TABLE VII

MYU TESTS: CATALYST COMPARISONS AT 880°F

Catalyst Type	Zeolite Y	Zeolite Beta	Zeolite HZSM-5
Run No.	031	042	055
Conversion, Wt%	83.0	83.3	83.8
Product Yields, Wt%:			
C_2^-	0.6	0.6	1.5
$C_3^=$	7.4	8.9	17.5
C_3^o	0.8	0.9	2.7
$C_4^=$	13.2	17.7	27.4
C_4^o	3.7	3.6	3.6
$C_5^=$	11.7	13.5	13.9
C_5^o	3.6	2.2	2.0
C_6-430°F	41.7	35.8	15.3
430°F$^+$	17.0	16.8	16.2
Coke	0.3	0.2	0.1
Isobutylene	5.8	9.4	12.3
Isoamylenes	7.7	9.2	9.8
C_5-430°F	57.0	51.4	31.1
RON	85.2	84.4	84.4
MON	76.2	74.6	76.0

4.1.3 Non-zeolitic Catalysts

Amorphous, non-zeolitic FCC catalysts are no longer used in commercial units because they have lower activity than zeolite-based FCC catalysts. However, amorphous, low-activity catalysts may not be a disadvantage for F-T wax cracking because, as our tests have shown, it cracks readily under mild conditions. One example of this type of amorphous catalyst is the matrix only fraction of Davison Chemical Company's commercial Octacat D series of FCC catalysts. This material consists of an active alumina phase and inert clay components. Table VIII compares the wax cracking of a steamed sample of this catalyst with diluted zeolite Y and zeolite beta, with all the runs made at 970°F and 3 catalyst to oil ratio. Although the conversion levels of the three catalysts were not equivalent (they were between 71 and 78%), some qualitative observations are possible. The amorphous matrix sample had excellent light olefin selectivities, comparable to the beta zeolite and superior to the Y zeolite sample. As with the zeolite-based catalysts, the high yields of light olefins with the Octacat D matrix catalyst came at the expense of gasoline yield.

TABLE VIII

MYU TESTS: COMPARISON OF AMORPHOUS CATALYST AT 970°F

Catalyst Type	AD Matrix	Zeolite Y	Zeolite Beta
Run No.	048	046	044
C/O	3.0	0.2	0.2
Conversion, Wt%	72.6	70.9	77.8
Product Yields, Wt%:			
C_2^-	1.4	1.1	1.1
$C_3^=$	9.6	5.7	8.4
C_3°	1.0	0.7	0.8
$C_4^=$	16.4	9.7	14.9
C_4°	2.3	1.8	2.5
$C_5^=$	12.1	9.8	13.4
C_5°	1.7	1.8	1.5
C_6-430°F	27.4	40.2	35.1
430°F$^+$	27.4	29.1	22.3
Coke	0.6	0.1	0.1
Isobutylene	7.2	4.2	7.6
Isoamylenes	8.1	5.9	8.0
C_5-430°F	41.2	51.9	50.0

4.1.4 Effect of HZSM-5 Source

The results described above for HZSM-5 were obtained using "ZCat Plus," which is Intercat Corporation's commercial FCC additive material. Two additional HZSM-5 type samples were tested to determine if the high yields of isobutylene and isoamylenes could be retained, but with lower propylene production. They were Davison's "Additive OH-S" and Intercat's "Isocat." A standard steam pre-treatment (100% steam at 1450°F for five hours) of these samples preceded the wax cracking tests. Table IX presents the results of these tests, all of which were obtained at the same process conditions of 880°F and 0.2 catalyst/oil ratio. Although there was considerable variability in the conversions, there were no major selectivity differences between the ZCat Plus and the other HZSM-5 catalysts; the ratio of propylene to isobutylene yields and the gasoline composition was similar for all samples.

4.1.5 HZSM-5 Zeolite Catalysts Containing Rare Earth

Table X shows the results of those tests with 1-3 % rare earth oxide added to HZSM-5 zeolite catalysts. At the same process conditions of 880 °F and 0.2 catalyst/oil ratio, the addition of 1, 2, or 3% rare earth oxide to the base HZSM-5 catalyst (ZCat Plus) lowered conversion to about 80% but had no effect on selectivity.

Tests of these catalysts at 880°F and 0.9 catalyst to oil weight ratio showed that wax conversion level varied with the catalyst to oil ratio, as shown in Figure 17. The rare earth oxide treated HZSM-5 samples and the

FIGURE 13

SASOL WAX MYU DATA:
EFFECT OF C/O ON COKE

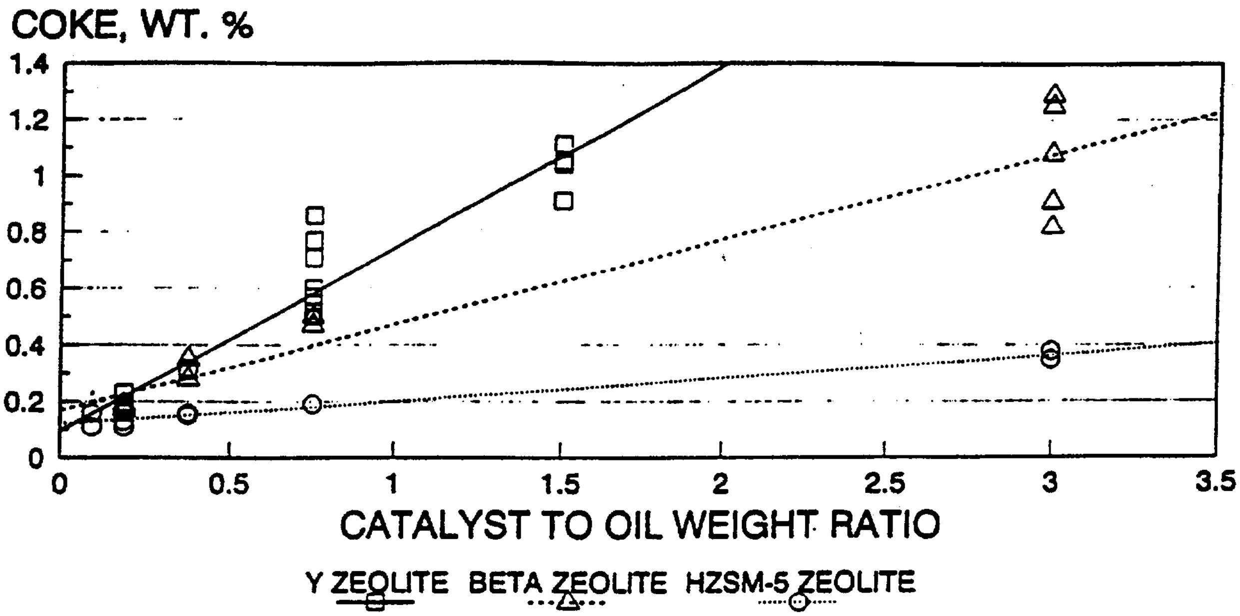

FIGURE 14

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON AROMATICS FORMATION

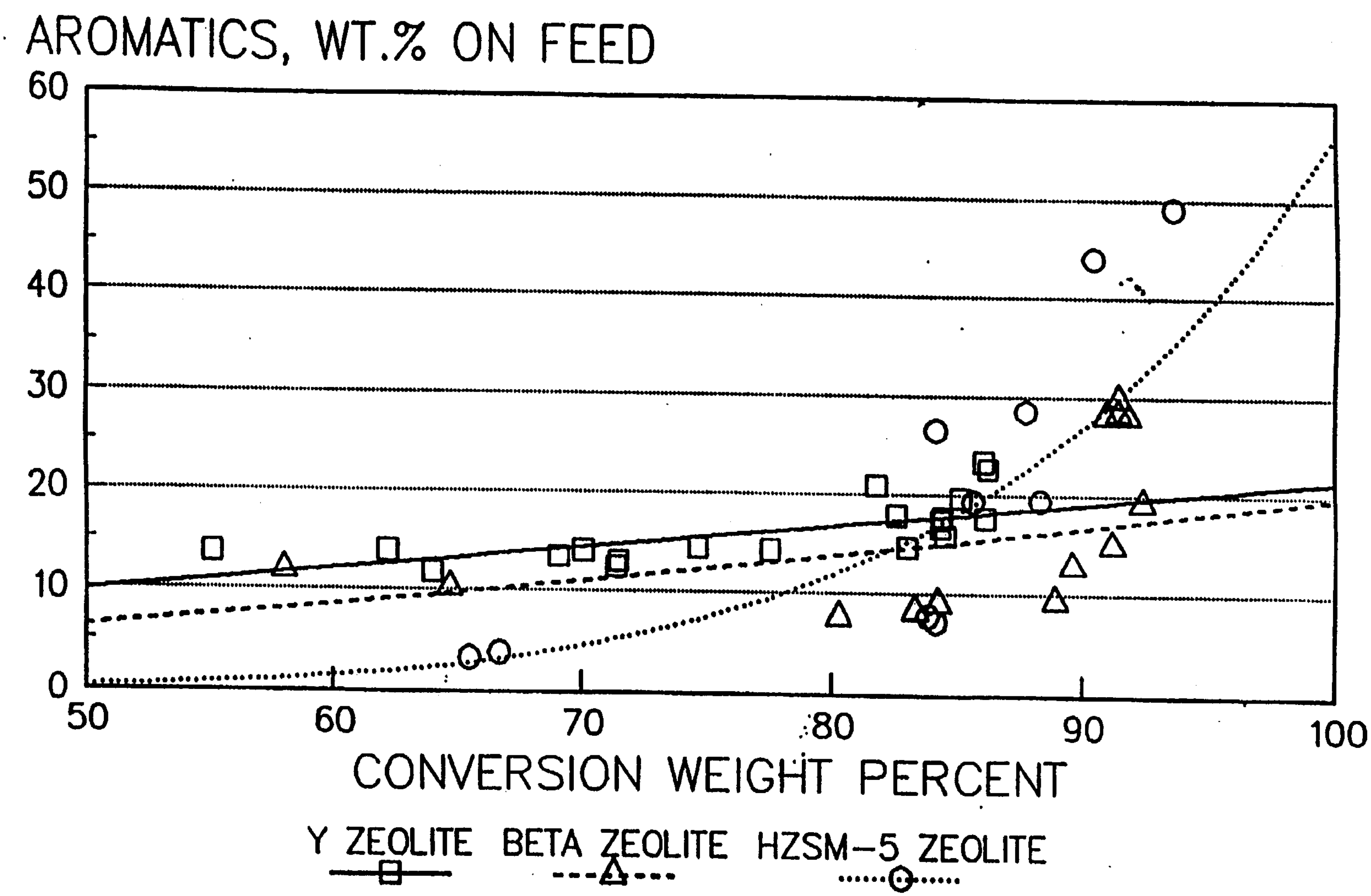

FIGURE 15

SASOL WAX MYU DATA: C5 ISOMER DISTRIBUTION

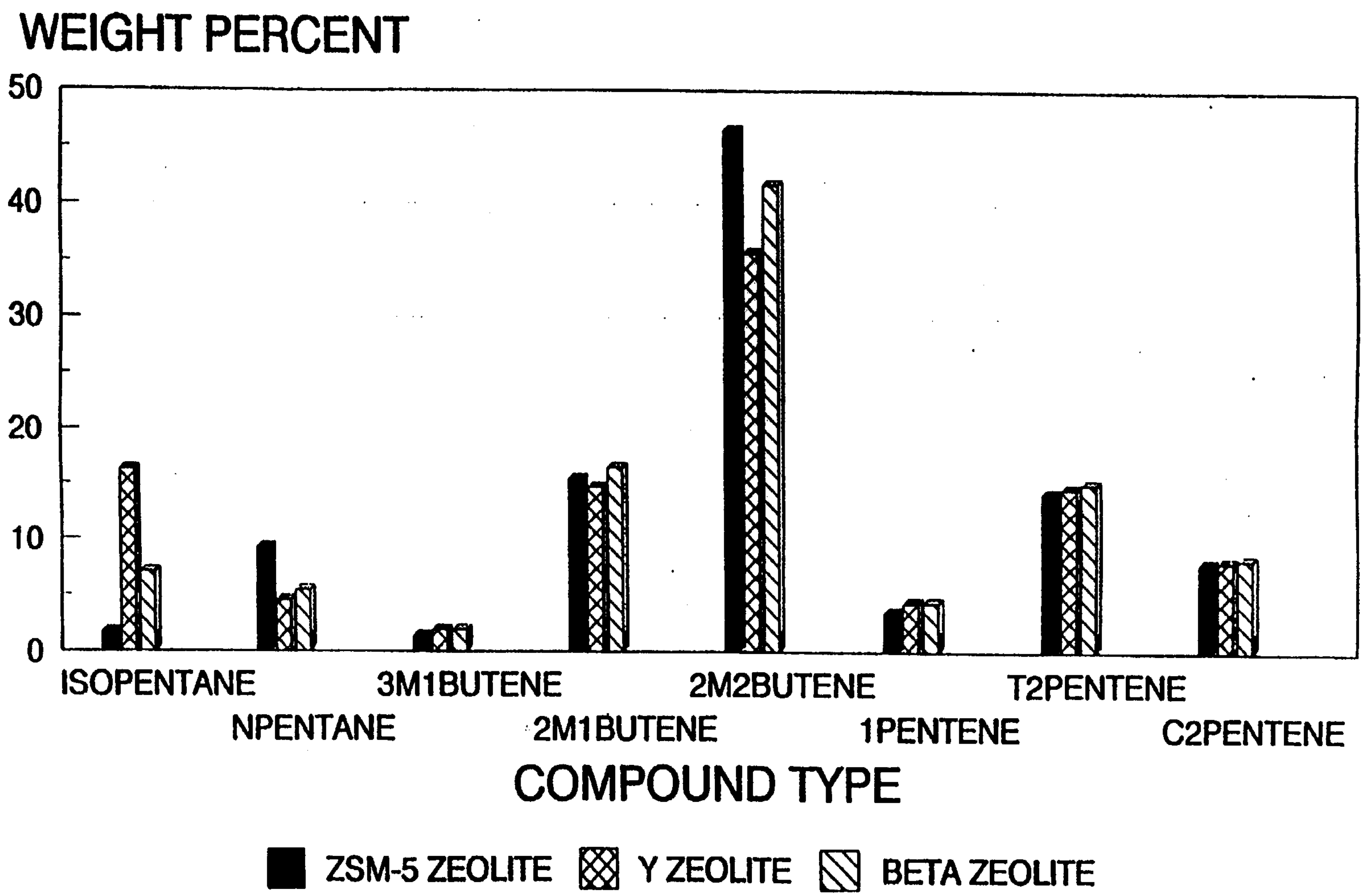

FIGURE 16

SASOL WAX MYU DATA: C4 ISOMER DISTRIBUTION

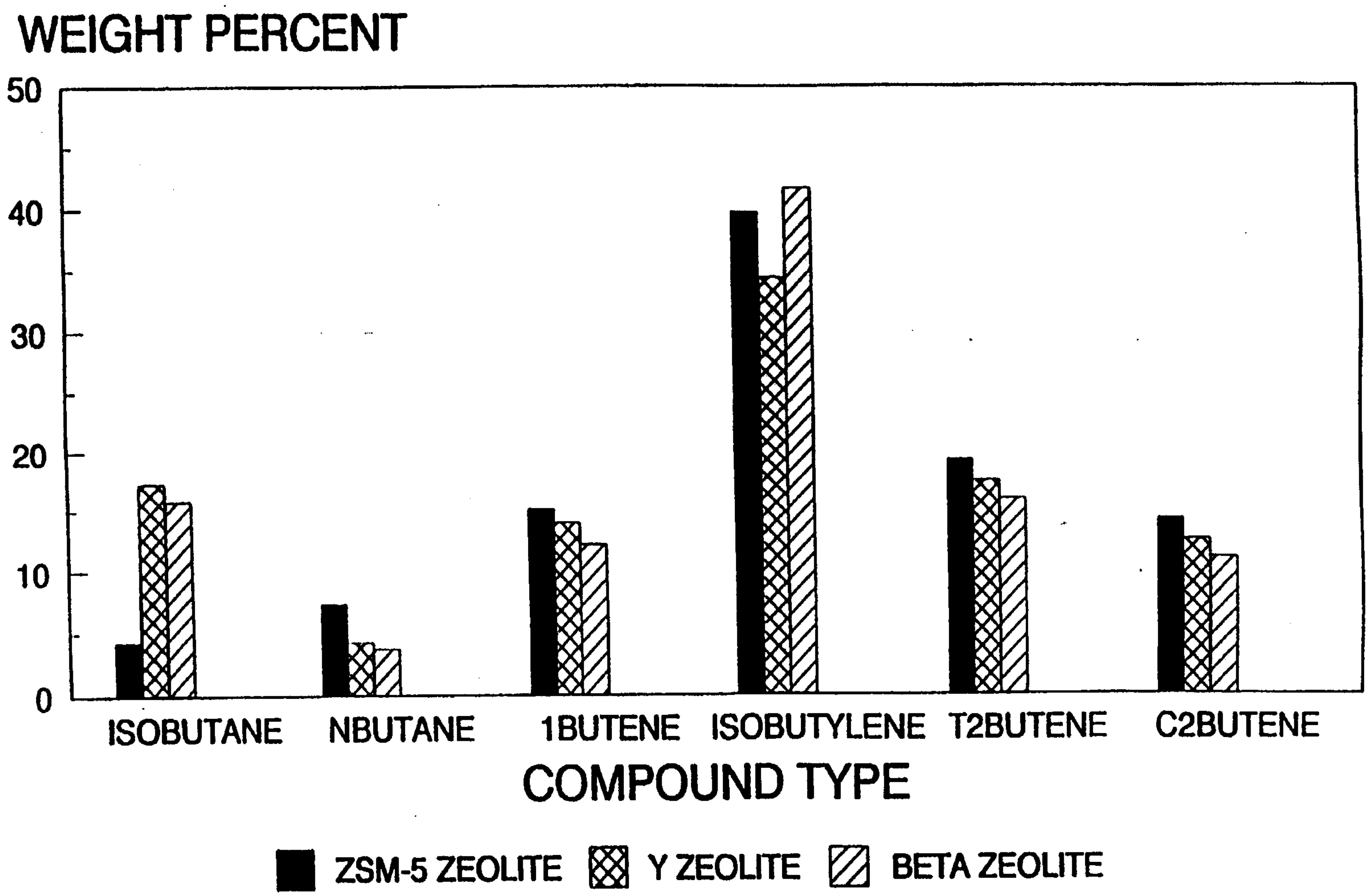

FIGURE 17

SASOL WAX MYU DATA: EFFECT OF C/O ON CONVERSION WITH HZSM-5 CATALYSTS

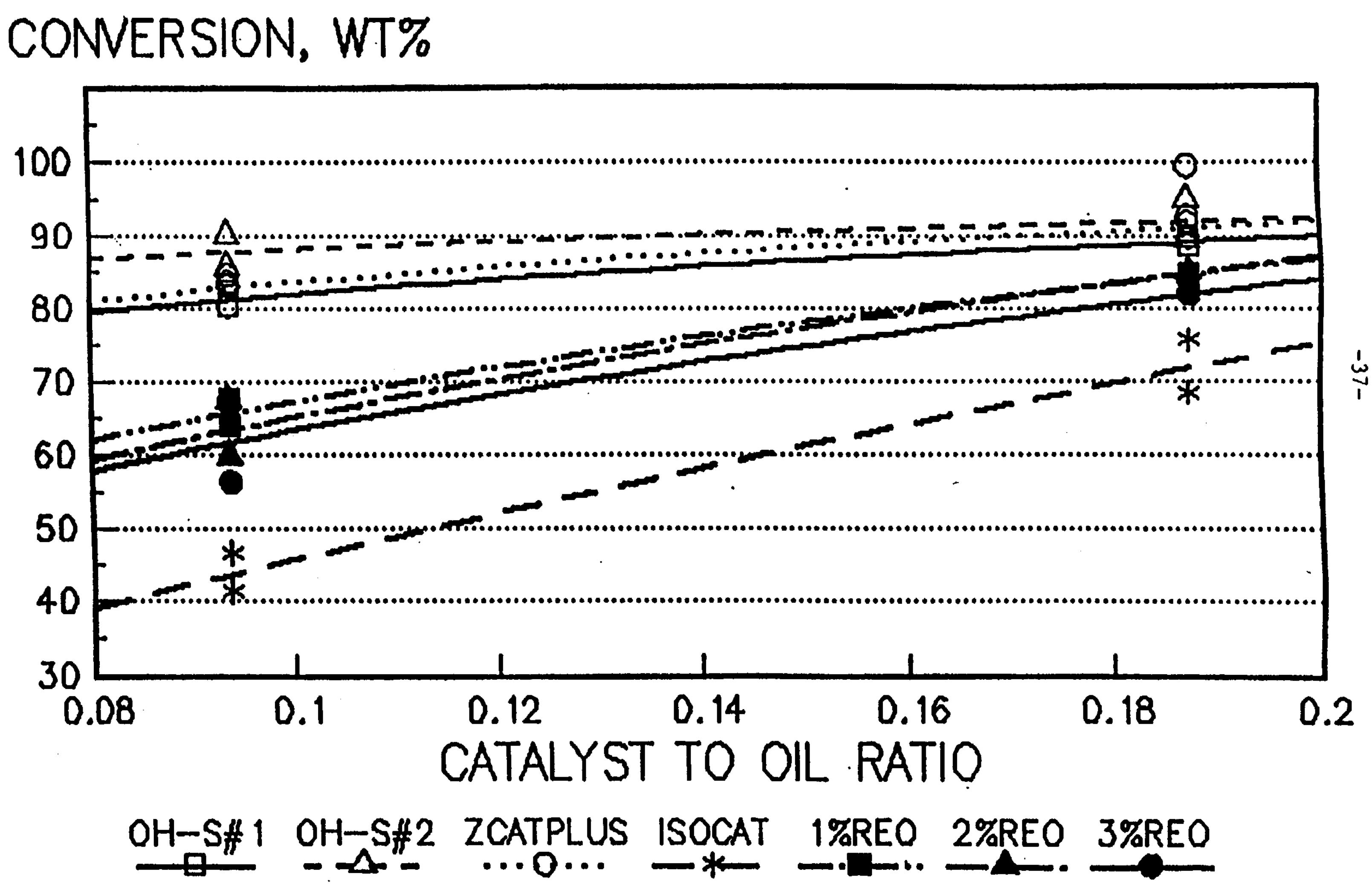

TABLE IX

MYU TEST: VARIOUS HZSM-5 CATALYSTS

(TEST CONDITIONS: 880°F, 0.187 CATALYST/OIL RATIO)

Run No.	054	055	087	088	089	090	094	084	091	085	092	086	093
Catalyst Description	<----------CCC-1891----------> ZCat Plus Large Steamer					CCC-1891 ZCat Plus Small Steamer		14040-43-1 OH-S Small Steamer		14040-43-2 OH-S Small Steamer		14040-43-3 Isocat Small Steamer	
Conversion Wt%	90.2	91.9	92.5	86.5	86.9	78.5	90.5	84.7	87.8	83.9	89.8	65.9	69.4
Product Yields Wt%													
C_2^-	1.6	1.5	2.8	1.6	2.2	1.2	2.1	1.9	1.7	1.7	3.0	0.9	0.8
C_3 + C_4	49.5	50.3	49.4	42.4	48.9	37.3	47.7	41.5	45.1	39.9	47.2	30.1	32.0
C_5-430°F	40.0	38.0	39.8	41.2	35.6	39.9	40.6	42.1	40.9	42.2	39.4	34.8	36.5
430°F+	8.8	10.0	7.5	13.5	13.1	21.1	9.5	15.6	12.2	16.1	9.3	34.1	30.6
Coke	0.1	0.2	0.5	1.3	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.1
$C_3^=$	16.6	17.4	13.8	12.5	14.8	12.8	14.4	10.7	14.5	11.0	15.9	9.5	11.9
$iC_4^=$	12.2	12.1	12.5	10.7	11.8	9.7	12.4	11.5	10.6	10.7	10.6	8.9	8.6
$iC_5^=$	10.8	10.9	9.5	12.0	11.5	12.5	15.5	13.6	11.0	12.1	9.8	12.6	13.9
C_5-430°F													
RON	85.4	84.4	80.9	84.3	82.5	84.3	83.5	84.4	81.7	86.2	85.0	83.6	84.8
MON	76.4	76.0	74.2	75.1	74.8	74.9	75.2	75.0	74.2	75.7	76.5	74.3	75.3

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TABLE X

MYU TESTS: RARE EARTH/HZSM-5 CATALYSTS
Test Conditions: 880°F, 0.187 Catalyst/Oil Ratio

Run No.	096	097	098
Catalyst	14040-42-1	14040-42-2	14040-42-3
Description	1% ReO	2% ReO	3% ReO
Conversion, wt%	80.3	80.5	76.7
Product Yields, wt%:			
C_2-	1.2	1.3	1.1
C_3+C_4	39.5	39.0	36.6
C_5-430°F	39.5	40.1	38.9
430°F^{-1}	19.7	19.5	23.3
Coke	0.1	0.1	0.1
C_3=	13.3	12.7	11.8
iC_4=	9.9	9.5	9.5
iC_5=	10.1	10.8	10.1
C_5-430°F	83.3	83.7	83.3
RON	74.7	75.0	74.8
MON			

Isocat material were less active (lower wax conversion) than the other two commercial HZSM-5 samples, Intercat's ZCatPlus and Davison's OH-S. Catalytic activity is a function of the available Bronsted acid site concentration, or framework aluminum content. The lower catalytic activity of the Isocat sample is explained by its higher silica to alumina ratio (low framework alumina) HZSM-5 zeolite. Since the rare earth samples also showed lower activity, it is likely that the impregnation treatment lowered their acidity by lowering the framework aluminum content.

Figures 18-21 show there were no major selectivity differences in product yields of propylene, isobutylene, isoamylenes, and gasoline, respectively, among these HZSM-5 samples. The Isocat sample had lower propylene and isobutylene yields than the other HZSM-5 samples, but the differences were small. Figures 22 and 23 show that the total aromatic and olefin contents of the gasoline from the various catalysts varied with conversion. At >90% conversion levels, the olefins converted to aromatics.

This study of various HZSM-5 samples, with and without added rare earth, showed that there were differences in activity, but product selectivity changes were small and difficult to measure accurately.

4.1.6 Y Zeolite Catalysts Containing Rare Earth

A series of USY faujasite FCC catalyst samples with 0.3-1.5% rare earth was prepared and tested at two severity levels, catalyst to oil ratios of 0.75 and 0.1875 at 880°F. Table XI shows the results of those tests.

FIGURE 18

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON PROPYLENE YIELD WITH HZSM-5 CATALYSTS

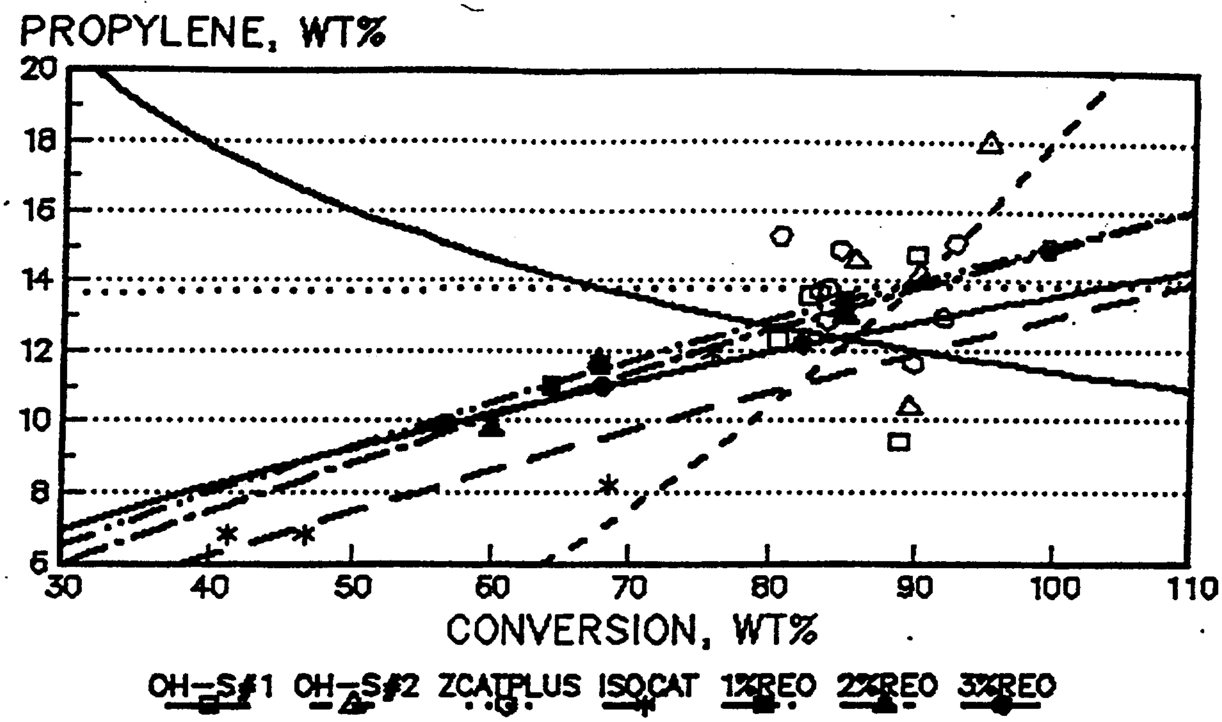

FIGURE 19

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON ISOBUTYLENE YIELD WITH HZSM-5 CATALYSTS

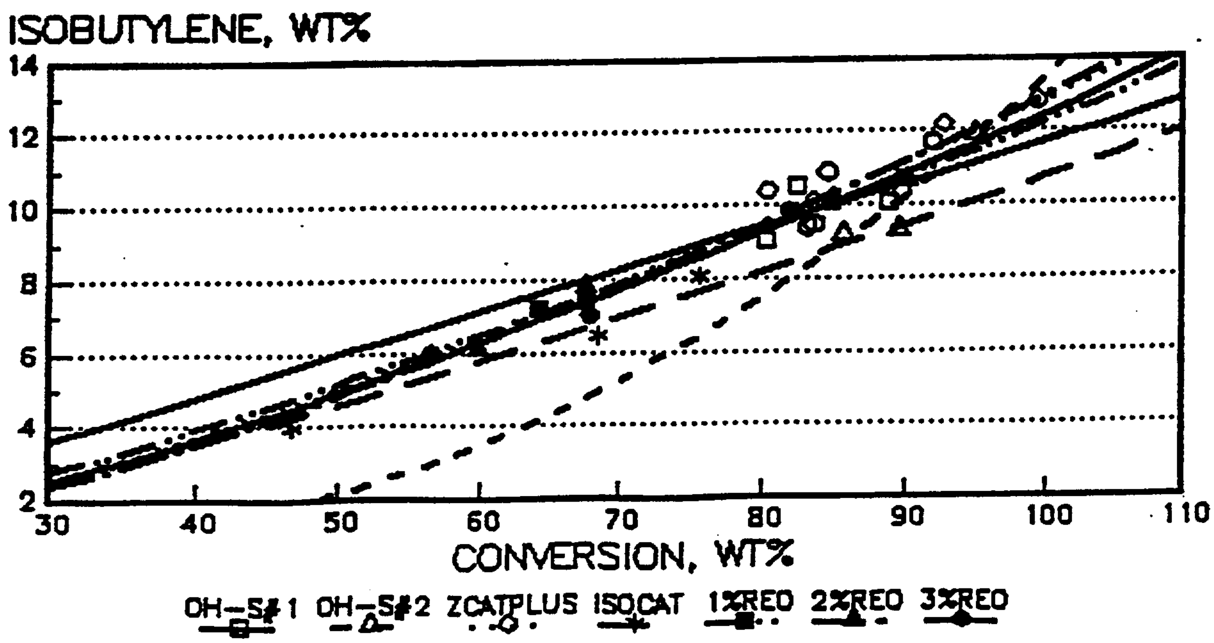

FIGURE 20

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON ISOAMYLENES YIELD WITH HZSM-5 CATALYSTS

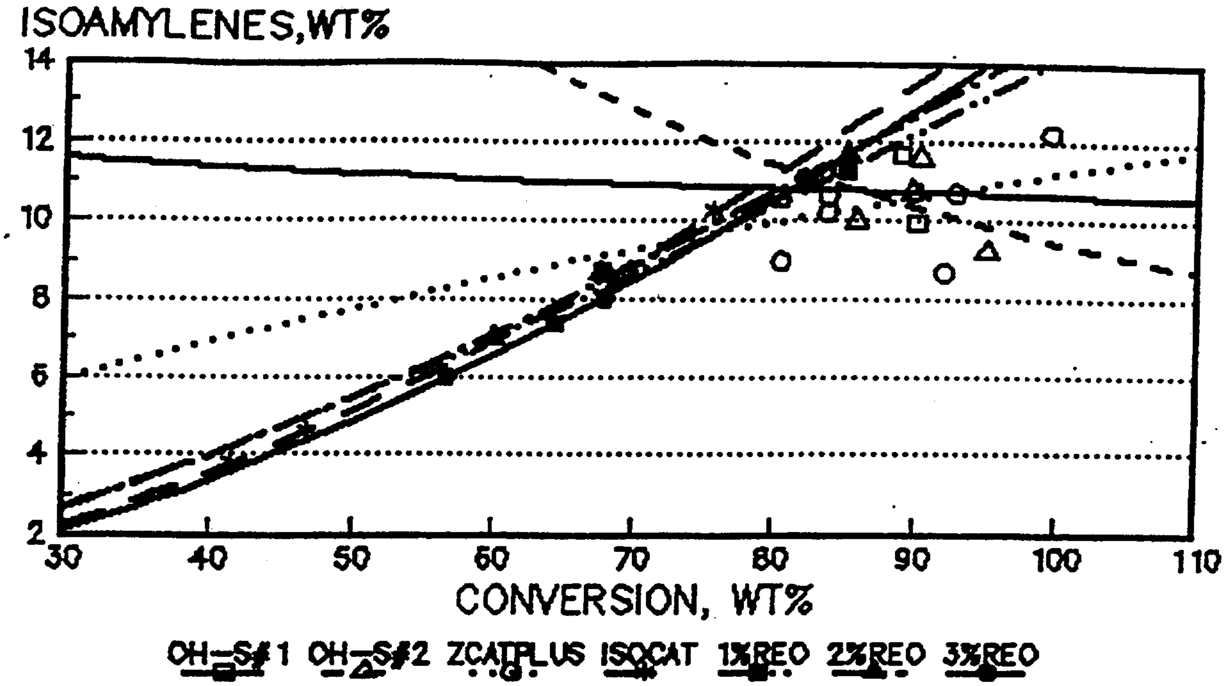

FIGURE 21

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON C5-430F NAPHTHA YIELD WITH HZSM-5 CATALYSTS

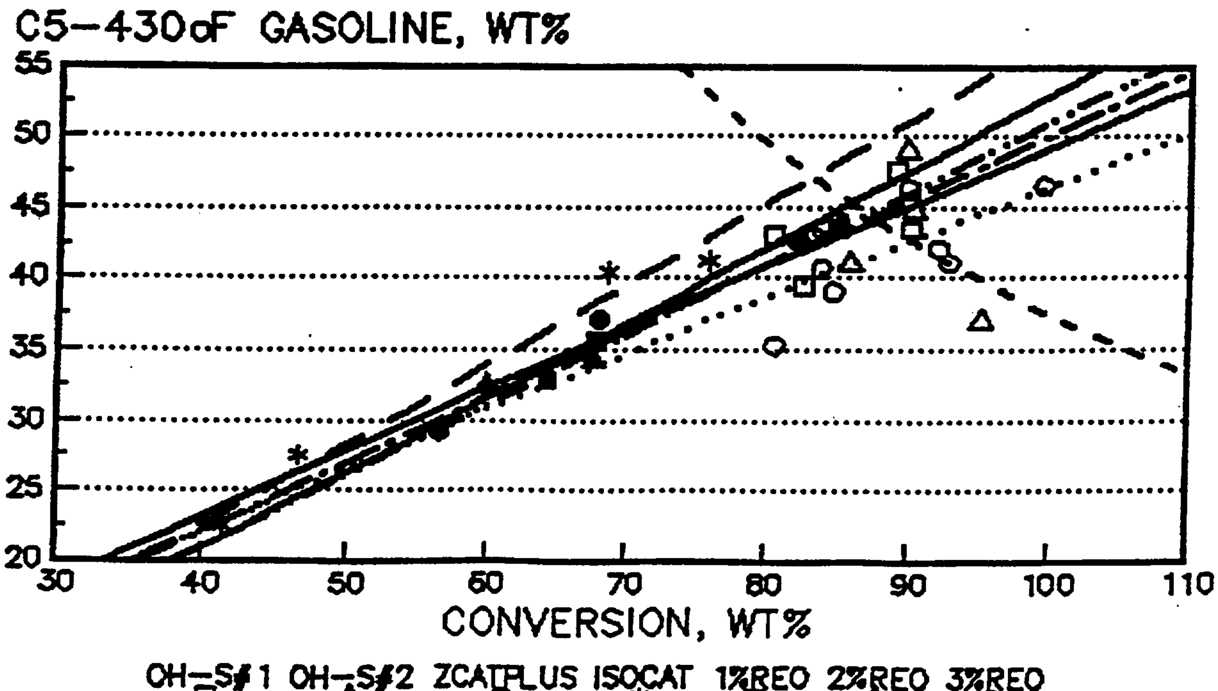

FIGURE 22

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON AROMATICS FORMATION WITH HZSM-5 CATALYSTS

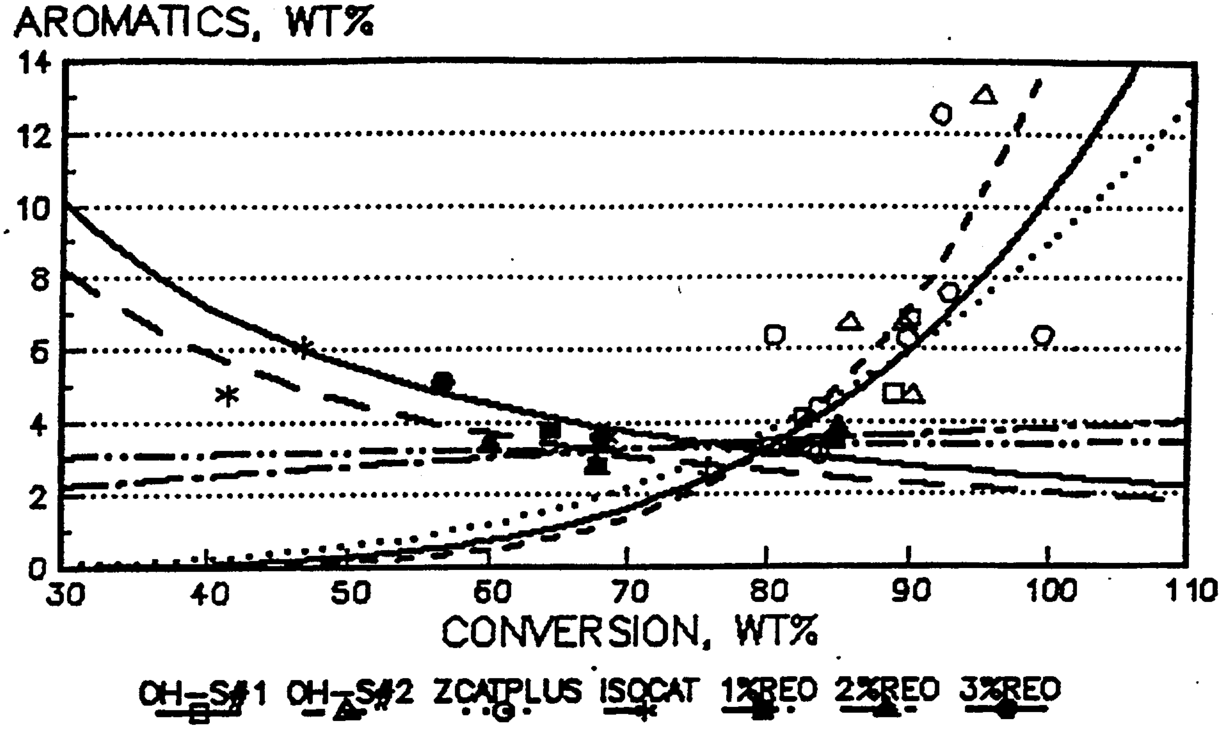

FIGURE 23

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON OLEFIN YIELD WITH HZSM-5 CATALYSTS

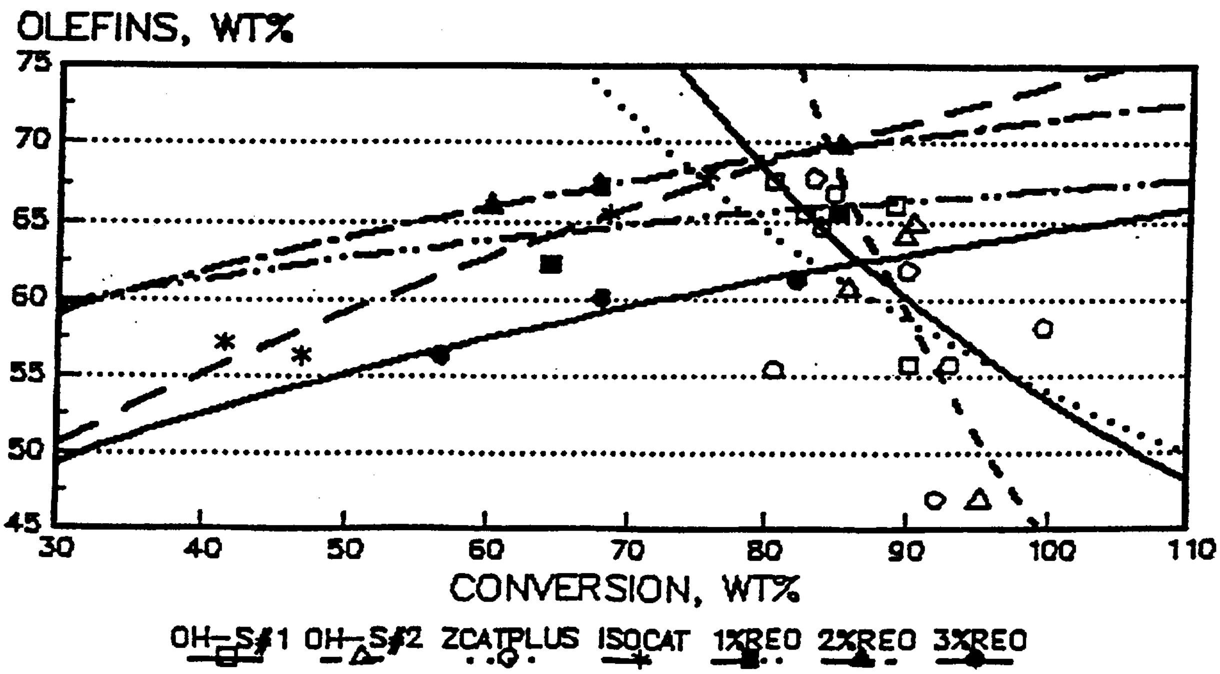

TABLE XI

MYU TESTS: RARE EARTH/USY CATALYSTS
Test Conditions: 880°F, 0.75 Catalyst/Oil Ratio

Run No.	0.99	100	101	102	103
Catalyst Description	CCC-1701[a]	CCC-1702[a]	CCC-1703[a]	CCC-1704[a]	CCC-1705[b]
Wt% Rare Earth	<0.04	0.27	0.34	0.96	1.49
Conversion, wt%	92.4	87.8	85.5	91.5	87.3
Product Yields, wt%:					
C_2-	0.8	0.6	0.6	0.8	0.7
C_3+C_4	28.7	23.4	20.8	23.2	11.3
C_5-430°F	62.1	63.0	63.2	66.5	66.5
430°F^{-1}	7.6	12.2	14.5	8.5	12.7
Coke	0.8	0.8	0.9	0.9	0.8
C_3=	7.6	6.6	5.8	6.5	5.3
iC_4=	5.9	4.5	4.1	4.3	3.8
iC_5=	7.8	6.4	5.6	6.4	5.9
RON	89.7	88.7	87.4	88.0	86.5
MON	78.0	76.3	74.5	76.0	74.0

(a) 100% steam; 1450°F; 8.5 hours
(b) 100% steam; 1450°F; 16 hours
(c) 100% steam; 1450°F; 8 hours

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Figures 24 summarizes the conversion data and Figures 25-31 summarize the selectivity data for the runs at both 0.75 and 0.1875 catalyst to oil ratio.

At 0.75 catalyst to oil ratio, in general, the addition of rare earth to conventional Y faujasite FCC catalysts lowered conversion, increased gasoline but lowered olefin yields, RON, and MON. These wax cracking test results with rare earth exchanged Y catalysts confirm the findings of other workers with regular gas oil feedstocks. There were wide variations in the wax conversion levels at 0.1875 catalyst to oil ratio that could not be resolved by running 4-6 tests on each of these samples. As Figures 18-24 show, there was too much scatter for differences between the catalysts to be distinguished. An attempt to resolve this difficulty was made by plotting selected points from the power law equations that were used to correlate the data for the various catalysts. Plots of this type for propylene, isobutylene, isoamylenes, and gasoline yield, in Figures 32-35, respectively, show that two of the high rare earth samples (1704,1705) had the expected "rare earth effect" of higher gasoline and lower olefin yields. The other high rare earth sample (1706) had a product selectivity more like the low or no rare earth samples.

4.1.7 Effect of Coke Deposition

Although the coke yields from all the HZSM-5 catalysts were very low, <0.2 wt%, coke deposition is a major contributor to the rapid (but regenerable) catalyst deactivation in the fluid catalytic cracking process. The effects of coke deposition on activity and product selectivity were evaluated in a series of sequential MYU tests on the same coked HZSM-5 catalyst. This sequential experiment involved one HZSM-5 catalyst sample (CCC-1891) and five consecutive wax contact cracking tests. The catalyst sample remained in the reactor and the coke determination occurred only after the final wax cracking test. The test conditions were 880°F and 0.2 catalyst to oil ratio.

Figure 36 shows that wax conversion decreased with each subsequent test, which was expected due to the fouling of the active sites of the catalyst with coke. Note that the MYU conversion value for test #5 did not follow the conversion decrease and probably is in error.

Figures 37-41 show the effects of the multiple HZSM-5 wax cracking test run sequence on product selectivities for propylene, isobutylene, isoamylenes, gasoline, and C_3+C_4 gases, respectively. These figures show each of the "multiple" run product yield points and those of the other "individual" HZSM-5 catalyst runs. These results show that coke deposition had only a small impact on the wax cracking product selectivities of the HZSM-5 catalyst. This effect may be unique to the HZSM-5 type zeolite catalyst due to its medium pore geometry. Other zeolite catalysts may not respond to coke deposition in the same way.

4.1.8 Low Zeolite-content Catalysts

A series of FCC catalysts, with *nominal* zeolite concentrations of 10 and 40% of Y zeolite or 10% beta zeolite and a low activity matrix, was prepared and tested to further examine the relationships between type and amount of zeolite in the catalyst on wax conversion and selectivity. Table XII presents the nominal compositions of these catalyst samples, all of which were prepared using conventional raw materials and experimental

FIGURE 24

SASOL WAX MYU DATA: EFFECT OF C/O ON CONVERSION WITH RARE EARTH/USY CATALYSTS

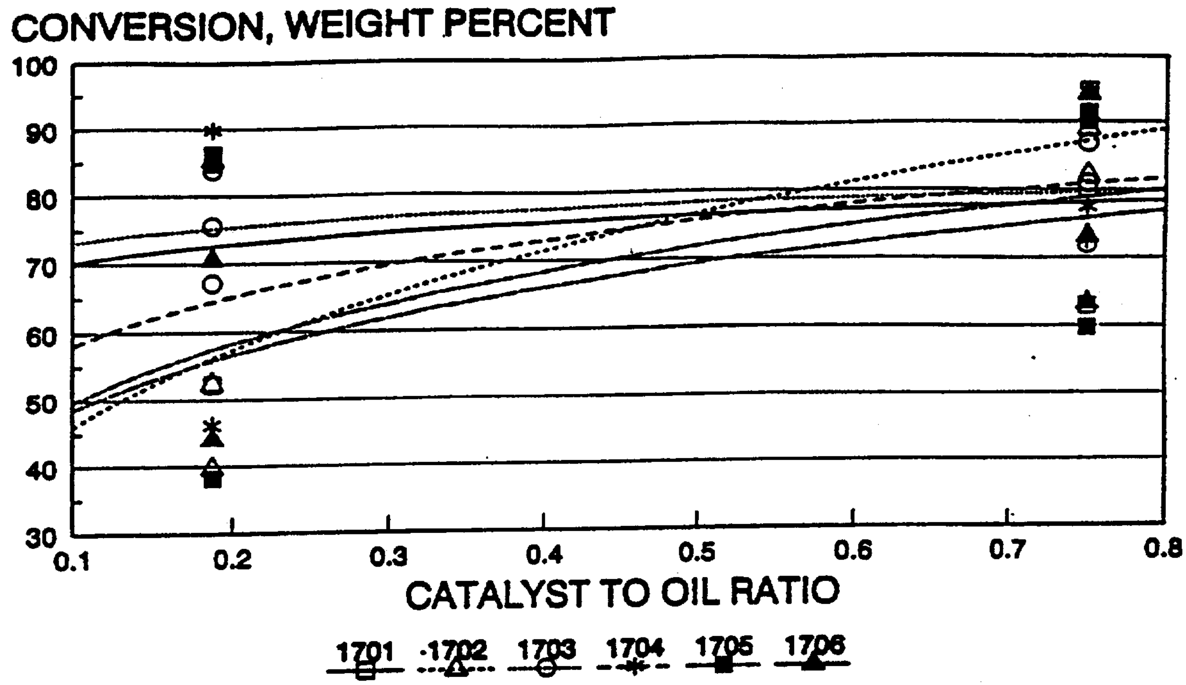

FIGURE 25

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON PROPYLENE YIELD WITH RARE EARTH/USY CATALYSTS

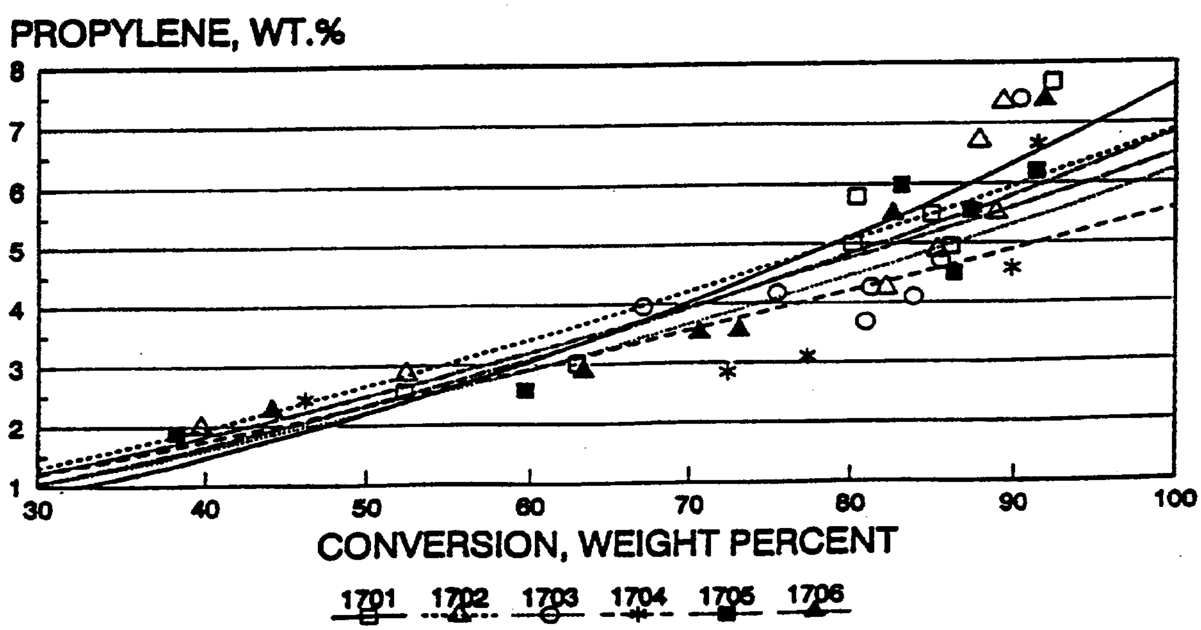

FIGURE 26

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON PROPYLENE YIELD WITH RARE EARTH/USY CATALYSTS

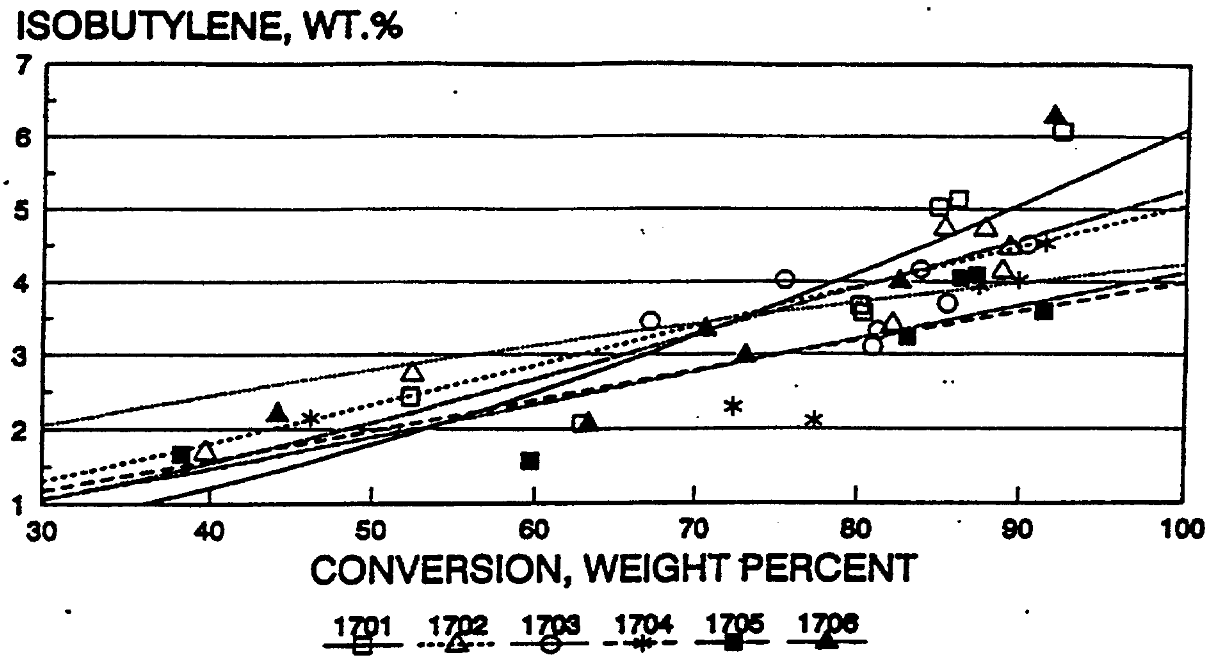

FIGURE 27

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON ISOAMYLENES YIELD WITH RARE EARTH/USY CATALYSTS

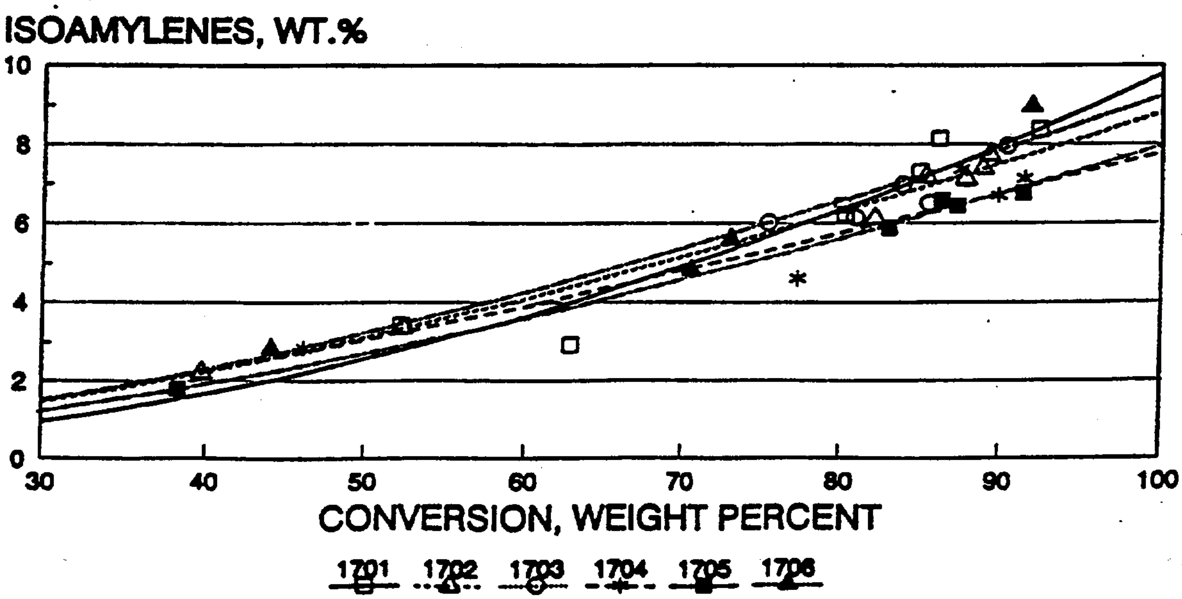

FIGURE 28

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON C5-430F YIELD WITH RARE EARTH/USY CATALYSTS

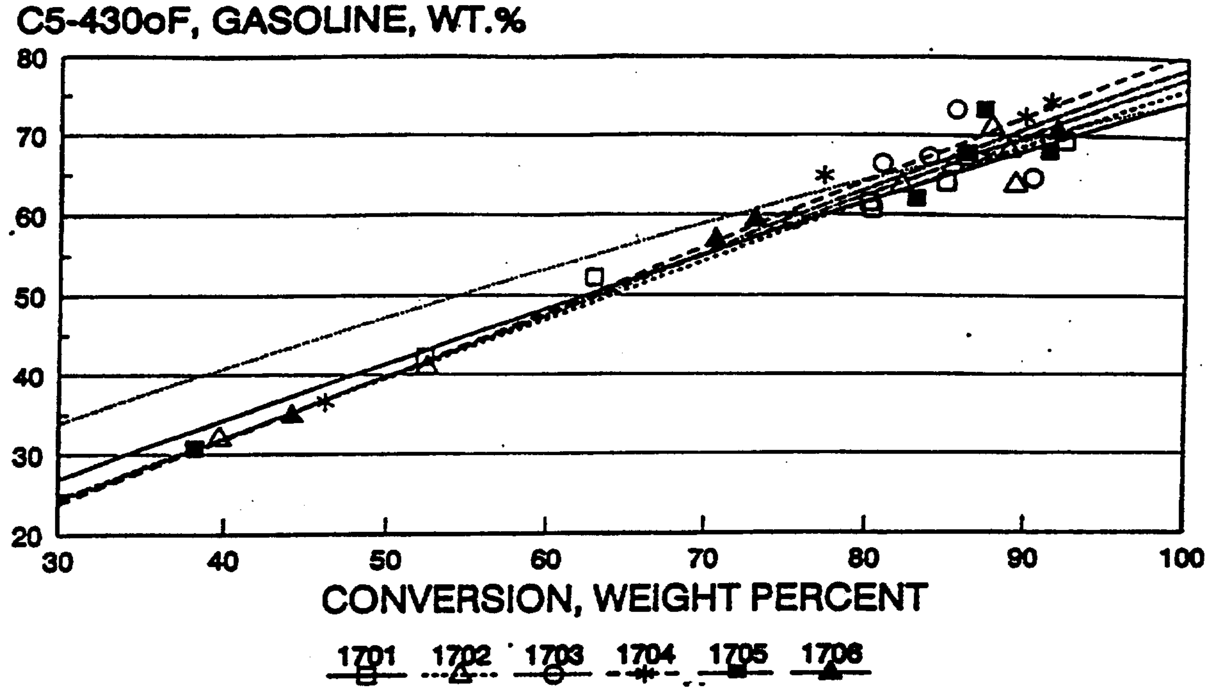

FIGURE 29

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON C3 AND C4 YIELD WITH RARE EARTH/USY CATALYSTS

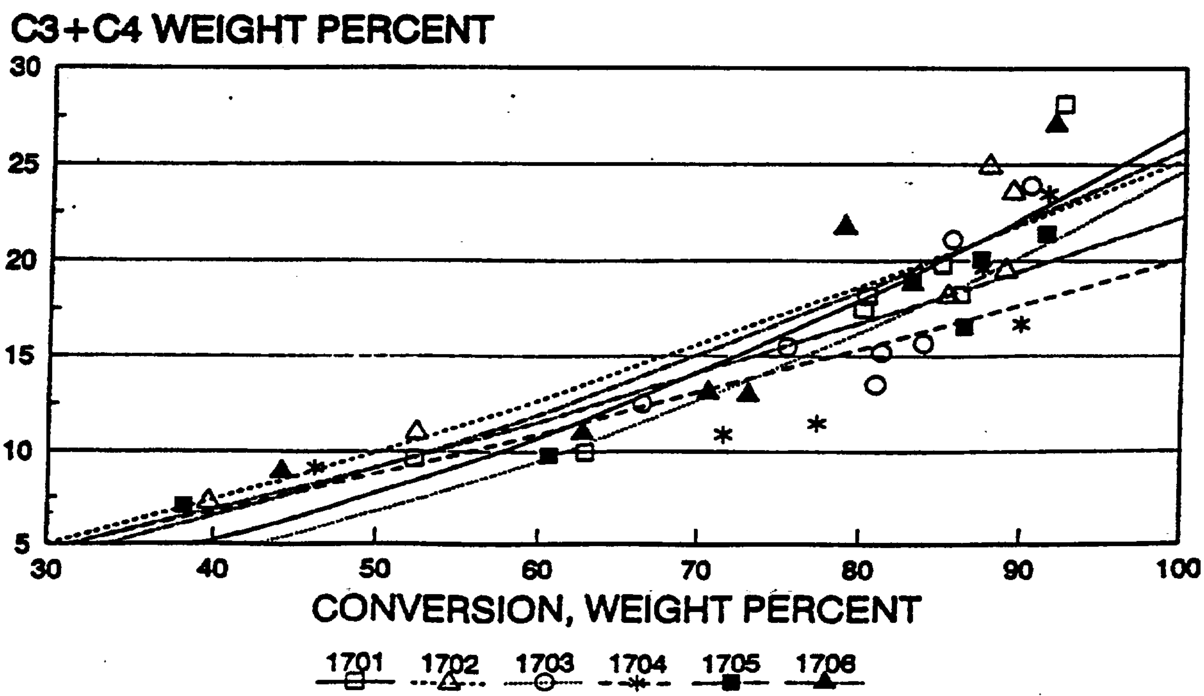

FIGURE 30

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON RON WITH RARE EARTH/USY CATALYSTS

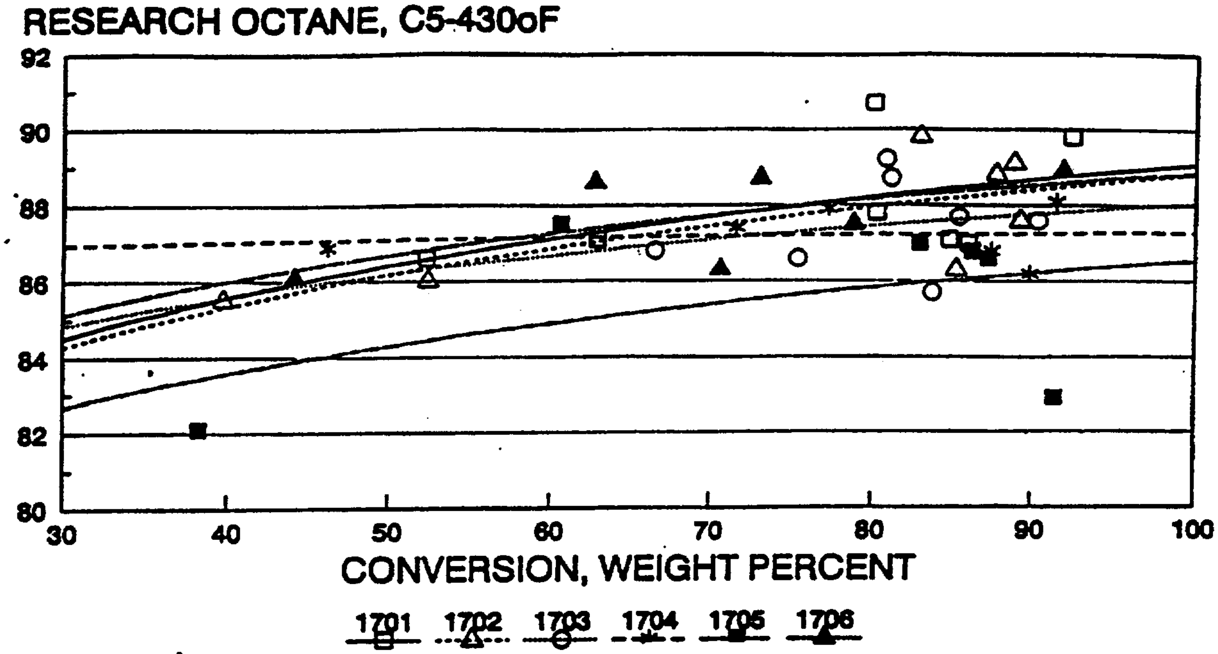

FIGURE 31

SASOL WAX MYU DATA: FISCHER-TROPSCH WAX CATALYTIC CRACKING VARIABLE RARE EARTH Y CATALYSTS

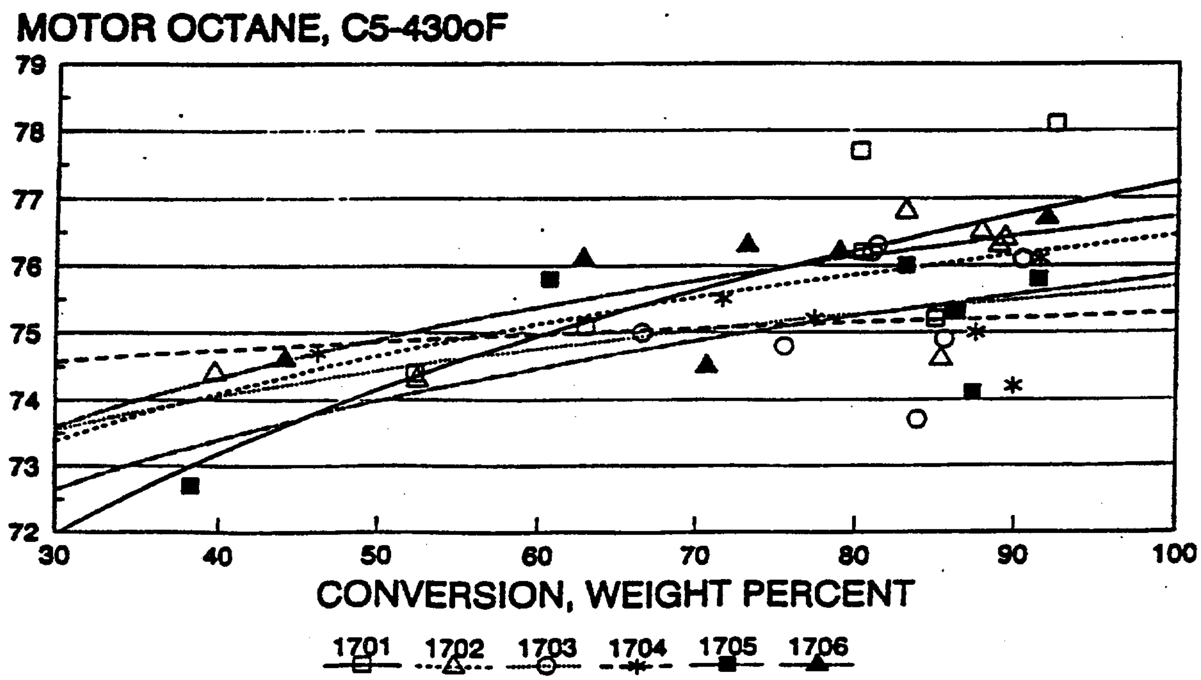

FIGURE 32

SASOL WAX MYU DATA: POWER LAW PLOT OF PROPYLENE YIELD VS. CONVERSION WITH RARE EARTH/USY CATALYSTS

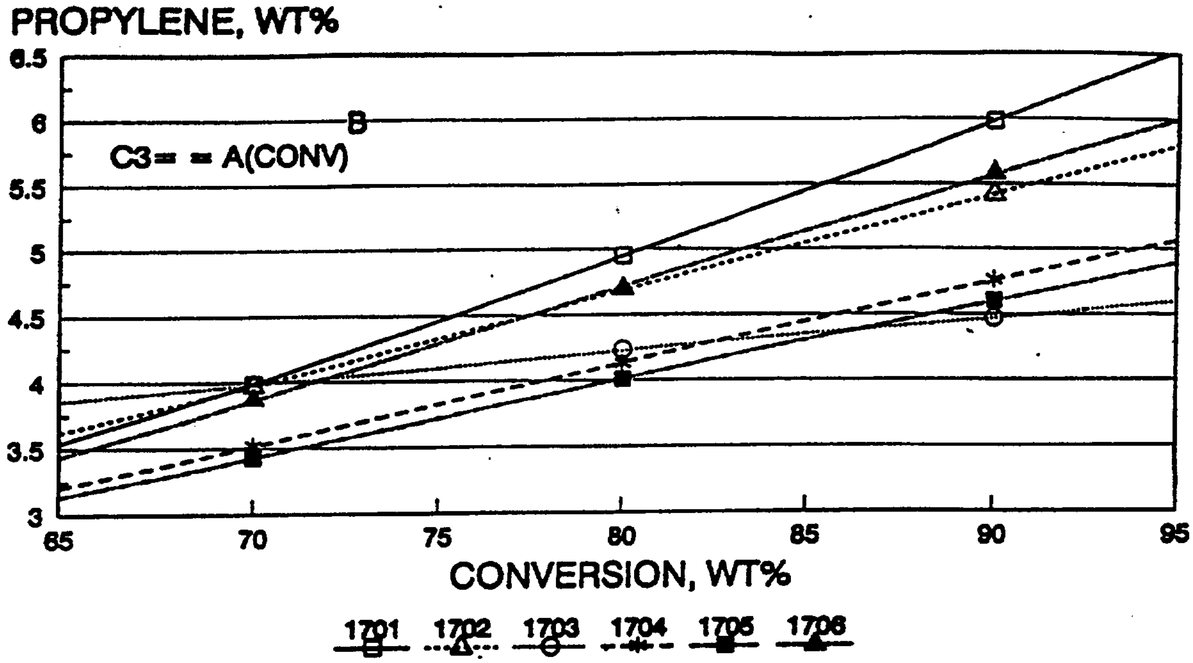

FIGURE 33

SASOL WAX MYU DATA: POWER LAW PLOT OF ISOBUTYLENE YIELD VS. CONVERSION WITH RARE EARTH/USY CATALYSTS

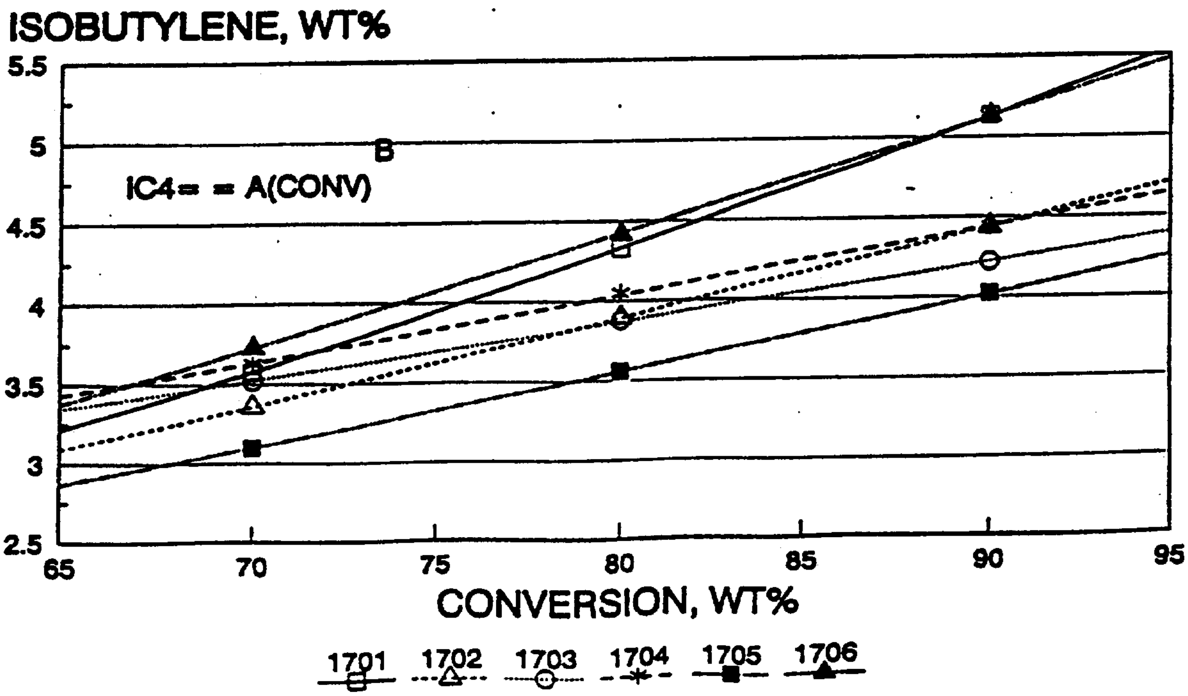

FIGURE 34

SASOL WAX MYU DATA: POWER LAW PLOT OF ISOAMYLENES YIELD VS. CONVERSION WITH RARE EARTH/USY CATALYSTS

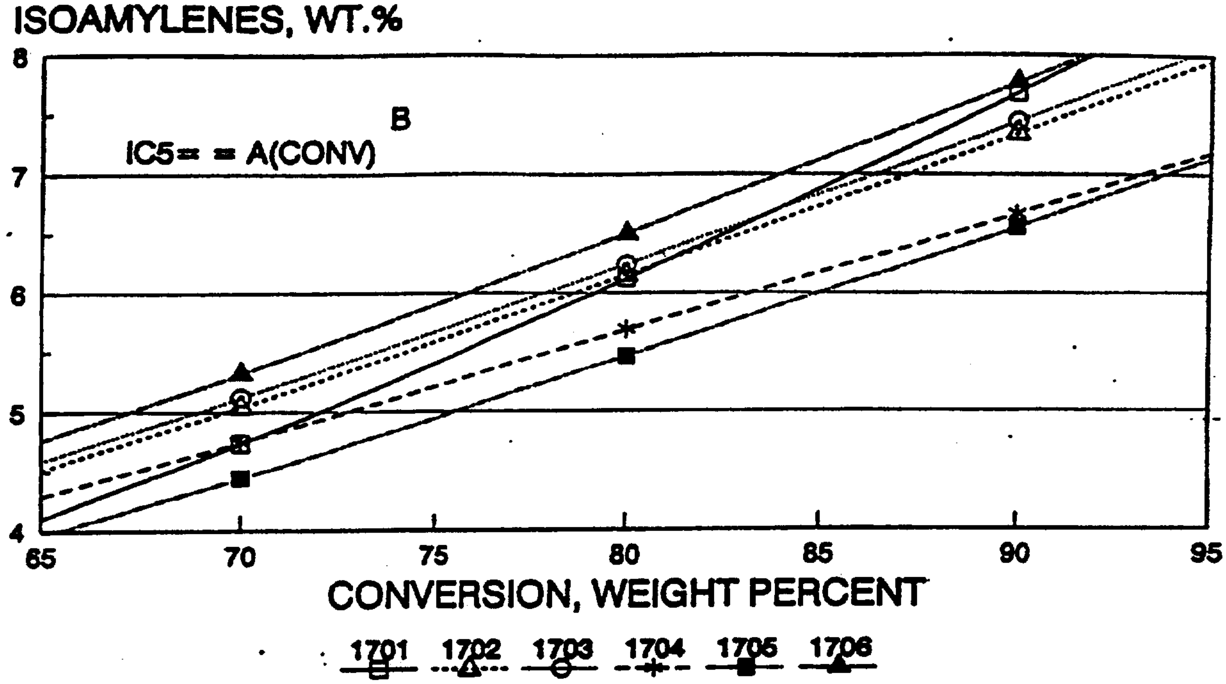

FIGURE 35

SASOL WAX MYU DATA: POWER LAW PLOT OF C5-430F NAPHTHA YIELD VS. CONVERSION WITH RARE EARTH/USY CATALYSTS

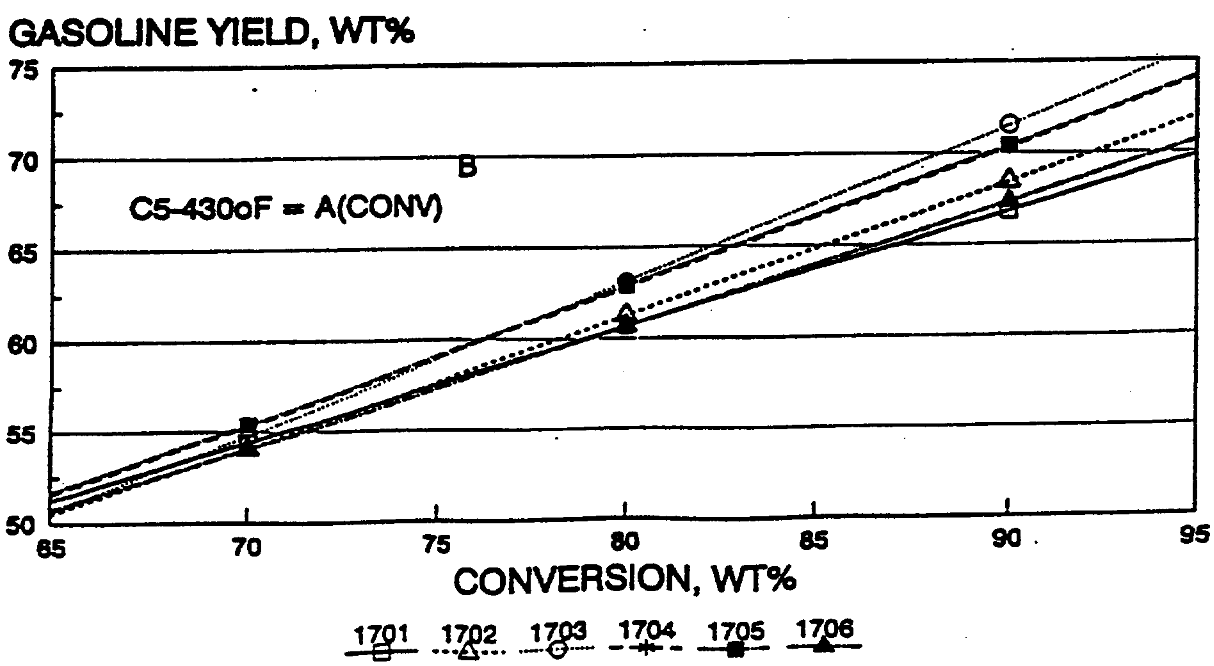

FIGURE 36

SASOL WAX MYU DATA: EFFECT OF MULTIPLE RUNS ON CONVERSION WITH HZSM-5 CATALYST

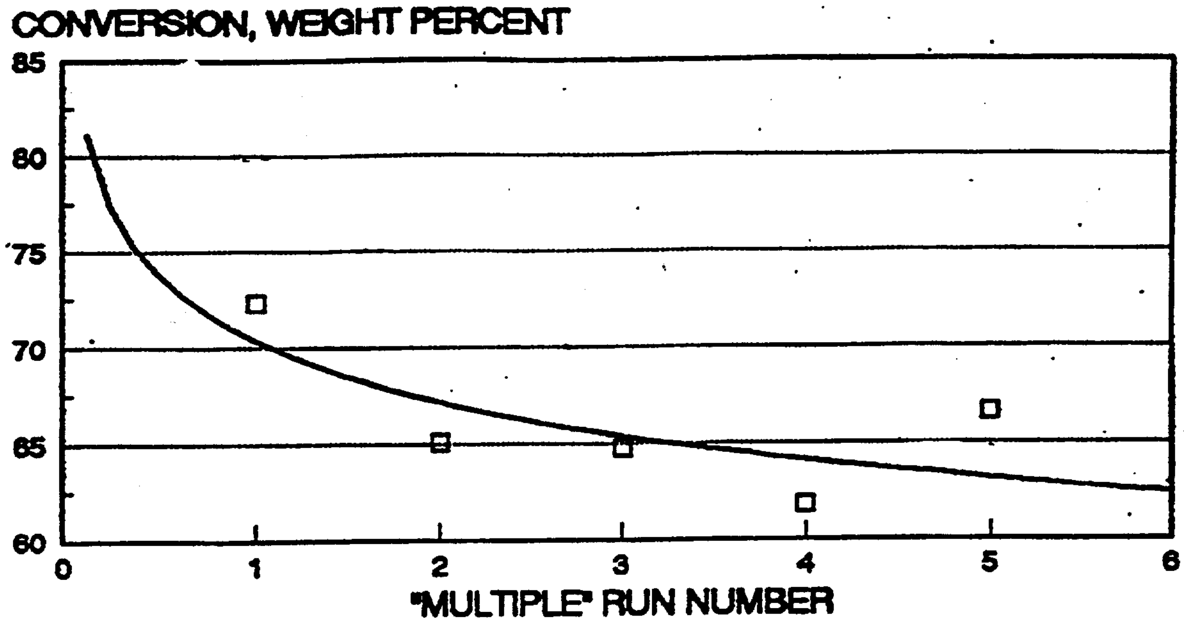

FIGURE 37

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON PROPYLENE YIELD IN MULTIPLE RUNS WITH HZSM-5 CATALYST

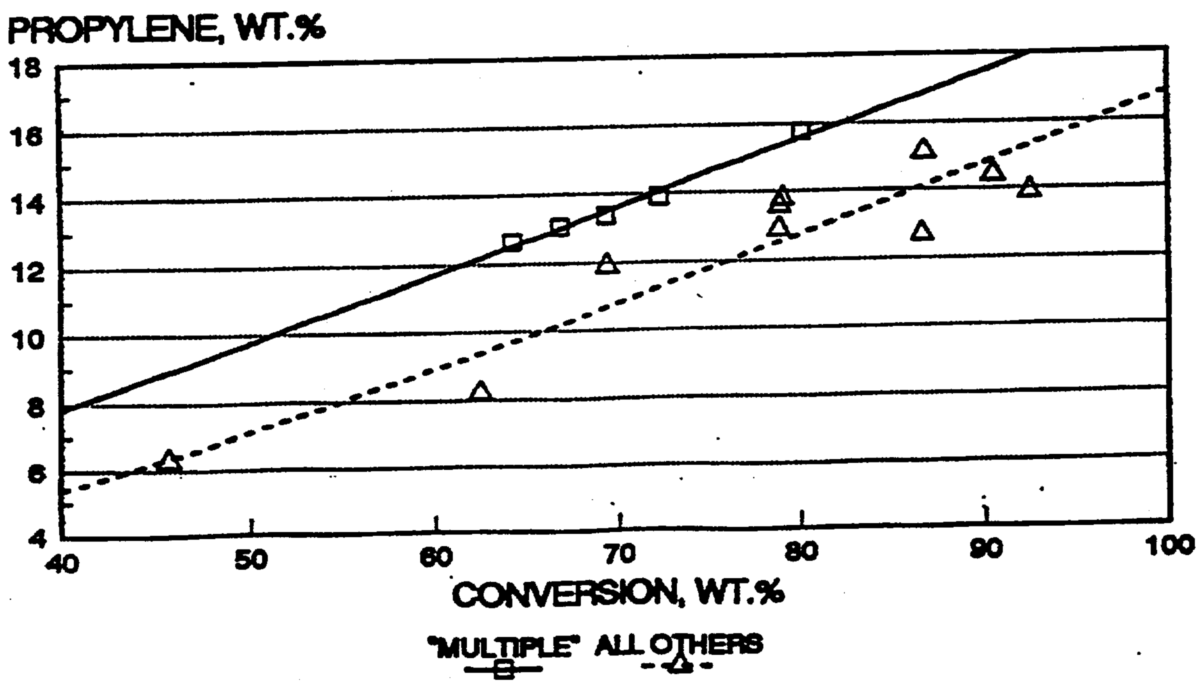

FIGURE 38

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON ISOBUTYLENE YIELD IN MULTIPLE RUNS WITH HZSM-5 CATALYST

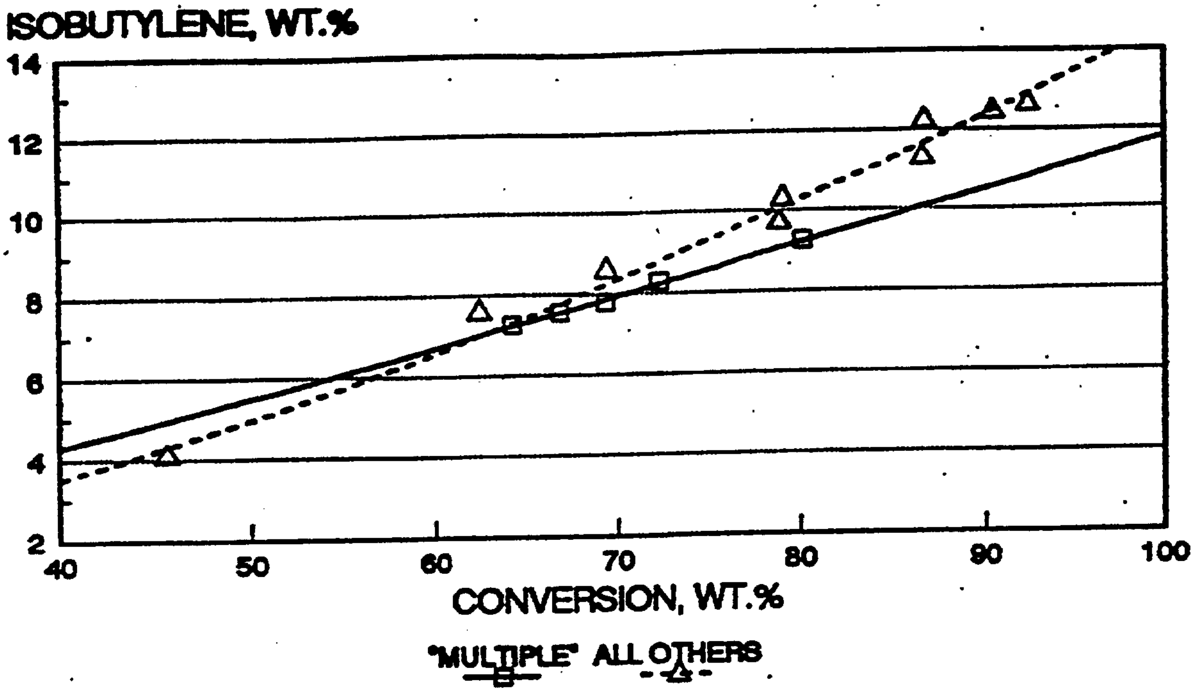

FIGURE 39

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON ISOAMYLENES YIELD IN MULTIPLE RUNS WITH HZSM-5 CATALYST

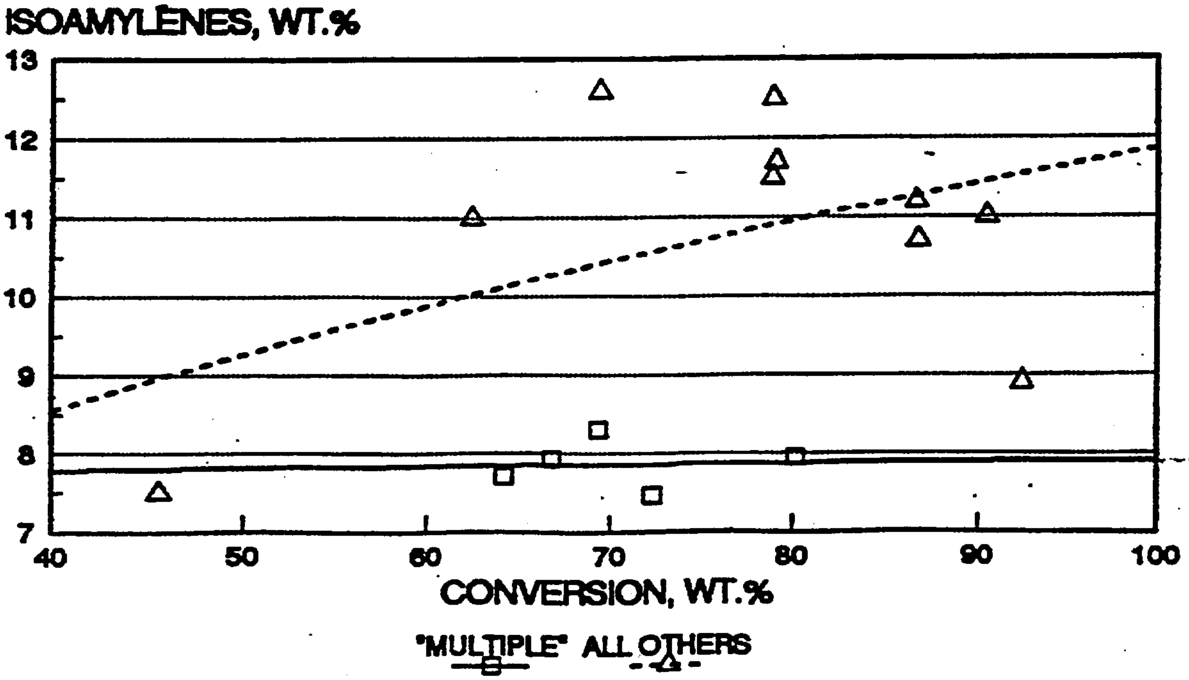

FIGURE 40

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON C5-430F NAPHTHA YIELD IN MULTIPLE RUNS WITH HZSM-5 CATALYST

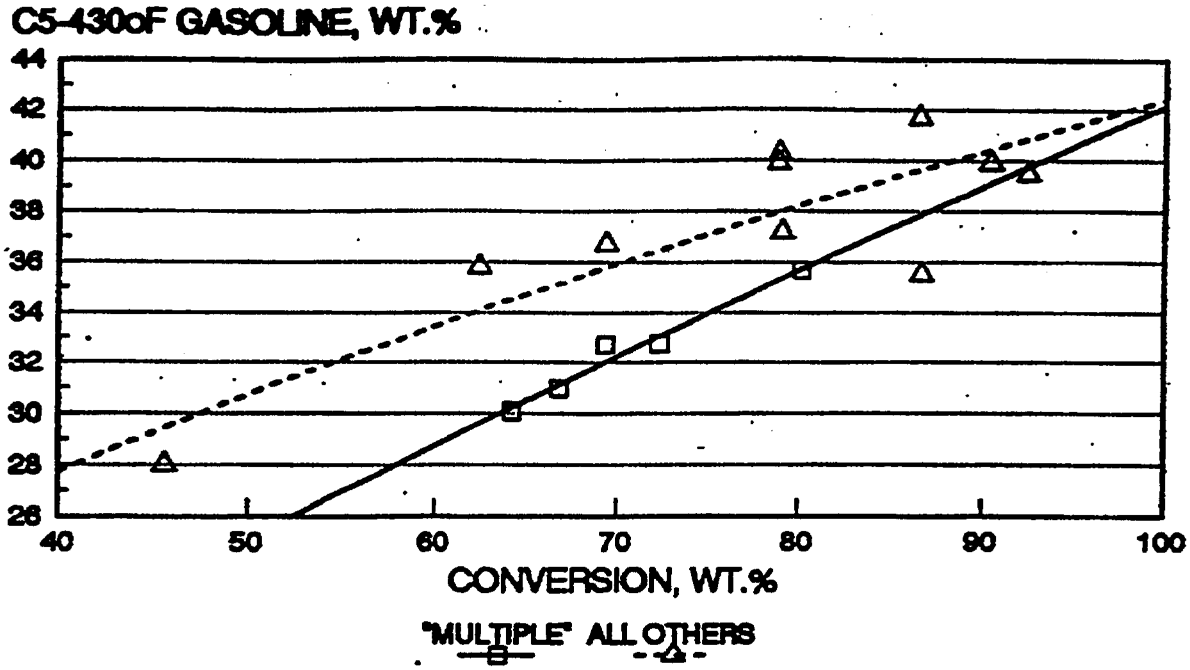

FIGURE 41

SASOL WAX MYU DATA: EFFECT OF CONVERSION ON C3 AND C4 YIELD IN MULTIPLE RUNS WITH HZSM-5 CATALYST