SELECTIVE CATALYTIC CRACKING OF FISCHER-TROPSCH LIQUIDS TO HIGH VALUE TRANSPORTATION FUELS. QUARTERLY TECHNICAL PROGRESS REPORT NO. 5, FIRST QUARTER FISCAL YEAR 1993, OCTOBER 1, 1992--DECEMBER 31, 1992

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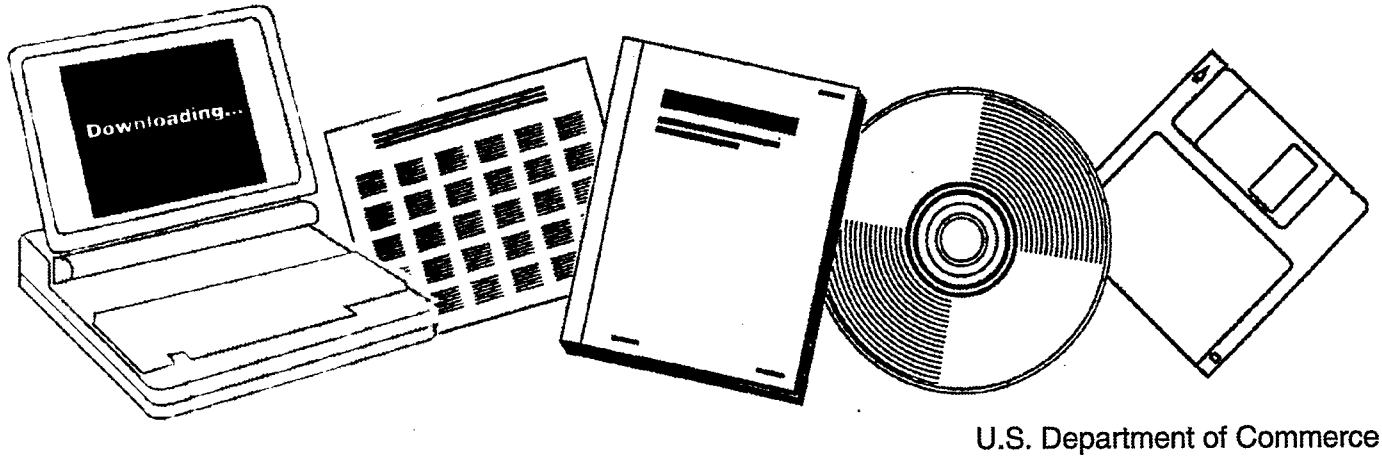
RESEARCH AND DEVELOPMENT DEPT

1995



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

REPORT NO. 25

QUARTERLY TECHNICAL PROGRESS REPORT

FOR

FIRST QUARTER FISCAL YEAR, 1993

(October 1, 1992 - December 31, 1992)

PROJECT MANAGER: R. D. HUGHES

PRINCIPAL INVESTIGATOR: W. J. REAGAN

WORK PERFORMED UNDER CONTRACT NO. DE-AC22-91PC90057

FOR

U.S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
PITTSBURGH, PENNSYLVANIA

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DISCLAIMER

TECHNICAL STATUS

This technical status report is being transmitted in advance of DOE review, and no further dissemination or publication will be made of this report without prior approval of the DOE Project/ Program Manager.

EXECUTIVE SUMMARY

Amoco Oil Company, under a contract with the United States Department of Energy, is investigating a selective catalytic cracking process to convert the Fischer-Tropsch gasoline and wax fractions to high value transportation fuels. This report describes the work in the first quarter, fiscal year, 1993, the sixth quarter of the two year project.

Task 1, Project Management Plan. The plan has been accepted by the Project Manager DOE/PETC. This report contains the most current and accurate information and projections of the scope of work, schedules, milestones, staffing/manpower plan and costs.

Task 2, Preparation of Feedstocks and Equipment Calibration. The work in this area is complete. The wax feedstock for this program, a commercial sample of Fischer-Tropsch product from Sasol, is a high melting point,(>220°F), high boiling range (50% boiling above 1000°F), largely paraffinic material.

Task 3, Catalytic Cracking Catalyst Screening Program. The wax feedstock readily converts over conventional fluid catalytic cracking (FCC) catalysts (85%+ conversion) to high yields of C_4- gas (high in propylene and C_4 olefins) and gasoline (C_5-430°F). The HZSM-5 zeolite catalyst has the highest isobutylene and isoamylenes yields among the catalysts tested to date. However, the production of propylene is too high. A series of five sequential MYU wax cracking tests on the same coked HZSM-5 catalyst show that the wax conversion declines from ~80% to ~65%. However, there are only small changes in product selectivities as a function of coke deposition. The wax cracking tests of a series of low zeolite (Beta and Y) catalysts show that conversion decreases with the lower zeolite levels, as expected. There is considerable scatter in the conversion values that may suggest a feedstock bypassing problem with the fixed bed unit. The Beta catalyst and a matrix only sample have higher isobutylene yields than the Y zeolite sample.

Task 4, Pilot Plant Tests. There was no activity in this area during this Quarter.

Task 5, Preparation of C_5-C_8 Ethers. A new ether synthesis test unit was commissioned for this section of the project. The project plan will be modified to eliminate the alcohol synthesis portion of this task. The primary feedstocks for these etherification runs are the light naphthas obtained from the pilot plant catalytic cracking runs with the Fischer-Tropsch wax. The initial runs with an Amberlyst 15 etherification catalyst and a light naphtha (200°F- fraction) show variable (30-90%) conversion of the reactive C_5 - C_6 isoolefins to ethers. The reaction products from these runs have a significant yellow color. This could be a serious product quality issue.

The catalytic cracking test results from both the small scale test unit and the pilot plant indicate that the wax feedstock readily converts to C_4- gas and gasoline. These tests suggest that very mild process conditions and low activity catalysts are needed to lower the overall wax

conversion. The target light olefin yields vary with catalyst type and the process conditions.

BACKGROUND

Fischer-Tropsch (F-T) synthesis technology produces liquid hydrocarbons from synthesis gas (hydrogen and carbon monoxide) derived from the gasification of coal. Domestic supplies of both high- and low- rank coals are extensive and represent a strategic resource to supplement dwindling petroleum reserves. The Fischer-Tropsch technology has been practiced commercially at Sasol in South Africa since the mid-1950's. The F-T liquid product consists of a broad range of normal paraffins (C_5-C_{30}) and a small quantity of oxygenates and olefins. The gasoline range C_5-C_{12} product fraction consists of 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. There are many studies on the upgrading of these F-T liquids. These products are further treated by conventional petroleum processes, such as hydrotreating, reforming and catalytic cracking to produce conventional gasoline and distillate fuels. There are no reported studies of the catalytic cracking processing of F-T liquids to produce C_3-C_8 olefins as feedstocks for the synthesis of gasoline range ethers and alcohols. This is the primary focus of this project.

Fuel oxygenates, particularly alcohols and ethers, represent a potential solution to environmental concerns due to conventional automotive fuels. 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. 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.

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

PROGRAM OBJECTIVES

The 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 C_4-C_8 product olefins would then be etherified with methanol to prepare the target ethers. Alcohols will be produced by direct hydration of C_3-C_8 product olefins. The gasoline and distillate products are also expected to be superior to

conventional fuels because of the unique combination catalysts to be used in this process.

PROJECT DESCRIPTION

A two year, multi-task program will be used to accomplish the objective to develop a selective catalytic cracking process to produce premium transportation fuels, including ethers and alcohols from Fischer-Tropsch gasoline and wax products.

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. Suitable mixtures of Fischer-Tropsch waxes (C_{18}+) and light olefin components (C_5-C_{12}) will be prepared to simulate full range F-T liquids without the premium distillate products. The necessary analytical equipment will be calibrated for the detailed identification of C_4-C_8 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 C_5-C_8 Ethers and C_3-C_8 Alcohols. These products will be prepared from the pilot plant C_3-C_8 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.

The DOE reporting requirements for this contract will be followed in all cases. This includes all project status, milestone schedule, and cost management reports. A final detailed project report will be submitted upon completion of the contract.

RESULTS AND DISCUSSION

During this quarter, project activities center on Tasks 3 and 5 of the contract.

TASK 1. Project Management Plan.

The draft Project Management Plan has been accepted by the Program Manager at DOE/PETC. This completes Task 1 of the contract. This document contains the most current and accurate information and projections of the scope of work, schedules, milestones,staffing/manpower plan and costs. This plan contains the following sections:

— Management Plan
— Technical Plan
— Milestone Schedule/Manpower Plan
— Cost Plan
— Notice of Energy RD&D Project

The technical approach builds from small scale tests of the selective cracking concept to pilot plant scale verification of product yields. The screening test results will serve as a preliminary milestone of this process scheme. An assessment of project directions, scope of work and objectives after this milestone will be appropriate.

TASK 2. Feedstock Characterization.

The wax feedstock has been analyzed by various analytical methods. The boiling point and the carbon number distributions of the largely paraffinic material are consistent with literature reports of similar Fischer-Tropsch samples. No further work in this area is planned.

TASK 3. Screening Catalytic Cracking Tests.

Activities under Task 3 of the contract continue on the small scale test unit, the MYU (Micro Yields Unit). Several pilot plant runs of the catalytic cracking of Fischer-Tropsch wax show very high conversion levels. (>85-90%) In addition, the product olefin yields depend to a great extent upon the zeolite component of the cracking catalyst. The HZSM-5 zeolite catalysts have the highest yields of the target olefins. These products occur at the expense of gasoline yield. The details of these runs have been presented in earlier reports. The Monthly Technical Status Report for July, 1992, Report No. 17, discusses the evaluation of different types of HZSM-5 catalysts. These tests occur at the normal small scale (MYU) test conditions, where the wax feedstock and catalyst contact occurs for 50 seconds. The test run ends with catalyst and product recovery. The coke yields from these HZSM-5 catalysts are very low (<0.2 wt%). Coke deposition is a major contributor to the rapid (but regenerable) catalyst deactivation in the fluid catalytic cracking process. 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 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 1 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 (1,2) for the deactivation of cracking catalysts. Two different measurements of conversion ("MYU" and "SD") occur in Figure 1. The MYU conversion value is the normal calculated value of conversion: the sum of product C_4- gas, gasoline and coke, that has been used in earlier MYU studies. Note that the MYU conversion value for Test No. 5 does not follow the conversion decrease and probably is in error. However, the "SD" conversion values do decrease continuously with test number. The "SD" conversion value comes from a GC simulated distillation of the liquid products. Both methods are acceptable and have various positive and negative features. The "SD" method also presents a complete weight versus boiling point breakdown of the liquid product above the gasoline boiling range. This is useful for the determination of distillate yields, another important catalytic cracking product.

Figure 2 indicates that the two conversion calculation methods do not have identical conversion numbers for the same five multiple HZSM-5 runs in this study. There is a systematic offset between the two sets of values. Further effort will be required to resolve these differences.

It is of interest to compare the present results for the sequential or multiple HZSM-5 tests with the historical values for the same or similar (other commercial types or repeated steamings of the same starting material) HZSM-5 catalysts. This is part of our on-going efforts at quality control and maintenance of MYU test precision. Figure 3 shows that the conversion value (80.2%) for Run #1 of the present multiple test is on the low side of the other historical conversion values of MYU tests of HZSM-5 samples (88.2%,+/- 4.7%). The comparison of wax conversion values among catalysts with the MYU test must be done with caution.

Figures 4-8 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 5; total C_3+C_4, Figure 8) selectivity differences between these two types of tests for the HZSM-5 catalysts are small. However, the "multiple" run tests do show lower gasoline yields, Figure 7, lower isoamylenes yields, Figure 6, and higher propylene yields, Figure 4, than the individual test runs. The large differences between the isoamylene yields for the two sets of tests (Figure 6) suggests that the "multiple" runs may have a systematic error in this measurement. Further testing would be required to clearly distinguish these effects. However, 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.

The screening of other zeolite samples for catalytic cracking of Fischer-Tropsch wax will continue.

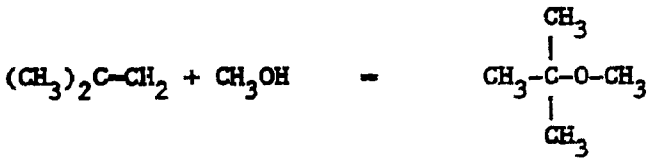
Several pilot plant runs of the catalytic cracking of Fischer-Tropsch wax show very high conversion levels. (>85-90%) The details of these runs have been discussed in earlier reports. (see Quarterly Technical Status Reports for the First and Second Quarter Fiscal Year, 1992, Report Nos. 10 and 13) The type and amount of zeolite in the catalyst have major impacts upon the wax conversion. These high conversion levels may not provide the optimum light olefin yields. A series of FCC catalysts with low (~10%) zeolite content should address this issue with lower catalytic activity. The details of the preparation and initial characterization of these samples are available in the September, 1992 Monthly Progress Report. The wax conversion levels and product selectivities of these samples in the small scale catalytic cracking test unit, the MYU, are under study.

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 880°F. Figure 9 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%. At the lower wax conversion levels, the fixed bed test unit may have feedstock channelling or bypassing problems. These physical effects will influence the reproducibility of the test. Figure 10 shows that the two methods of conversion calculation are in reasonable agreement. This issue of "catalyst activity" or wax conversion level will require further study.

The product selectivity measurements from these MYU tests are also important to the full characterization of these catalyst samples. Figures 11-20 show various product yields for the four catalyst samples as a function of overall wax conversion. In most cases, it is difficult to see clear trends that would distinguish between these catalysts. There is considerable scatter in the test results. Figures 12, 14 and 16, the yields of propylene, isobutylene and isoamylenes, show a reasonable fit of all points (R^2 ~ 0.9), without regard to sample type. Another factor is that the lower zeolite content samples are generally at a lower overall conversion than the higher zeolite content sample. This impedes a constant conversion comparison between the samples. The isobutylene yields, Figures 13, 14, do suggest 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. Further MYU testing of these samples will be needed before pilot plant tests of these catalysts are scheduled.

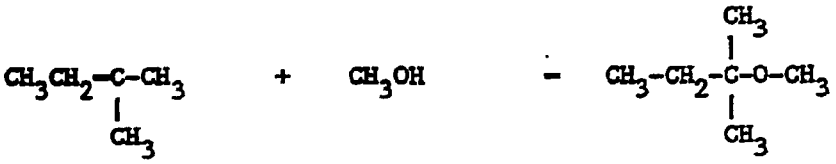
Work under Task 5 of the contract is under way. The initial focus of this ether synthesis activity is to commission a new test unit. AU 109, a fixed bed, high pressure micro-unit, will be used in place of the larger test unit, AU 6. The limited availability of the product naphthas from pilot plant wax cracking runs is the reason for this change from the project plan. In addition, the project plan will be modified to eliminate the alcohol synthesis portion of Task 5. This change reflects time and manpower constraints.

The DOE COR will be notified separately regarding the deletion of this component of Task 5. Relevant additional work shall be added to the project plan, in consultation with the DOE COR, to substitute the deleted portion of work in Task 5. Further, if such substitution results in a decrease in total project costs, the DOE COR shall be so notified. A brief review of the ether synthesis task objectives and ether synthesis chemistry is desirable. Several types of ethers are now commercially produced and used as gasoline blending components. (3) Recent studies of methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME) suggest that they may reduce carbon monoxide automotive emissions, have high blending octane ratings, R+M/2, (MTBE-108, TAME- 102), and have low Reid vapor pressures, (MTBE-8-10, TAME-1). MTBE has attracted the most attention in recent years. The growth rate for MTBE production could reach 25% per year by 1995. (4,5) 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:



isobutylene methanol MTBE.

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



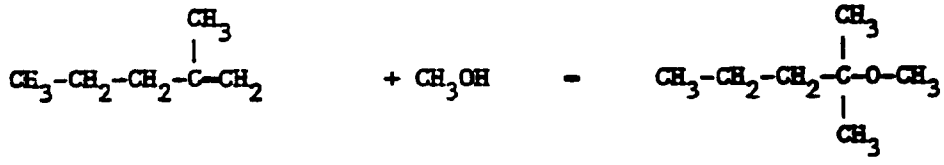
isoamylene methanol TAME

These etherification reactions were discovered in 1907. (6) Detailed catalysis studies of these reactions have only recently appeared in the scientific literature. (7) 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 (7) 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 C_6 olefins that are also present in significant quantities in fluid catalytic cracking product naphthas. The Etherol process (8) produces a mixed ether product from C_4-C_7 reactive iso-olefins in naphthas. One report (9) provides some information about the reaction of

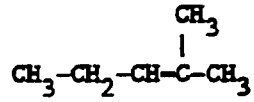
C_6 iso-olefins with methanol to produce the higher ethers, MTHE's, methyl tertiary hexyl ethers. Several C_6 olefins can react with methanol to produce three different THME ethers:

Scheme 1:



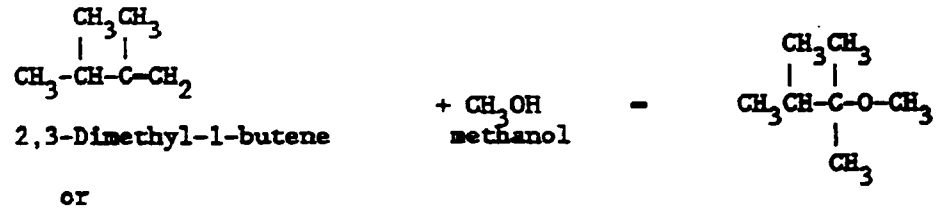
2-Methyl-1-pentene + methanol → 2-Methyl-2-methoxypentane

or



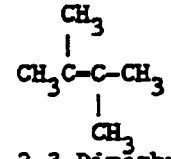
2-Methyl-2-pentene

Scheme 2:



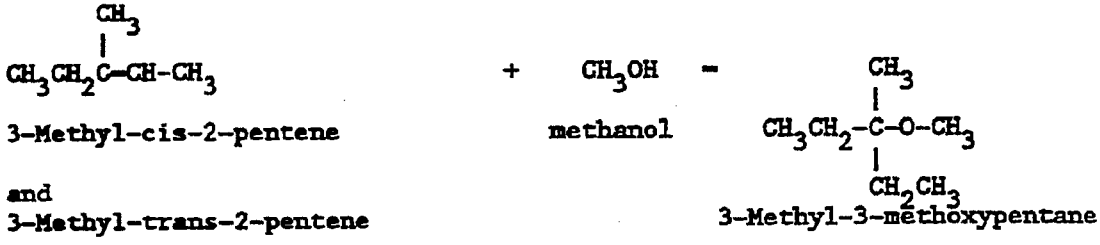
2,3-Dimethyl-1-butene + methanol → 2,3-Dimethyl-2-methoxybutane

or



2,3-Dimethyl-2-butene

Scheme 3:

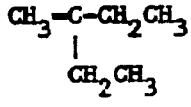


3-Methyl-cis-2-pentene

and

3-Methyl-trans-2-pentene

or



2-Ethyl-1-butene

methanol

3-Methyl-3-methoxypentane

The reactions of these C_6 olefins to the THME ethers can contribute significantly to the total ether yields from the FCC naphthas. Since the reactions of isobutylene and methanol to form MTBE are 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 21 shows the comparison of TAME yields (conversion of isoamylene to TAME: moles TAME out/moles isoamylene in*100) from the new unit, AU-109, with results from the larger unit, AU-6. 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. There is good agreement for the ether yields between the units. 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 feedstocks for these etherification studies are the light naphthas obtained from the pilot plant catalytic cracking runs with the Fischer-Tropsch wax. These details of these runs are available in previous reports. (see Quarterly Technical Status Reports, First and Second Quarters, Fiscal Year, 1992, Reports Nos. 10 and 13) The liquid products from two pilot plant runs, 939-01 and 939-02, 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.

The weight percent of each fraction is listed below:

Fraction Identification	Weight Percent Recovery	API Gravity @ 60°F
#1 200°F-	48.3	75.8
#2 200-430°F	40.7	47.7
#3 430°F+	10.3	23.8
Sample Loss	0.7	

This liquid product represents a high (~93%) wax conversion run in the catalytic cracking pilot plant. The Y faujasite catalyst, used in these runs, does not yield the maximum olefin concentrations. However, this sample is representative of the type of gasoline products from Fischer-Tropsch wax catalytic cracking. Figure 22 shows the simulated distillation curves for the three samples. The fraction of major interest, 200°F-, has some material boiling higher than 200°F,(12%), but is suitable as an etherification feedstock. Table I presents the detailed composition of this light naphtha. The carbon number distributions of the various hydrocarbon types center on C_6 for this particular naphtha. The reactive isoamylenes, 2-Methyl-2-butene and 2-Methyl-1-butene for TAME synthesis and the reactive C_6 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 sample and methanol are the feedstock for a new series of etherification runs at the same process conditions for the earlier 2-Methyl-2-butene/methanol tests. Due the limited availability of the gasoline, only two reaction temperatures are available. Table II shows the major product analyses of these light naphtha/methanol runs. Each run represents a weight balance period of at least 6 hours. The first sample at each temperature is a line-out period that is not representative of the other three balances. There is good agreement in the product analyses for each test condition, except for the variability in the methanol analyses. In addition, the methanol and isobutylene components are not completely separated on the capillary GC column. This situation does not allow for the quantification of the production of MTBE from the reaction of methanol and the minor amount of isobutylene in the naphtha sample. A summary of the conversion of the various C_5 and C_6 iso-olefins to their respective methyl ethers, Table III, 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. (7,9) Further analyses of these results will be needed to determine the extent of olefin isomerization, which is a competing reaction to etherification.

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 C_{10}+ 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. Another possible solution is to distill the ether product to remove the high molecular weight color bodies. The THME ethers boil at the high end of the product gasoline fraction and it is not clear whether such a separation is feasible.

The blending octane numbers for several of these mixed ether-gasoline fractions will be determined. Several additional etherification process runs, especially with the hydrogenation catalyst and hydrogen gas co-feed, are also planned.

CONCLUSIONS

Task 1 of the contract, the Project Management Plan, and Task 2, Feedstock Characterization are complete.

The catalytic cracking screening tests of the wax feedstock under Task 3 (small scale) and the etherification of light naphtha fractions under Task 5 (pilot plant scale) of the contract are underway.

A series of sequential wax cracking tests on the small scale MYU unit with the HZSM-5 catalyst shows that wax conversion decreases with coke deposition but product selectivity changes are small. The wax cracking tests of a series of low (~10%) zeolite FCC catalysts suggest that wax conversion roughly correlates with zeolite content, as expected. The typical product selectivity trends for these samples are similar to the more conventional FCC catalysts with 35-40% zeolite levels. In this series of tests, the low zeolite Beta and matrix only catalysts have higher olefin selectivity than the Y zeolite catalysts.

The etherification studies of the light naphtha fractions from the pilot plant wax conversion runs indicate that the C_5 and C_6 isoolefins in the naphtha react with methanol to form ethers at widely different conversion levels, 30-90%. The ether product fraction from these tests have a yellow color. This color may be a product quality issue.

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ACKNOWLEDGEMENT

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NOTICE

Prepared by
Amoco Oil Company (Amoco Corporation)
Naperville, Illinois

QUARTERLY MANPOWER REPORT

For FIRST QUARTER FISCAL YEAR, 1993

(October 1, 1993 - December 31, 1993)

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

IDENTIFICATION NUMBER: DE-AC22-91PC90057

START DATE: June 1, 1991
COMPLETION DATE: May 31, 1993

PARTICIPANT NAME AND ADDRESS:

AMOCO OIL COMPANY
P. O. BOX 3011
NAPERVILLE, ILLINOIS 60566

Manpower In Hours by Task

Name	1	2	3	4	5	6	7	Total
W. J. Reagan	0	0	32	169	240	20	0	461
D. M. Washecheck	0	0	0	0	0	0	0	0
R. D. Hughes	0	0	2	5	13	0	0	20
Other Professionals	0	0	0	0	0	0	0	0
Technical Support	0	0	53	227	282	0	0	562
Secretarial	0	0	6	14	0	0	0	20
Total Hours	0	0	93	415	535	0	0	1063

TABLE I

HYDROCARBON COMPOSITION OF 200°F- NAPHTHA FRACTION
PILOT PLANT RUNS 939-01, 02

	Weight%	Reactive Iso-Olefins, Wt%
Total Paraffins:	6.69	
C_4	0.18	C_5
C_5	0.93	2-methyl-1-Butene: 1.25
C_6	4.03	2-methyl-2-Butene: 4.26
C_7	1.45	
C_8	0.08	
Total Iso-Paraffins:	42.71	C_6
C_4	0.32	2,3-dimethylbutene: 0.8
C_5	3.77	2-methyl-1-pentene: 2.35
C_6	22.94	2-methyl-2-pentene: 4.01
C_7	13.87	3-methyl-trans-2-pentene: 2.49
C_8	1.82	3-methyl-cis-2-pentene: 3.98
Total Aromatics:	1.74	
C_6	0.34	
C_7	1.33	
C_8	0.05	
Total Naphthenes:	3.96	
C_5	0.05	
C_6	1.23	
C_7	1.92	
C_8	0.75	
Total Olefins:	44.51	
C_3	.01	
C_4	1.25	
C_5	8.71	
C_6	23.88	
C_7	10.36	
C_8	0.3	

TABLE II

AW-109 ETHERIFICATION RUNS
200 PSIG, AMBERLIST 15, 2.9 GRAMS
FEED RATE: METHANOL, 1.37 G/HR, 200°F- NAPHTHA, 5.5 G/HR

Run No.	Feed + MeOH	024-1	024-2	024-3	024-4	024-5	024-6	024-7	024-8
Date									
Temp		125°F	125°F	125°F	125°F	150°F	150°F	150°F	150°F
Wt% Product:									
C4-5 Olefins:									
1C4=	0.22761	0.066	0.44	0.408	0.443	0.441	0.477	0.467	0.466
3M1BUTENE	0.10959	0.066	0.101	0.094	0.104	0.101	0.103	0.103	0.104
2M1BUTENE	1.05375	0.324	0.161	0.146	0.153	0.121	0.108	0.109	0.101
2M2BUTENE	3.59118	4.37	2.719	2.403	2.247	1.717	1.267	1.237	1.208
C6 Olefins:									
3M1PENTENE	0.79242	0.646	0.774	0.769	0.791	0.789	0.795	0.81	0.796
23DMBUTENE	0.69126	0.143	0.293	0.296	0.313	0.175	0.116	0.113	0.115
4Mt2PENTENE	0.30348	0.278	0.334	0.326	0.352	0.339	0.341	0.361	0.353
4Mo2PENTENE	1.07904	0.931	1.048	1.047	1.087	1.062	1.072	1.094	1.083
2M1PENTENE	1.98105	0.406	0.657	0.667	0.701	0.385	0.253	0.25	0.245
HEXENE-1	0.6744	0.503	0.659	0.664	0.682	0.671	0.671	0.684	0.675
tHEXENE-3	1.48682	1.302	1.443	1.454	1.488	1.462	1.474	1.497	1.481
cHEXENE-3	2.28453	2.198	2.252	2.271	2.316	2.276	2.291	2.331	2.3
2M2PENTENE	3.38043	2.65	2.636	2.668	2.731	1.991	1.733	1.724	1.75
tHEXENE-2	0.06744	0.05	0.063	0.064	0.067	0.067	0.07	0.071	0.067
3Mt2PENTENE	2.09907	1.514	1.615	1.635	1.677	1.366	1.278	1.299	1.285
cHEXENE-2	1.22235	1.067	1.209	1.22	1.238	1.216	1.23	1.247	1.232
3Mo2PENTENE	3.35514	2.955	2.617	2.654	2.694	2.369	2.329	2.402	2.331
Oxygenates:									
MeOH	15.7	0	10.586	10.353	9.614	9.439	9.953	8.593	9.535
MTBE	0	0.119	0.362	0.379	0.396	0.392	0.407	0.401	0.394
TAME	0	3.452	4.193	4.264	4.027	5.251	5.271	5.356	5.299
TMME1	0	0.194	0.557	0.563	0.556	0.841	0.978	1.002	0.981
TMME2	0	1.341	2.984	2.931	2.929	4.202	4.771	4.937	4.815
TMME3	0	0.786	2.941	2.361	2.353	3.122	3.361	3.397	3.42
nHEXANE	3.39729	16.19	4.792	4.708	4.207	4.382	3.552	3.53	3.449
TOLUENE	1.127091	1.036	1.132	1.154	1.16	1.132	1.146	1.165	1.154
2MPENTANE	9.9474	9.229	9.726	9.775	10.027	9.884	9.968	10.163	10.064
3MPENTANE	6.909228	7	6.877	6.899	7.039	6.939	6.96	7.095	7.011

TABLE III

REACTIVE ISO-OLEFINS CONVERSION TO ETHERS

Reaction Temperature
(Averages of Three Weight Balance Tests--Table II Conditions)

Iso-olefin Component	125°F	150°F
C_5	Wt%	Wt%
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

WR/lkv/93135
7/16/93

FIGURE 1

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

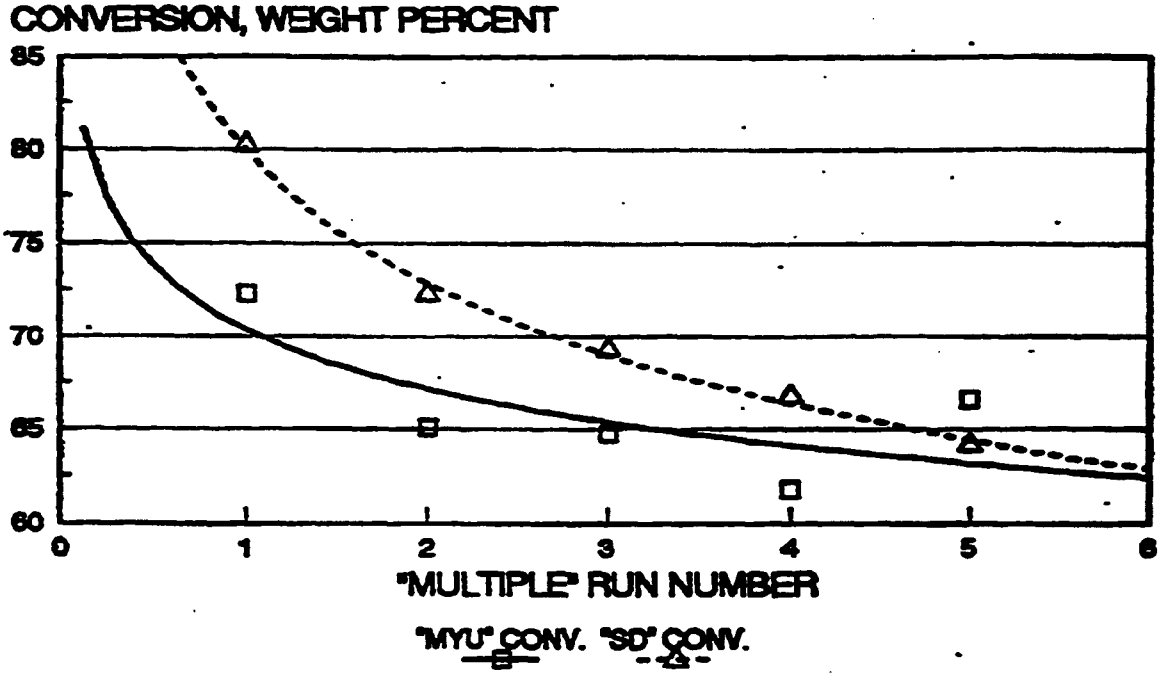


FIGURE 2

FISCHER-TROPSCH WAX CATALYTIC CRACKING:MYU RUNS
COMPARISON OF CONVERSION CALCULATIONS

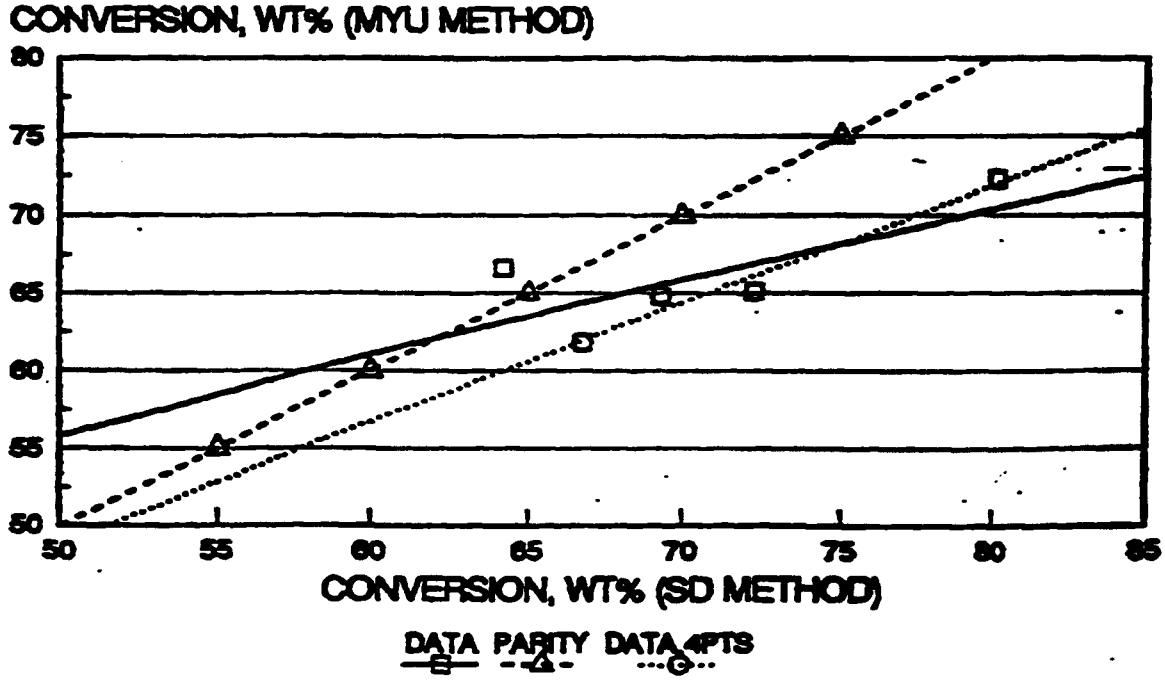
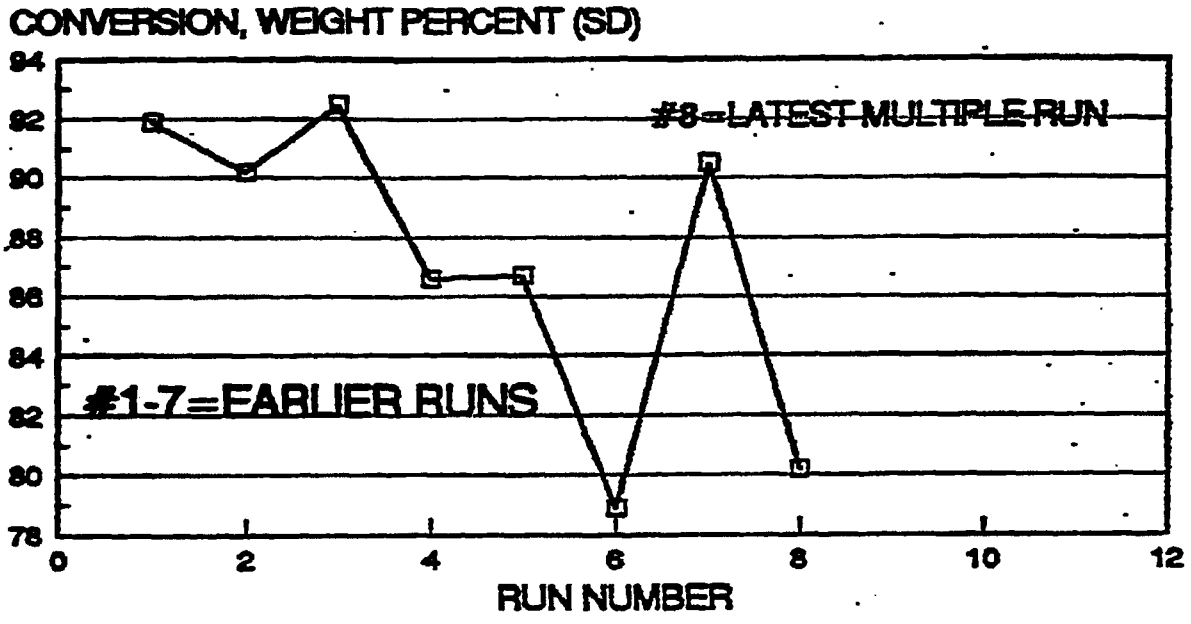


FIGURE 3

FISCHER-TROPSCH WAX CATALYTIC CRACKING:MYU RUNS
WAX CONVERSION OF ALL HZSM-5 CATALYST RUNS



ALL HZSM-5 TESTS AT 880oF, C/O=0.2

FIGURE 4

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

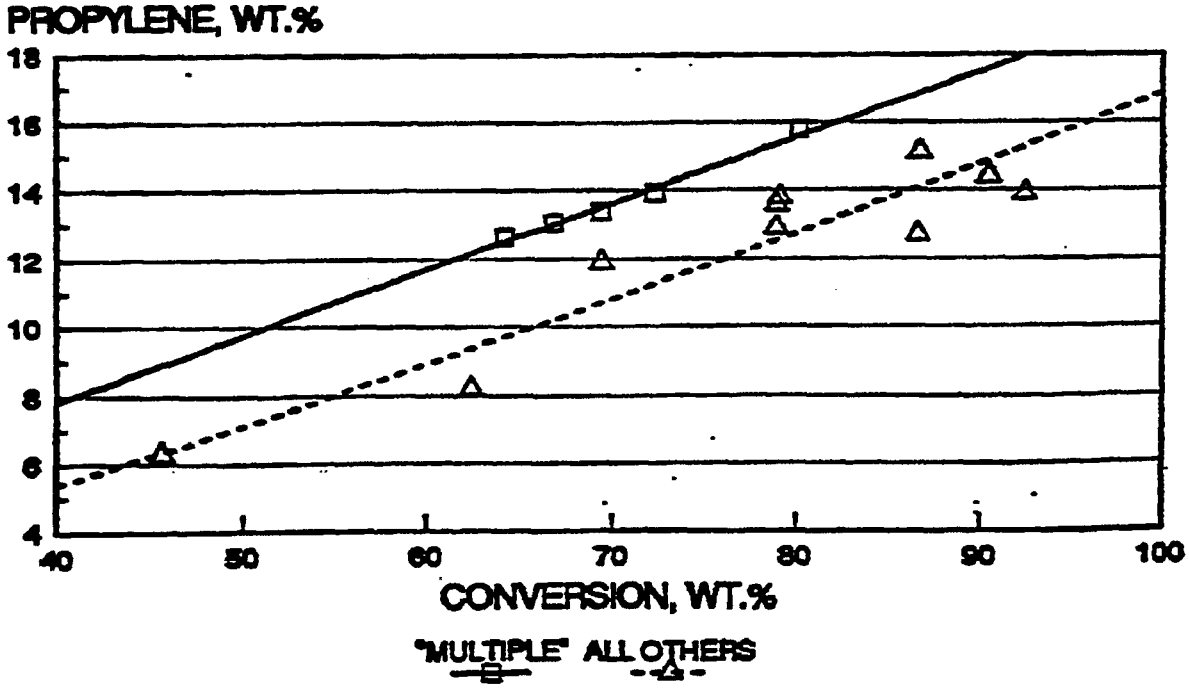


FIGURE 5

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

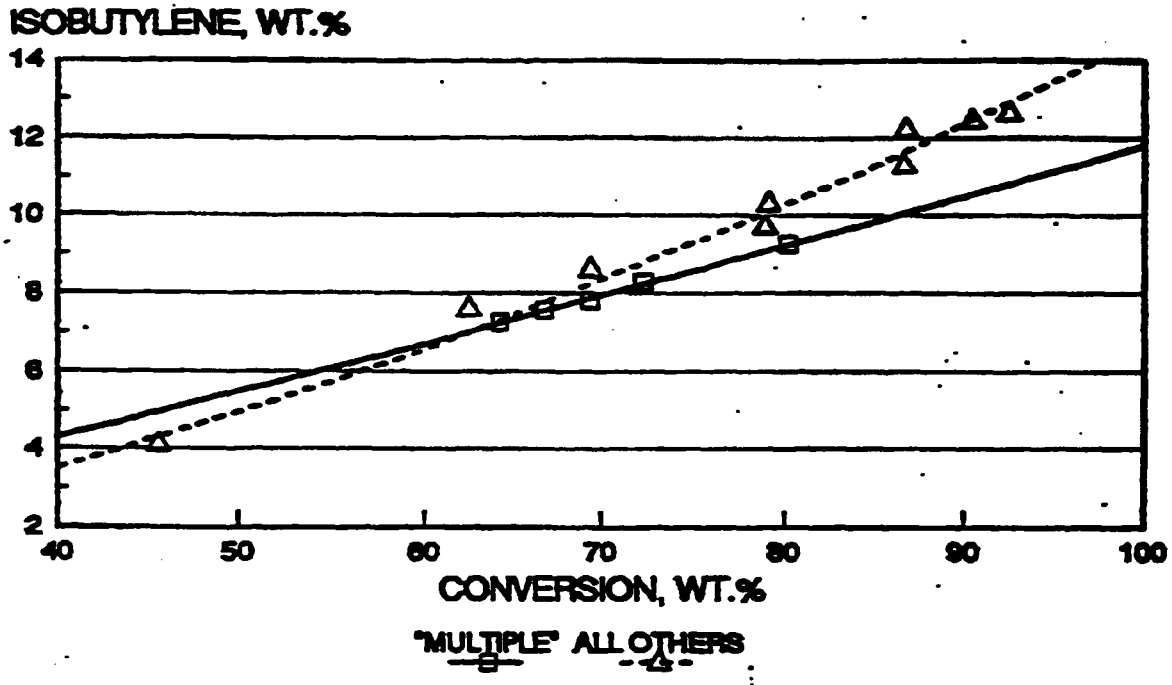


FIGURE 6

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

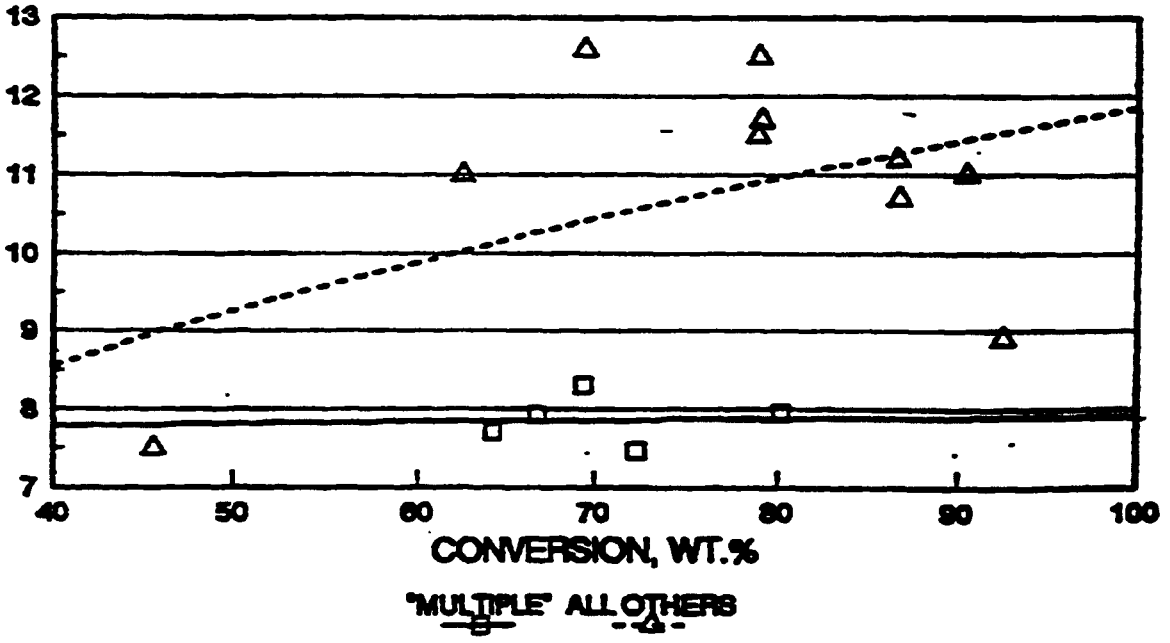


FIGURE 7

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

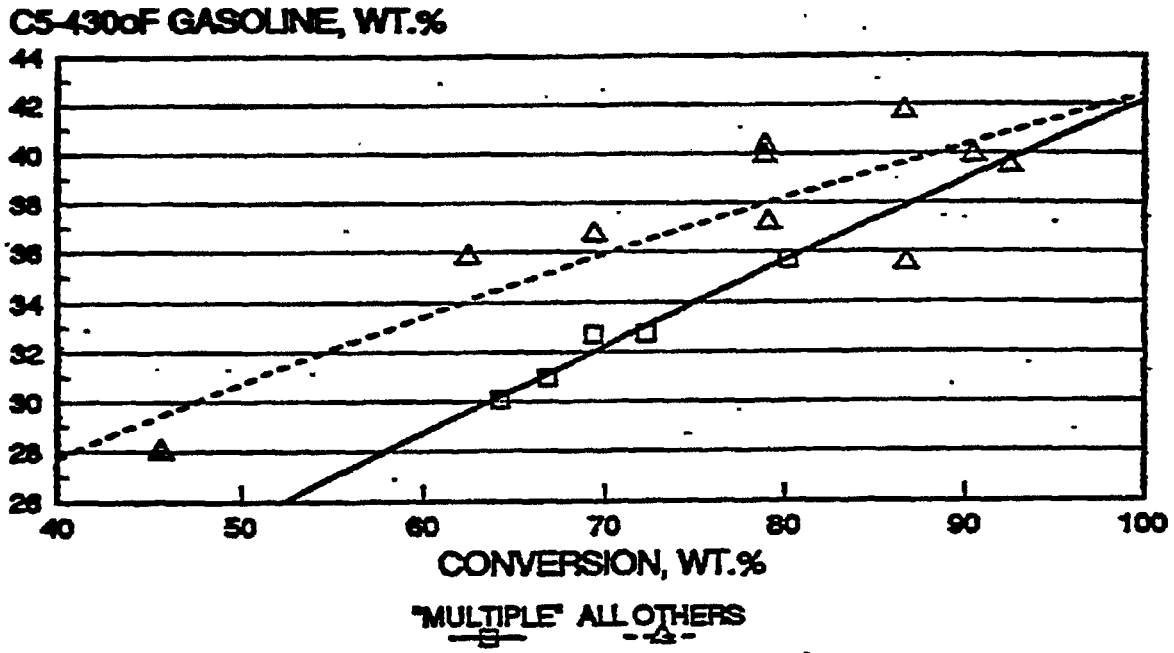


FIGURE 8

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

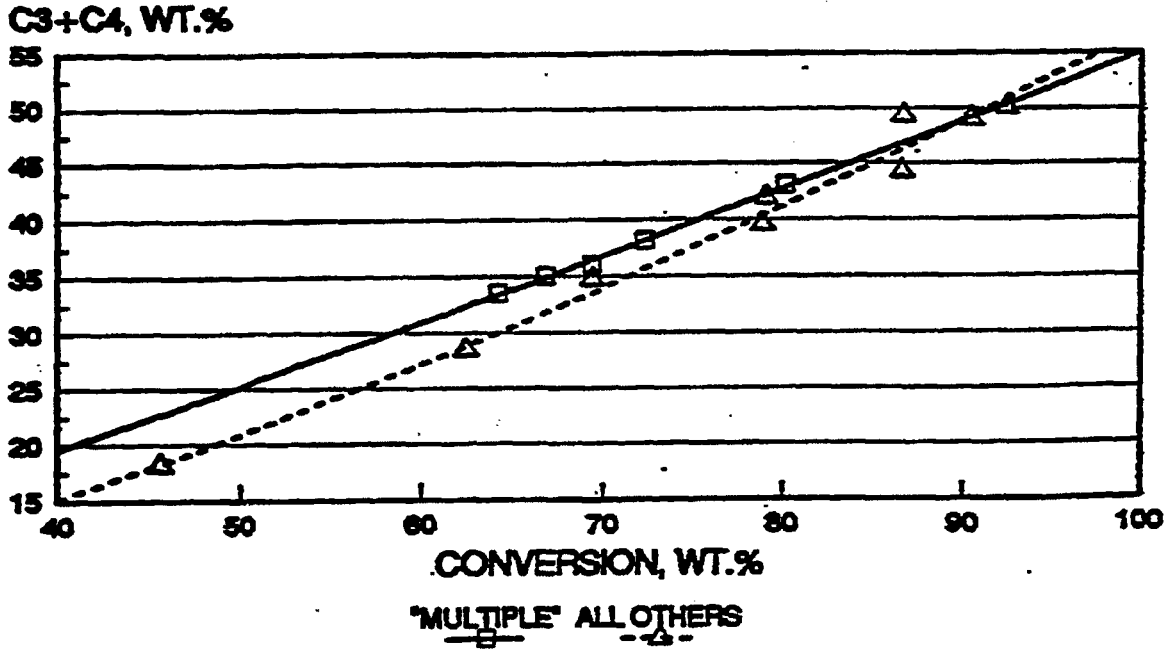


FIGURE 9

FISCHER-TROPSCH WAX CATALYTIC CRACKING

WAX CONVERSION STUDIES - LOW ZEOLITE CATALYSTS

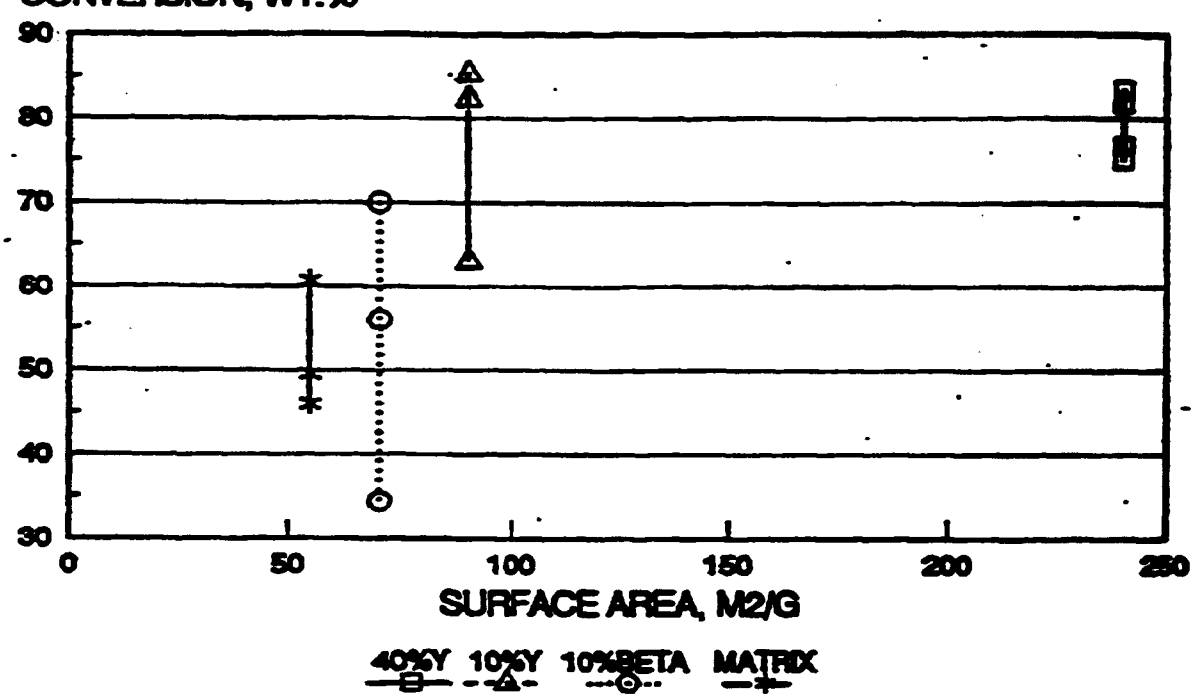


FIGURE 10

FISCHER-TROPSCH WAX CATALYTIC CRACKING

CONVERSION CALCULATIONS - LOW ZEOLITE CATALYSTS

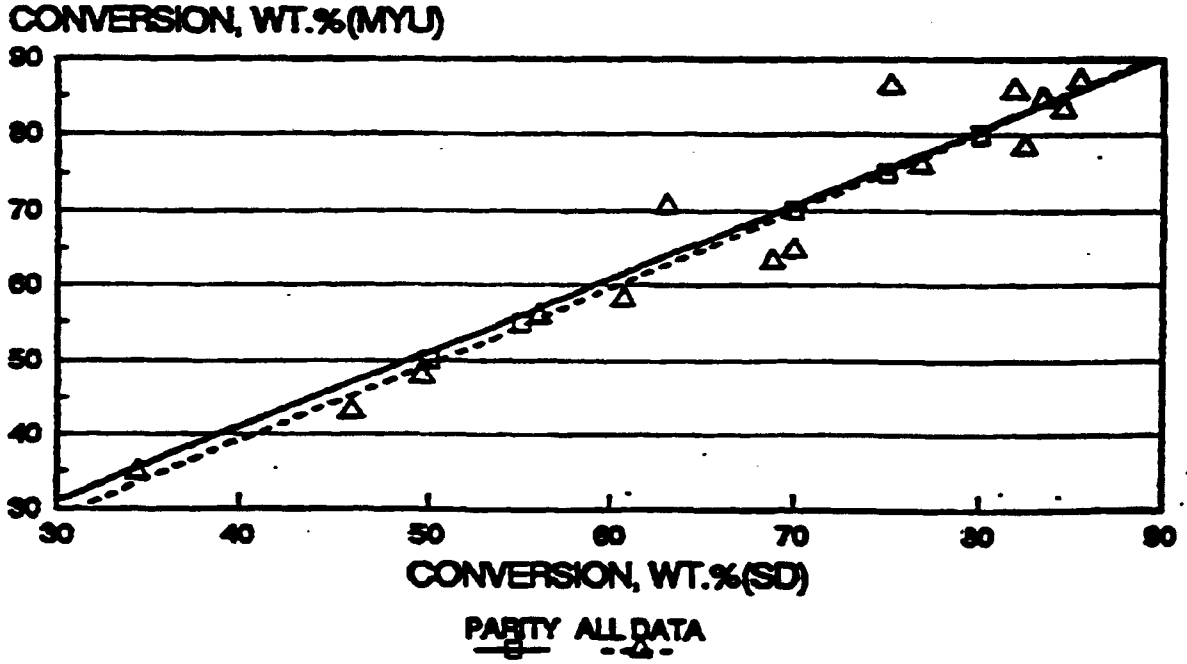


FIGURE 11

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

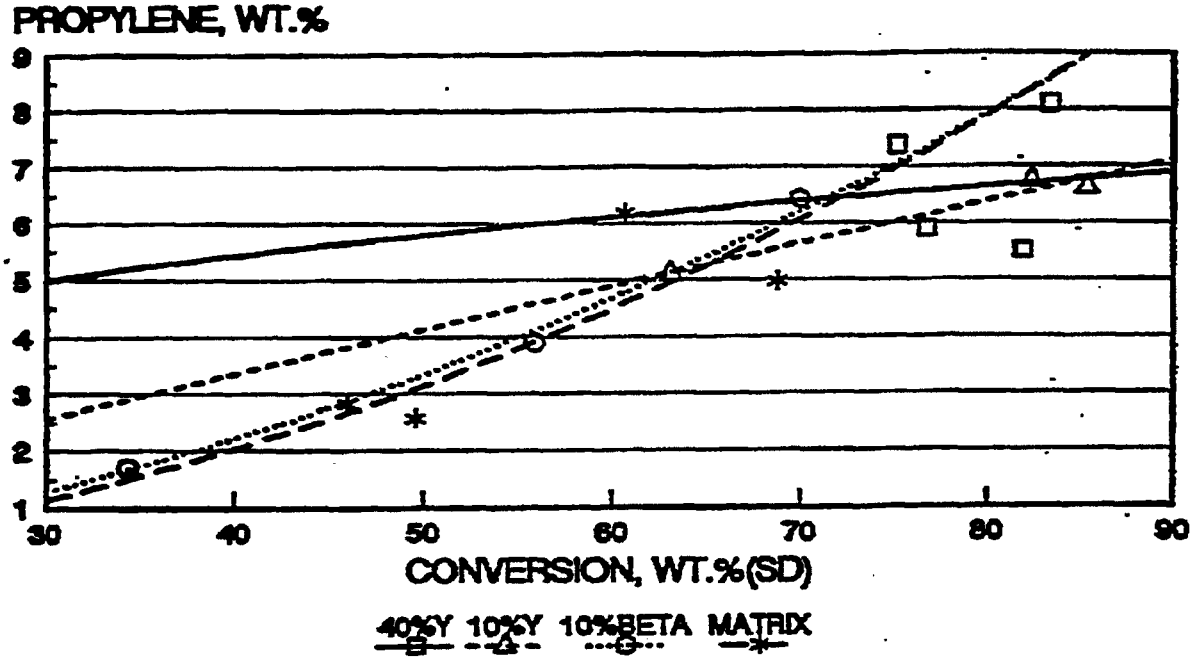


FIGURE 12

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

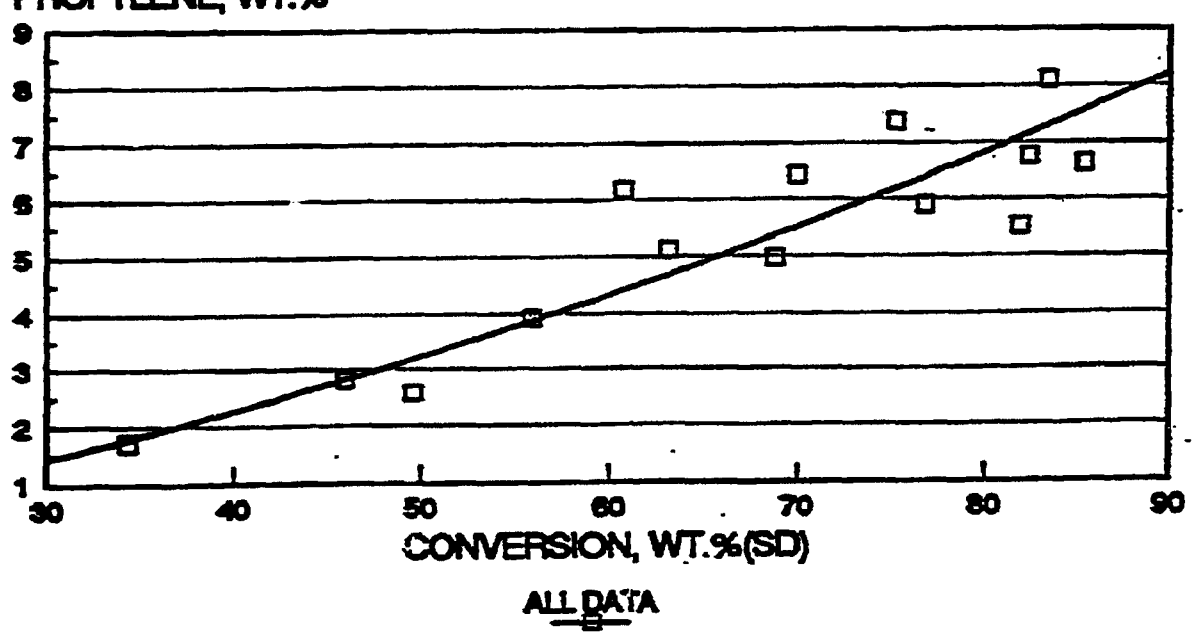


FIGURE 13

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

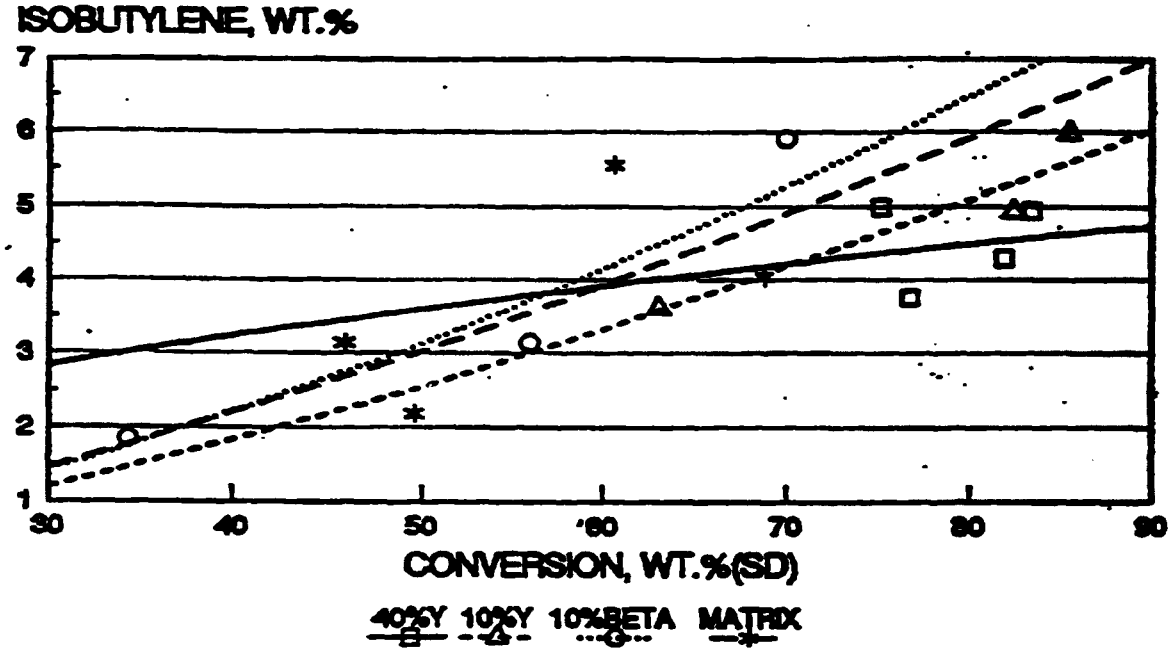


FIGURE 14

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

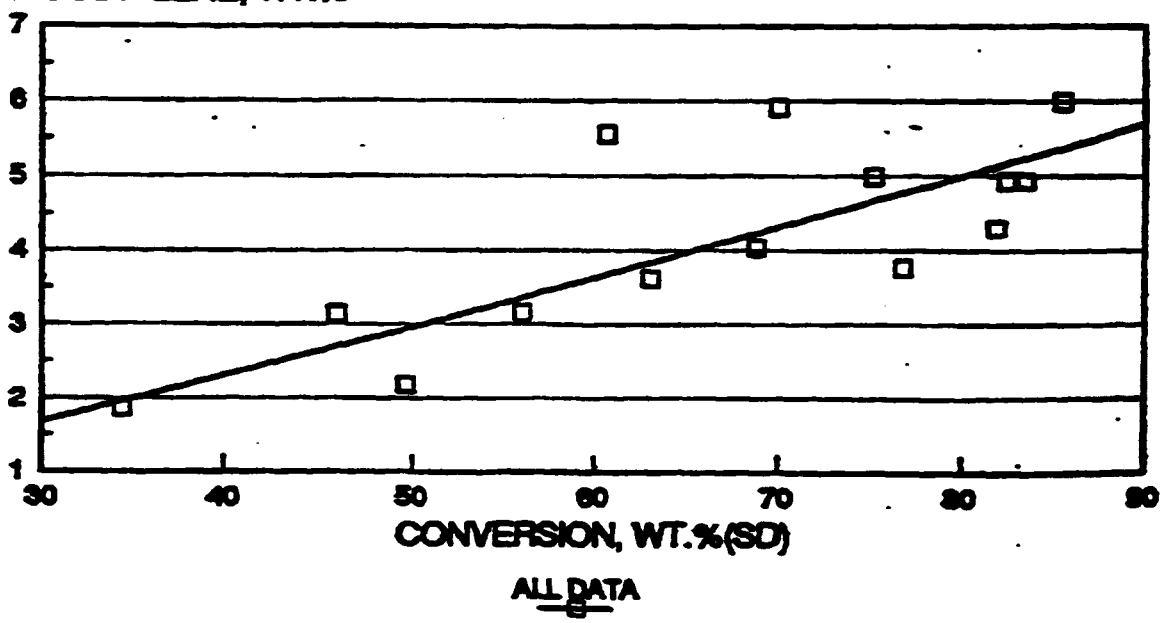


FIGURE 15

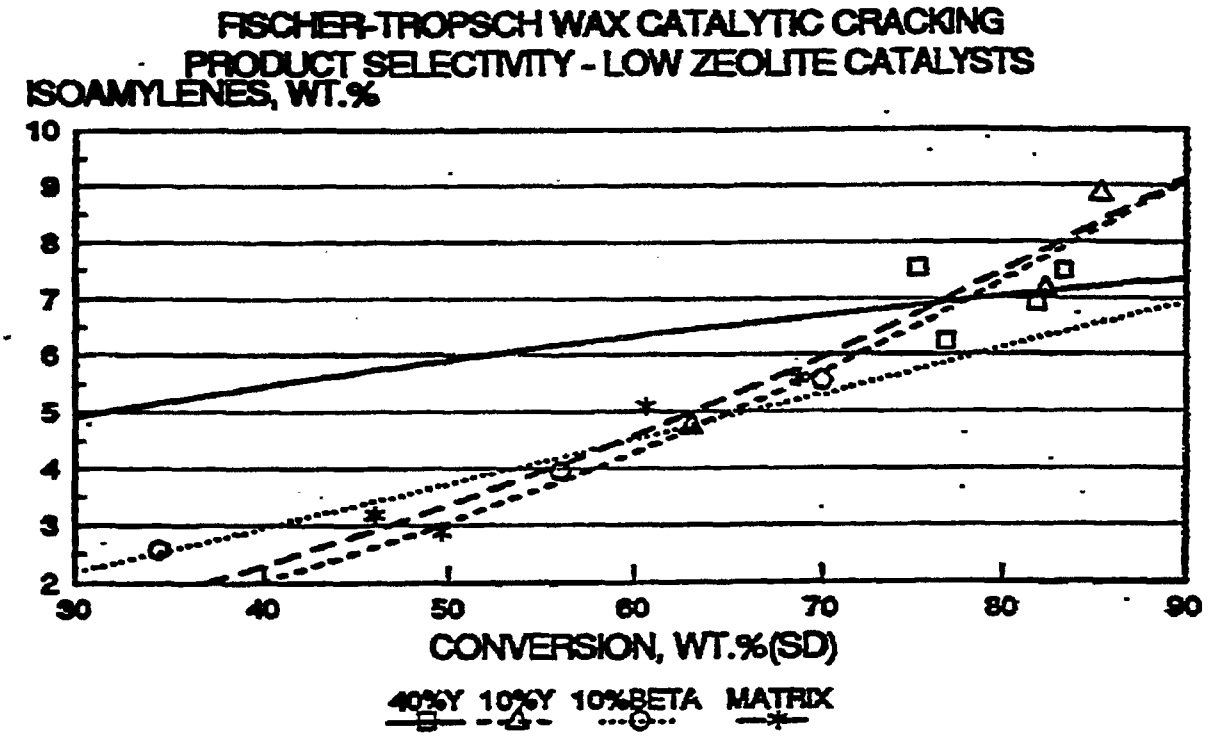


FIGURE 16

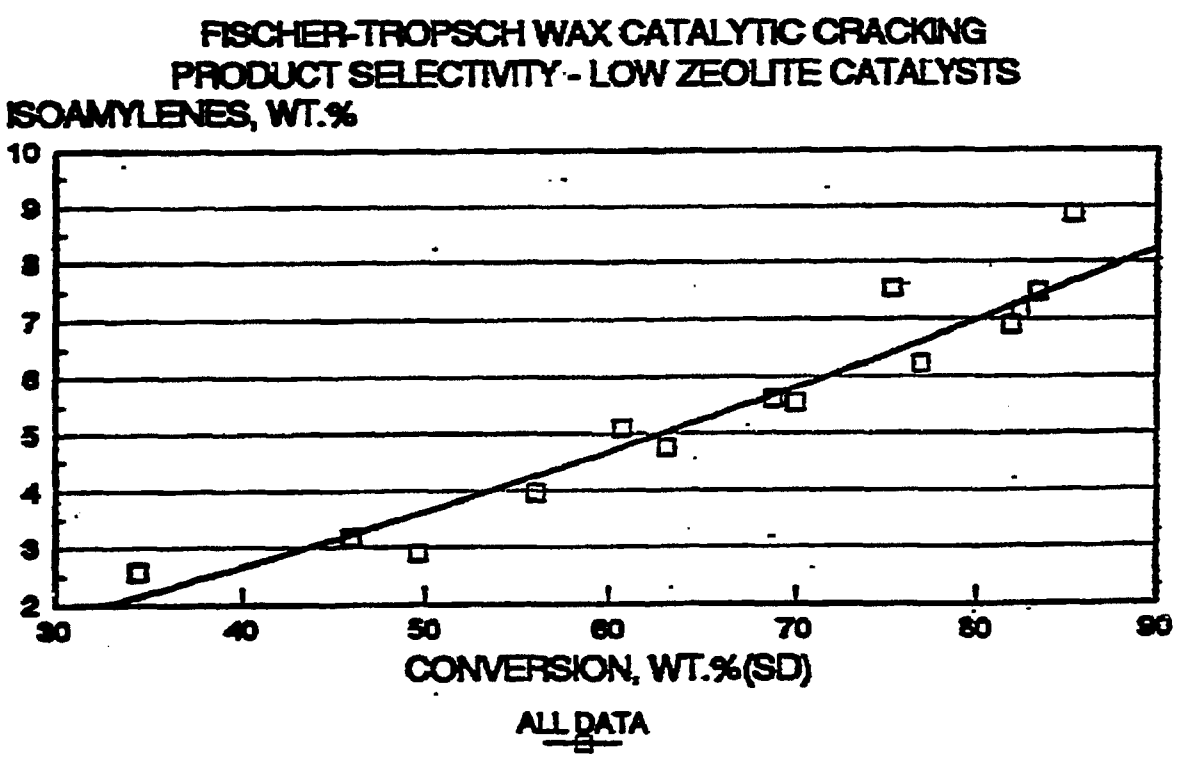


FIGURE 17

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

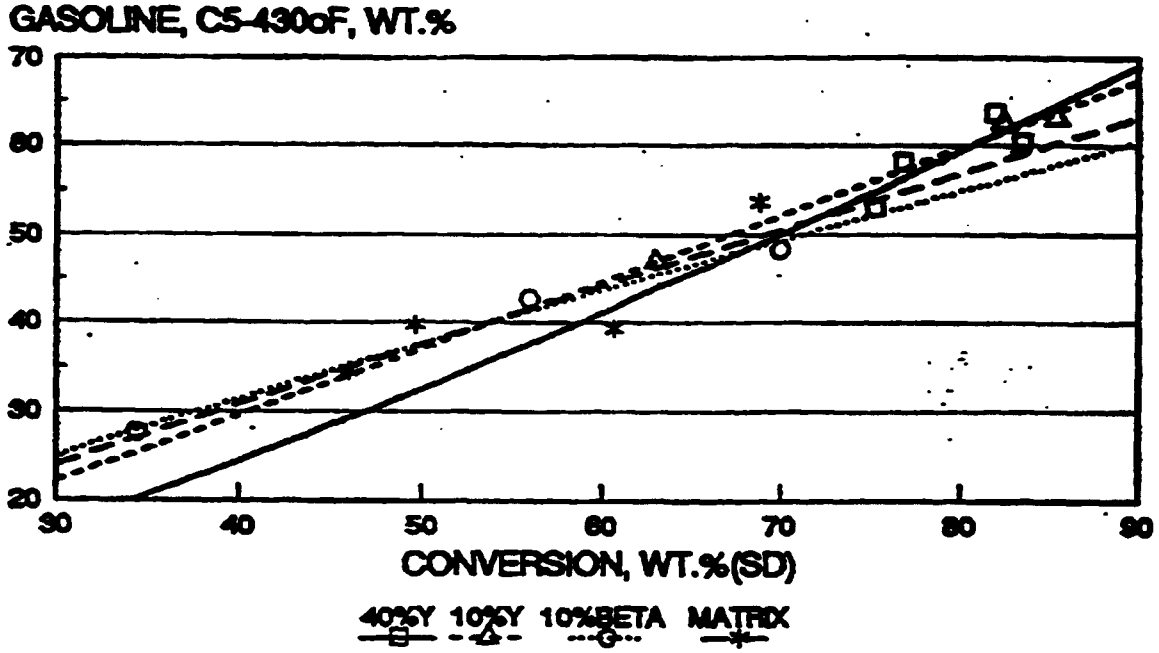


FIGURE 18

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

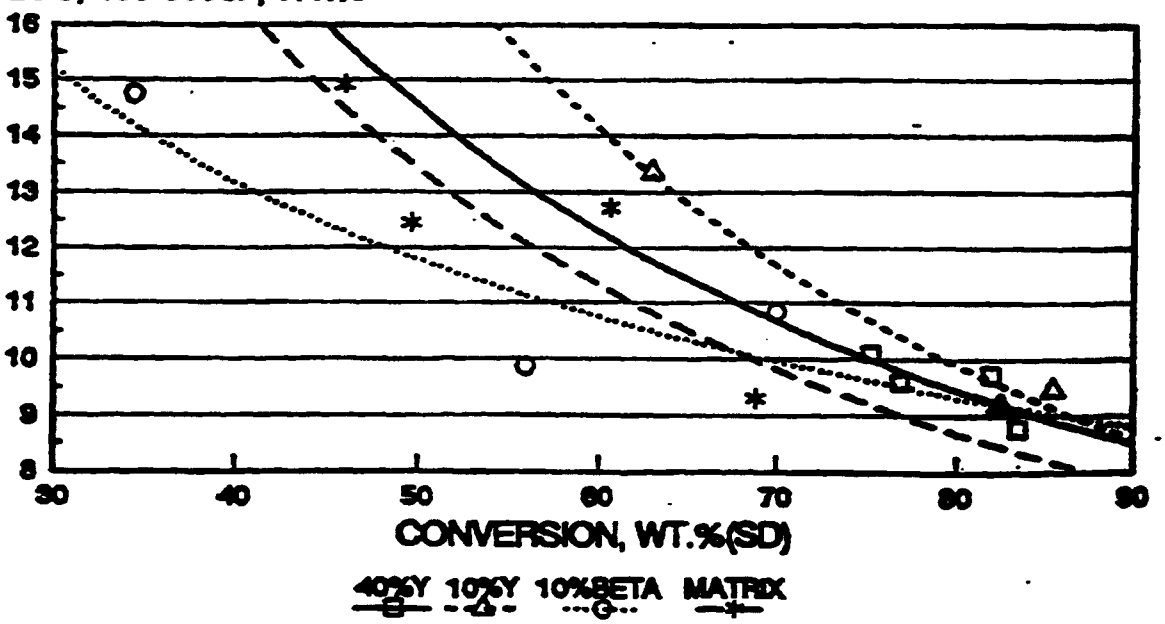


FIGURE 19

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

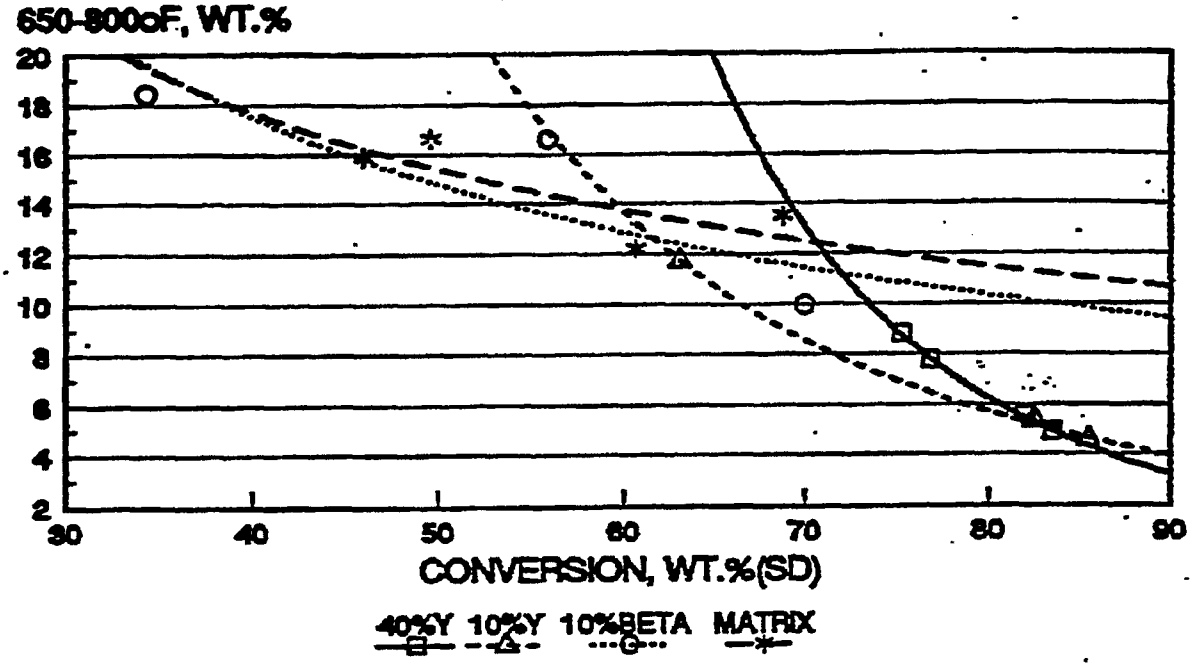


FIGURE 20

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

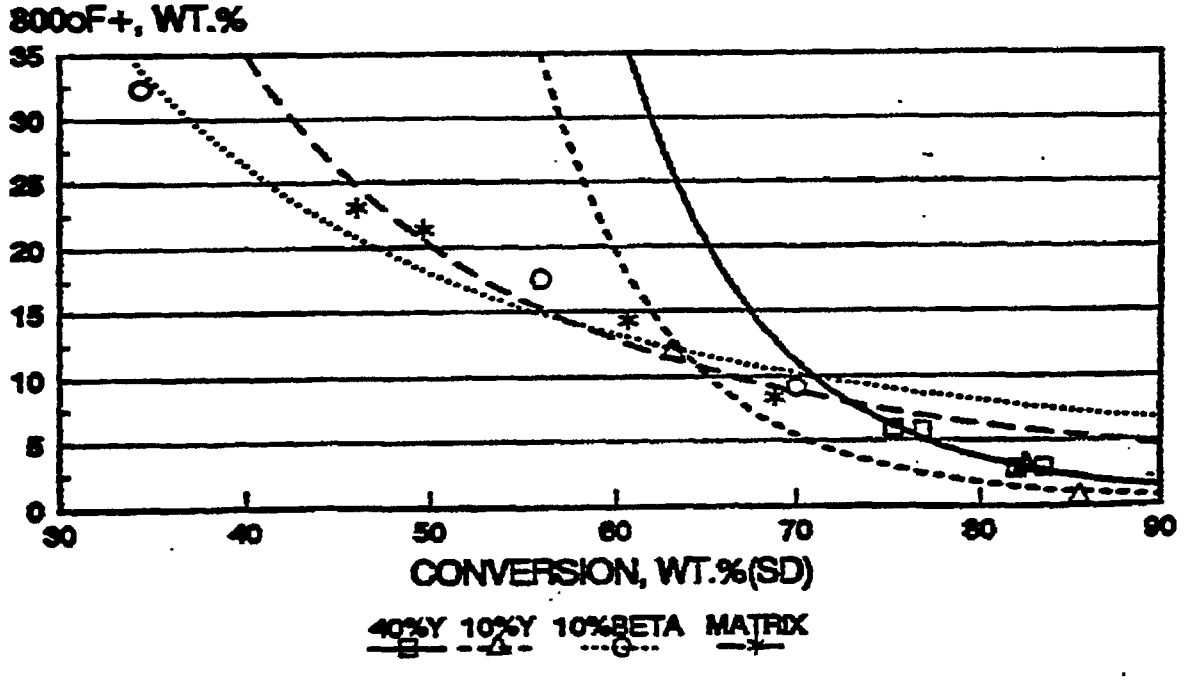


FIGURE 21
COMPARISON OF TAME PRODUCTION AU-6 - AU-109
METHANOL/2METHYL2BUTENE FEED

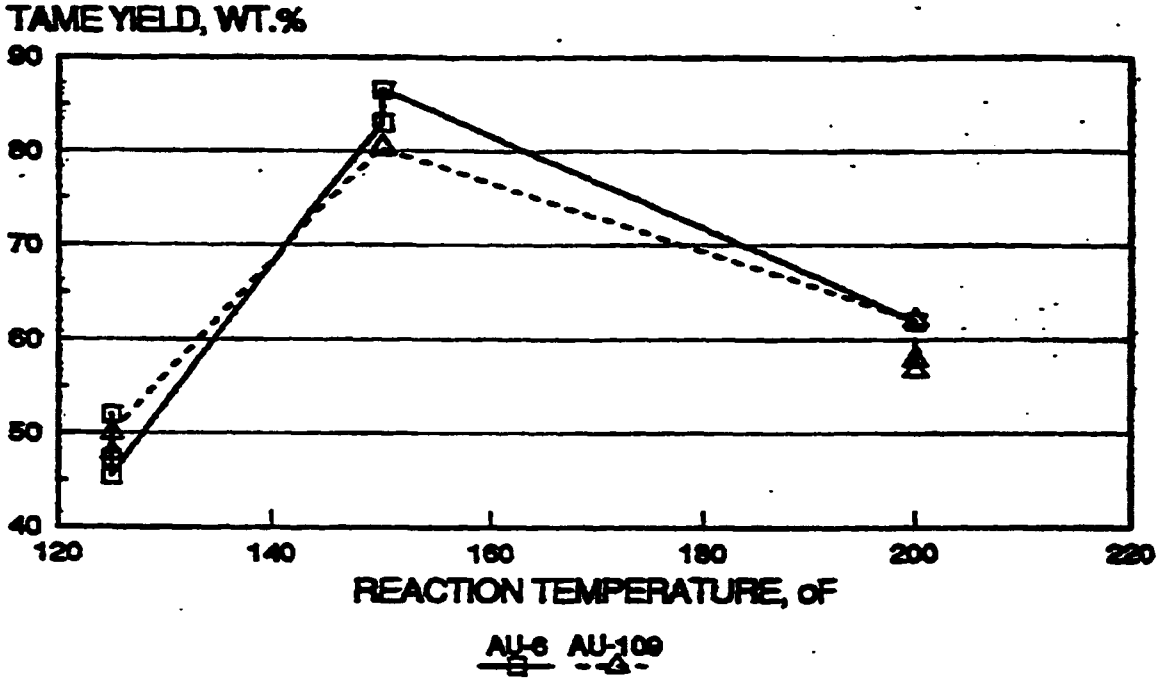
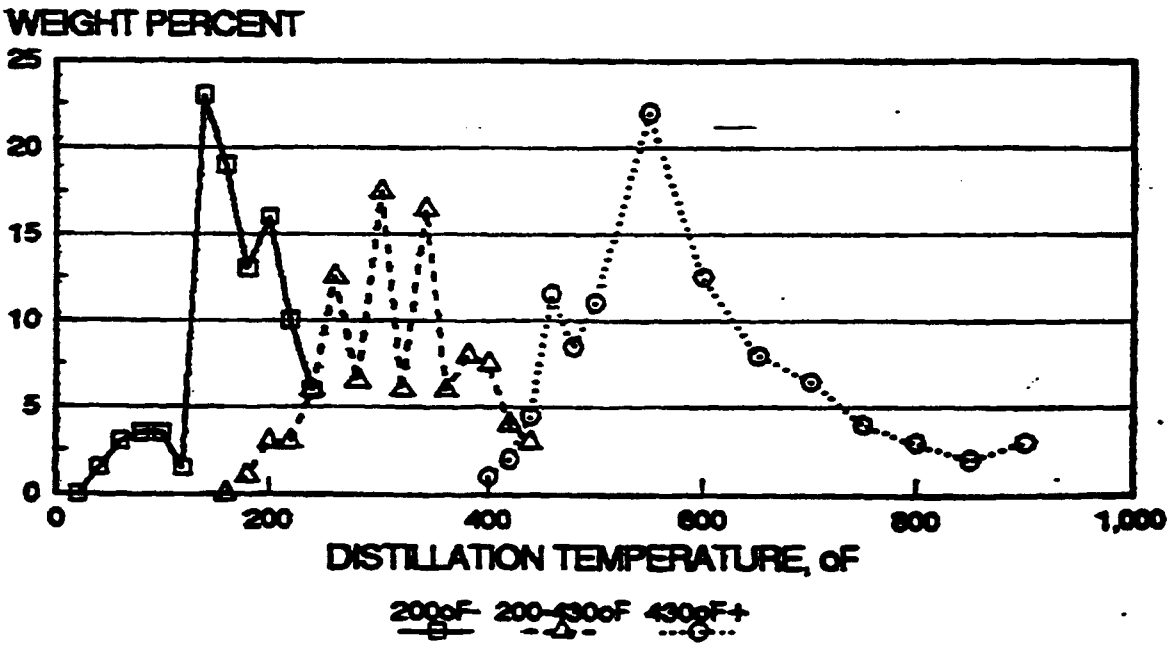


FIGURE 22
SIMULATED DISTILLATION RESULTS FOR NAPHTHA
THREE FRACTIONS BY ASTM D-2892



QUARTERLY MANPOWER REPORT

For FIRST QUARTER FISCAL YEAR, 1993

(October 1, 1993 - December 31, 1993)

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

IDENTIFICATION NUMBER: DE-AC22-91PC90057

START DATE: June 1, 1991
COMPLETION DATE: May 31, 1993

PARTICIPANT NAME AND ADDRESS:

AMOCO OIL COMPANY
P. O. BOX 3011
NAPERVILLE, ILLINOIS 60566

Manpower In Hours by Task

Name	1	2	3	4	5	6	7	Total
W. J. Reagan	0	0	32	169	240	20	0	461
D. M. Washecheck	0	0	0	0	0	0	0	0
R. D. Hughes	0	0	2	5	13	0	0	20
Other Professionals	0	0	0	0	0	0	0	0
Technical Support	0	0	53	227	282	0	0	562
Secretarial	0	0	6	14	0	0	0	20
Total Hours	0	0	93	415	535	0	0	1063

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