steaming the catalyst (run 939-5) while using the process conditions of run 939-4 gave essentially the same conversion (85%). The final run in this program, run 945-2, used the equilibrium USY catalyst with low process severity similar to run 949-4. There was excellent agreement in the conversion and product yields for runs 939-4 and 945-2, except for coke. Run 945-2 gave 1.8% coke, which was more in line with the 2-2.3% coke obtained in runs 39-1 and -2, than the 0.6% coke in run 939-4. A 50% dilution of the equilibrium Y zeolite catalyst with inert clay microsphere (run No. 942-2) did not lower conversion substantially. The use of added diluent to lower conversion was abandoned because the diluent had a higher particle density than normal FCC catalysts, which caused circulation problems in the pilot plant test of this catalyst mixture. One run (943-1) was also made with a steamed 10% USY zeolite catalyst using mild catalytic cracking severity. This run was made with the objective of using a less active catalyst plus mild cracking severity to get yield data at a lower conversion than was obtained in the run with steamed equilibrium USY (run 939-5). Lowering the activity had little effect; the conversion and product yields with the steamed 10% USY catalyst (RMA=77) were virtually identical to those with the steamed equilibrium USY catalyst (RMA=85) (run 939-5).

The two runs (940-1 and 940-2) with the steamed 40% beta zeolite catalyst confirmed the conclusions of the MYU tests: the beta zeolite converted a greater fraction of the wax feedstock to light olefins, including propylene, isobutylene and isoamylenes, than the steamed equilibrium USY zeolite catalyst; but the higher olefin yields were accompanied by a

significantly lower C_6-430°F naphtha yield (27-32% with steamed beta versus 46% with steamed equilibrium USY catalyst). One run (944-2) was made with steamed 10% beta zeolite catalyst using mild catalytic cracking process severity. This run was made with the objective of using a less active catalyst plus mild cracking severity to get yield data at a lower conversion than was obtained in the runs with steamed 40% beta (runs 940-1 and -2). Lowering the zeolite content lowered conversion--to about 90% versus 97% with 40% beta--and also had a beneficial effect on the product yields. High yields of olefins and propylene were obtained with the 10% beta catalyst, but with a higher C_6-430°F naphtha yield (44%) than the steamed 40% beta catalyst (27-32%).

The test results for the 25% steamed HZSM-5 catalyst mixture with steamed equilibrium USY (run 941-1) were similar to the steamed 40% beta zeolite. High yields of the target light olefins were produced, but gasoline yield was much lower than the Y zeolite catalyst. This trade-off of light olefin and gasoline yield can be adjusted by the amount of the HZSM-5 additive and the process conditions. Additional work would be needed to determine the optimal combination of HZSM-5 catalyst and process conditions.

5.2 Product Quality

The liquid products from runs 943-1 (steamed 10% USY catalyst), 939-05 (steamed equilibrium USY catalyst), 945-2 (equilibrium USY catalyst), and 944-2 (steamed 10% beta catalyst) were fractionated by an atmospheric distillation procedure (ASTM D-2892) to yield 430-°F and 430+°F fractions. Table XIX gives the following analyses for the IBP-430°F naphtha fractions: API, RON by gc, RON by engine test, MON by engine test, simulated distillation, and PIANO by gc. The 430+°F fractions were then distilled under vacuum (10mm Hg) to give 430-650°F distillate and 650+°F cycle oil fractions. Table XX lists the following properties of the 430-650°F distillates: API, pour point, cloud point, cetane index, C_A (by NMR), and simulated distillation. Table XXI gives the following properties for the 650+°F cycle oils: API, C_A (by NMR), and simulated distillation.

5.2.1 Properties of 430-°F Product (Naphtha)

The PIANO analyses show that the *distribution of compound types* and the *carbon number distribution* within the compound types were strongly affected by both catalyst activity and catalyst type. Figure 70 shows the effect of activity for USY zeolite on the distribution of n-paraffins, i-paraffins, i/n-paraffin ratio, naphthenes, aromatics, and olefins. With increasing activity (steamed 10% Y with 77 RMA < steamed equilibrium Y with 85 RMA < equilibrium Y with 120 RMA), olefin content decreased while naphthene and aromatics contents increased. Increasing activity had no

TABLE XIX

ANALYSIS OF IBP-430F PRODUCTS FROM FCC PILOT PLANT RUNS

Run ID:	943-1	939-5	945-2	944-2
Catalyst Type:	Stm'd 10% USY	Stm'd Eq USY	Eq USY	Stm'd 10 % Beta
API	68.5	63.6	58	63.5
RON, gc	84.3	81.6	81.3	81.1
RON	90.3	86.7	81.3	85.4
MON	79.4	78.1	74.9	76.4
(RON+MON)/2	84.8	82.4	78.1	80.9
Sim Dist., F				
IBP	72		-22	-25
5 %	104		136	91
10 %	136		159	133
20 %	151		196	162
30 %	162		216	203
40 %	189		245	223
50 %	206		274	253
60 %	235		292	279
70 %	268		326	302
80 %	307		350	337
90 %	362		387	384
95 %	394		409	413
FBP	446		455	475
PIANO, Distribution of Compound Types, wt %				
n-Paraffins	5.41	5.05	5.56	7.18
i-Paraffins	23.23	20.4	24.88	16.02
i/n	4.3	4.04	4.5	2.2
Naphthenes	8.97	13.2	15.98	15.49
Aromatics	8.86	11.57	22.57	8.9
Olefins	51.17	46.03	26.95	46.87
Oxygenates	0.24	0.08	0.26	0.46
Unknowns	2.08	3.68	3.8	5.08

TABLE XIX (Cont)

ANALYSIS OF IBP-430F PRODUCTS FROM FCC PILOT PLANT RUNS

Run ID:	943-1	939-5	945-2	944-2
Catalyst Type:	Stm'd 10 % USY	Stm'd Eq USY	Eq USY	Stm'd 10 % Beta
PIANO, Distribution by Carbon Number, wt %				
Propane	0.02	0.04	0.02	0.03
Butanes	1.78	1.1	1.43	2.83
Pentanes	17.87	6	4.13	11.06
Hexanes	30.07	25.95	10.68	15.62
Heptanes	20.98	23.49	23.08	21.34
Octanes	11.79	17.2	22.27	19.08
Nonanes	7.7	10.86	17.02	12.52
Decanes	5.31	7.81	11.82	8.84
C11's	2.04	3.17	4.68	3.01
C12's	0.37	0.7	1.06	0.59
C13's	0	0	0	0
Unknowns	2.08	3.68	3.8	5.08
PIANO, Compound Types by Carbon Number, wt %				
Paraffins:				
C4	0.12	0.08	0.012	0.19
C5	0.9	0.28	0.22	0.63
C6	1.92	1.33	0.79	1.39
C7	0.7	0.85	1.02	1.16
C8	0.78	1.13	1.4	1.74
C9	0.35	0.49	0.69	0.81
C10	0.24	0.35	0.54	0.53
C11	0.23	0.3	0.45	0.44
C12	0.18	0.24	0.32	0.3
Isoparaffins:				
C4	0.25	0.14	0.3	0.29
C5	3	0.86	1.24	1.29
C6	8.06	5.64	3.31	2
C7	6.06	5.6	7.21	3.06
C8	2.85	3.37	5.94	3.18
C9	1.06	1.39	2.12	2.12
C10	1.28	2.24	3.08	2.77
C11	0.68	1.1	1.61	1.25
C12	0	0.06	0.06	0.06
Aromatics:				
C6	0	0	0.14	0
C7	0.39	0.46	0.97	0.25
C8	1.92	2.33	5.28	1.7
C9	2.63	3.29	6.84	2.53
C10	2.79	3.72	6.54	3.18
C11	0.94	1.39	2.14	1.03
C12	0.2	0.36	0.64	0.21

TABLE XIX (Cont)

Table II, concl.

ANALYSIS OF IBP-430F PRODUCTS FROM FCC PILOT PLANT RUNS

Analysis of IBP-430 F Products from AU-2L Pilot Plant Runs

Run ID:	943-1	939-5	945-2	944-2
Catalyst Type:	Stm'd 10 % USY	Stm'd Eq USY	Eq USY	Stm'd 10 % Beta
PIANO, Compound Types by Carbon Number, wt %				
Naphthenes:				
C6	0.45	0.4	0.3	0.18
C7	0.84	1.29	1.38	0.59
C8	3	4.36	5.06	5.46
C9	3.57	5.47	7.3	6.86
C10	0.98	1.45	1.62	2.31
C11	0.1	0.21	0.33	0.1
C12	0	0	0	0
Olefins:				
C4	1.33	0.81	0.97	2.29
C5	13.94	4.86	2.67	9.09
C6	19.63	18.58	6.15	12.06
C7	12.82	15.29	12.27	15.92
C8	3.24	6	4.6	7
C9	0.09	0.21	0.06	0.2
C10	0.02	0.04	0.03	0.06
C11	0.09	0.17	0.15	0.2
C12	0	0.03	0.03	0.02

TABLE XX

ANALYSIS OF 430-650F PRODUCTS FROM FCC PILOT PLANT RUNS

Run ID:	943-1	939-5	945-2	944-2
Catalyst Type:	Stm'd 10 % USY	Stm'd Eq USY	Eq USY	Stm'd 10 % Beta
API	38.9	39.5	36.9	42.2
Pour Pt, F	0	0	-6	-6
Cloud Pt, F	1	2	-1	-1
Cetane Index	56.3	58.9	50.8	60.9
C-sub-A (NMR), wt %	19.4		24.8	15
Sim Dist, F				
IBP	403	395	400	393
5 %	434	438	428	431
10 %	443	453	440	444
20 %	466	478	455	467
30 %	486	501	475	485
40 %	511	525	489	503
50 %	534	550	515	521
60 %	559	576	532	542
70 %	585	602	553	562
80 %	613	627	576	586
90 %	642	651	615	624
95 %	651	661	647	649
FBP	691	694	733	741

TABLE XXI

ANALYSIS OF 650+F PRODUCTS FROM FCC PILOT PLANT RUNS

Run ID:	943-1	939-5	945-2	944-2
Catalyst Type:	Stm'd 10 % USY	Stm'd Eq USY	Eq USY	Stm'd 10 % Beta
API	32.8	37.1	29.6	36.8
C-sub-A (NMR), wt %	16		24.1	10.6
Sim Dist, F				
IBP	236	273	233	224
5 %	670	397	604	600
10 %	690	664	625	624
20 %	704	693	649	649
30 %	717	711	672	674
40 %	730	726	695	697
50 %	741	741	712	715
60 %	759	758	730	734
70 %	781	776	752	762
80 %	808	802	786	794
90 %	856	845	838	844
95 %	910	897	895	892
FBP	1189	1265	1132	1155

FIGURE 70

SASOL WAX FCC PILOT PLANT DATA:
EFFECT OF USY ZEOLITE CATALYST ACIDITY
ON PIANO DISTRIBUTION BY COMPOUND TYPE IN IBP-430F NAPHTHA

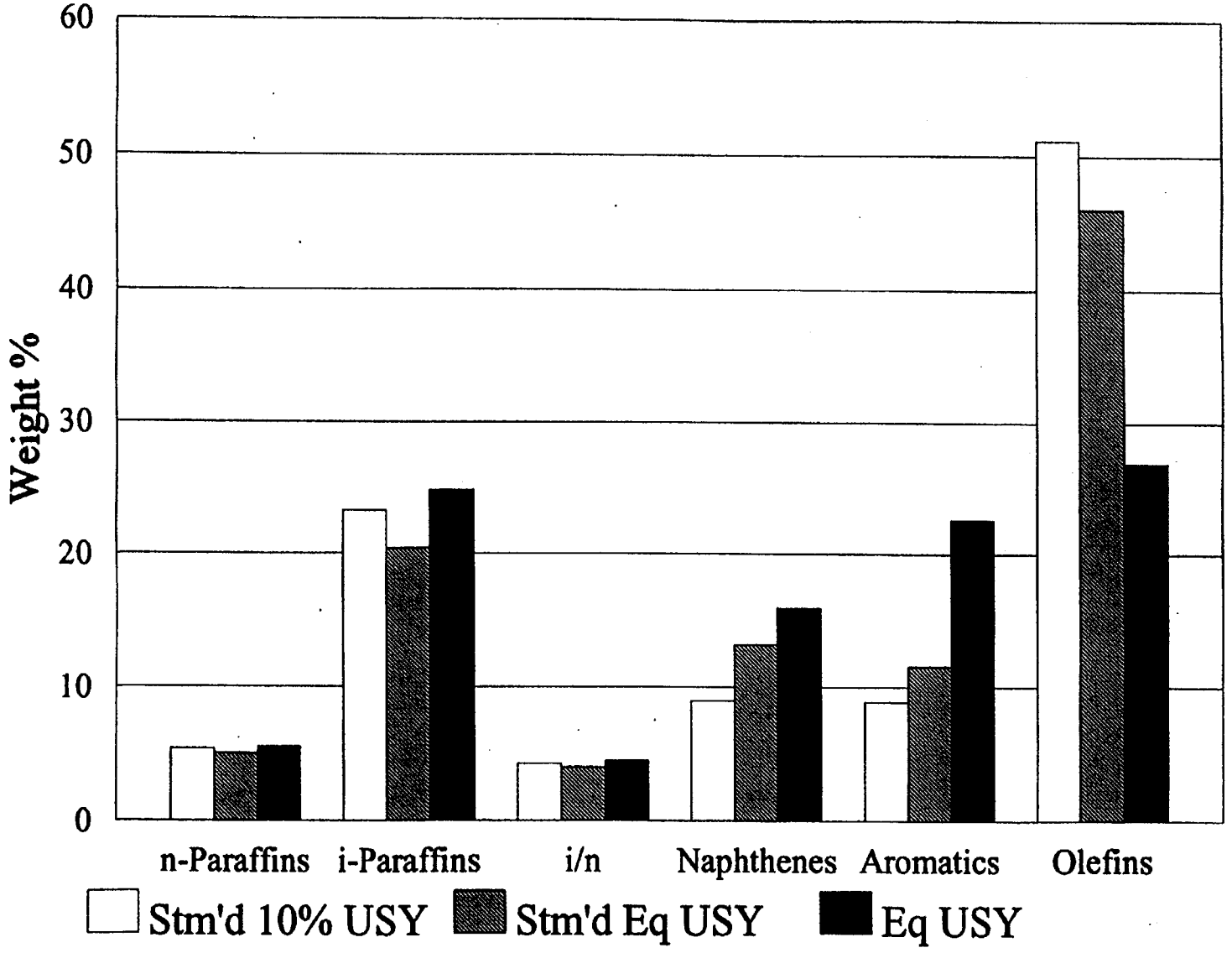
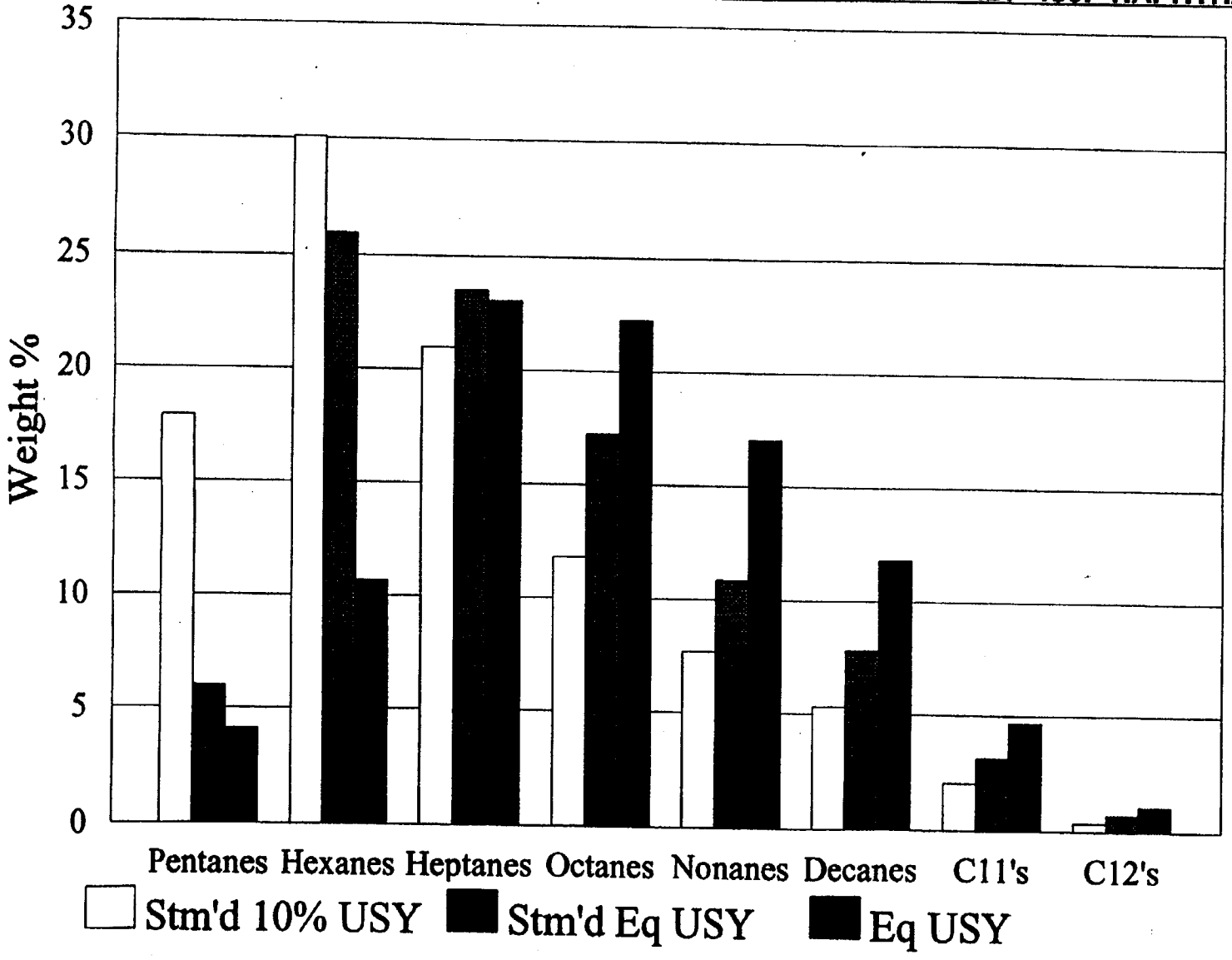


FIGURE 71

SASOL WAX FCC PILOT PLANT DATA:
EFFECT OF USY ZEOLITE CATALYST ACTIVITY
ON PIANO DISTRIBUTION BY CARBON NUMBER IN IBP-430F NAPHTHA



effect on either n- or i-paraffin content. The naphtha from the 10% steamed USY catalyst contained 9% naphthenes, 9% aromatics, 51% olefins, and had a 4.3 ratio of *i*- to *n*-paraffins. The naphtha from the standard equilibrium USY catalyst contained 16% naphthenes, 23% aromatics, 27% olefins and had a 4.5 ratio of *i*- to *n*-paraffins. Comparison of the steamed 10% USY catalyst with the steamed 10% beta catalyst shows that catalyst type had a strong effect on naphtha compound type. The 10% steamed beta catalyst produced more naphthenes (15%) and had a 2.2 ratio of *i*- to *n*-paraffins.

Figure 71 shows the effect of activity for USY zeolite on the C_5 through C_{12} distributions. With increasing activity (steamed 10% Y with 77 RMA < steamed equilibrium Y with 85 RMA < equilibrium Y with 120 RMA), the distribution shifted to heavier products. Naphtha from the 10% steamed USY catalyst was much lighter (38% C_5-C_6s and 8% C_{10}-C_{13}s) than the naphtha made with the standard equilibrium USY catalyst (15% C_5-C_6s and 18% C_{10}-C_{13}s). Comparison of the steamed 10% USY catalyst with the steamed 10% beta catalyst shows that catalyst type had an effect on carbon number distribution. The naphtha from the steamed 10% USY catalyst was also lighter than the naphtha from the steamed 10% beta catalyst (27% C_5-C_6s and 12% C_{10}-C_{13}s)).

These PIANO results show that the primary products from cracking over the steamed 10% USY catalyst are olefins distributed around C_6, but that they increasingly cyclize, aromatize, and disproportionate into higher molecular weight products over the more active steamed equilibrium USY and standard equilibrium USY catalysts. Both catalyst and process parameters should influence this aromatics formation reaction. Although further studies will be required to elucidate the mechanism of aromatics formation, these results suggest the following direction for future work: modification of the catalyst to lower activity, such as by the addition of phosphorus,[8] should be a successful strategy for producing more olefins and decreasing the formation of naphthenes and aromatics.

The steamed 10% USY catalyst produced naphtha with an API gravity of 68.5, which was much higher than the gravity produced by either the steamed 10% beta or standard equilibrium USY catalysts, which were 63.5 and 58, respectively. These gravities reflect the PIANO analyses which showed that the steamed 10% USY made low naphthenes and low aromatics, the steamed 10% beta made high naphthenes and low aromatics, and the standard equilibrium USY made high naphthenes and high aromatics.

The engine tests of RON and MON showed that both decreased with increasing acidity for the USY catalysts. The steamed 10% USY catalyst produced naphtha with an (R+M)/2 octane number of 84.8, versus 82.4 for the steamed equilibrium USY and 78.1 for the equilibrium USY catalyst. The steamed 10% USY catalyst gave a higher octane than the steamed 10% beta catalyst (80.9). These results are also explained by the PIANO analyses. The high octane number of the naphtha from the steamed 10% USY catalyst is produced by its high content of low molecular weight olefins. The naphtha from the steamed 10% beta catalyst was lower in octane number because it had lower total olefins, the olefins were of higher molecular weight, and it had a high naphthene content. The low octane number of the naphtha from the standard equilibrium USY catalyst was surprising because, although it had the lowest olefin content, it had the highest content of aromatics plus olefins. Apparently the increase in molecular weight of the olefins and aromatics over those made by the steamed 10% USY catalyst, and the high content on naphthenes, combined to lower the octane of the naphtha that was made with the standard equilibrium USY catalyst.

5.2.2 Properties of 430-650 °F Product (LCCO)

Any 430-650°F fraction is "distillate" and is the boiling range for products such as diesel fuel, jet fuel, kerosene, and heating oil. The 430-650°F product from catalytic cracking is called "light cat cycle oil," which is abbreviated LCCO. The cetane index rating is the major property

of interest for diesel oil. Cetane index, which is calculated from the API gravity and simulated distillation, is proportional to the paraffin content; it is a measurement of diesel fuel quality analogous to octane number for gasoline. Weight percent C_A(NMR) is usually used as the indicator of aromatic carbon content, but is really the amount of sp_2-hybridized carbon. Because these samples are expected to have high olefin contents, the C_A might not be proportional to the aromatic carbon content. Additional analysis would be required to distinguish the olefinic from the aromatic carbon.

Table XX shows that the 10% beta catalyst produced LCCO with the highest API gravity (42.2) and cetane index (60.9) and lowest weight percent C_A(NMR) (15) of the four catalysts.

The effect of activity with the three USY catalysts on LCCO properties was not as unambiguous as the effect on naphtha properties. The highest activity catalyst, the standard equilibrium USY catalyst, produced LCCO with the lowest API gravity (36.9) and cetane index (50.8) and highest weight percent C_A(NMR) (24.8). However, the LCCO from the intermediate activity catalyst (steamed equilibrium USY) had a higher API and cetane index than the LCCO from the steamed 10% USY catalyst, 39.5 vs 38.9 °API and 58.9 vs 56.3 cetane index, respectively. As expected, the C_A (NMR) for the steamed 10% USY catalyst (19.4 wt%) was lower than the C_A (NMR) from the equilibrium USY catalyst, but the analysis of the LCCO from the steamed equilibrium USY catalyst is not available to confirm the trend.

Although the steamed 10% beta catalyst made the highest cetane index product, the LCCOs from all four catalysts would be excellent stock for blending into diesel fuel.

The relative ranking of the LCCO from the standard equilibrium USY catalyst--heaviest and most aromatic--is consistent with the trends observed in the naphtha (discussed above). However, the relative rankings of the APIs of the LCCOs from the steamed 10% USY and steamed 10% beta catalysts are reversed from those of the naphtha. This implies that the LCCO fraction is not simply partially converted paraffinic feed, but that the LCCO contains products of condensation, cyclization, and aromatization. The lower API gravity and higher C_A(NMR) of the LCCO made with the steamed 10% USY catalyst versus the steamed 10% beta catalyst is consistent with those processes.

The pour points (0 to -6°F) and cloud points (2 to -1°F) of all four products were not significantly different.

5.2.3 Properties of 650+°F Product (Heavy Cycle Oil)

Table XXI shows that the 10% steamed beta catalyst produced the 650+°F cycle oil with the highest API gravity (36.8) and lowest weight percent C_A(NMR) (10.6) of the four catalysts. Consistent with the above-mentioned effect of activity for the USY catalysts, the standard equilibrium USY catalyst produced 650+°F cycle oil with the highest C_A(NMR) (24.1) and lowest API gravity (29.9). LCCO from the steamed 10% USY catalyst had 16 wt % C_A(NMR) and a 32.8 API gravity. The steamed equilibrium USY catalyst gave LCCO with the highest (37.1) API. This result is not understood; it may be erroneously high because of the presence of 5% 400-°F material that was not removed in the distillation. The observed trends in API gravity and C_A(NMR) are consistent with those of the LCCOs from the steamed 10% USY, equilibrium USY, and steamed 10% beta catalysts: more condensation, cyclization, and aromatization (high API and low C_A(NMR)) with either USY-based catalyst than the beta-based catalyst, and more aromatization with the standard equilibrium USY catalyst than the steamed 10% USY catalyst.

6.0 PREPARATION OF C_5-C_8 ETHERS (TASK 5)

Table XXII identifies the three feedstocks, A-C, that were prepared by combining the 200-°F distillate from FCC cracking runs. Tables XXIII-XXV show the major product analyses of these light naphtha/methanol runs with feedstocks "A," "B," and "C," respectively. Table XXVI summarizes the iso-olefin conversions for the three feedstocks with two catalysts, with and without the presence of hydrogen gas.

6.1 Model Compound Runs

Scoping runs were made using the model compound 2-methyl-2-butene with methanol to produce TAME before using the naphtha that was made in the pilot plant. The initial scoping runs were made in pilot plant AU-6. Those runs were repeated in pilot plant AU-109 because it was a smaller unit. The limited volume of 200-°F pilot plant product that was to be the feedstock for the etherification runs required the smaller pilot plant. Figure 72 shows that equivalent results were obtained in pilot plants AU-6 and AU-109. The test conditions were: variable temperatures between 125 and 200°F; 200 PSIG unit pressure; 0.66 WHSV (olefin); 1.2 mole ratio of methanol/olefin; and Amberlyst 15 catalyst (a commercial etherification catalyst). Figure 72 shows that the reaction temperature had a strong influence on the etherification reaction. The decrease in TAME yield at 200°F versus 150°F shows that the reaction is equilibrium limited with these process conditions at a reaction temperature of about 150°F. Additional experiments would be needed to determine the reaction temperature between 125 and 150°F where equilibrium control begins, or to establish the process conditions for equilibrium control below 150°F.

6.2 Feedstock Variation

The primary feedstock for these etherification studies was the light naphtha obtained from the pilot plant catalytic cracking runs with the Fischer-Tropsch wax. Table XXII identifies the three feedstocks, A-C, that were prepared by combining the 200-°F distillate from FCC cracking runs. The iso-olefin contents of feeds "B" and "C" were higher than feed "A." Feed "B" had a high iso-olefin content because it was made using the olefin selective beta and HZSM-5 zeolite FCC catalysts in the pilot plant runs, Nos. 940-01,02 and 941-01. It is not known why the iso-olefin content was higher in "C" than in "A" because the same Y zeolite catalyst was used in the runs for both of those feeds.

TABLE XXII

HYDROCARBON COMPOSITION OF 200°F- NAPHTHAS FROM FCC PILOT PLANT RUNS

Feed ID:	92-0490-01A Feed A*	93-0024-01A Feed B	93-0024-01C Feed C
Pilot Plant Run Nos.	939-01, + 02 eq. USY catalyst conversion = 93.6%	940-01, 02 941-01 Beta/HZSM-5 catalyst Conversions = 90, 96%	939-04 eq. USY catalyst conversion = 83%
Total Paraffins wt%	6.69	8.44	4.32
C_4	0.18	0.37	0.16
C_5	0.93	1.04	0.72
C_6	4.03	4.50	2.35
C_7	1.45	1.67	1.02
C_8	0.08	0.69	0.06
C_9	--	0.13	--
Total Iso-paraffins wt%	42.71	17.64	22.88
C_4	0.32	0.56	0.28
C_5	3.77	2.03	2.19
C_6	22.94	6.22	10.55
C_7	13.87	6.12	8.86
C_8	1.82	2.16	0.99
C_9	--	0.44	--
Total Aromatics wt%	1.74	2.62	0.35
C_6	0.34	0	0
C_7	1.34	1.03	0.35
C_8	0.05	1.38	0
C_9	--	0.22	--
Total Naphthenes wt%	3.96	5.55	3.16
C_5	0.05	0.06	0.05
C_6	1.23	0.92	0.71
C_7	1.92	1.71	1.63
C_8	0.75	1.82	0.80
C_9	--	1.03	--
Total Olefins wt%	44.51	64.47	68.65
C_3	0.01	0.11	0.04
C_4	1.25	3.72	1.82
C_5	8.701	12.10	12.03
C_6	23.88	29.54	33.79
C_7	10.36	15.65	19.95
C_8	0.31	3.31	1.02
Reactive iso-olefins wt%			
C_5's			
2-methyl-1-butene	1.25	2.15	1.76
2-methyl-2-butene	4.26	5.67	5.64
C_6's			
2,3-dimethylbutene	0.8	0.73	0.97
2-methyl-1-pentene	2.35	2.49	3.02
2-methyl-2-pentene	4.01	5.27	5.46
3-methyl-trans-2-pentene	2.49	3.13	3.29
3-methyl-cis-2-pentene	3.98	5.48	5.35

*This light naphtha was used in the initial etherification runs reported in the December 1992 Monthly Report.xxii

TABLE XXIII

ETHERIFICATION RUNS WITH NAPHTHA "A"
(200 PSIG, AMBERLYST 15, 2.9 GRAMS
FEED RATE: METHANOL, 1.37 G/HR; 200F,- NAPHTHA, 5.5 G/HR)

Run No.	Feed + MeOH	024-2	024-3	024-4	024-6	024-7	024-8
Temp, F		125	125	125	150	150	150
Wt% Product:							
C4-5 Olefins:							
iC4=	0.22761	0.44	0.408	0.443	0.477	0.467	0.466
3M1BUTENE	0.10959	0.101	0.094	0.104	0.103	0.103	0.104
2M1BUTENE	1.05375	0.161	0.146	0.153	0.108	0.109	0.101
2M2BUTENE	3.59118	2.719	2.403	2.247	1.267	1.237	1.208
C6 Olefins:							
3M1PENTENE	0.79242	0.774	0.769	0.791	0.795	0.81	0.796
23DMBUTENE	0.69126	0.293	0.296	0.313	0.116	0.113	0.115
4Mt2PENTENE	0.30348	0.334	0.326	0.352	0.341	0.361	0.353
4Mc2PENTENE	1.07904	1.048	1.047	1.087	1.072	1.094	1.083
2M1PENTENE	1.98105	0.657	0.667	0.701	0.253	0.25	0.245
HEXENE-1	0.6744	0.659	0.664	0.682	0.671	0.684	0.675
tHEXENE-3	1.46682	1.443	1.454	1.488	1.474	1.497	1.481
cHEXENE-3	2.28453	2.252	2.271	2.316	2.291	2.331	2.3
2M2PENTENE	3.38043	2.636	2.668	2.731	1.733	1.724	1.75
tHEXENE-2	0.06744	0.063	0.064	0.067	0.07	0.071	0.067
3Mt2PENTENE	2.09907	1.615	1.635	1.677	1.278	1.299	1.285
cHEXENE-2	1.22235	1.209	1.22	1.238	1.23	1.247	1.232
3Mc2PENTENE	3.35514	2.617	2.654	2.694	2.329	2.402	2.331
Oxygenates:							
MeOH	15.7	10.586	10.553	9.614	9.953	8.593	9.535
MTBE	0	0.362	0.379	0.396	0.407	0.401	0.394
TAME	0	4.193	4.264	4.027	5.271	5.356	5.299
THME1	0	0.557	0.563	0.556	0.978	1.002	0.981
THME2	0	2.904	2.931	2.929	4.771	4.937	4.815
THME3	0	2.341	2.361	2.353	3.361	3.397	3.42
nHEXANE	3.39729	4.792	4.708	4.207	3.552	3.53	3.449
TOLUENE	1.127091	1.132	1.154	1.16	1.146	1.165	1.154
2MPENTANE	9.9474	9.726	9.773	10.027	9.968	10.163	10.064
3MPENTANE	6.909228	6.877	6.899	7.039	6.96	7.095	7.011

MMS/ml/94156
2/11/94