

THE SELECTIVE CATALYTIC CRACKING OF FISCHER-TROPSCH LIQUIDS TO
HIGH VALUE TRANSPORTATION FUELS

by

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ABSTRACT

The objective of this program is to prepare high-value transportation fuels, including gasoline, distillate, and gasoline range ethers and alcohols from the selective catalytic cracking of Fischer-Tropsch wax. The test results from both small scale (1-5 grams catalyst) and pilot plant (2500 grams catalyst) units show that the wax (Sasol) feedstock readily converts (>85%) to C₄- gas (high in propylene and C₄ olefins) and naphtha products. The major products of interest, isobutylene, isoamylenes, and C₅-430°F naphtha vary with the level of conversion of the wax feedstock and the type of zeolite (Y, HZSM-5, Beta) catalyst. Further zeolite modification studies show only minor variations in wax conversion and product selectivity among the zeolite types. The reactive isoolefins in the light naphtha product fractions from the pilot plant runs readily form methyl ethers by reaction with methanol. The ether yields are dependent on equilibrium constraints and carbon chain length of the olefin. Economic analysis of the product distributions from the eight pilot plant runs show that the net product values (\$/d) for a complex refinery (contains ether unit) are always higher than for a simple refinery (no ether unit).

INTRODUCTION

Fischer-Tropsch (F-T) synthesis technology (1) produces liquid hydrocarbons from synthesis gas (hydrogen and carbon monoxide) derived from the gasification of coal. The F-T liquid product consists of a broad range of normal paraffins (C_5 - C_{50+}) and a small quantity of oxygenates and olefins. The gasoline range C_5 - C_{12} product fraction consists of oxygenates, linear paraffins and olefins of low octane number. The distillate fraction, C_{12} - C_{18} , is an excellent quality fuel. The largest product fraction, C_{18+} , is primarily wax and is useless as a transportation fuel.

These products are further treated by conventional petroleum processes, such as hydrotreating, reforming and catalytic cracking to produce conventional gasoline and distillate fuels. (2) Fluid catalytic cracking, and hydrocracking, studies have been reported by Mobil (3) and UOP. (4) Heavy wax (C_{20+}) fractions have also been treated with hydroisomerization and hydrocracking processes at Exxon. (5) Hydrodewaxing and catalytic cracking treatments of heavy wax from slurry F-T processing are also reported by Mobil. (6) In addition, pure component cracking studies (decanol, decanal) over the intermediate-pore zeolite HZSM-5 have been reported. (7) The catalytic cracking of F-T liquids was examined in some detail by Wojciechowski over large-pore faujasite (zeolite Y) and over HZSM-5 zeolite catalysts. (8,9)

Governmental regulations, most recently in the Clean Air Act Amendments of November 1990, have resulted in the phase-out of lead additives, lowering of the Reid vapor pressure of gasoline and in some geographical areas, the mandated use of oxygenates. Several types of ethers are now commercially produced and used as gasoline blending components. (10) Recent studies of methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME) suggest that these compounds may reduce automotive carbon monoxide emissions, have high blending gasoline octane ratings, R+M/2, (MTBE-108, TAME-102) and have low Reid vapor pressure. These ethers are produced commercially by the etherification of the appropriate olefin by methanol (MTBE, isobutylene; TAME, isoamylenes). These olefins are derived from conventional petroleum processes such as catalytic cracking or steam/thermal reforming. MTBE has attracted the most attention in recent years. The growth rate for its production could reach 25% per year by 1995. (11,12)

There is a growing need for alternative sources of olefins for ethers and alcohol syntheses as demand for these materials escalates beyond the capacity of conventional petroleum processes. This project addresses this requirement to produce C_3 - C_8 olefin feedstock for oxygenate synthesis.

During the first year of this contract, (13) the catalytic cracking of the Fischer-Tropsch wax feedstock was studied in a small scale (1-5 grams catalyst) test unit and the circulating pilot plant (2500 grams catalyst). The wax feedstock readily converts (>85%) to product gas (C_4 -) and naphtha (C_5 -430°F). Under similar test conditions, a normal gas oil feedstock would have much lower conversion levels. (65%) The yields of the target product olefins, isobutylene and isoamylenes, from wax cracking are more than twice the levels found with gas oil cracking. Three different types of zeolite catalysts show wide variations of product yields as a function of wax feedstock conversion. The HZSM-5 zeolite catalyst produces the highest yields of the target products, isobutylene and isoamylenes. The

Beta zeolite has lower light olefin yields than the HZSM-5 sample but greater olefin yields than the Y zeolite catalyst. These high olefin yields form at the expense of naphtha product. The Y zeolite catalyst has the highest naphtha yields among the catalysts tested. The major areas of work during the second year of this contract include further catalyst testing, ether synthesis experiments and some preliminary economic evaluations.

PROGRAM OBJECTIVES

The overall objective of this program is to prepare high-value transportation fuels, including gasoline, distillate, and gasoline range ethers and alcohols from non-petroleum resources. A selective catalytic cracking process of Fischer-Tropsch liquids is proposed. The C₄-C₈ product olefins would then be etherified with methanol to prepare the target ethers.

PROJECT DESCRIPTION

A two year, multi-task program will be used to accomplish the program.

Task 1. -- Project Management Plan. A plan will be prepared which describes the work to be done, milestones, and manpower and cost requirements.

Task 2. -- Preparation of Feedstocks and Equipment Calibration. The necessary analytical equipment will be calibrated for the detailed identification of C₄-C₈ olefins and ethers and other paraffin, aromatic and naphthene gasoline range components.

Task 3. -- Catalytic Cracking Catalyst Screening Program. Various zeolite catalysts and process variables will be studied with small scale test equipment.

Task 4. -- Pilot Plant Tests of the Optimized Catalyst and Process. The optimized process will be tested on a pilot plant scale. The target light olefin products, gasoline and distillate products will be produced in sufficient quantities for complete characterization.

Task 5. -- Preparation of C₅-C₈ Ethers and C₃-C₈ Alcohols. These products will be prepared from the pilot plant C₃-C₈ olefin products.

Task 6. -- Evaluation of Gasoline Blending Properties of Ethers and Alcohol Products. The gasoline blending properties of the product ethers and alcohols will be measured. The properties of the distillate products will also be evaluated.

Task 7. -- Scoping Economic Evaluation of the Proposed Processes. An economic analysis of the proposed process will be compared with conventional petroleum processes and ether and alcohol synthesis routes.

RESULTS AND DISCUSSION

I. EXPERIMENTAL

The details of the analytical methods and testing procedures are described in a previous publication. (13)

II. CATALYTIC CRACKING STUDIES

A. Screening of ZSM-5 Zeolite FCC Catalysts.

The catalytic cracking results from both the small scale test unit (MYU) and the pilot plant indicate that the wax feedstock readily converts to product gas (C₄-) and naphtha. The HZSM-5 zeolite catalyst has the highest isobutylene and isoamylenes yields among the catalysts tested to date. However, the production of propylene is also high. These results are from one sample of Intercat Corp.'s ZCAT PLUS[®] commercial FCC additive material. Further catalyst screening studies center on various types of HZSM-5 catalysts. Another commercial HZSM-5 catalyst sample from Davison Chemical Co., Additive OH-S[®], and a sample of Intercat's ISOCAT[®] material, are under study with the small scale test unit. A series of HZSM-5 samples with added rare earth oxide levels are also under study. The rare earth oxide is added to the base HZSM-5 catalyst (ZCAT PLUS[®]) by standard impregnation techniques. A standard steam pre-treatment, 100% steam, 1450°F, five hours, of these samples precedes the wax cracking tests. Table I lists the descriptions of these catalysts. Table II presents the results of the initial tests of these catalysts at one set of process conditions, (880°F, 0.2 catalyst/oil ratio). The wax conversion levels, (the sum of C₄- gas, gasoline and coke) of the various catalysts vary with the catalyst/oil ratio (Figure 1). The rare earth oxide treated HZSM-5 samples (~80%) and the ISOCAT[®] material (~68%) are lower in conversion than the other two commercial HZSM-5 samples, Intercat Corp.'s ZCAT PLUS[®] and Davison's OH-S[®] (~85-90%). This variation in activity does not correlate directly with the surface area of the samples. The results from nitrogen adsorption measurements (Table III) show similar BET surface areas for the catalysts. These measurements probably reflect the relative zeolite content of the samples, which are about 25%. The catalytic activity (wax conversion) is a function of the available Bronsted acid site concentration, or framework aluminum content. This explains why the ISOCAT[®] sample has a lower catalytic activity. It has a higher silica to alumina ratio (low framework alumina) HZSM-5 zeolite. Since the rare earth samples also show lower activity, it is likely that the impregnation treatment has lowered the framework aluminum (acidity level) content. The activity (overall conversion) of the two conventional HZSM-5 samples, ZCAT PLUS[®] and OH-S[®] are similar. Another key aspect of these various HZSM-5 samples is to observe changes in product selectivity among the light gas and gasoline products. Figure 2 presents a plot of isobutylene yield as a function of wax conversion. There are no major selectivity differences in product yields among these HZSM-5 samples. The ISOCAT[®] sample has lower propylene and isobutylene yields than the other HZSM-5 samples but the differences are small. This study of various HZSM-5 samples shows that activity (wax conversion levels) differences are readily apparent. However, product selectivity changes are small and difficult to measure accurately.

B. Screening of Y Faujasite FCC Catalysts.

A series of rare earth exchanged zeolite Y catalysts are under study to determine the effects of rare earth ions on olefin selectivities. These catalysts have similar zeolite and matrix levels and vary only in rare earth content.

In general, the addition of rare earth to conventional Y faujasite FCC catalysts raises the activity level, increases the gasoline selectivity and lowers the olefin yields and gasoline octane values. This series of rare earth Y FCC samples are described in Table IV. The matrix and zeolite levels are constant with only the rare earth level varying. The steam treatments should yield samples of comparable activity. The last sample of high rare earth content (1.49%) was steamed at two different conditions to produce catalysts of two different activity levels (No. 1705, 1706). The preliminary catalytic test results in Table V show some interesting trends. The non rare earth sample, CCC-1701, has the highest gas (C_3+C_4) yields and the lowest $C_5-430^\circ\text{F}$ naphtha yields and highest octane ratings. Two of the high rare earth samples (No. 1704, 1705) show the expected "rare earth effect" of higher naphtha and lower olefin yields and octane ratings. The other high rare earth sample, (No. 1706) appears to have a different product selectivity, more like the non-rare earth sample. Further wax cracking tests of these samples were carried out at two severity levels, catalyst to oil ratios of 0.75 and 0.1875 at 880°F . Figure 3 summarizes these tests. There are wide variations in the wax conversion levels (the sum of $C_5-430^\circ\text{F}$ naphtha, C_1 -gas and coke) of the various samples. These multiple wax cracking test runs with the variable rare earth Y zeolite catalysts do represent an excellent source of product selectivity information. Figure 4 presents the conventional propylene product yield versus conversion plot for all of these runs. It is difficult to distinguish among the various catalysts due to the scatter in the data. One approach to resolving this difficulty is to plot selected points from the power law equations that have been used to correlate the data for the various catalysts. Plots of this type (Figures 5-6) show that two of the high rare earth samples (1704, 1705) have the expected "rare earth effect": higher gasoline and lower olefin yields. These wax cracking test results confirm the findings of other workers with regular gas oil feedstocks that "zero" rare earth FCC catalysts provide the maximum yields of the desirable light olefins.

C. Sequential Catalytic Cracking with HZSM-5 FCC Catalysts.

The HZSM-5 zeolite catalysts have the highest yields of the target olefins. A series of sequential MYU tests on the same coked HZSM-5 catalyst would evaluate the effects of coke deposition on the activity (wax conversion) and product selectivity of this catalyst. This type of information may lead to alternative wax processing schemes. The amount of coke on regenerated catalyst can be controlled in a commercial FCC unit by various operational methods.

This sequential experiment involves one HZSM-5 catalyst sample (CCC-1891) and five consecutive wax contact cracking tests. The catalyst sample remains in the reactor and the coke determination occurs only after the final wax cracking test. The test conditions of 880°F , 0.2 catalyst-to-oil ratio and 50 seconds contact time, are the standard ones for previous MYU catalyst evaluation. Figure 7 shows that wax conversion decreases

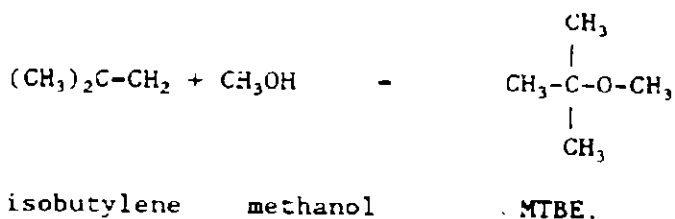
with each subsequent test. This is expected due to the fouling of the active sites of the catalyst with coke. This deactivation curve can be modelled with a hyperbolic decay function of time-on-stream. This formalism is described by B. Wojciechowski (14,15) for the deactivation of cracking catalysts. Figures 8-9 show the effects of the multiple HZSM-5 wax cracking test run sequence on product selectivities. Each of the "multiple" run product yield points of the present study are plotted versus other "individual" HZSM-5 catalyst runs. In some cases, the product (isobutylene, Figure 9) selectivity differences between these two types of tests for the HZSM-5 catalysts are small. However, the "multiple" run tests do show higher propylene yields (Figure 8) than the individual test runs. These initial results show that coke deposition has 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.

D. Low Zeolite Content FCC Catalysts.

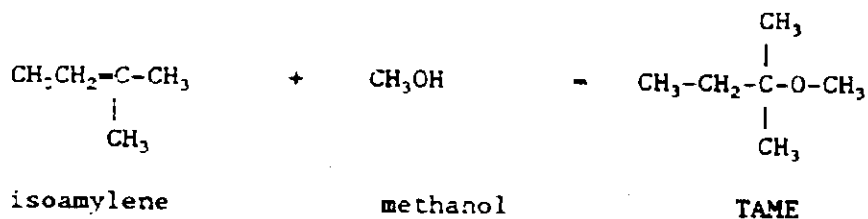
Several pilot plant runs of the catalytic cracking of Fischer-Tropsch wax show very high conversion levels (>85-90%). These high conversion levels may not provide the optimum light olefin yields. The zeolite content is the major factor that affects catalyst activity. A series of FCC catalysts with low zeolite content (~10%) should address this issue with lower catalytic activity. Table VI presents the nominal compositions of several catalyst samples, with either zeolite Y or Beta and a low activity matrix. These preparations use conventional raw materials and experimental techniques. The BET surface areas of these catalysts, after a steam treatment at 1450°F, 5 hours, are found in Table VII. The surface areas and pore volumes decrease with the lower zeolite levels, as expected. The 10% Beta zeolite catalyst (69 m²/g) has a significantly lower surface area than the 10% Y zeolite sample (90 m²/g). Similar differences are evident for the 40% Y and Beta samples. This may indicate that the Beta zeolite has a lower hydrothermal stability than the Y zeolite sample. The two different surface area results (Table VII) for the 40% Y sample (14040-48-1,-2) illustrates the variability in the steaming treatments. The wax conversion levels of the four steamed catalyst (40%Y, 10%Y, 10% Beta and Matrix only) samples are available at one set of process conditions: a catalyst to oil ratio of 0.75 and reaction temperatures of 970°F and 980°F. Figure 10 presents the wax conversion levels as a function of catalyst B.E.T. surface area. This measurement roughly corresponds to the zeolite content, since the matrix of the four samples is the same. The wax conversion level does decrease with zeolite content. The matrix only sample has the lowest conversion values. However, there is considerable scatter in the results for each sample. This is especially true where the overall conversion level is below 70%. The product selectivity measurements from these MYU tests are also important to the full characterization of these catalyst samples. In most cases, it is difficult to see clear trends that would distinguish between these catalysts. There is considerable scatter in the test results. The isobutylene yield plot, Figures 11, suggests that the Beta and Matrix samples are more selective for this target olefin than the Y zeolite samples. This conclusion is in line with previous catalyst testing results.

III. ETHER SYNTHESIS

A brief review of the ether synthesis task objectives and ether synthesis chemistry is desirable. These ethers are synthesized by the reaction of methanol with a reactive olefin to form the corresponding tertiary alkyl methyl ether. This reaction is catalyzed by acidic ion exchange resins at low temperatures (100-200°F) and moderate pressures (100-400 psig). For MTBE, this reaction is:



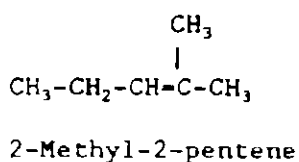
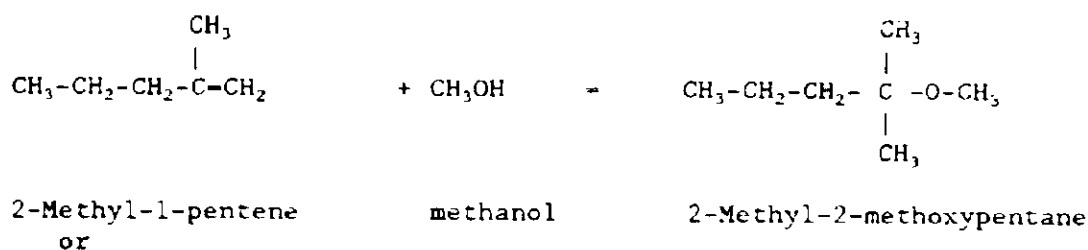
TAME forms by the reaction of the isoamylene isomers, 2-Methyl-1-butene and 2-Methyl-2-butene with methanol:



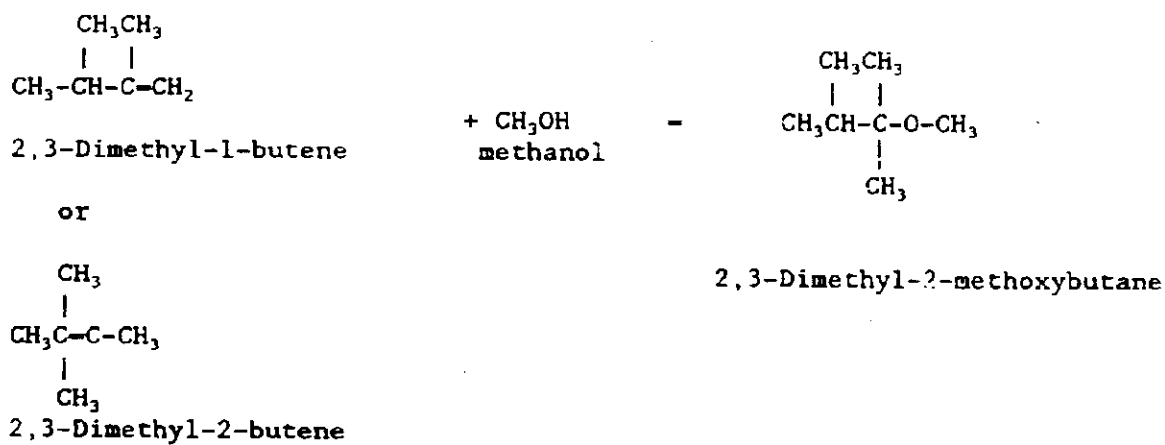
These etherification reactions were discovered in 1907. (16) Detailed catalysis studies of these reactions have only recently appeared in the scientific literature. (17) These reactions are mildly exothermic and equilibrium limited. At low temperatures, the equilibrium is shifted to the right, and at high temperatures the equilibrium is shifted to the left. The original study of these reactions by Snamprogetti workers (17) shows that the ratio of etherification rates for isobutylene and isoamylenes is 1.85. Both isomerization and etherification reactions are observed with the two reactive isoamylenes, 2-Methyl-1-butene and 2-Methyl-2-butene. The other isomer, 3-Methyl-1-butene is not reactive.

There is less information in the open literature about the etherification reactions of C₆ olefins that are also present in significant quantities in fluid catalytic cracking product naphthas. The Etherol process (18) produces a mixed ether product from C₄-C₇ reactive iso-olefins in naphthas. One report (19) provides some information about the reaction of C₆ iso-olefins with methanol to produce the higher ethers, MTHE's, methyl tertiary hexyl ethers. Several C₆ olefins can react with methanol to produce three different THME ethers:

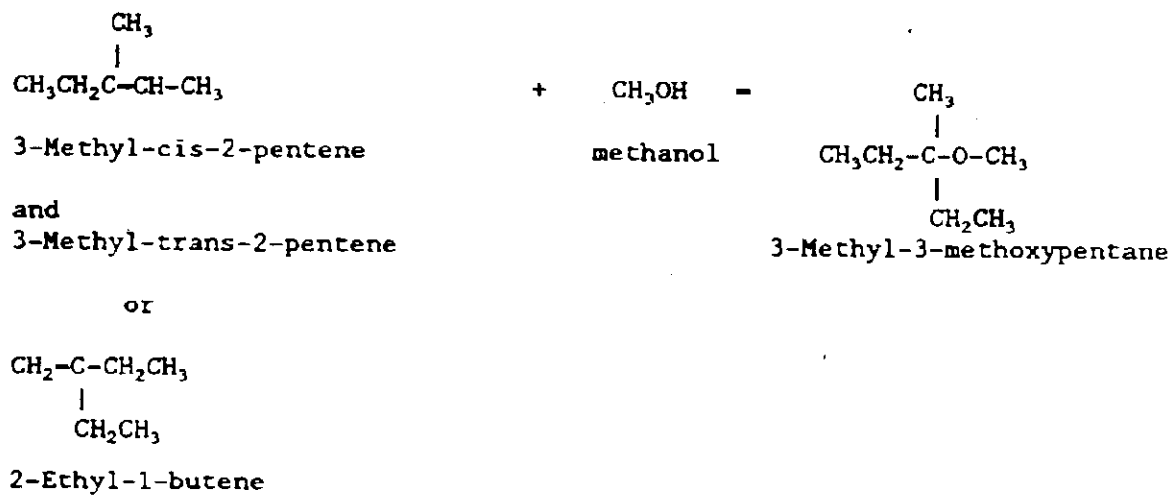
Scheme 1:



Scheme 2:



Scheme 3:



The reactions of these C₆ olefins to the THME ethers can contribute significantly to the total ether yields from the FCC naphthas. Since the reaction of isobutylene and methanol to form MTBE is well known, this process will not be studied in this program. The focus of this task will be to produce TAME and THME ethers from the light naphtha products of the pilot plant wax cracking studies.

A small, fixed bed unit, AU-109, is in use for these etherification studies. The initial test runs involve the reaction of 2-Methyl-2-butene with methanol to produce TAME. Figure 12 shows the TAME yields (conversion of isoamylene to TAME: moles TAME out/moles isoamylene in *100) from the new unit, AU-109. The test conditions are: variable temperatures, 200 psig unit pressure, 0.66 WHSV (olefin) and 1.2 mole ratio of methanol/olefin. The catalyst for these runs is Amberlyst 15, a commercial etherification catalyst. The reaction temperature is a major factor in this etherification reaction. The sharp rise in TAME yield at 150°F and the decline at 200°F suggests that equilibrium limitations exist at these temperatures and reaction conditions. The maximum yields of ethers will occur at these equilibrium conditions. The primary feedstock for these etherification studies is the light naphthas obtained from the pilot plant catalytic cracking runs with the Fischer-Tropsch wax. The details of these runs are available in a previous publication. (13) The liquid products from several pilot plant runs were combined and then distilled into three fractions, 200°F-, 200-430°F, and 430°F+, according to ASTM Method D-2892, an atmospheric distillation procedure. Table VIII presents the detailed composition of these light naphtha samples. The iso-olefin contents of the samples, feeds "B" and "C", are higher than the light naphtha sample, feed "A". This is due to the use of high olefin selective FCC catalysts, Beta and HZSM-5, in the pilot plant runs, Nos. 940-01,02 and 941-01. The same Y zeolite catalyst was used in the runs for feed "A" and "C". The high iso-olefin content of feed "C" results from the lower conversion level. The reactive isoamylenes, 2-Methyl-2-butene and 2-Methyl-1-butene for TAME synthesis and the reactive C₆ iso-olefins, 2-Methyl-1-pentene, 2-Methyl-2-pentene, 2,3-Dimethyl-1-butene, and cis and trans 3-Methyl-2-pentene for THME synthesis are the important components. This light naphtha, feed "A" sample, and methanol are the feedstock for a series of etherification runs at the same process conditions for the 2-Methyl-2-butene/methanol tests. Due to the limited availability of the gasoline, only two reaction temperatures are available. A summary of the conversion of the various C₅ and C₆ iso-olefins to their respective methyl ethers, Table IX, shows that reaction temperature is a major factor in the etherification reaction. The decrease in conversion with the increase in the carbon number of the iso-olefin agrees with other literature etherification studies. (17,19) The reaction products from these runs have a significant yellow color, especially at the higher reaction temperature of 150°F. This color is not present for the pure component 2-methyl butene-2 tests. It is likely that polymerization of olefins to C₁₀+ hydrocarbon "color bodies" is responsible for the colored product. The color of the ether product could be a significant product quality issue. Additional runs with a catalyst that contains a hydrogenation metal component and hydrogen gas in the reactor may solve this problem.

Table X presents the summary of the etherification runs with the "A", "B" and "C" light naphthas at 150°F. In these runs, both Amberlyst 15 and another commercial etherification catalyst, Bayer's K2634 are under study. The Bayer catalyst contains a noble metal in addition to the strong acid

functionality. The noble metal is available for olefin isomerization and diolefin saturation, in the presence of hydrogen. The nominal reaction conditions are the same as the previous set of runs, 200 psig, 2.9 grams of catalyst, methanol 1.37 g/hr, naphtha, 5.5g/hr except that only one reaction temperature, 150°F, is available. The results are similar for both catalysts and the three feedstocks, in the absence of hydrogen gas in the reactor. The calculated research octane values for the products of these etherification runs are 2-4 numbers higher than the starting light naphtha feedstocks, Table XI. As expected, this octane increase depends to some extent upon the concentrations of the ethers in the product. Blending octane numbers for the mixed ether light naphtha fractions are also shown in Table XI. There is only fair agreement with the calculated (by GC) octane numbers.

When hydrogen gas is present, Run No. 034-1, Table X, there is a major loss of iso-olefin conversion. These reaction conditions result in the hydrogenation of both reactive iso-olefins and linear olefins. This is an undesirable result since both the production of ethers and the octane number of the product decreases significantly. The run with added hydrogen gas, 034-1, has a lower research octane rating (79.5) than the feedstock (84.6) or the run with no added hydrogen, 034-3, (85.8), (Table XI). This octane loss is due to the conversion of high octane value olefins to low octane value paraffins. There is a significant improvement in the color of the etherification products in the presence of hydrogen gas.

These etherification runs clearly demonstrate that the light naphtha fractions from the catalytic cracking of Fischer-Tropsch wax are excellent ether synthesis feedstocks.

IV. CATALYTIC CRACKING OF LAPORTE FISCHER-TROPSCH WAX

The primary Fischer-Tropsch wax feedstock for all catalytic cracking studies thus far in this program is a sample from Sasol. Another Fischer-Tropsch wax feedstock (one 55 gallon drum) has been received from the DOE sponsored Liquid Phase Fischer-Tropsch (LPFT) synthesis demonstration run (19 day run, August 4-23, 1992) at the LaPorte, Texas 0.7 T/D plant. These runs used a silica supported iron catalyst. The presence of some initial catalyst fines and some attrition in the reactor caused a significant contamination (2-4 wt.%) of the wax product with F-T catalyst. (20) A brief study of the catalytic cracking of this wax is of interest since the high level of catalyst contamination would preclude any fixed bed conversion processing (e.g., hydrocracking) of this material. The Fluid Catalytic Cracking process operates with a circulating catalyst inventory. This FCC operation may tolerate the high contaminant F-T catalyst level found in this LaPorte wax feedstock.

The boiling point distribution (by GC simulated distillation) of the new LaPorte wax feedstock is similar to the standard Sasol wax feedstock, Figure 13. The LaPorte wax (61% >1000°F) contains more high boiling material than the Sasol wax (52% >1000°F). Table XII presents the solids content analyses of this particular LaPorte drum sample. The wax is ashed and the residue is then analyzed by Atomic Absorption Spectroscopy for individual metals content. The value of 2.46% solids (oxide basis) agrees with the average values reported by the contractor for these runs, 2-4%. (20) A simple centrifuge experiment did not provide for a satisfactory separation of the F-T catalyst solids from the hot wax

sample. The chemical analysis results of the centrifuged wax sample in Table XII indicate that the catalyst solids are distributed in an increasing gradient from top (3681 ppm) to bottom (9490 ppm) into the sample. However, the ash composition values from this centrifuge experiment do not agree with the overall analysis (Table XII). This discrepancy suggests that the catalyst may not be distributed homogeneously in the wax. The Fluid Catalytic Cracking unit may tolerate this level of Fischer-Tropsch catalyst fines in the wax feedstock if the F-T catalyst can be selectively removed from the FCC unit. These F-T fines will deposit on the external surfaces of the FCC catalyst microspheres. One possible removal method is to selectively attrit the F-T catalyst from the external surfaces of the FCC catalyst. This would be done with high velocity air jets in the regenerator of a commercial FCC unit. The fines would then be removed from the flue gas by conventional electrostatic precipitators or other collection devices. A series of laboratory experiments describes the results of this processing option. The first experiment is the simple sequential catalytic cracking of the LaPorte wax with one reference FCC catalyst. This would simulate a working FCC unit and catalyst with the LaPorte wax as the feedstock. Ten individual cracking runs (1 g LaPorte wax feedstock, 970°F, 5 g catalyst) were carried out with the same catalyst (CCC-1397) sample, a commercial equilibrium FCC catalyst. This wax cracking sequence results in a significant deposition of F-T catalyst fines from the wax onto the FCC catalyst. The iron content of the FCC catalyst increases from 0.42% to 1.05%, Table XIII, Part A. This F-T fines contaminated catalyst is then treated in a laboratory attrition test. A high velocity air jet subjects this catalyst sample to severe attrition conditions. After the attrition test, the catalyst and fines are recovered and analyzed for contaminant metals. The results of this attrition experiment, Table XIII, Part B, No.2, indicate that the F-T catalyst fines are selectively attritted from the contaminated FCC catalyst into the fines. The iron content of the contaminated FCC catalyst decreases from 1.05% to 0.62% after the attrition experiment. The iron content of the fines generated in this experiment is nearly 3%. A control attrition experiment, with the base catalyst, CCC-1397, without F-T catalyst fines is also detailed in Table XIII, Part B, No.1. Note that the composition of the fines, especially the iron content, is similar to the starting catalyst, suggesting that no selective attrition occurs with the uncontaminated, control sample.

The catalytic cracking tests of the LaPorte wax feedstock and new test runs with the Sasol wax were carried out with three types of FCC catalysts (USY, HZSM-5, Beta). The three catalysts represent different zeolite structures with varying olefin selectivities. These catalysts have been used throughout this program. The first question of interest is whether there is any variation in conversion values between these two wax feedstocks. There is considerable variation in the conversion values for each of the catalyst and wax feedstock combinations, Figure 14. The conversion number is the sum of the cracked products: gas(C₄-), naphtha(C₅-430°F) and coke. However, the scatter of conversion values for both feedstocks and catalyst combinations between 80-90% at cat-to-oil ratios of 0.9-1.0 suggest that both feedstocks have similar conversion values. Further tests at a wider variety of catalyst to oil ratios would be required to verify this tentative conclusion. The next issue is whether product selectivities vary with the two wax feedstocks. The coke and hydrogen gas yields for the LaPorte wax are significantly higher than the Sasol wax (Figures 15, 16). This is the result of the iron Fischer-

Tropsch catalyst fines in the LaPorte wax. These fines are deposited upon the surfaces of the cracking catalysts during the test runs. The HZSM-5 catalyst, CCC-1891, has a lower coke yield but similar hydrogen yield compared to the other two catalysts for the LaPorte wax tests. The intermediate pore structure of the HZSM-5 catalyst apparently inhibits coke formation even in the presence of the active dehydrogenation iron F-T fines.

V. SCOPING ECONOMIC EVALUATION OF THE PROPOSED PROCESSES

The initial economic analysis for the proposed cracking process centered on the calculation of simple product values of each of the pilot plant runs. Table XIV shows the catalyst-to-oil ratios and reactor temperatures used and the conversions obtained in these pilot plant runs. Table XV shows the results of economic analysis of one of the above-mentioned pilot plant runs. The rate basis for all the analyses was 283,687 lb/hr. Net product values (which accounts for the external energy required to maintain heat balance) were calculated for both simple (no ether unit) and complex (contains ether unit) refinery configurations. Table XVI summarizes the net product values for simple and complex refineries, and the difference between the two, for all the pilot plant runs. The net product values (\$/d) for a simple refinery ranged from about \$555,500 for Run 941-1 to about \$584,500 for Run 940-2. The net product values (\$/d) for a complex refinery ranged from about \$605,600 for Run 939-4 to about \$653,300 for Run 940-2. The delta in net product values for the complex and simple refineries was greatest (about \$74,900/d) for the run that used HZSM-5 catalyst (941-1); the delta for the runs with Beta catalyst was about \$67,000-69,000/d; and the delta for the runs using only USY catalyst were about \$43,000-55,000/d.

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TABLE I

DESCRIPTIONS OF HISEN-5 FCC CATALYSTS

Catalyst I.D.	Catalyst Description
CCC-1891	Intercat ZCAT Plus® Large steamer, 5,000 g., 1450°F, 5 hrs., 100X steam
14040-45-1	Intercat ZCAT Plus® small steamer, 25 g., 1450°F, 5 hrs., 100X steam
14040-43-3	Intercat Isocat® small steamer, 25g., 1450°F, 5 hrs., 100X steam
14040-43-1	Devison Additive OH-S® small steamer, 25 g., 1450°F, 4 hrs., 100X steam
14040-43-2	Repeat of above
14040-42-1	1X ReO/ZCAT Plus®, 1450F, 5 hrs., 100X steam
14040-42-2	2X ReO/ZCAT Plus®, 1450F, 5 hrs., 100X steam
14040-42-3	3X ReO/ZCAT Plus®, 1450F, 5 hrs., 100X steam

TABLE II

MTU TEST RESULTS - FISCHER-TROPSCH WAX CRACKING VARIOUS HISEN-5 CATALYSTS
(TEST CONDITIONS: 890°F, 0.187 CATALYST/OIL RATIO)

Run No.	054	055	087	088	089	090	094	084	091	085	092	086	093	096	097	098
Catalyst Description	←-----CCC-1891-----→		ZCAT Plus Large Steamer		ZCAT Plus Small Steamer		CCC-1891 ZCAT Plus Small Steamer	14040-43-1 OH-S Small Steamer	14040-43-1 OH-S Small Steamer	14040-43-2 OH-S Small Steamer	14040-43-3 Isocat Small Steamer	14040-43-3 Isocat Small Steamer	14040-42-1 1X ReO	14040-42-2 2X ReO	14040-42-3 3X ReO	
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	80.3	80.5	76.7
Product Yields Wt%																
C ₁	1.6	1.5	2.8	1.6	2.2	3.2	2.1	1.9	1.7	1.7	3.0	0.9	0.8	1.2	1.3	1.1
C ₁ + C ₂	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	39.5	39.0	36.6
C ₃ -430°F	40.0	38.0	39.8	41.2	35.6	35.9	40.6	42.1	40.9	42.2	39.4	34.8	36.5	39.5	40.1	38.9
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	19.7	19.5	23.3
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	0.1	0.1	0.1
C ₁	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	13.3	12.7	11.8
IC ₁	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	9.9	9.5	9.5
IC ₂	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	10.1	10.8	10.1
C ₁ -430°F RON	85.4	84.4	80.9	84.3	82.5	86.3	83.5	84.4	81.7	86.2	85.0	83.6	84.8	83.3	83.7	83.3
MON	76.6	76.0	74.2	75.1	74.8	74.9	75.2	75.0	74.2	75.7	76.5	74.3	75.3	74.7	75.0	74.8

TABLE III
B.E.T. SURFACE AREAS OF STEAMED HZSM-5 SAMPLES
 Steam Treatment: 1450°F, 5 Hours, 100% Steam

Sample ID	Total B.E.T. Surface Area (m ² /g)	Zeolite Surface Area (m ² /g)	Matrix Surface Area (m ² /g)
ZCAT Plus (#1)	70	39	31
ZCAT Plus (#2)	70	30	40
1% ReO/ZCAT Plus	63	41	22
2% ReO/ZCAT Plus	62	38	24
3% ReO/ZCAT Plus	60	42	18
OH-S (#1)	54	31	23
OH-S (#2)	56	25	31
Isocat	53	30	23

TABLE IV
DESCRIPTION OF RARE EARTH OXIDE/FAUJASITE CATALYSTS

Catalyst I.D.	Wt% Rare Earth	Steam Treatment
CCC-1701	<0.04	1450°F, 8.5 hours, 100% steam
CCC-1702	0.27	1450°F, 8.5 hours, 100% steam
CCC-1703	0.34	1450°F, 8.5 hours, 100% steam
CCC-1704	0.96	1450°F, 8.5 hours, 100% steam
CCC-1705	1.49	1450°F, 16 hours, 100% steam
CCC-1706	1.49	1450°F, 8 hours, 100% steam

TABLE V
MYU TEST RESULTS - FISCHER-TROPSCH MAX CRACKING
 Rare Earth Oxide/Faujasite Catalysts
 Test Conditions: 880°F, 0.75 Catalyst/Oil Ratio

Run No.	099	100	101	102	103	104
Catalyst Description	CCC-1710	CCC-1702	CCC-1703	CCC-1704	CCC-1705	CCC-1706
Conversion Wt%	92.4	87.8	85.5	91.5	87.3	91.9
Product Yields, Wt%:						
C ₂ -	0.8	0.6	0.6	0.8	0.7	0.5
C ₂ +C ₃	28.7	23.4	20.8	23.2	11.3	26.6
C ₂ -430°F	62.1	63.0	63.2	66.5	66.5	63.9
430°F+	7.6	12.2	14.5	8.5	12.7	8.9
Coke	0.8	0.8	0.9	0.9	.8	0.1
C ₃ -	7.6	6.6	5.8	6.5	5.3	7.2
iC ₃ -	5.9	4.5	4.1	4.3	3.8	6.0
iC ₃ -	7.8	6.4	5.6	6.4	5.9	8.3
C ₃ -430°F						
RON	89.7	88.7	87.4	88.0	86.5	88.8
MON	78.0	76.3	74.5	76.0	74.0	76.6

TABLE VI

CHEMICAL COMPOSITIONS OF ZEOLITE FCC CATALYSTS

Catalyst ID	Nominal Composition	Comment
9669-146-148	40% Beta zeolite 20.8% silica sol 4.2% alumina 35% Kaolin clay	Standard Beta
9669-152	40% LZY-84 zeolite 20.8% silica sol 4.2% alumina 35% Kaolin clay	Standard Y
9669-153	34.7% silica sol 7% alumina 58.3% Kaolin clay	Matrix only
9669-154	10% LZY-84 20.8% silica sol 4.2% alumina 65% Kaolin clay	Low Y zeolite
9669-155	10% Beta 20.8% silica sol 4.2% alumina 65% Kaolin clay	Low Beta

TABLE VII

PHYSICAL PROPERTIES OF ZEOLITE FCC CATALYSTS

Steam Treatment: 1450°F, 5 hours, 100% steam

Catalyst ID	Description	BET Surface Area, m ² /g			Micropore Volume (cc/g)
		Total	Zeolite	Matrix	
14059-81-4	40% Beta	211	143	68	.066
14040-48-1	40% Y	253	183	70	.084
14040-48-2	40% Y	233	167	66	.077
14040-50-5	Matrix	55	3.0	52	.001
14040-50-6	10% Y	90	48	42	.022
14040-50-7	10% Beta	69	19	50	.009

TABLE VIII

HYDROCARBON COMPOSITION OF 200°F- NAPHTHAS

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 ₅	0.18	0.37	0.16
C ₆	0.93	1.04	0.72
C ₇	4.03	4.50	2.35
C ₈	1.45	1.67	1.02
C ₉	0.08	0.69	0.06
C ₁₀	--	0.13	--
Total Iso-paraffins wt%	42.71	17.64	22.88
C ₅	0.32	0.56	0.28
C ₆	3.77	2.03	2.19
C ₇	22.94	6.22	10.55
C ₈	13.87	6.12	8.86
C ₉	1.82	2.16	0.99
C ₁₀	--	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 ₆	0.05	0.06	0.05
C ₇	1.23	0.92	0.71
C ₈	1.92	1.71	1.63
C ₉	0.75	1.82	0.80
C ₁₀	--	1.03	--
Total Olefins wt%	44.51	64.47	68.65
C ₅	0.01	0.11	0.04
C ₆	1.25	3.72	1.82
C ₇	8.701	12.10	12.03
C ₈	23.88	25.54	33.79
C ₉	10.36	15.65	19.95
C ₁₀	0.31	3.31	1.02
Reactive iso-olefins wt%			
C ₄ 's			
2-methyl-1-butene	1.25	2.15	1.76
2-methyl-2-butene	4.26	5.67	5.64
C ₅ '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-vis-2-pentene	3.98	5.48	5.35

WR/lkv/93465
9/8/93

TABLE IX

REACTIVE ISO-OLEFINS CONVERSION TO ETHERS

Reaction Temperature
(Averages of Three Weight Balance Tests)

Feed A

Iso-olefin Component	125°F	150°F
C ₅	<u>Wt%</u>	<u>Wt%</u>
2-Methyl-1-butene	85.4	89.9
2-Methyl-2-butene	29.9	65.5
C ₆		
2,3 Dimethyl-1-butene	56.5	83.4
2-Methyl-1-pentene	65.9	87.5
2-Methyl-2-pentene	20.7	48.6
3-Methyl-cis-2-pentene	21.7	38.6
3-Methyl-trans-2-pentene	20.8	29.8

TABLE X

REACTIVE ISO-OLEFINS CONVERSION TO ETHERS

	FEED A	FEED B			FEED C	
200°F- Naptha	92-049-01A	93-0024-01A			93-0024-01C	
Reaction Temp, °F	150	150	150	150	150	150
Catalyst	Amberlyst 15	Amberlyst 15	K2634	K2634	K2634	K2634
			No H ₂	H ₂	H ₂	No H ₂
<u>iso-olefin component:</u>						
C ₅ 's						
2-methyl-1-butene	89.9	90.2	87.1	77.2	78.1	87.7
2-methyl-2-butene	65.5	62.2	66.2	42.9	38.2	61.2
C ₆ 's						
2,3, dimethyl-1-butene	83.4	--	--	--	--	--
2-methyl-1-pentene	87.5	85.5	84.1	72.2	78.6	86.9
2-methyl-2-pentene	48.6	56.1	62.7	44.2	31.5	51.5
3-methyl-Cis-2-pentene	38.6	31.0	43.4	23.8	7.3	25.8
3-methyl-trans-2-pentene	29.8	32.2	43.7	25.9	20.7	33.3

TABLE XI
 LIGHT NAPHTHA ETHERIFICATION RUNS
 HYDROCARBON COMPOSITION OF FEED AND PRODUCTS

Run No.	Reaction Temp	Catalyst	Research Octane Number*	Blending Research Octane Number	Paraffins	iso-paraffins	Aromatics	Naphthenes	Diolefins	Oxygenates	Unknowns
Feed A											
92-0490-01A			80.92	66.9	6.689	42.712	1.736	3.956	44.507	0.071	0.33
15586-024-2	125°F	Amberlyst 15	82.09	77.9	7.804	40.230	1.985	4.474	33.762	11.406	0.34
15586-024-6	150°F	Amberlyst 15	83.76	79.9	6.463	40.429	2.247	4.576	29.671	16.294	0.32
15586-024-8	150°F	Amberlyst 15	83.88	--	6.337	40.466	2.263	4.586	29.58	16.436	0.33
Feed B											
93-0024-01A			83.12	83.9	8.437	17.637	2.623	5.549	64.172	0.17	1.11
15586-031-2	150°F	Amberlyst 15	87.43	87.9	7.417	17.989	3.687	6.424	41.847	21.815	0.821
15586-033-1	150°F	Bayer K2634	87.48	85.9	7.381	17.340	3.691	6.583	41.716	22.445	0.844
15586-033-3	150°F	Bayer K2634	85.78	84.9	8.205	17.668	3.62	6.512	45.889	17.277	0.83
Feed C											
93-0024-01C			84.56	95.9	4.315	24.881	0.353	3.161	68.651	0.15	0.49
15586-034-1	150°F	Bayer H2 K2634	79.47	88.9	14.535	24.733	2.405	5.436	35.369	17.332	0.19
15586-034-3	150°F	Bayer no H2 K2634	85.76	95.9	5.921	22.489	1.977	4.497	43.51	21.192	0.415

*Calculated

TABLE XII

CHEMICAL ANALYSES OF LA PORTE FISCHER-TROPSCH WAX

Sample ID 15586-012					
Chemical Composition (ppm) of Ash:					
Si	=	1,710	SiO ₂	=	3,659
K	=	1,350	K ₂ O	=	1,626
Fe	=	13,900	Fe ₂ O ₃	=	17,882
Cu	=	<u>1,150</u>	CuO	=	<u>1,439</u>
		18,110			24,606
<u>Centrifuge Experiment to Separate Solids</u>					
Chemical Composition (ppm)					
<u>Top:</u>	Si	540	<u>Bottom:</u>	Si	1200
	K	430		K	820
	Fe	2620		Fe	6900
	Cu	<u>91</u>		Cu	<u>570</u>
		3681			9490

TABLE XIII

SELECTIVE ATTRITION EXPERIMENTS

	(ppm)				
	Si	K	Fe	Cu	Al
A. F-T catalyst fines deposition, chemical analyses of samples (from La Porte wax)					
1. Base Catalyst CCC-1397	226000	121	4200	26	258000
2. Treated Catalyst: 5.0 g catalyst, 10 g La Porte wax in 1-g segments I.D. No. 9363005 (15586-030-2P)	225000	266	10500	610	231000
B. Selective Attrition Experiments					
1. Control					
a. Starting sample CCC-1397	226000	121	4200	26	258000
b. After attrition (15586-030-1B)	200000	108	4200	21	254000
c. Fines (15586-030-1F)	252000	204	4100	14	235000
2. F-T catalyst contaminator sample 9363005					
a. Starting sample (15586-030-2P)	225000	266	10500	610	231000
b. After attrition (15586-030-2B)	212000	159	6200	289	267000
c. Fines (15586-030-2F)	219000	125	29600	2020	213000

TABLE XIV

PILOT PLANT FCC RUN DATA SUMMARY

Run Number	Catalyst	Catalyst to Oil Ratio	Reactor Temperature, °F	Conversion, %
939-1	Eq USY	5.2	944	93.5
939-2	Eq USY	4.1	932	93.7
939-4	Eq USY	2.3	982	83
939-5	Stmd. Eq USY	2.4	979	85
940-1	Stmd. Beta	1.5	934	96.6
940-2	Stmd. Beta	3.4	910	96.5
941-1	75% Stmd. Eq USY, 25% Stmd. H-ZSM5	2.8	965	89
942-2	50% Eq USY, 50% Diluent	1.6	937	90

TABLE XV

Fischer Tropach Wax Economics
Pilot Plant Results of Wax Run Through an FCCU
03/19/93

Rate Basis: 283,657 lb/hr
Run No. 939-1

Component	normalized wt % Yield	lb/hr	BBU/Day	--- Simple Configuration ---			--- Complex Configuration ---				
				cpg	\$/Day	Valued as	cpg	\$/Day	Valued as		
Hydrogen	0.040	113	111	6.0	279	Fuel Gas	2	6.0	279	Fuel Gas	2
Methane	0.360	1,021	233	10.8	1,059	Fuel Gas	2	10.8	1,059	Fuel Gas	2
Ethylene	0.480	1,362	252	12.0	1,356	Fuel Gas	2	12.0	1,356	Fuel Gas	2
Ethane	0.260	738	142	12.1	721	Fuel Gas	2	12.1	721	Fuel Gas	2
Propylene	9.263	26,274	3,450	17.1	24,777	Fuel Gas	2	17.1	24,777	Fuel Gas	2
Propane	1.861	5,277	713	16.8	5,028	Fuel Gas	2	16.8	5,028	Fuel Gas	2
i-Butane	7.932	22,500	2,739	37.2	42,792	Alkylation	3	37.2	42,792	Alkylation	3
n-Butane	2.081	5,902	692	29.8	8,662	Gasoline	5	29.8	8,662	Gasoline	5
1-Butene	1.470	4,171	475	63.9	12,756	Alkylation	3	63.9	12,756	Alkylation	3
i-Pentene	5.912	16,769	1,914	63.8	51,289	Alkylation	3	63.8	51,289	Alkylation	3
i-2-Butene	4.191	11,888	1,336	64.8	36,349	Alkylation	3	64.8	36,349	Alkylation	3
c-2-Butene	3.121	8,852	968	66.6	27,065	Alkylation	3	66.6	27,065	Alkylation	3
i-Pentane	8.492	24,089	2,652	49.4	55,017	Gasoline	5	49.4	55,017	Gasoline	5
n-Pentane	1.250	3,547	385	33.8	5,469	Gasoline	5	33.8	5,469	Gasoline	5
3M-1-Butene	0.086	244	27	50.3	560	Gasoline	5	53.6	597	Alkylation	3
2M-1-Butene	0.993	2,817	294	50.3	6,216	Gasoline	5	86.5	10,689	Ether Unit	4
7M-2-Butene	3.781	10,725	1,101	50.3	23,268	Gasoline	5	88.0	40,707	Ether Unit	4
1-Pentene	0.797	843	89	50.3	1,889	Gasoline	5	54.9	2,062	Alkylation	3
i-2-Pentene	1.400	3,972	417	50.3	8,803	Gasoline	5	55.5	9,713	Alkylation	3
c-2-Pentene	0.806	2,287	240	50.3	5,068	Gasoline	5	55.5	5,592	Alkylation	3
2-1-nM-1-Butene	0.187	531	53	59.2	1,326	Gasoline	5	68.6	1,537	Ether Unit	4
2-M-1-Pentene	0.490	1,362	137	59.2	3,395	Gasoline	5	68.7	3,940	Ether Unit	4
2-M-2-Pentene	0.812	2,304	229	59.2	5,689	Gasoline	5	69.4	6,669	Ether Unit	4
c-3-M-2-Pentene	0.812	2,304	227	59.2	5,634	Gasoline	5	70.1	6,671	Ether Unit	4
1-3-M-2-Pentene	0.520	1,475	144	59.2	3,586	Gasoline	5	70.5	4,270	Ether Unit	4
C6-430	34.299	97,292	8,416	59.7	211,018	Gasoline	5	59.7	211,018	Gasoline	5
430-650	4.971	14,102	1,019	52.1	22,296	Diesel	6	52.1	22,296	Diesel	6
650+	1.500	4,256	275	31.8	3,666	No 6 FO	7	31.8	3,666	No 6 FO	7
Sub-total	97.659	277,018	28,728		575,833				619,411		
Coke	2.341	6,639									
Grand Total	100.000	283,657									
Coke Amount for Heat Balance, wt % lb/hr		5% 14,929									
Coke Deficit, lb/hr MMBTU/Day \$/Day		8,290 3,382 6,765									
					(6,765)				(6,765)		
Net \$/Day					568,269				612,646		

TABLE XVI

SUMMARY OF NET PRODUCT VALUES FOR PILOT PLANT FCC RUNS

Run Number	Catalyst	Net Product Value, \$/d		
		Simple Refinery	Complex Refinery	Δ (Complex-Simple)
939-1	Eq. USY	568,269	612,646	44,377
939-2	Eq. USY	572,805	622,337	49,532
939-4	Eq. USY	562,181	605,612	43,431
939-5	Stmd. Eq. USY	570,631	625,664	55,033
940-1	Stmd. Beta	578,548	646,035	67,487
940-2	Stmd. Beta	584,479	653,299	68,820
941-1	75% Stmd. Eq. USY; 25% Stmd. H-ZSM5	555,461	630,327	74,866
942-2	50% Eq. USY; 50% Diluent	571,358	616,859	45,501

FIGURE 1

FISCHER-TROPSCH WAX CATALYTIC CRACKING
ACTIVITY OF HZSM-5 SAMPLES

CONVERSION, WT%

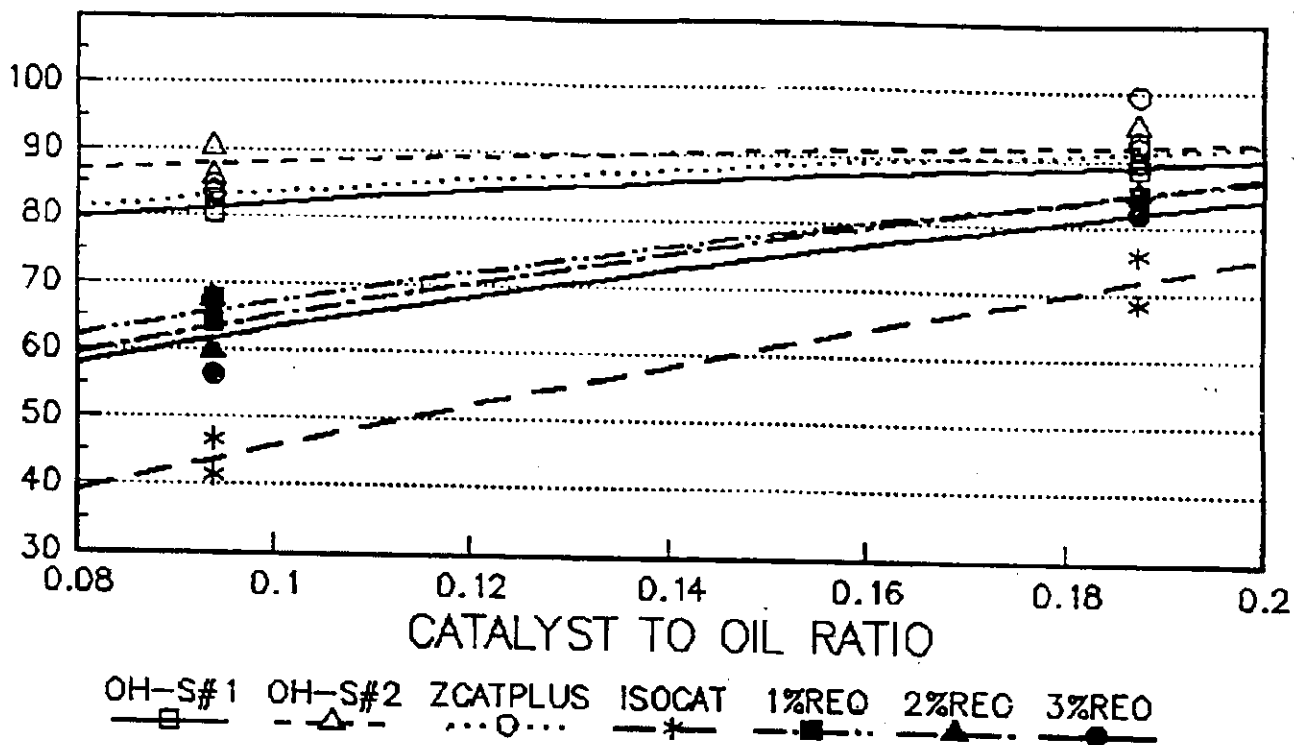


FIGURE 2

PRODUCT SELECTIVITIES OF HZSM-5 SAMPLES

ISOBUTYLENE, WT%

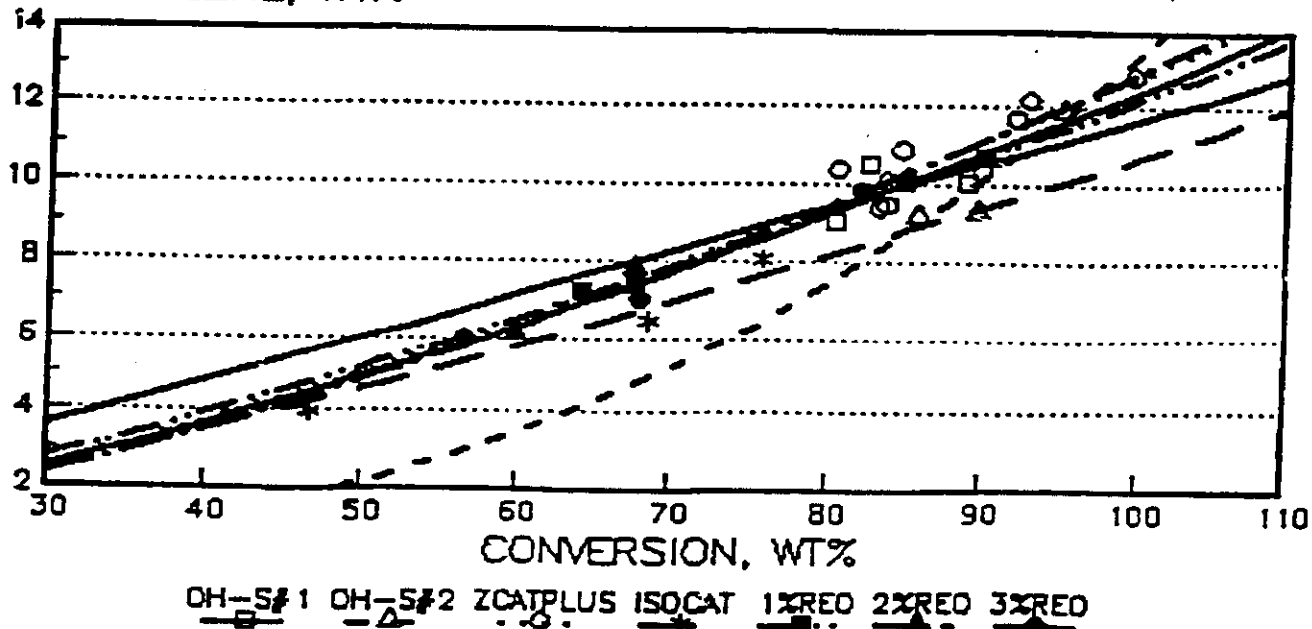


FIGURE 3

FISCHER-TROPSCH WAX CATALYTIC CRACKING
VARIABLE RARE EARTH Y ZEOLITE CATALYSTS

CONVERSION, WEIGHT PERCENT

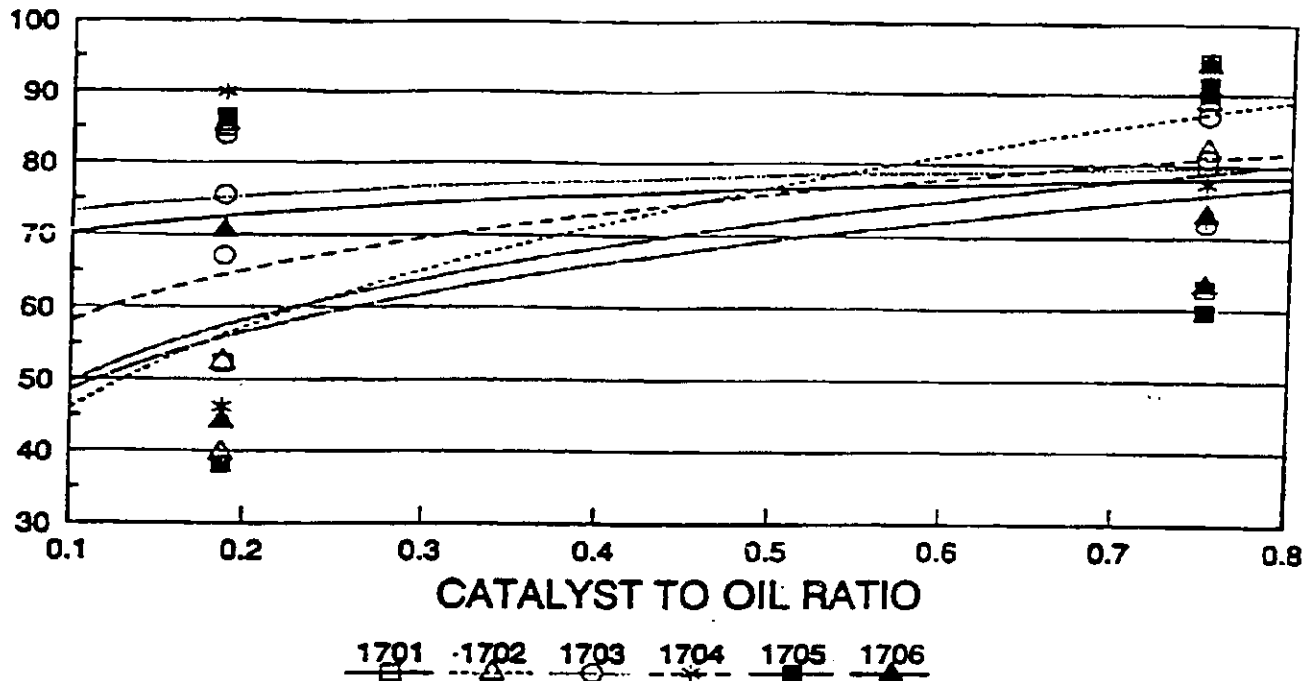


FIGURE 4

FISCHER-TROPSCH WAX CATALYTIC CRACKING
VARIABLE RARE EARTH Y ZEOLITE CATALYSTS

PROPYLENE, WT. %

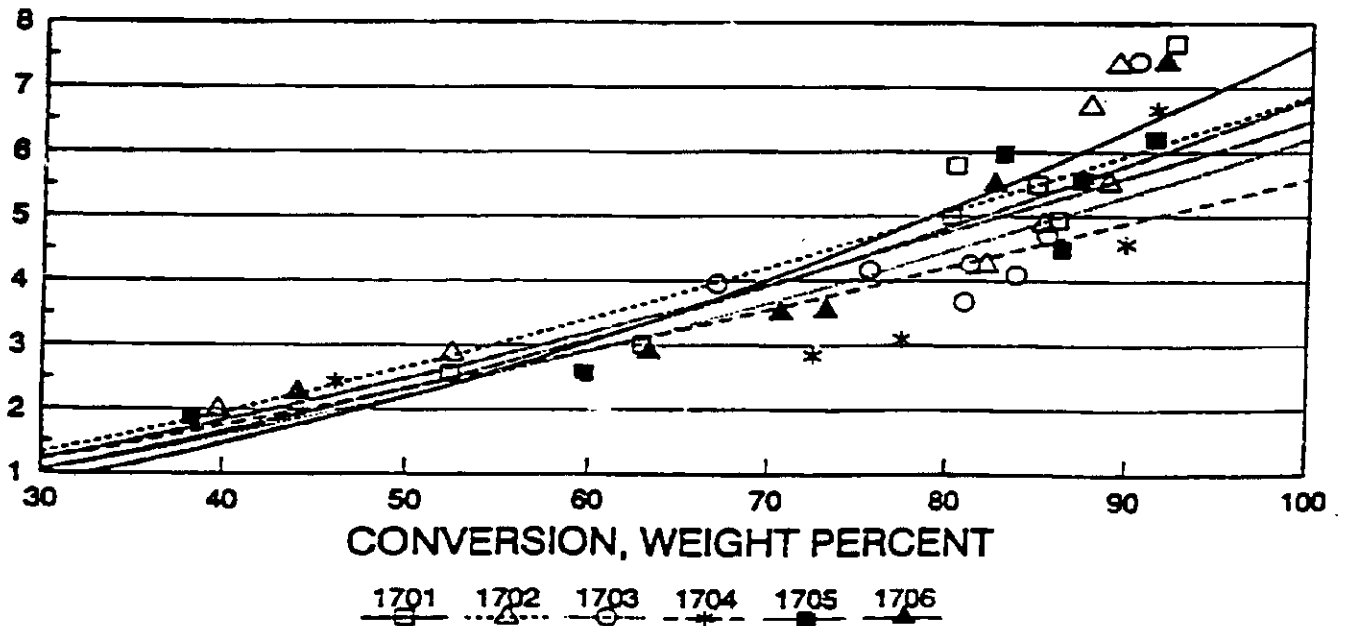


FIGURE 5

FISCHER-TROPSCH WAX CATALYTIC CRACKING
 RARE EARTH Y CATALYSTS-INTERPOLATED DATA
 PROPYLENE, WT%

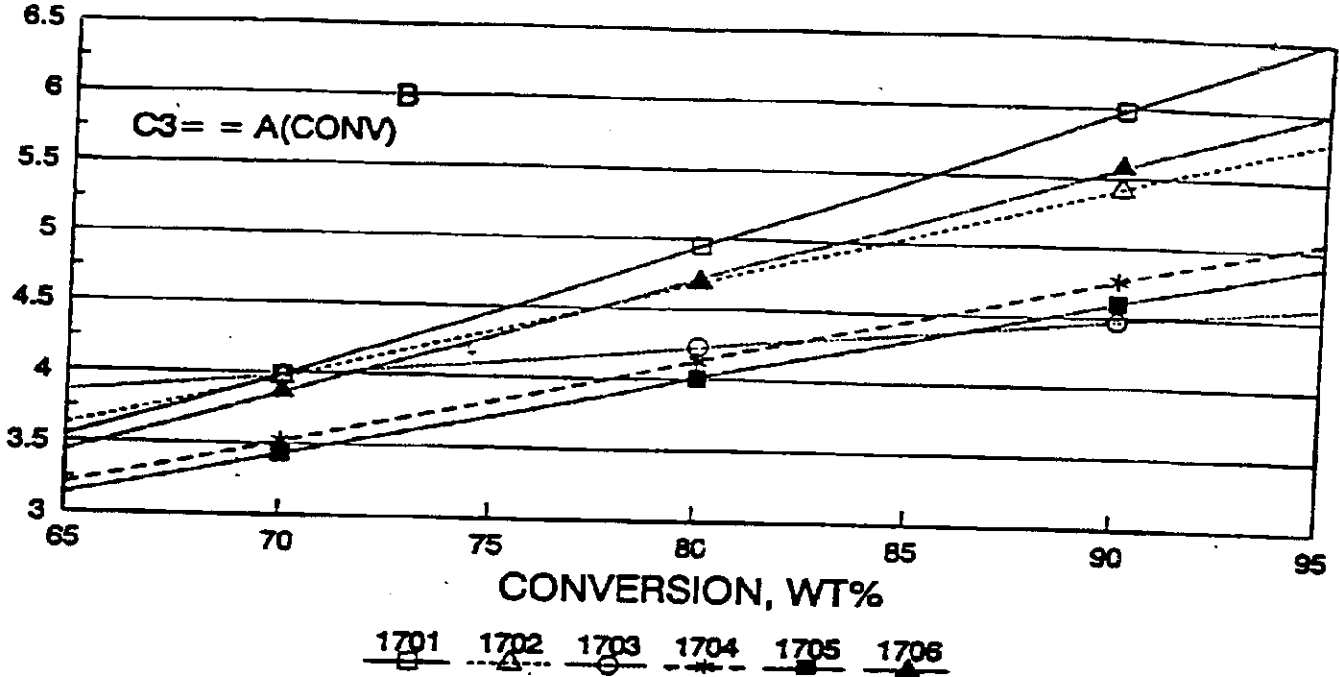


FIGURE 6

FISCHER-TROPSCH WAX CATALYTIC CRACKING
 RARE EARTH Y CATALYSTS-INTERPOLATED DATA
 GASOLINE YIELD, WT%

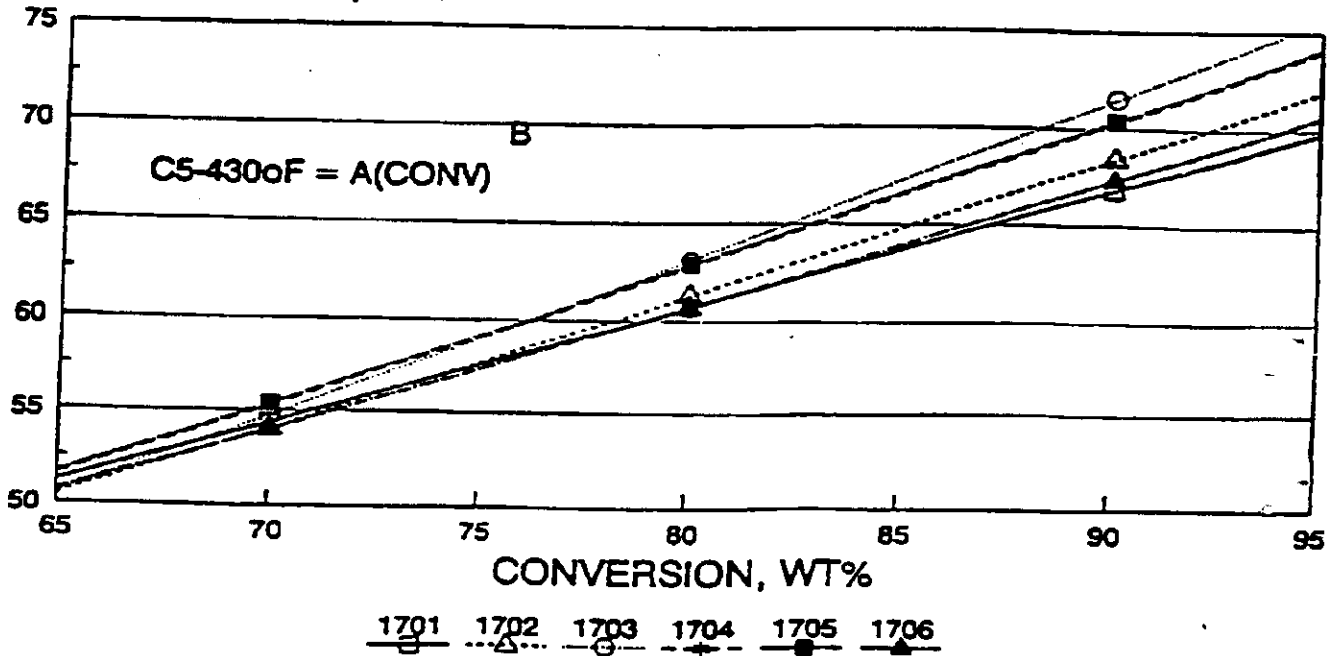


FIGURE 7

FISCHER-TROPSCH WAX CATALYTIC CRACKING:MYU RUNS
"MULTIPLE" HZSM-5 RUNS

CONVERSION, WEIGHT PERCENT

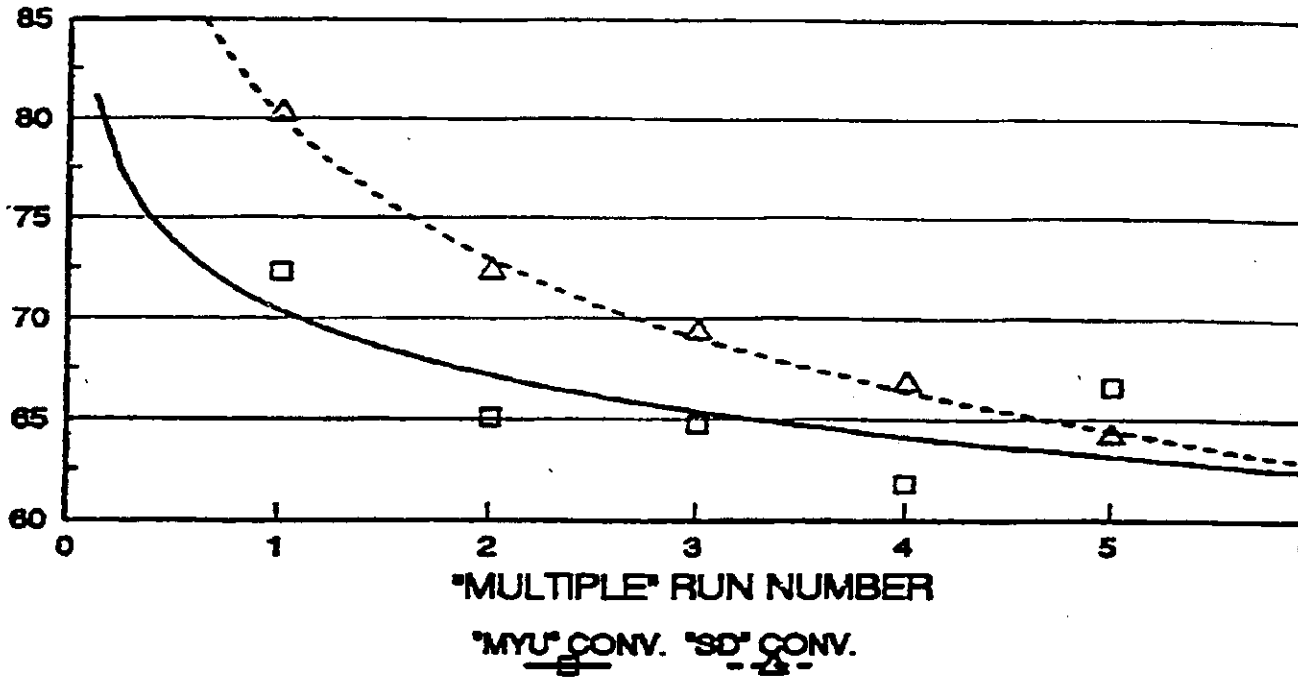


FIGURE 8

FISCHER-TROPSCH WAX CATALYTIC CRACKING:MYU RUNS
PRODUCT SELECTIVITIES OF "MULTIPLE" HZSM-5 TESTS

PROPYLENE, WT. %

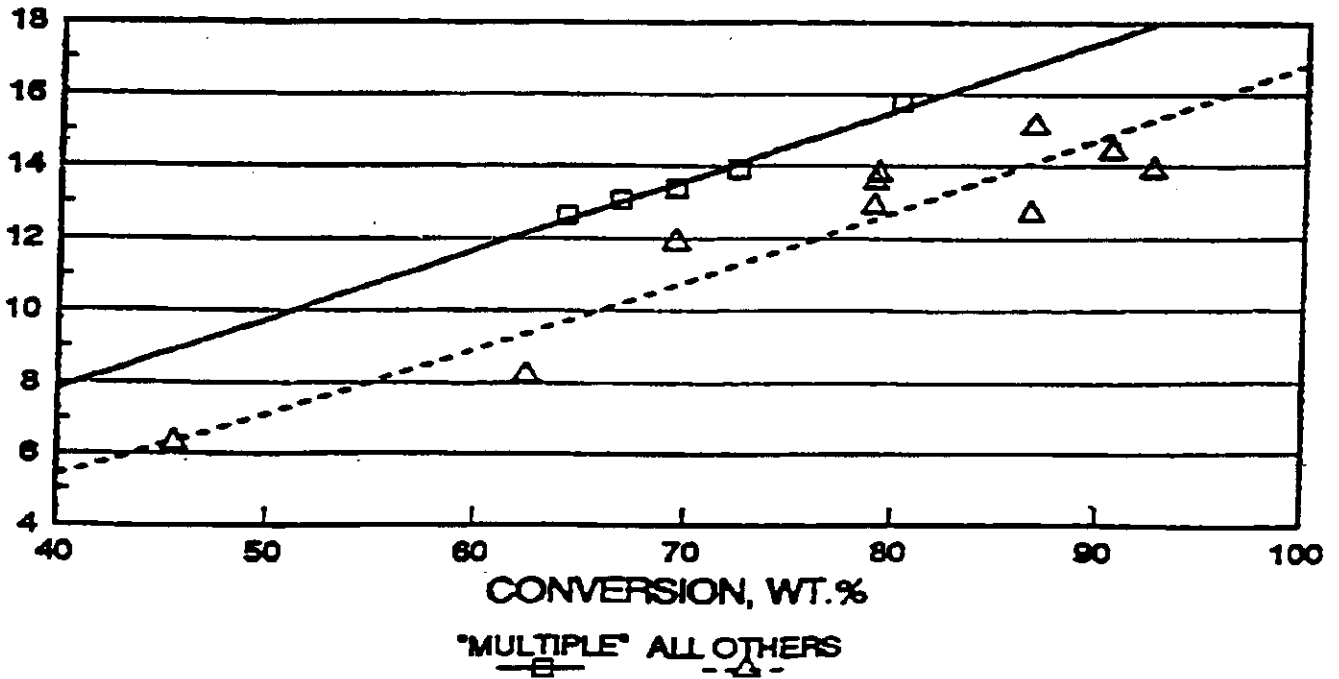


FIGURE 9

FISCHER-TROPSCH WAX CATALYTIC CRACKING: MYU RUNS
 PRODUCT SELECTIVITIES OF "MULTIPLE" HZSM-5 TESTS

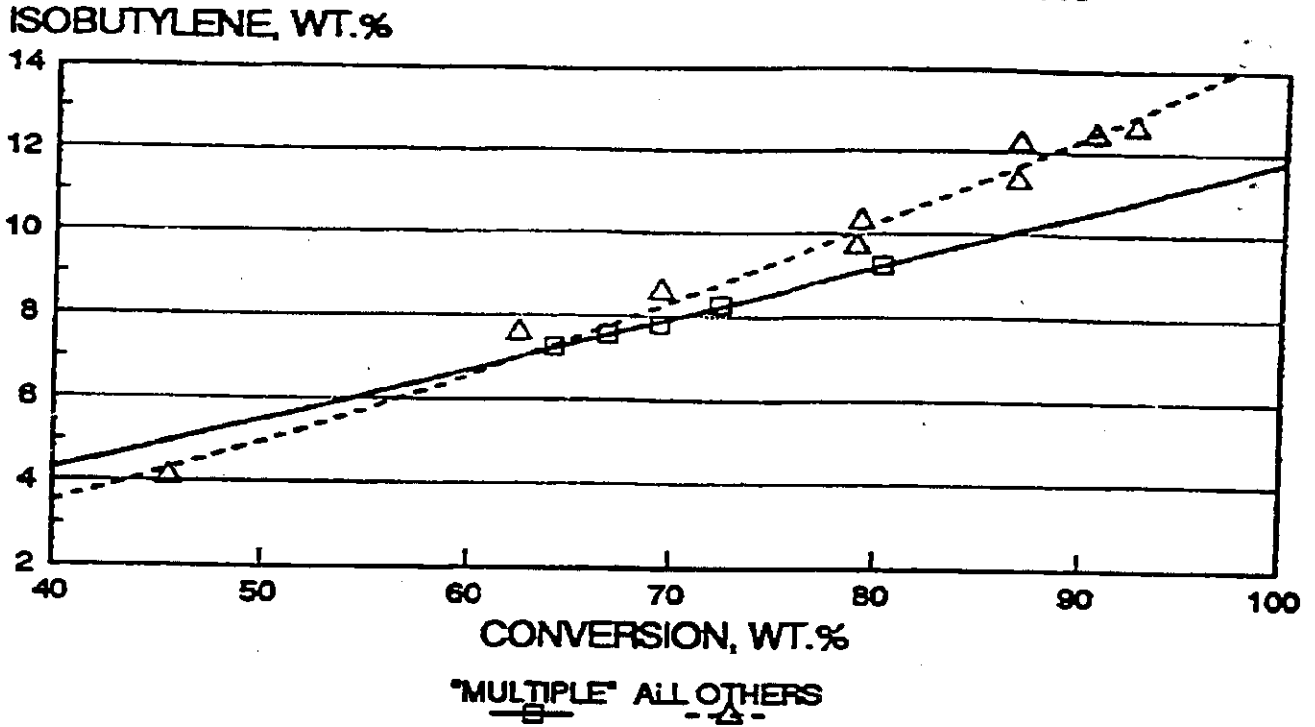


FIGURE 10

FISCHER-TROPSCH WAX CATALYTIC CRACKING
 WAX CONVERSION STUDIES - LOW ZEOLITE CATALYSTS

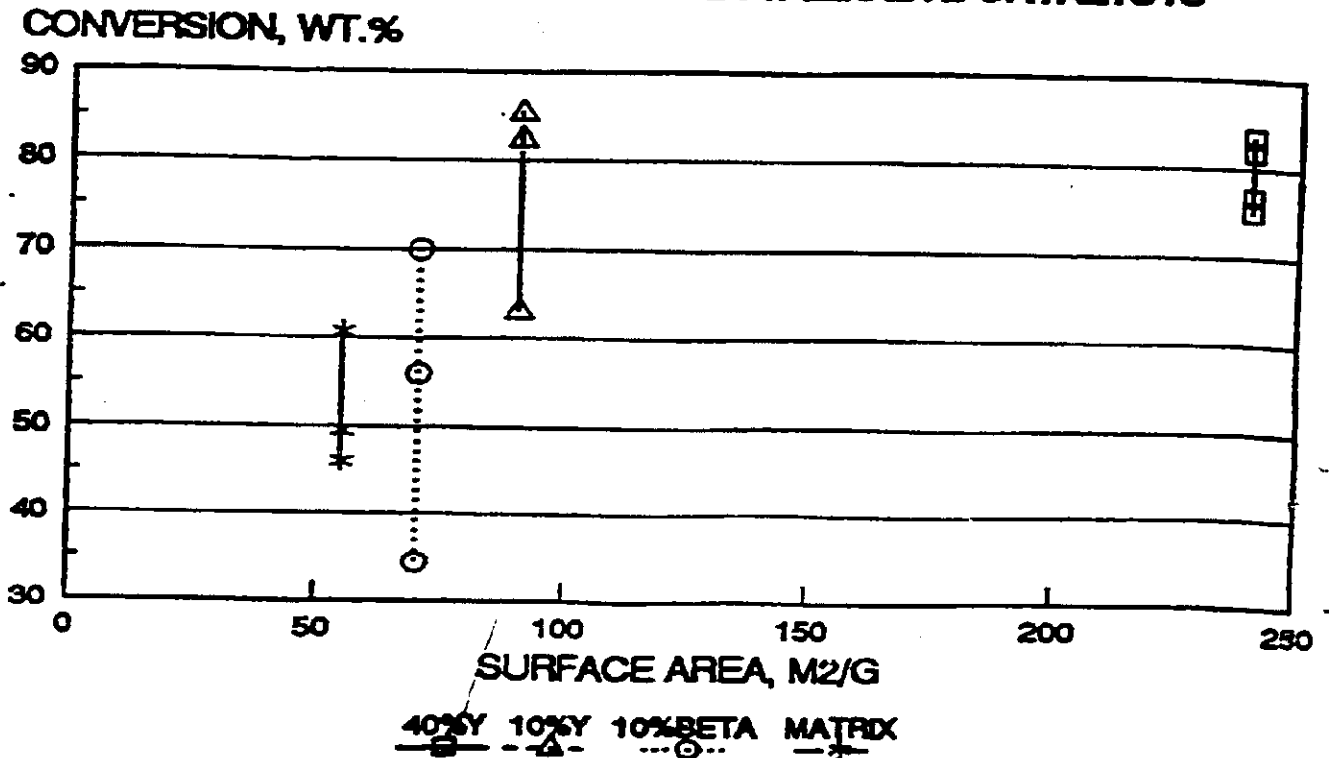


FIGURE 11

FISCHER-TROPSCH WAX CATALYTIC CRACKING
PRODUCT SELECTIVITY - LOW ZEOLITE CATALYSTS

ISOBUTYLENE, WT. %

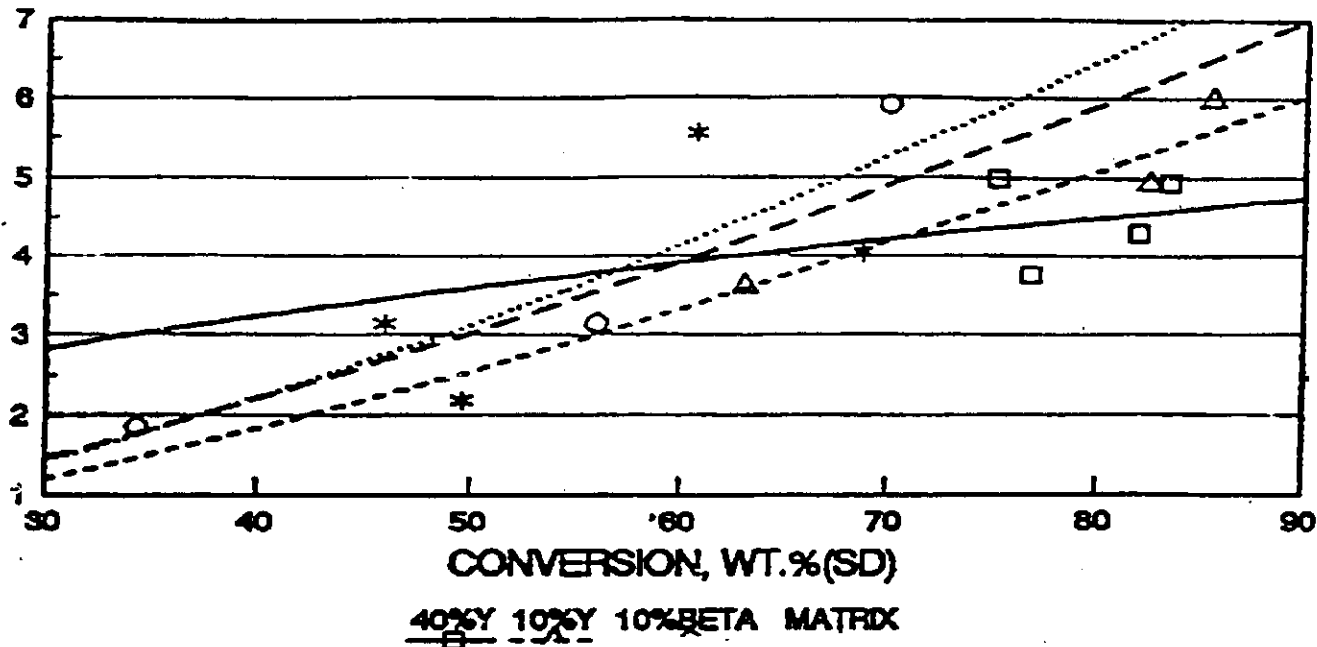
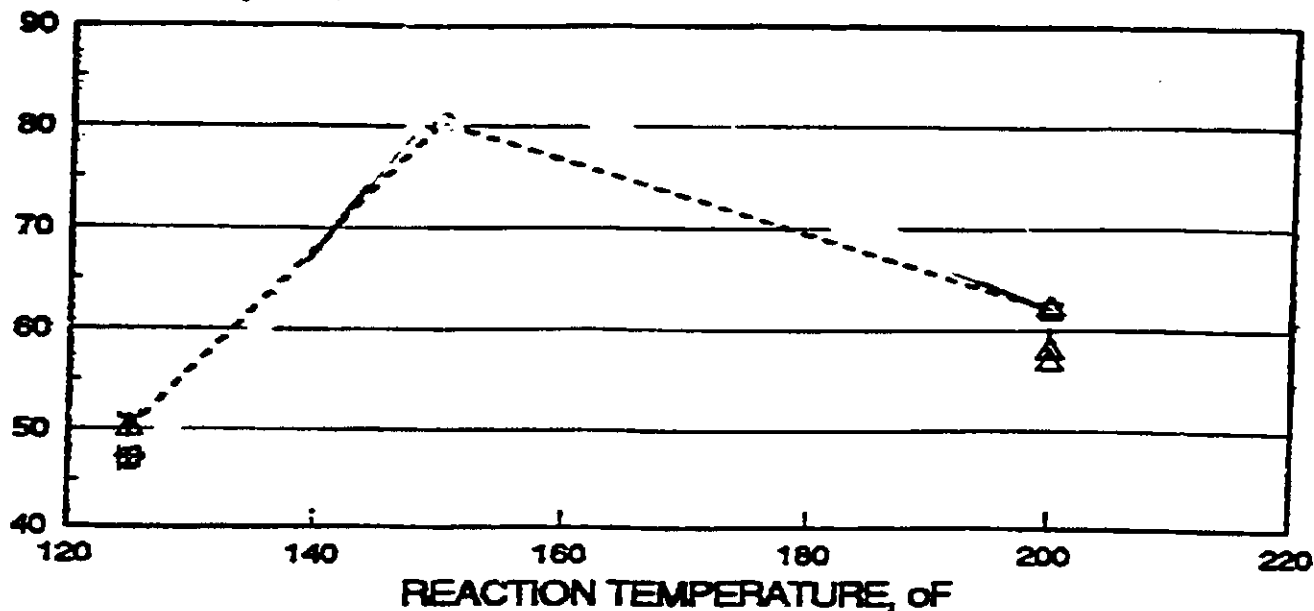


FIGURE 12

TAME PRODUCTION AU-109
METHANOL/2METHYL2BUTENE FEED

TAME YIELD, WT. %



AU-109
-△-

FIGURE 13

HIGH TEMPERATURE SIMULATED DISTILLATION
SASOL AND LAPORTE WAX FEEDSTOCKS

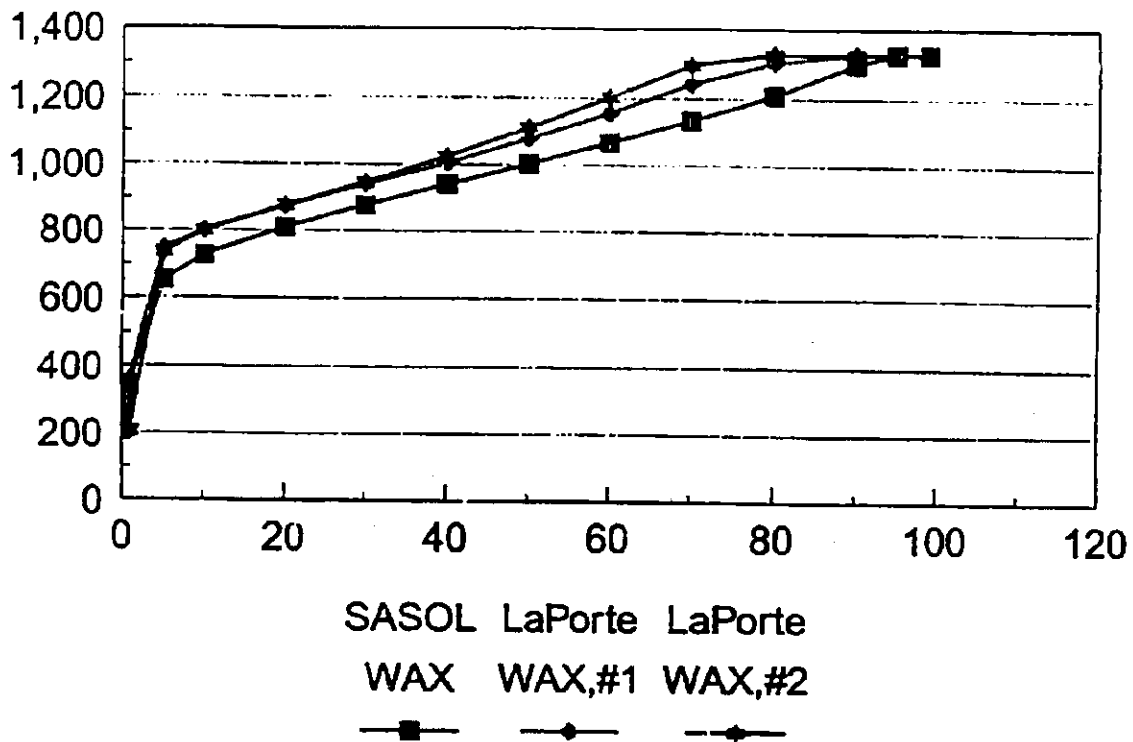


FIGURE 14

WAX CONVERSION - CATALYST TO OIL RATIO
CONVERSION, WT. %

