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

REPORT NO. 30

QUARTERLY TECHNICAL STATUS REPORT

FOR

SECOND QUARTER FISCAL YEAR, 1993

(January 1, 1993 - March 31, 1993)

PROJECT MANAGER: R. D. HUGHES

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

FOR

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

BY

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#### 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 second quarter, fiscal year, 1993, the seventh 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 virtually complete. The primary 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. A second feedstock being used is also a high melting point paraffinic wax. It was produced by the Liquid Phase F-T demonstration plant at LaPorte, Texas, and is contaminated with about 2.5% of finely dispersed iron F-T catalyst.

Task 3, Catalytic Cracking Catalyst Screening Program. MYU experiments with the LaPorte wax as feedstock demonstrated the feasibility of the concept of selective attrition of the FCC catalyst. An invention disclosure was submitted for a process modification of the FCC unit and catalyst that would allow the use of wax feedstocks that contained high levels of F-T catalyst fines.

MYU experiments comparing the Sasol and LaPorte wax feedstocks with USY, Beta and HZSM-5 catalysts showed that the type of FCC catalyst has a major impact upon product yields and quality. For a given catalyst, both feedstocks have similar conversion values. The yields of the major catalytic cracking products, light olefins, naphtha and distillate, do not vary significantly with the two wax feedstocks. However, the presence of the iron F-T fines in the LaPorte wax increases the coke and hydrogen gas yields. In addition, small increases occur in the octane quality of the naphtha products from the LaPorte wax feedstock.

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

Task 5, Preparation of C<sub>5</sub>-C<sub>8</sub> Ethers. The methanol etherification of the light naphtha product from the pilot plant F-T wax cracking runs yields a mixed ether product. Etherification runs were completed on two additional pilot plant light naphthas using two commercial etherification catalysts, one of which contains a noble metal, in addition to the strong acid functionality. Isoolefin conversion values were similar for the two catalysts and three feedstocks in the absence of H<sub>2</sub>. With H<sub>2</sub> present, product color is improved; but overall the presence of H<sub>2</sub> is not desirable because olefins are saturated, which results in decreased production of ethers and decreased product octane number.

Task 7, Scoping Economic Evaluation of the Proposed Processes. Economic analysis of the eight pilot plant runs that were performed under Task 4 showed that the net product values (\$/d) for a complex refinery (contains ether unit) were always higher than for a simple refinery (no ether unit).

The delta in net product values for the complex and simple refineries was greatest (about \$74,900/d) for run that used HZSM-5 catalyst (941-1); the delta for the runs using only USY catalyst were about \$43,000-55,000/d.

#### 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 ( $C_5-C_{50}$ ) 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. These studies are 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 2, 3, 5, and 7 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.

Activities under Task 2 of the contract continue. The primary Fischer-Tropsch wax feedstock for all catalytic cracking studies thus far in this contract is a sample from Sasol. The Sasol 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. Except for a pending measurement of viscosity, no further characterization of the Sasol wax is planned.

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.<sup>(1)</sup> 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 1. The LaPorte wax (61% >1000°F) contains more high boiling material than the Sasol wax (52% >1000°F). The normal paraffin distributions for the two samples also reflects this difference, as Figure 2 shows.

Table I 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%.<sup>(1)</sup> 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 I 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 I. This

discrepancy suggests that the catalyst may not be distributed homogeneously in the wax. No further efforts are planned on catalyst and wax separations.

**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).

The Fluid Catalytic Cracking unit may tolerate the high level of Fischer-Tropsch catalyst fines in the LaPorte 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 II, 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 II, 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 II, 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.

A brief Scanning Electron Microscopy (SEM) study of the catalyst and fines samples from these selective attrition experiments supports the conclusions of the chemical analyses. A series of SEM photographs, Figures 3 - 6, illustrates the fate of the F-T catalyst fines in these laboratory tests. The base FCC catalyst, Figure 3, consists of varied shaped microspheres with smooth, rounded surfaces. This morphology is characteristic of the particular type of FCC catalyst and the abrasive nature of the circulating catalyst inventory of a commercial FCC unit. Figures 4, and 5 illustrate the composition of the FCC catalyst after the sequential wax cracking experiments. It is clear that the F-T catalyst fines (small bright spots, due to the high iron content) are deposited mainly on the external surfaces of the FCC catalyst microspheres.

Figure 6 illustrates the FCC catalyst sample after the selective attrition experiment. Most of the external F-T catalyst fines have been removed from the external surfaces of the FCC catalyst. Figures 7 and 8 show that the fines from the attrition experiment consist largely of very small, high iron content fragments.

These laboratory experiments demonstrate the feasibility of the selective attrition concept. The FCC unit and catalyst can be adapted to process these wax feedstocks with high levels of F-T catalyst fines. No fixed bed conversion process, such as hydrocracking, could tolerate such a highly contaminated feedstock. An invention disclosure has been submitted for this process. Further effort would be required to optimize the selective attrition process. However, no additional work in this area will be performed under the present contract.

After it was determined that the FCC process can tolerate the high level of iron catalyst fines in the LaPorte wax -- by the use of the novel selective attrition process discussed above -- the catalytic cracking properties of this new LaPorte wax feedstock were measured and compared with those of the Sasol wax.

The catalytic cracking tests of the LaPorte wax feedstock with three types of FCC catalysts (USY, HZSM-5, Beta) present an effective testing program. The three catalysts represent different zeolite structures with varying olefin selectivities. These catalysts have been used throughout this program. Table III presents the detailed results of the catalytic cracking tests on the small scale test unit, the Micro Yields Unit, MYU. Both the LaPorte wax and new test runs with the Sasol wax are shown. This is due, in part, to the training of a new operator.

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. The conversion number is the sum of the cracked products: gas( $C_4$ -), naphtha( $C_5$ -430°F) and coke. Two methods to calculate the conversion are listed in Table III. One method is from the analysis of the liquid product by GC simulated distillation. The other MYU method derives from a correlation of GC area counts of the gasoline products. The two methods provide similar but not identical conversion values. The variations in conversion values among the samples may be due to operator variability and other test variables, such as, feed delivery precision. This series of MYU tests should be at the same test conditions, (970°F, 0.8 catalyst to oil weight ratio) but Figure 9 suggests that a wide range of catalyst to oil ratios are actually recorded. 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. Figures 10 to 18 present product yields versus conversion plots for the wax feedstock and catalyst combinations. The coke and hydrogen gas yields for the LaPorte wax are significantly higher than the Sasol wax (Figures 10, 11). 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. One test

(Table III, Run No. 021) of the USY catalyst that has over 1% iron from repeated LaPorte wax cracking runs also has high coke and hydrogen yields with the Sasol wax feedstock. This sample was used in the selective attrition experiments reported in the January, 1993, Monthly Technical Status Report. 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 catalyst, iron F-T fines. Figures 12-15 show several light gas and gasoline selectivity plots for the two wax feedstocks and the three catalysts. The major differences in product selectivities are from catalyst differences rather than feedstock differences. The HZSM-5 produces the highest yields of propylene, regardless of feed. The HZSM-5 and the Beta zeolite catalysts have higher yields of isobutylene than the USY catalyst with both wax feedstocks. The higher light gas yields for the HZSM-5 and Beta catalysts occur at the expense of the naphtha (Figure 15) and distillate (Figure 16) yields. The 650 °F+ liquid yields (Figures 17, 18) do not vary significantly with wax feedstock or catalyst. The research octane quality of the naphtha products from the LaPorte wax feedstock are 1-2 octane numbers higher than the naphtha products from the Sasol wax, (Figure 19). This may be another effect of the dehydrogenation activity of the iron F-T catalyst fines. The higher octane numbers are the result of higher olefin contents (Table III) for the LaPorte naphtha products.

The yields of the major catalytic cracking products, light olefins, naphtha and distillate do not vary significantly with the two wax feedstocks. The type of FCC catalyst has a major impact upon product yields and quality. However, the presence of the iron F-T fines in the LaPorte wax increases the coke and hydrogen gas yields. In addition, small increases occur in the octane quality of the naphtha products from the LaPorte wax feedstock.

#### TASK 5. Preparation of Ethers.

Activities under Task 5 of the contract continue.

The methanol etherification of a light naphtha product (200°F- fraction) from the pilot plant Fischer-Tropsch wax catalytic cracking runs yields a mixed ether product. This ether product consists of TAME, (tertiary amyl methyl ether) and the three C<sub>6</sub> ethers, THME, (tertiary hexyl methyl ethers), which are 2-methyl-2-methoxypentane, 2,3-dimethyl-2-methoxybutane and 3-methyl-3-methoxypentane.

Two new light naphtha samples are available from the atmospheric distillation (ASTM Method D-2892) of pilot plant liquid products. Table IV shows the composition of these new naphtha, along with the previous sample, discussed in the December, 1992 Monthly Status Report. The iso-olefin contents of these samples, feeds "B" and "C", are higher than the previous 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. Tables V and VI present the results of the etherification runs with these two light naphtha. 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 from the previous set of runs, 200 psig, 2.9 grams of catalyst, methanol 1.37 g/hr, naphtha, 5.5 g/hr are the same except that only one reaction temperature, 150°F, is available. There is again some scatter in the methanol analysis results. This may be due to some separation of alcohol and hydrocarbon product phases. Table VII summarizes the iso-olefin conversion values for the two catalysts and feedstocks. The results are similar for both catalysts and the three feedstocks, in the absence of hydrogen gas in the reactor. As Table VIII shows, the calculated research octane values for the products of these etherification runs are 2-4 numbers higher than the starting light naphtha feedstocks. As expected, this octane increase depends to some extent upon the concentrations of the ethers in the product. Several of these etherification products will be submitted for blending octane measurements. This will verify the calculated research octane values shown in Table VIII. When hydrogen gas is present, run No. 034-1, Table VII, 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. Table VIII illustrates this point with comparisons of feeds and etherification products from several of the runs. 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). 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. Further experiments would be required to clarify the particular experimental conditions for hydrogen gas addition to the etherification reactor.

These etherification runs clearly demonstrate that the light naphtha fractions from the catalytic cracking of Fischer-Tropsch wax are excellent ether synthesis feedstocks. The measurements of blending octane values for the etherification products will conclude this portion of the contract.

#### TASK 7. Scoping Economic Evaluation.

Activities under Task 7 of the contract continue.

The results of eight pilot plant tests performed under Task 4 have been previously reported (Reports #10, 13, and 23, which are, respectively, the First, Second, and Third Quarterly Status Reports Fiscal Year, 1992). Runs 939-1, -2, and -4 used Equilibrium USY catalyst; Run 939-5 used steamed Equilibrium USY; Runs 940-1 and -2 used steamed Beta; Run 941-1 used a mixture of 75% steamed Equilibrium USY with 25% steamed HZSM-5; and Run 942-2 used 50% Equilibrium USY with 50% diluent. Table IX shows the catalyst-to-oil ratios and reactor temperatures used and the conversions obtained in these pilot plant runs.

Tables X-XVII show the results of economic analysis of each of eight above-mentioned pilot plant runs, respectively. 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 XVIII 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 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.

#### CONCLUSIONS

Task 1 of the contract, the Project Management Plan, and Task 2, Feedstock Characterization are essentially complete. Additionally, wax that is contaminated with about 2.5% iron F-T catalyst, from the LPFT plant at LaPorte, Texas was also characterized and used this Quarter.

Catalytic cracking screening tests of the LaPorte wax feedstock under Task 3 (small scale) showed that it was potentially feasible to use wax that is contaminated with F-T catalyst fines as feedstock in the FCC process. Experiments comparing the Sasol and LaPorte wax feedstocks with USY, Beta and HZSM-5 catalysts showed that the type of FCC catalyst has a major impact upon product yields and quality. For a given catalyst, both feedstocks have similar conversion values and yields of the major catalytic cracking products, light olefins, naphtha and distillate. However, the presence of the iron F-T fines in the LaPorte wax increases the coke and hydrogen gas yields. In addition, small increases occur in the octane quality of the naphtha products from the LaPorte wax feedstock.

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

Work under Task 5, Preparation of C<sub>5</sub>-C<sub>8</sub> Ethers, continued. This Quarter, methanol etherification runs were completed on two additional pilot plant light naphthas using two commercial etherification catalysts, one of which contains a noble metal, in addition to the strong acid functionality. The methanol etherification yields a mixed ether product. Isoolefin conversion values were similar for the two catalysts and three feedstocks in the absence of H<sub>2</sub>. With H<sub>2</sub> present, product color is improved; but overall the presence of H<sub>2</sub> is not desirable because olefins are saturated, which results in decreased production of ethers and decreased product octane number.

Work under Task 7, Scoping Economic Evaluation of the Proposed Processes, continued. Economic analysis of the eight pilot plant runs that were performed under Task 4 showed that the net product values (\$/d) for a complex refinery (contains ether unit) were always higher than for a simple refinery (no ether unit). The delta in net product values for the complex and simple refineries was greatest (about \$74,900/d) for run that used HZSM-5 catalyst (941-1); the delta for the runs using only USY catalyst were about \$43,000-55,000/d.

#### REFERENCES

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QUARTERLY MANPOWER REPORT

For SECOND QUARTER FISCAL YEAR, 1993

(January 1, 1993 - March 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	0	0	287
D. M. Washecheck	0	0	0	0	0	0	0	0
M. M. Schwartz								
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	28
Total Hours	0	0	93	415	535	0	0	1063

TABLE I

CHEMICAL ANALYSES OF LA PORTE FISCHER-TROPSCH WAX

Sample ID 15586-012

Chemical Composition (ppm) of Ash: Si - 1,710       $\text{SiO}_2$  - 3,659  
                                  K - 1,350       $\text{K}_2\text{O}$  - 1,626  
                                  Fe - 13,900      $\text{Fe}_2\text{O}_3$  - 17,882  
                                 Cu - 1,150      CuO - 1,439  
    18,110      24,606

Centrifuge Experiment to Separate Solids

Chemical Composition (ppm)

<u>Top:</u>	Si	540	<u>Bottom:</u>	Si	1200
	K	430		K	820
	Fe	2620		Fe	6900
	Cu	91		Cu	570
		3681			9490

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TABLE II

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 III

**HICRO-YIELDS UNIT EVALUATIONS--LAPORTE, SASOL WAX**  
 (Catalytic Cracking, 970°F, 0.8 Catalyst/Oil)

Feed: LaPorte Wax		Weight Percent Product Yields						Gasoline Composition, Vt% on Feed <sup>a</sup>										
Catalyst	Run #	*	Conv.	H <sub>2</sub>	C <sub>3</sub> -	I C <sub>4</sub> -	I C <sub>5</sub> -	Coke	410°- 650°F	650°- 800°F	RON	MON	P+H	T+K	A+K	N+K	O+K	
CCC 1397 (USY)	008	A	86.4	0.15	6.65	4.15	7.58	63.42	1.02	--	87.8	77.3	5.76	18.39	16.07	9.14	45.99	
		B	85.6	--	6.66	4.33	7.72	64.88	1.03	11.40	2.65	0.37	--	--	--	--	--	
	017	A	84.9	0.16	7.01	3.67	6.17	62.87	1.32	--	87.8	77.2	5.30	18.6	19.9	10.9	41.8	
CCC 1891 (HZSM-5)		B	82.3	--	7.09	3.98	6.15	60.63	1.31	11.62	3.55	0.5	--	--	--	--	--	
	006	A	81.8	0.19	20.53	9.14	6.15	28.45	0.75	--	--	92.0	80.1	10.17	5.10	28.79	5.67	42.7
		B	83.17	--	20.66	9.23	7.12	28.89	0.74	4.81	4.45	7.56	--	--	--	--	--	
CCC 1875 (Beta)	015	A	80.1	0.22	17.11	9.26	6.05	31.23	0.44	--	87.7	77.4	13.45	6.36	21.98	6.49	44.66	
		B	81.7	--	17.0	9.29	6.72	31.89	0.45	6.39	4.91	6.99	--	--	--	--	--	
	007	A	88.2	0.16	9.6	7.69	8.83	57.18	1.19	--	--	88.2	76.4	6.66	10.55	11.73	9.56	54.24
Feed: Sasol Wax		B	86.8	--	9.4	7.76	8.27	57.46	1.21	8.50	2.81	1.87	--	--	--	--	--	
	016	A	83.4	0.15	8.76	5.92	6.81	57.16	1.71	--	88.6	76.6	5.63	9.89	13.02	11.71	51.61	
		B	79.4	--	8.72	6.00	7.19	53.08	1.73	13.34	4.18	3.1	--	--	--	--	--	
Feed: Sasol Wax																		
CCC 1397 (USY)	011	A	94.0	0.03	11.01	6.08	8.19	60.52	0.67	--	--	84.8	76.9	8.70	23.85	19.69	7.54	36.44
		B	93.01	--	11.11	6.18	6.87	60.42	0.68	6.18	.80	0	--	--	--	--	--	
	013	A	85.8	0.02	7.95	4.96	7.94	59.53	0.54	--	86.7	76.7	6.39	20.38	13.84	9.07	46.11	

TABLE III (con't)

Catalyst	Feed:	Gasol Wax		Weight Percent Product Yields						Gasoline Composition, Vt on Feed										
		Run #	#	Conv.	Vt <sup>a</sup>	C <sub>5</sub> <sup>b</sup>	C <sub>6</sub> <sup>b</sup>	C <sub>7</sub> <sup>b</sup>	C <sub>8</sub> <sup>b</sup>	C <sub>9</sub> - 430°F	C <sub>9</sub> - 650°F	Coke	430- 650°F	650- 800°F	RON	I&M	P**	HON	A**	NH*
9163005*	021	A	86.2	0.16	9.89	4.16	4.57	53.11	2.60	--	--	--	86.4	78.7	--	--	--	--	--	--
	022	B	88.73	--	10.07	4.24	4.20	56.96	2.61	9.23	1.64	.397	85.3	76.5	6.93	20.48	25.52	12.37	31.1	
	023	A	75.7	0.02	9.03	4.43	3.49	49.38	0.95	--	--	--	84.0	74.5	5.77	19.09	18.17	15.13	35.58	
	023	B	81.74	--	7.66	3.79	2.68	59.13	1.04	10.73	5.91	1.61	--	--	--	--	--	--	--	
	024	A	56.4	0.02	3.79	1.88	2.08	45.15	0.45	--	--	--	84.0	74.5	5.77	19.09	18.17	15.13	35.58	
	024	B	62.2	--	3.68	1.93	4.40	51.54	.45	13.53	11.60	12.65	--	--	--	--	--	--	--	
	024	A	62.0	0.01	5.18	3.71	4.93	43.28	0.46	--	--	--	86.9	76.6	4.31	20.03	16.57	14.60	38.60	
	025	B	66.42	--	5.29	4.05	6.58	48.09	.46	11.46	9.91	12.19	--	--	--	--	--	--	--	
	025	A	67.2	0.02	5.20	3.69	5.41	48.52	0.44	--	--	--	87.0	76.5	4.59	19.37	15.87	14.0	40.07	
	026	B	66.1	--	5.33	3.96	6.76	47.61	0.45	12.44	10.03	11.42	--	--	--	--	--	--	--	
	026	A	78.2	0.02	6.36	4.42	6.70	56.5	0.43	--	--	--	87.0	76.4	5.03	20.41	12.86	11.43	43.9	
	027	B	79.99	--	6.22	4.63	7.82	60.41	.435	9.597	6.49	3.91	--	--	--	--	--	--	--	
	027	A	61.6	0.01	4.65	2.78	4.02	46.88	0.38	--	--	--	86.0	75.5	4.66	19.44	15.64	14.19	39.71	
		B	64.03	--	4.67	3.00	5.89	49.87	.38	13.36	10.67	11.97	--	--	--	--	--	--	--	
CCC 1891 (HZSH-5)	009	A	87.7	--	10.13	7.64	36.94	0.19	--	--	--	--	84.4	75.5	15.5	6.88	11.81	8.48	46.84	
	018	A	90.35	18.56	10.13	7.85	39.87	0.86	4.44	1.2	1.99	--	85.7	76.3	15.59	7.66	18.49	10.25	39.13	
		B	76.7	16.53	8.94	6.74	28.23	0.25	--	--	--	8.36	7.10	--	--	--	--	--	--	
		B	79.86	16.38	9.01	6.96	31.00	.25	4.67	--	--	--	--	--	--	--	--	--	--	
CCC 1875 (Beta)	010	A	90.9	--	14.89	9.15	7.91	47.32	0.62	--	--	--	85.5	76.5	10.38	12.03	15.21	9.87	41.31	
	012	B	89.6	14.96	9.26	7.06	46.41	.44	6.29	2.70	1.38	--	--	--	--	--	--	--	--	
	0	A	79.8	10.76	7.59	7.72	46.25	.38	--	--	--	86.0	75.8	8.85	13.37	12.47	11.60	48.0*		
	0.19	A	79.16	10.65	7.73	8.59	47.00	.40	8.39	7.11	5.33	--	--	--	--	--	--	--	--	
		B	57.2	6.74	4.19	3.95	37.04	0.42	--	--	--	84.6	75.8	7.98	16.68	19.34	15.85	33.16		
		B	64.53	6.88	4.33	4.39	43.81	.436	13.05	10.16	12.25	--	--	--	--	--	--	--	--	

<sup>a</sup>A = MTO Conversion Calculation<sup>b</sup>B = Simulated Distillation Conversion Calculation

\*P = paraffin

I = isoparaffin

A = aromatic

N = naphthalene

O = olefin

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TABLE IV  
HYDROCARBON COMPOSITION OF 200°F- NAPHTHA'S

Feed ID:	92-0490-01A Feed A*	93-0024-01A Feed B	93-0024-01C Feed C
Pilot Plant Run No.	939-01, + 02 eq. UST catalyst conversion = 93.6%	940-01, 02 941-01 Beta/EZSM-5 catalyst Conversions = 90.96%	939-04 eq. UST catalyst conversion = 83%
Total Paraffins wt%	6.69	8.44	4.32
C <sub>2</sub>	0.18	0.37	0.16
C <sub>3</sub>	0.93	1.04	0.72
C <sub>4</sub>	4.03	4.50	2.35
C <sub>5</sub>	1.45	1.67	1.02
C <sub>6</sub>	0.08	0.69	0.06
C <sub>7</sub>	--	0.13	--
Total Iso-paraffins wt%	42.71	17.64	22.88
C <sub>2</sub>	0.32	0.56	0.28
C <sub>3</sub>	3.77	2.03	2.19
C <sub>4</sub>	22.94	6.22	10.55
C <sub>5</sub>	13.87	6.12	8.86
C <sub>6</sub>	1.82	2.16	0.99
C <sub>7</sub>	--	0.44	--
Total Aromatics wt%	1.74	2.62	0.35
C <sub>6</sub>	0.34	0	0
C <sub>7</sub>	1.34	1.03	0.35
C <sub>8</sub>	0.05	1.38	0
C <sub>9</sub>	--	0.22	--
Total Naphthalenes wt%	3.96	5.55	3.16
C <sub>7</sub>	0.05	0.06	0.05
C <sub>8</sub>	1.23	0.92	0.71
C <sub>9</sub>	1.92	1.71	1.63
C <sub>10</sub>	0.75	1.82	0.80
C <sub>11</sub>	--	1.03	--
Total Olefins wt%	44.51	64.47	68.65
C <sub>2</sub>	0.01	0.11	0.04
C <sub>3</sub>	1.25	3.72	1.82
C <sub>4</sub>	8.701	12.10	12.03
C <sub>5</sub>	23.88	29.54	33.79
C <sub>6</sub>	10.36	15.65	19.95
C <sub>7</sub>	0.31	3.31	1.02
Reactive iso-olefins wt%			
C <sub>4</sub> 's			
2-methyl-1-butene	1.25	2.15	1.76
2-methyl-2-butene	4.26	5.67	5.64
C <sub>5</sub> '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

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

TABLE V

AU-109 ETHERIFICATION RUNS  
200 PSIG, METHANOL 1.37 G/HR, 200°F - NAPHTHA 5.5 G/HR  
NAPHTHA ID = 93-0024-01A

Run No.	Feed:MeOH	031-2	032-1	033-1	033-2	033-3	033-4
Temp		150°F	150°F	150°F	150°F	150°F	150°F
Catalyst		Amberlyst	Amberlyst	E2634	E2634	E2634	E2634
Product, Wt% C4-5 Olefins:							H2 added
Isobutylene IC4=	1.036047	0.405	0.385	0.441	0.367	0.374	0.468
3M1PENTENE	0.225081	0.192	0.267	0.203	0.261	0.149	0.143
2M1BUTENE	1.81245	0.141	0.199	0.153	0.215	0.335	0.414
2M2BUTENE	4.778967	1.464	2.016	1.358	1.906	1.581	2.731
C6 OLEFINS							
3M1PENTENE	0.689574	0.66	0.767	0.6	0.748	0.423	0.429
23DIBUTENE	0.612861	0.512	0	0.038	0.048	0.03	0.083
4M-2PENTENE	0.30348	0.293	0.368	0.289	0.363	0.221	0.262
4McPENTENE	1.041105	0.995	1.159	0.912	1.136	0.69	0.929
2M1PENTENE	2.099913	0.276	0.329	0.239	0.335	0.424	0.583
HEXENE1	0.649953	0.622	0.696	0.544	0.68	0.368	0.387
1-HEXENE3	1.620246	1.551	1.718	1.358	1.695	1.011	1.298
cHEXENE3	2.695914	2.569	2.633	2.086	2.601	1.594	2.207
2M2PENTENE	4.440081	1.81	2.08	1.497	2.008	1.46	2.478
tHEXENE2	0.06744	0.114	0	0.067	0.067	0.07	0.071
3M-2PENTENE	2.640276	1.542	1.893	1.398	1.851	1.208	1.957
cHEXENE2	1.422141	1.359	1.482	1.169	1.468	0.863	1.04
3Mc2PENTENE	4.621326	2.969	3.378	2.436	3.289	2.127	3.521
OXYGENATES:							
MEOH	15.7	15.3	17.148	39.317	17.586	49.193	22.108
MBBE	0	1.558	2.031	1.459	1.991	0.927	1.835
TAME	0	6.17	6.328	4.452	6.338	2.853	4.644
TEME1	0	1.172	0.67	0.466	0.677	0.386	0.32
TEME2	0	5.535	4.369	2.866	4.397	2.45	3.542
TEME3	0	4.142	3.003	2.148	3.113	1.782	2.376
NON-REACTIVE COMPOUNDS:							
nHEXANE	3.796872	3.25	3.598	2.883	3.484	2.48	4.653
TOLUENE	0.865761	0.851	0.746	0.499	0.739	0.461	0.714
2MPENTANE	3.153663	3.271	3.796	2.867	3.538	2.228	3.7
3MPENTANE	1.608444	1.746	1.972	1.455	1.794	1.121	1.878

TABLE VI

AU-109 ETHERIFICATION RUNS  
200 PSIG, METHANOL 1.37 G/HR, 200°F - NAPHTHA 5.5 G/HR  
NAPHTHA ID = 93-0024-01C

Run No.	Feed-MeOH	034-1	034-2	034-3	034-4
Temp		150°F	150°F	150°F	150°F
NEOGENE		E2634	E2634	E2634	E2634
CASORATE		H2 added	H2 added	no H2	no H2
Product:					
CA-5 OL:					
Isobutylene	0.427401	0.3	0.206	0.435	0.3
3MIBUTENE	0.15174	0.019	0.008	0.111	0.159
2MIBUTENE	1.483366	0.348	0.302	0.213	0.151
2M2BUTENE	4.752834	3.095	2.778	2.094	1.595
C6 OLEFINS:					
3MIPENTENE	1.012443	0.073	0.052	0.709	1.012
23DMBUTENE	0.820239	0.115	0.115	0.115	0.115
4Me2PENTENE	0.418971	0.145	0.123	0.458	0.46
4Mc2PENTENE	1.353858	0.751	0.651	1.481	1.404
2MC2PENTENE	2.54586	0.54	0.548	0.351	0.318
HEXENOL	0.96943	0.067	0.048	0.407	0.957
t-HEXENE3	2.128575	0.891	0.786	2.009	2.167
c-HEXENE3	3.339966	1.884	1.692	3.589	3.43
2MC2PENTENE	4.606152	3.087	3.219	2.281	2.187
t-HEXENE2	0.06744	0.067	0	0.067	0.067
3M-2PENTENE	2.774313	2.185	2.215	1.868	1.834
c-HEXENE2	1.797276	0.588	0.518	1.609	1.817
3Mc2PENTENE	4.509207	4.125	4.237	3.399	3.29
OXGENATES:					
MEOH	15.7	15.88	11.402	13.721	10.7
MEBE	0	1.318	1.117	1.082	1.049
LAWE	0	4.555	4.854	5.838	6.819
TEME1	0	0.494	0.597	0.679	0.893
TEME2	0	3.876	4.932	5.012	6.114
TEME3	0	2.087	2.589	3.366	4.166
NON-REACTIVE COMPOUNDS:					
nHEXANE	1.978521	7.371	7.847	2.943	2.151
TOLUENE	0.292521	0.375	0.335	0.269	0.325
2MPELANE	4.517637	5.961	6.157	5.233	4.731
3MPELANE	3.250608	3.691	3.973	3.571	3.316

TABLE VII

REACTIVE ISO-OLEFINS CONVERSION TO ISOPERS  
Table II and III Run Conditions

200°F- Isopercs	92-049-01A*	93-0024-01A			93-0024-01C	
Reaction Temp, °F	150	150	150	150	150	150
Catalyst	Ambardyst 15	Ambardyst 15	E2634	E2634	E2634	E2634
	No E2	E2	No E2	E2	No E2	E2
<u>iso-olefin component:</u>						
C5's						
2-methyl-1-butene	89.9	90.2	87.1	77.2	78.1	87.7
2-methyl-2-butene	65.3	62.2	66.2	42.9	38.2	61.2
C6'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	52.7	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

\*These runs were reported in the December 1992 Monthly Report

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TABLE VIII

## LIGHT MAPITHA ETHERIFICATION RUNS HYDROCARBON COMPOSITION OF FEED AND PRODUCTS

Run No.	Reaction Temp	Research Octane Number*	Catalyst	Iso-paraffins			Aromatics			Naphthalenes			Olefins			Unsatens		
				Paraffins														
Feed A 92-0190-01A	80.92	6.089	42.712	1.736	3.256		46.307	0.011	1	0.011	0.31							
15586-024-2 125°F	82.09	7.804	40.210	1.985	4.174		33.762	11.106		0.34								
15586-024-6 150°F	81.76	6.163	40.129	2.247	4.576		29.671	16.294		0.32								
15586-024-8 150°F	81.88	6.137	40.466	2.263	4.586		29.38	16.416		0.33								
Feed B 91-0024-01A	83.12	8.137	17.637	2.623	5.519		64.472	0.17		1.11								
15586-031-2 150°F	87.43	7.417	17.989	3.687	6.424		61.887	21.815		0.821								
15586-033-1 150°F	87.48	7.381	17.340	3.691	6.383		41.716	22.145		0.844								
15586-033-3 150°F	85.78	8.205	17.668	3.62	6.312		45.889	17.277		0.83								
Feed C 91-0024-01D	84.56	4.315	22.881	0.153	3.161		68.651	0.15		0.49								
15586-034-1 150°F	79.47	14.515	24.733	2.405	5.416		55.369	17.312		0.19								
15586-034-3 150°F	85.78	5.921	22.489	1.977	4.497		43.51	21.192		0.415								

### Calculated

14/23/99

TABLE IX

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	882	83
939-5	Stmd. Eq. USY	2.3	879	85
940-1	Stmd. Beta	5.1	934	96.6
940-2	Stmd. Beta	3.4	910	96.5
941-1	75% Stmd Eq. USY; 25% Stmd H-ZSMS	2.8	965	89
942-2	50% Eq. USY; 50% Diluent	1.6	937	90

TABLE X

Fischer Tropach Wax Economics Pilot Plant Results of Wax Run Through an FCU 03/19/93		Rate Basis: 283,657 lb/hr Run No. 939-1		<-- Simple Configuration --> \$/Day Valued as cpg		<-- Complex Configuration --> \$/Day Valued as cpg	
Component	Normalized Wt % Yield	lb/hr	MMBtu/Day	Fuel Gas	Fuel Gas	Fuel Gas	Fuel Gas
Hydrogen	0.040	113	111	6.0	279	6.0	279
Methane	0.360	1,021	233	10.8	1,059	10.8	1,059
Ethylene	0.480	1,362	252	12.8	1,356	12.8	1,356
Ethane	0.260	738	142	12.1	721	12.1	721
Propylene	9.263	26,274	3,450	17.1	24,777	17.1	24,777
Propane	1.061	5,277	713	16.8	5,028	16.8	5,028
1-Butane	7.932	22,500	2,739	37.2	42,792	37.2	42,792
n-Butane	2.001	5,902	692	29.8	0,662	29.8	0,662
1-Butene	1.470	4,171	475	63.9	12,756	63.9	12,756
1-Pentene	5.912	16,769	1,914	63.8	51,289	65.4	68,654
1-2-Diolenes	4.191	11,088	1,330	64.8	36,349	64.8	36,349
C-2-Diolenes	3.121	8,852	960	66.6	27,065	66.6	27,065
1-Pentane	6,492	24,009	2,652	49.4	55,017	49.4	65,017
n-Pentane	1.250	3,547	305	33.8	5,469	33.8	6,469
3M-1-Bulene	0.086	244	27	50.3	50.3	53.0	59.7
2M-1-Bulene	0.993	2,017	294	50.3	6,216	58.5	10,689
2M-2-Bulene	3.781	10,725	1,101	50.3	23,260	58.5	40,707
1-Pentene	0.297	843	89	50.3	1,869	64.9	2,062
1-2-Pentene	1.400	3,972	417	50.3	8,003	55.5	9,713
C-2-Pentene	0.806	2,207	240	50.3	5,068	55.5	5,592
2,3-dim-1-Bulene	0.187	531	53	59.2	1,326	68.6	1,537
2-M-1-Pentene	0.480	1,362	137	59.2	3,395	68.7	3,940
2-M-2-Pentene	0.812	2,304	229	59.2	5,689	69.4	6,669
C-3-M-2-Pentene	0.812	2,304	227	59.2	5,634	70.1	6,671
1-3-M-2-Pentene	0.520	1,475	144	59.2	3,506	70.5	4,270
C6-4J0	34.259	97,292	8,416	59.7	211,010	69.7	211,018
430-650	4,971	14,102	1,019	62.1	22,296	62.1	22,290
650+	1,500	4,256	275	31.0	3,066	7	31.0
Sub-Total Coke	97,659	277,018	28,728	575,033		819,411	
Grand Total	100.000	283,657					
Coke Amount for Heat Balance, wt %							
Ib/hr	5%						
Coke Defall, lb/hr	8,280						
MMBTU/Day	3,382						
\$/Day	6,765						
					(6,765)		
Net \$/Day	568,269						
						612,846	

TABLE XI

Fischer Tropsch Wax Economics  
Pilot Plant Results of Wax Run Through an FCU  
Date Basis: 203,557 lb/hr  
Run No. 939-2  
07/10/01

TABLE XII

Fischer Tropsch Wax Economics  
Pilot Plant Results of Wax Run Through an FCU  
03/19/93

Component	normalized wt % Yield	Rate Basis: 283,657 lb/hr Run No. 939-4			<---Simple Configuration---> \$/Day Valued as			<---Complex Configuration---> \$/Day Valued as			
		lb/hr	BBU/Day	cpg	Fuel Gas	2	6.0	209	Fuel Gas	2	
Hydrogen	0.030	85	83	6.0	209	Fuel Gas	2	10.8	529	Fuel Gas	2
Methane	0.180	510	117	10.8	529	Fuel Gas	2	12.8	734	Fuel Gas	2
Ethylene	0.260	737	137	12.8	734	Fuel Gas	2	12.1	443	Fuel Gas	2
Ethano	0.160	454	87	12.1	443	Fuel Gas	2	17.1	19,471	Fuel Gas	2
Propylene	7.279	20,647	2,711	17.1	19,471	Fuel Gas	2	16.8	2,891	Fuel Gas	2
Propane	1.070	3,035	410	16.8	2,891	Fuel Gas	2	37.2	22,384	Alkylation	3
1-Butane	4.149	11,770	1,433	37.2	22,384	Alkylation	3	29.8	5,036	Gasoline	5
n-Butane	1.210	3,432	402	29.8	5,036	Gasoline	5	63.9	12,144	Alkylation	3
1-Butene	1,400	3,971	452	63.9	12,144	Alkylation	3	85.4	72,920	Ether Unit	4
1-Butylene	6.229	17,811	2,033	63.8	54,176	Alkylation	3	64.8	31,997	Alkylation	3
1-2-Butene	3.689	10,465	1,176	64.8	31,997	Alkylation	3	69.6	23,151	Alkylation	3
c-2-Butene	2,670	7,572	828	66.6	23,151	Alkylation	3	86.5	32,185	Ether Unit	4
n-Pentane	3,379	9,586	1,055	49.4	21,893	Gasoline	5	49.4	21,893	Gasoline	5
m-Pentane	0.770	2,184	237	33.8	3,367	Gasoline	5	33.8	3,367	Gasoline	5
3M-1-Butene	0.092	261	28	50.3	599	Gasoline	5	63.6	63.8	Alkylation	3
2M-1-Butene	0.936	2,655	277	60.3	5,056	Gasoline	5	86.5	10,071	Ether Unit	4
2M-2-Butene	2,089	8,480	871	50.3	18,397	Gasoline	5	88.0	54.9	Alkylation	3
1-Pentene	0.312	885	94	50.3	1,983	Gasoline	5	54.9	2,165	Alkylation	3
1-2-Pentene	1.248	3,539	371	50.3	7,844	Gasoline	5	55.5	8,655	Alkylation	3
c-2-Pentene	0.716	2,032	213	50.3	4,504	Gasoline	5	65.5	4,970	Alkylation	3
2,3-dim-1-Butene	0.330	936	94	69.2	2,339	Gasoline	5	68.6	2,710	Ether Unit	4
2-M-1-Pentene	0.718	2,035	204	69.2	5,074	Gasoline	5	68.7	5,888	Ether Unit	4
2-M-2-Pentene	1.287	3,650	362	59.2	9,013	Gasoline	5	69.4	10,566	Ether Unit	4
c-3-M-2-Pentene	1.306	3,704	364	59.2	9,058	Gasoline	5	70.1	10,725	Ether Unit	4
1-3-M-2-Pentene	0.822	2,331	228	59.2	5,066	Gasoline	5	70.5	6,747	Ether Unit	4
C6-430	39,423	111,827	9,673	59.7	242,542	Gasoline	5	59.7	242,542	Gasoline	5
430-650	10,078	20,588	2,066	52.1	45,201	Diesel	6	62.1	45,201	Diesel	6
650+	6,609	16,746	1,209	31.8	16,149	No FO	7	31.8	16,149	No FO	7
Sub-total	99,390	261,927	27,216		572,952				616,383		
Coke	0.610	1,730									
<b>Grand Total</b>	<b>100,000</b>	<b>283,657</b>									
Coke Amount for Heat Balance, wt %	5%										
Coke Deficit, lb/hr	14,929										
MMBTU/Day	13,189										
\$/Day	5,385										
	10,771										
	(10,771)										
<b>Net \$/Day</b>	<b>562,181</b>										
	<b>605,612</b>										

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TABLE XIII

Fischer Tropsch Wax Economics  
Pilot Plant Results of Wax Run Through an FCU  
03/19/93

Component	Rate Basis: Run No. 939-5		<--Simple Configuration-->		<--Complex Configuration-->	
	normalized wt % Yield	lb/hr	BBL/Day	cpg	\$/Day	Valued as \$/Day
Hydrogen	0.020	57	55	6.0	140	Fuel Gas 2
Methane	0.140	397	91	10.8	412	Fuel Gas 2
Ethylene	0.210	696	110	12.0	593	Fuel Gas 2
Ethane	0.140	397	76	12.1	308	Fuel Gas 2
Propylene	6.281	17,816	2,339	17.1	16,802	Fuel Gas 2
Propane	0.900	2,553	345	16.8	2,432	Fuel Gas 2
1-Butene	3.401	9,646	1,174	37.2	18,345	Alkylation 3
n-Dutene	0.990	2,009	329	29.0	4,122	Gasoline 5
1-Dutene	1.220	3,461	394	63.9	10,586	Alkylation 3
1-Buylene	5.531	15,609	1,791	63.8	47,986	Alkylation 3
1-2-Buylene	3.190	9,050	1,017	64.0	27,671	Alkylation 3
c-2-Buylene	2.310	8,553	716	66.0	20,036	Alkylation 3
c-Pentane	3.351	9,504	1,046	49.4	21,706	Gasoline 5
n-Pentane	0.960	2,724	298	33.0	4,199	Gasoline 5
3M-1-Buylene	0.160	477	52	60.3	1,091	Gasoline 5
2M-1-Buylene	1.516	4,301	449	50.3	9,410	Gasoline 5
2M-2-Buylene	5.070	14,403	1,479	50.3	31,247	Gasoline 5
1-Pentene	0.505	1,433	152	50.3	3,211	Gasoline 5
1-2-Pentene	2.069	5,870	616	60.3	13,008	Gasoline 5
c-2-Pentene	1.203	3,413	350	60.3	7,564	Gasoline 5
2,3-dIM-1-Buylene	0.369	1,047	105	59.2	2,610	Gasoline 5
2-M-1-Pentene	0.803	2,278	228	59.2	5,678	Gasoline 5
2-M-2-Pentene	1.419	4,026	400	59.2	9,940	Gasoline 5
c-3-M-2-Pentene	1.419	4,026	396	59.2	9,845	Gasoline 5
c-3-M-2-Pentene	0.907	2,573	252	59.2	6,254	Gasoline 5
c8-430	41.166	116,771	10,101	59.7	253,266	Gasoline 5
430-650	6.951	25,391	1,835	52.1	40,147	Diesel 6
650+	5.101	14,469	933	31.0	12,464	No 6 FO 7
Sub-total	99,320	281,728	27,136		581,240	
Coke	0.680	1,929				636,272
<b>Grand Total</b>	<b>100,000</b>	<b>283,657</b>				
Coke Amount for Heat Balance, wt %			5%			
lb/hr			14,929			
Coke Deficit, lb/hr			13,000			
MMBTU/Day			5,304			(10,600)
\$/Day			10,608			
Net \$/Day			670,661			625,664

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TABLE XIV

Fischer Tropsch Wax Economics  
Pilot Plant Results of Wax Run Through an FCU  
03/19/93

Component	normalized wt % Yield	lb/hr	DBBL/Day	<---Simple Configuration--->			<---Complex Configuration--->		
				cpg	\$/Day	Valued as	cpg	\$/Day	Valued as
Hydrogen	0.020	57	65	0.0	140	Fuel Gas	2	6.0	140
Methane	0.100	284	65	10.0	294	Fuel Gas	2	10.0	294
Ethylene	0.660	1,973	347	12.6	1,066	Fuel Gas	2	12.6	1,066
Ethane	0.110	312	60	12.1	305	Fuel Gas	2	12.1	305
Propylene	13.939	39,531	5,192	17.1	37,287	Fuel Gas	2	17.1	37,287
Propane	2.111	5,979	809	16.8	5,706	Fuel Gas	2	16.8	5,706
1-Butene	9.046	25,659	3,123	37.2	40,800	Alkylation	3	37.2	40,800
n-Butane	2.582	7,323	659	29.0	10,746	Gasoline	5	29.0	10,746
1-Butene	2.221	6,301	718	63.9	19,272	Alkylation	3	63.9	19,272
1-Butene	10.247	29,065	3,318	63.8	69,901	Alkylation	3	65.4	118,999
1-2-Butene	5.654	16,937	1,802	64.8	49,034	Alkylation	3	64.8	49,034
C-2-Butene	4.163	11,808	1,291	66.6	36,100	Alkylation	3	60.6	36,100
1-Pentane	5.113	14,504	1,597	49.4	33,127	Gasoline	5	49.4	33,127
n-Pentane	1.731	4,910	533	33.8	7,571	Gasoline	5	33.8	7,571
3M-1-Butene	0.167	531	58	60.3	1,210	Gasoline	5	63.6	1,208
2M-1-Butene	1.681	4,769	490	50.3	10,520	Gasoline	5	66.5	16,091
2M-2-Butene	5.033	14,277	1,466	50.3	30,974	Gasoline	5	88.0	54,188
1-Pentene	0.476	1,351	143	60.3	3,020	Gasoline	6	64.9	3,305
1-2-Pentene	1.769	5,018	528	50.3	11,122	Gasoline	6	65.5	12,271
c-2-Pentene	1.001	2,838	298	50.3	6,290	Gasoline	5	65.5	6,941
2,3-dM-1-Butene	0.193	648	65	59.2	1,369	Gasoline	6	60.6	1,586
2-M-1-Pentene	0.579	1,643	165	59.2	4,096	Gasoline	5	68.7	4,754
2-M-2-Pentene	1.066	3,923	300	59.2	7,464	Gasoline	5	69.4	8,750
c-3-M-2-Pentene	1.079	3,060	301	59.2	7,403	Gasoline	6	70.1	8,860
1-3-M-2-Pentene	0.689	1,956	191	69.2	4,753	Gasoline	5	70.6	5,660
C6-430	23.755	67,384	6,829	59.7	146,150	Gasoline	5	69.7	146,160
430-650	2.722	7,720	558	52.1	12,207	Diesel	6	62.1	12,207
650+	0.871	2,469	159	31.8	2,127	No #FO	7	31.8	2,127
Sub-Total		98,799	280,251	30,315				655,438	
Coke		1,201	3,406						
Grand Total		100,000		283,657					
Coke Amount for Heat Balance, wt %				5%					
Coke Delivl. lb/hr				14,929					
MMBTU/Day					11,523				
\$/Day					4,701				
					9,403				(9,403)
									646,035

TABLE XV

Fischer Tropsch Wax Economics

Rate Basis: 283,657 lb/hr  
CU Run No. 940-2

TABLE XVI

Fischer Tropsch Wax Economics  
Pilot Plant Results of Wax Run Through an FCU  
03/19/93

Component	Fisher Tropsch Wax Economics			Flare Basis: 283,657 lb/hr			Run No. 941-1		
	normalized wt %	Yield lb/hr	BDL/Day	<--> Simple Configuration	\$/Day	Value as	<--> Complex Configuration	\$/Day	Value as
Hydrogen	0.020	57	55	6.0	140	Fuel Gas	2	6.0	140 Fuel Gas
Methane	0.090	255	50	10.8	265	Fuel Gas	2	10.8	265 Fuel Gas
Ethylene	1.010	2,865	531	12.0	2,854	Fuel Gas	2	12.0	2,854 Fuel Gas
Ethane	0.100	204	55	12.1	277	Fuel Gas	2	12.1	277 Fuel Gas
Propylene	16.032	45,477	5,971	17.1	42,887	Fuel Gas	2	17.1	42,887 Fuel Gas
Propane	2.470	7,007	946	16.8	6,676	Fuel Gas	2	16.8	6,676 Fuel Gas
1-Butane	3.401	9,646	1,174	37.2	18,345	Alkylation	3	37.2	18,345 Alkylation
n-Butene	1.920	6,447	639	29.8	7,994	Gasoline	5	29.8	7,994 Gasoline
1-Butene	2.200	6,241	711	63.9	19,009	Alkylation	3	63.9	19,009 Alkylation
1-Buylene	10.752	30,498	3,481	63.8	93,202	Alkylation	3	85.4	124,063 Ether Unit
1-2-Buylene	5.331	15,121	1,699	64.8	46,233	Alkylation	3	64.8	46,233 Alkylation
C-2-Buylene	3.761	10,667	1,166	66.6	32,613	Alkylation	3	66.6	32,613 Alkylation
1-Pentane	2.160	6,126	675	49.4	13,996	Gasoline	5	49.4	13,996 Gasoline
n-Pentane	1.400	3,972	431	33.8	6,124	Gasoline	5	33.8	6,124 Gasoline
3M-1-Buylene	0.279	792	86	50.3	1,816	Gasoline	5	53.6	1,935 Alkylation
2M-1-Buylene	2.300	6,525	601	50.3	14,395	Gasoline	5	86.5	24,755 Ether Unit
2M-2-Buylene	5.941	16,852	1,731	50.3	36,559	Gasoline	5	89.0	63,960 Ether Unit
1-Pentene	0.620	1,759	187	50.3	3,942	Gasoline	5	64.9	4,303 Alkylation
1-2-Pentene	2.145	6,085	638	50.3	13,486	Gasoline	5	65.5	14,880 Alkylation
C-2-Pentene	1.180	3,348	351	50.3	7,419	Gasoline	5	55.5	8,186 Alkylation
2,3-dim-1-Buylene	0.085	241	24	59.2	603	Gasoline	5	68.6	698 Ether Unit
2-M-1-Pentene	0.266	765	76	59.2	1,001	Gasoline	5	68.7	2,183 Ether Unit
2-M-2-Pentene	0.602	1,935	192	59.2	4,778	Gasoline	5	69.4	5,601 Ether Unit
C-3-M-2-Pentene	0.840	2,303	234	59.2	5,928	Gasoline	5	70.1	6,901 Ether Unit
1-3-M-2-Pentene	0.448	1,271	124	59.2	3,009	Gasoline	5	70.5	3,679 Ether Unit
C6-430	22,493	63,804	5,519	59.7	138,385	Gasoline	5	69.7	138,385 Gasoline
430-650	7,471	21,192	1,531	52.1	33,500	Diesel	6	62.1	33,508 Diesel
650+	4,131	11,717	756	31.8	10,093	No 6 FO	7	31.8	10,093 No 6 FO
Sub-Total	99,530	282,324	29,723		506,555			641,421	
Coke	0.470	1,333							
Grand Total	100,000	283,657							
Coke Amount for Heat Balance, wt %		5%							
lb/hr	14,929								
Coke Deficit, lb/hr	13,696								
MMBTUDay	5,547								
\$/Day	11,094								
Net \$/Day	655,461								
									(11,094)
									630,327

TABLE XVII

Fischer Tropsch Wax Economics 03/19/93		Rate Basis: Run No. 942-2		<----Simple Configuration---->		<----Complex Configuration---->				
Component	normalized wt % Yield	lb/hr	BBL/Day	cpg	\$/Day	Valued as	cpg	\$/Day	Valued as	
Hydrogen	0.020	57	55	6.0	140	Fuel Gas	2	6.0	140	Fuel Gas
Methane	0.160	454	104	10.8	471	Fuel Gas	2	10.8	471	Fuel Gas
Ethylene	0.340	965	179	12.8	961	Fuel Gas	2	12.8	961	Fuel Gas
Ethane	0.150	428	92	12.1	416	Fuel Gas	2	12.1	416	Fuel Gas
Propylene	0.041	25,361	3,330	17.1	23,916	Fuel Gas	2	17.1	23,916	Fuel Gas
Propane	1.250	3,546	479	16.8	3,378	Fuel Gas	2	16.8	3,378	Fuel Gas
1-Rutane	5.020	14,241	1,733	37.2	27,084	Alkylation	3	37.2	27,084	Alkylation
n-Butane	1.300	3,688	432	29.8	5,412	Gasoline	5	29.8	5,412	Gasoline
1-Butene	1.410	4,000	456	63.9	12,233	Alkylation	3	63.9	12,233	Alkylation
1-DiButene	6.261	17,758	2,027	63.8	54,316	Alkylation	3	85.4	72,706	Ether Unit
1-2-Butene	3.720	10,553	1,186	64.8	32,266	Alkylation	3	64.8	32,266	Alkylation
c-2-Butene	2.680	7,603	831	60.6	23,244	Alkylation	3	68.6	23,244	Alkylation
1-Pentane	3.970	11,262	1,240	49.4	25,722	Gasoline	5	49.4	25,722	Gasoline
n-Pentane	0.850	2,411	262	33.8	3,718	Gasoline	5	33.8	3,718	Gasoline
3M-1-Butene	0.128	357	39	60.3	820	Gasoline	5	63.6	874	Alkylation
2M-1-Butene	1.130	3,206	335	60.3	7,072	Gasoline	5	66.5	12,161	Ether Unit
2M-2-Butene	3,360	9,532	979	60.3	20,678	Gasoline	5	68.0	36,177	Ether Unit
1-Pentene	0.378	1,072	114	60.3	2,403	Gasoline	5	64.9	2,623	Alkylation
1-2-Pentene	1.450	4,113	432	50.3	9,116	Gasoline	5	55.5	10,058	Alkylation
c-2-Pentene	0.819	2,323	244	60.3	5,149	Gasoline	5	65.5	6,681	Alkylation
2,3-dim-1-Butene	0.220	624	63	59.2	1,560	Gasoline	5	68.6	1,807	Ether Unit
2-M-1-Pentene	0.570	1,617	162	59.2	4,031	Gasoline	5	68.7	4,677	Ether Unit
2-M-2-Pentene	1.136	3,223	320	59.2	7,957	Gasoline	5	69.4	9,328	Ether Unit
c-3-M-2-Pentene	1.210	3,433	338	59.2	8,394	Gasoline	5	70.1	9,940	Ether Unit
1-3-M-2-Pentene	0.733	2,079	203	59.2	5,054	Gasoline	5	70.5	6,018	Ether Unit
C6-430	41,493	117,699	10,181	59.7	255,276	Gasoline	5	59.7	255,276	Gasoline
430-650	7,471	21,191	1,531	52.1	33,506	Diesel	6	62.1	33,506	Diesel
650+	2,950	8,369	540	31.8	7,209	No 6 FO	7	31.8	7,209	No 6 FO
Sub-Total	89,120	281,161	27,874		581,503				627,004	
Coke	0.880	2,496								
Grand Total	100,000	283,657								

Coke Amount for Heat Balance, wt %	5%
lb/hr	14,929
Coke Deficit, lb/hr	12,433
MMBTU/Day	5,073
\$/Day	10,146

(10,145)

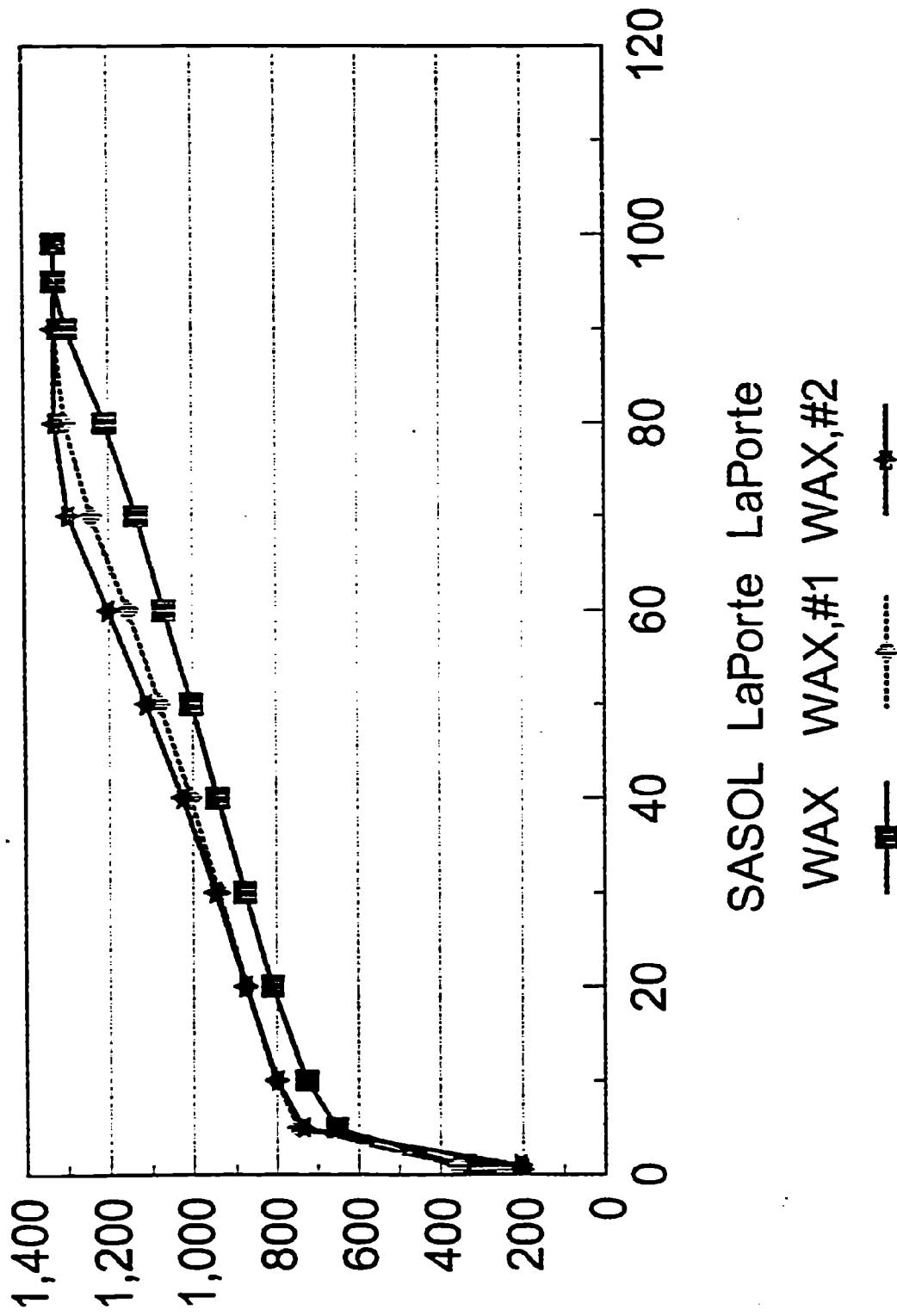
Net \$/Day	671,358
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TABLE XVIII  
SUMMARY OF NET PRODUCT VALUES FOR PILOT PLANT FCC RUNS

Run Number	Catalyst	Net Product Value, \$/d		
		Simple Refinery	Complex Refinery	$\Delta$ (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. HZSM-5	555,461	630,327	74,866
942-2	50% Eq. USY; 50% Diluent	571,358	616,859	45,501

**FIGURE 1**

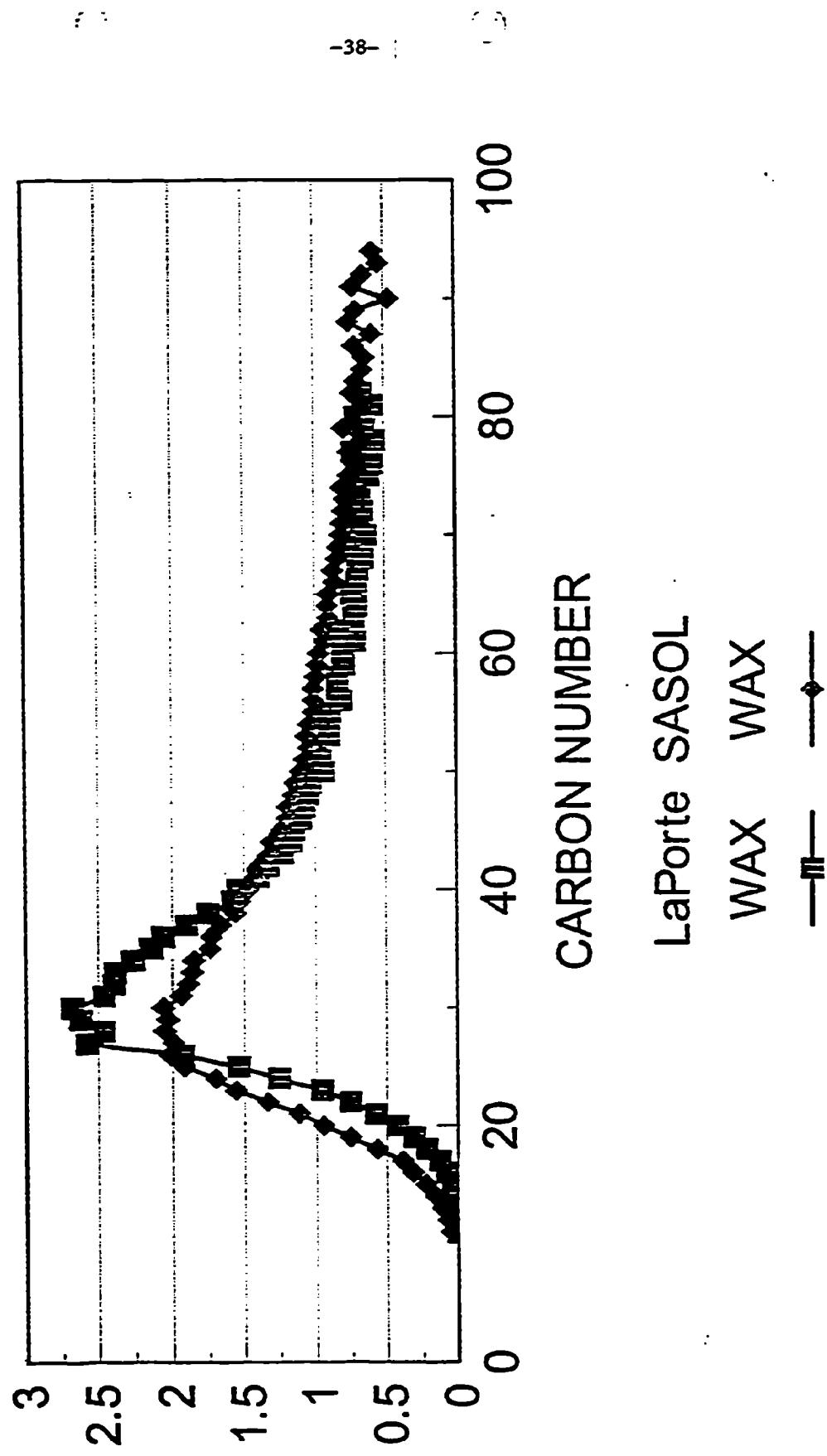
HIGH TEMPERATURE SIMULATED DISTILLATION  
SASOL AND LAPORTE WAX FEEDSTOCKS



## FIGURE 2

NORMAL PARAFFIN DISTRIBUTION  
SASOL AND LaPorte WAX FEEDSTOCKS

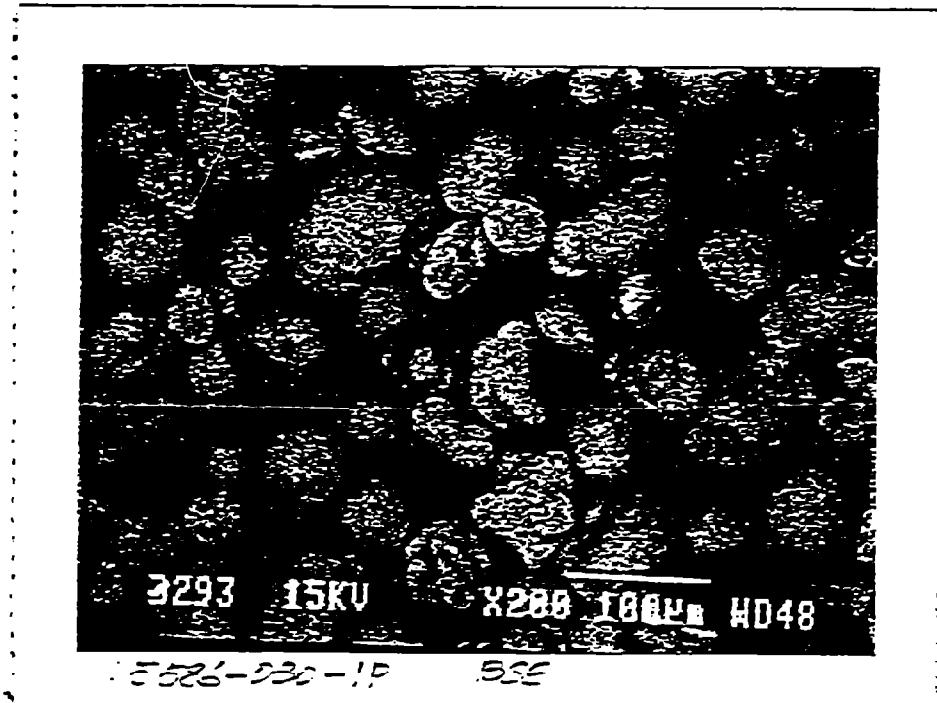
WEIGHT PERCENT



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FIGURE 3

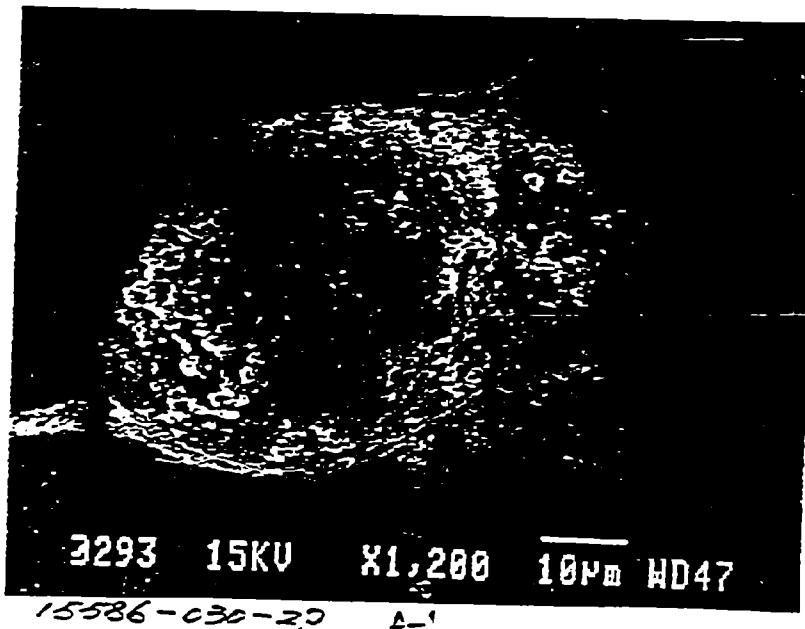
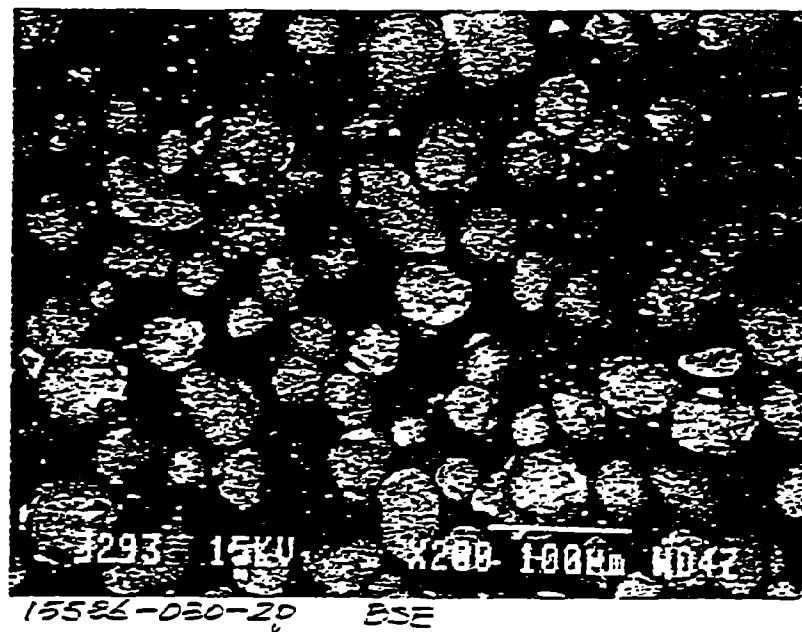
SEM PHOTOGRAPH  
BASE CATALYST - CCC-1397  
EQUILIBRIUM FCC CATALYST  
IRON CONTENT - 4200 PPM



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FIGURES 4 AND 5

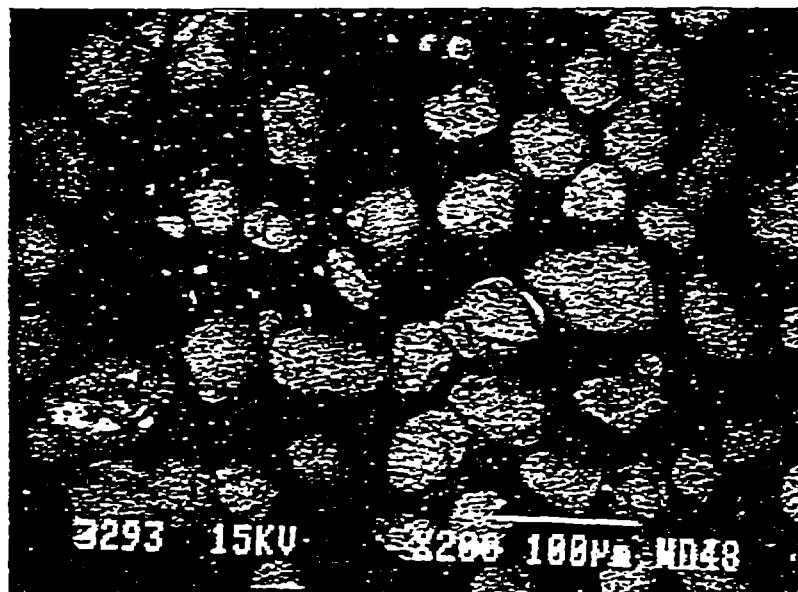
SEM PHOTOGRAPHS  
F-T Catalyst Fines Contaminated FCC Catalyst  
Before Selective Attrition Experiment  
ID No. 15586-030-2P  
Iron Content = 10500 ppm



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FIGURE 6

SEM PHOTOGRAPH  
F-T Catalyst Fines Contaminated FCC Catalyst  
After Selective Attrition Experiment  
ID No. 15586-030-23  
Iron Content = 6200 ppm



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FIGURES 7 AND 8

SEM PHOTOGRAPHS  
Fines from Selective Attrition Experiment  
ID No. 15586-030-2F  
Iron Content = 29600 ppm

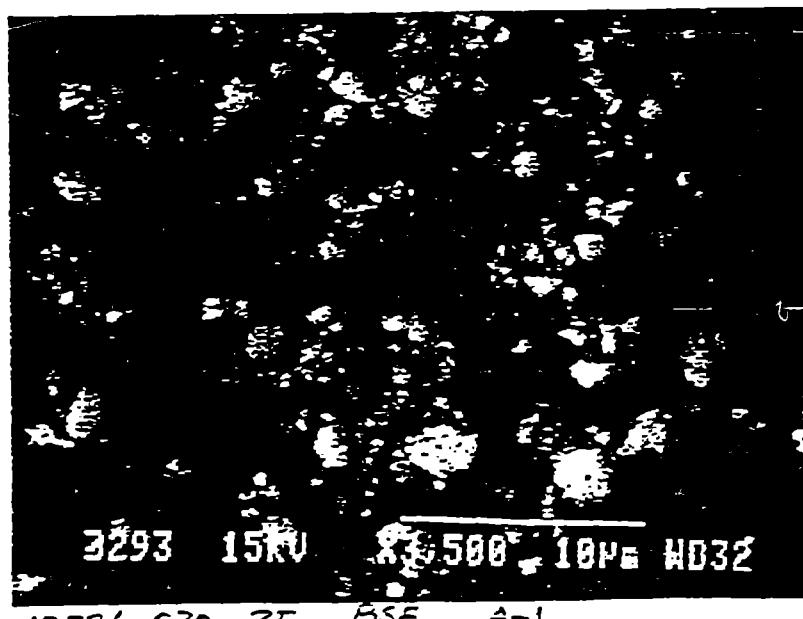
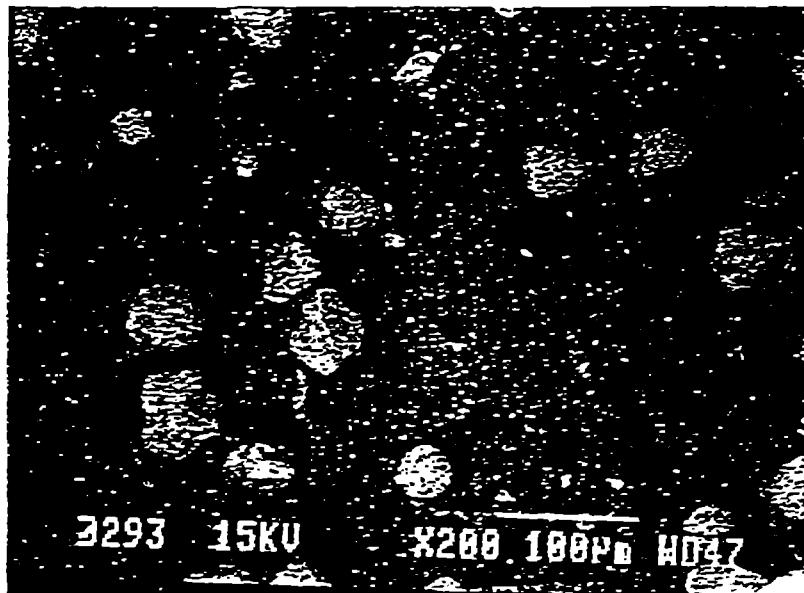


FIGURE 9

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

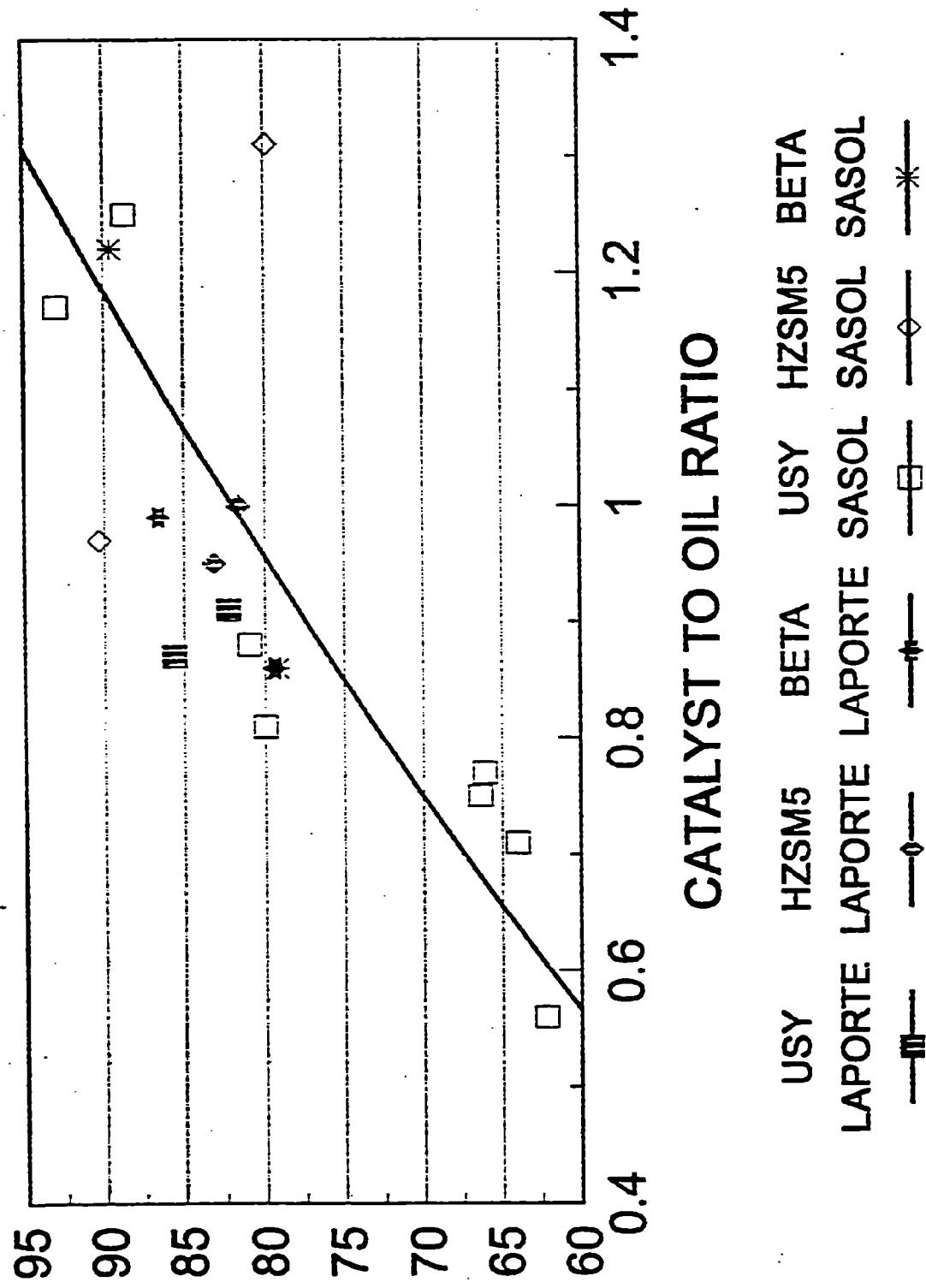


FIGURE 10

COKE SELECTIVITY SASOL AND LAPORTE WAX  
COKE, WT. %

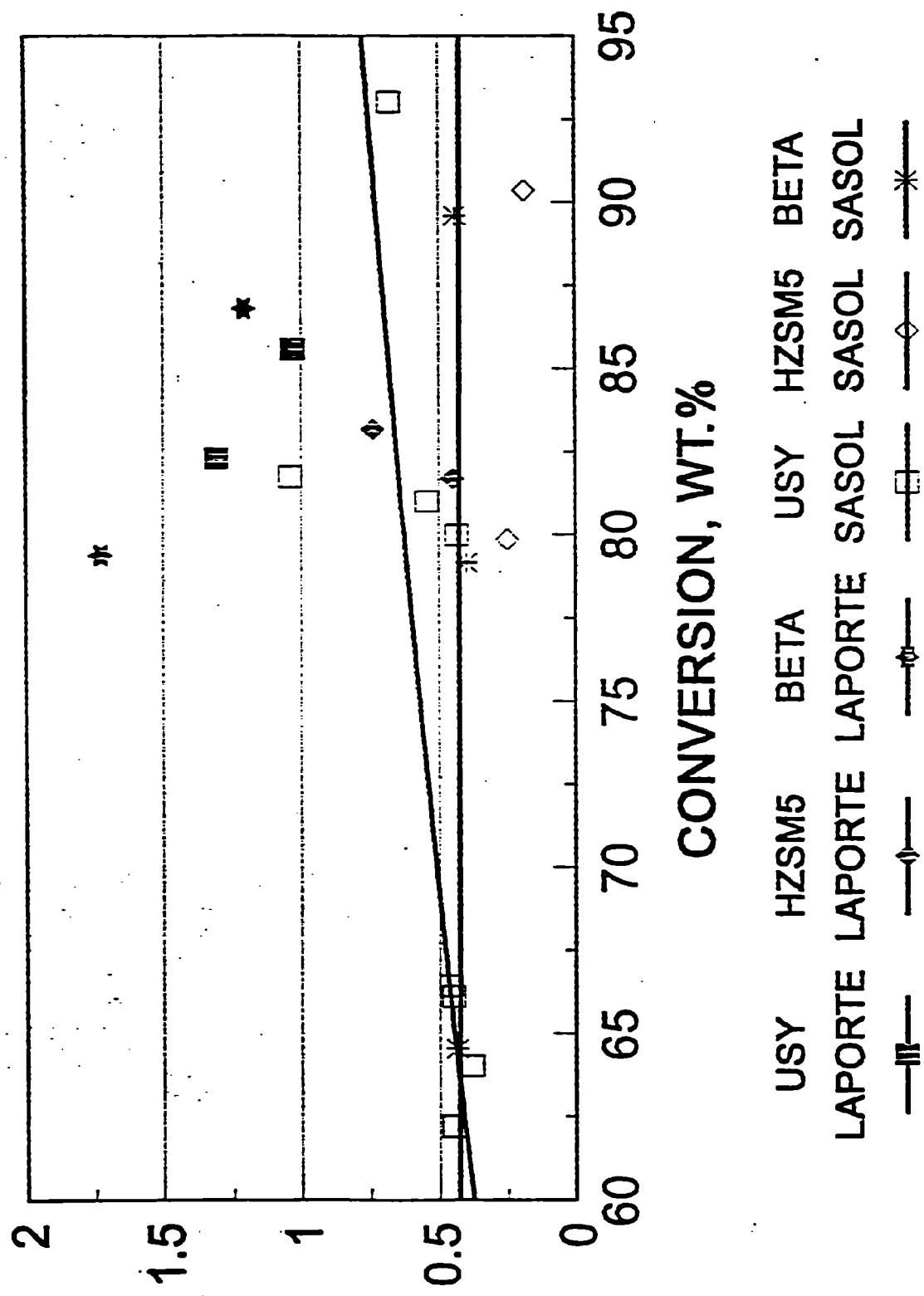


FIGURE 11

HYDROGEN PRODUCT SELECTIVITY LAPORTE / SASOL WAX  
HYDROGEN, WT. %

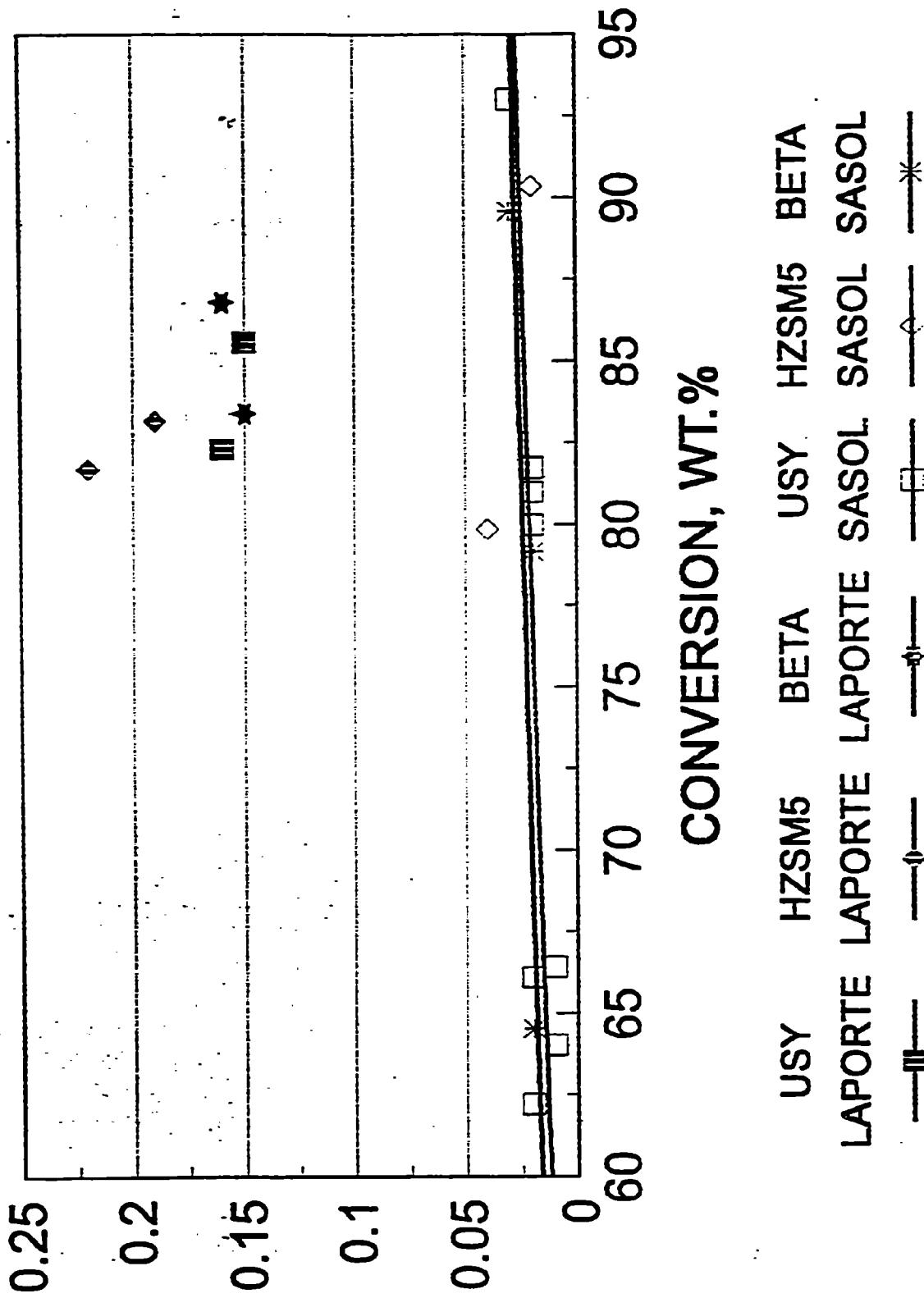


FIGURE 12

PROPYLENE SELECTIVITY LAPORTE AND SASOL WAX  
PROPYLENE, WT.%

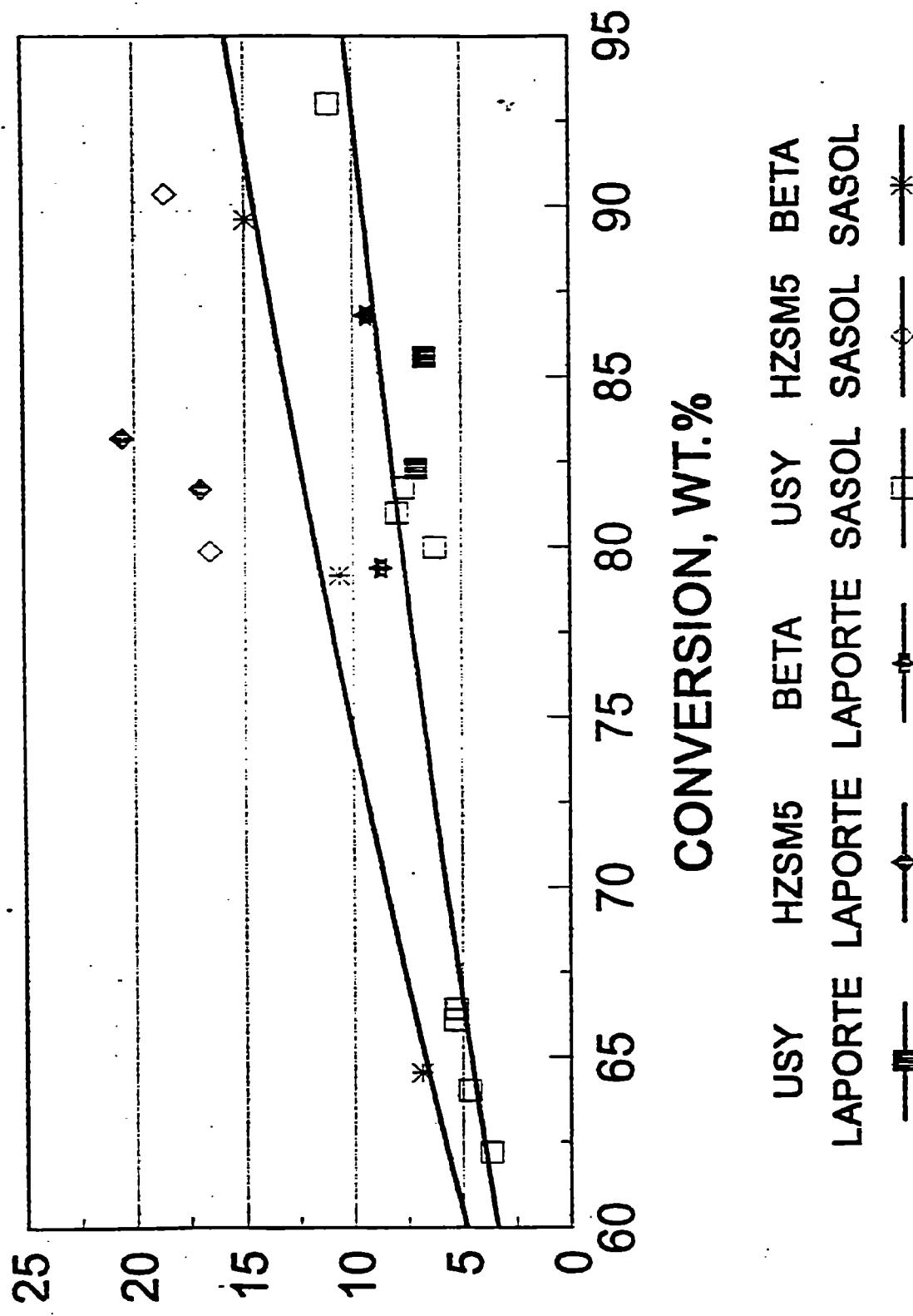


FIGURE 13

ISOBUTYLENE SELECTIVITY LAPORTE AND SASOL WAX  
ISOBUTYLENE, WT.%

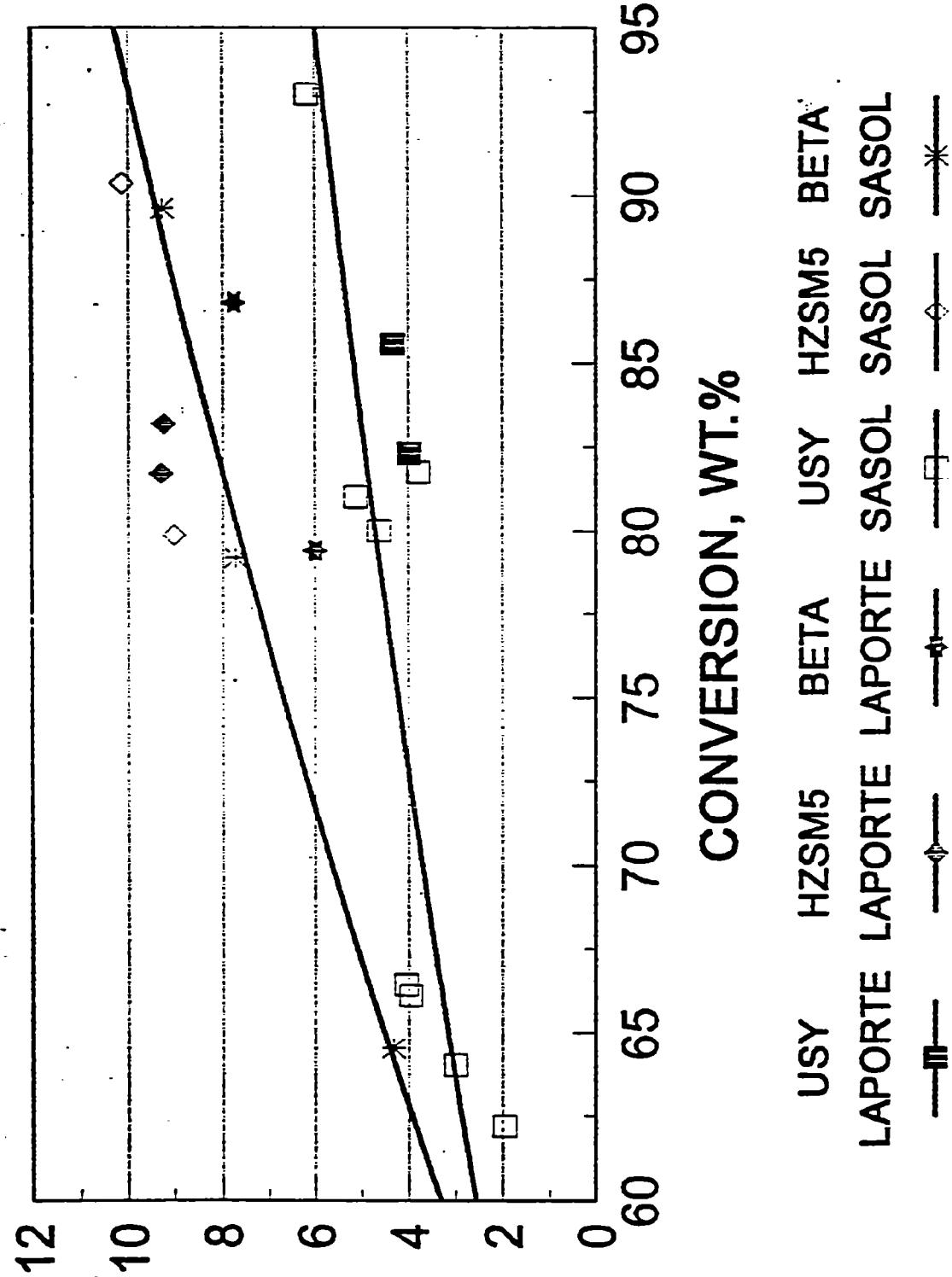


FIGURE 14

ISOAMYLENES SELECTIVITY SASOL AND LAPORTE WAX  
ISOAMYLENES, WT. %

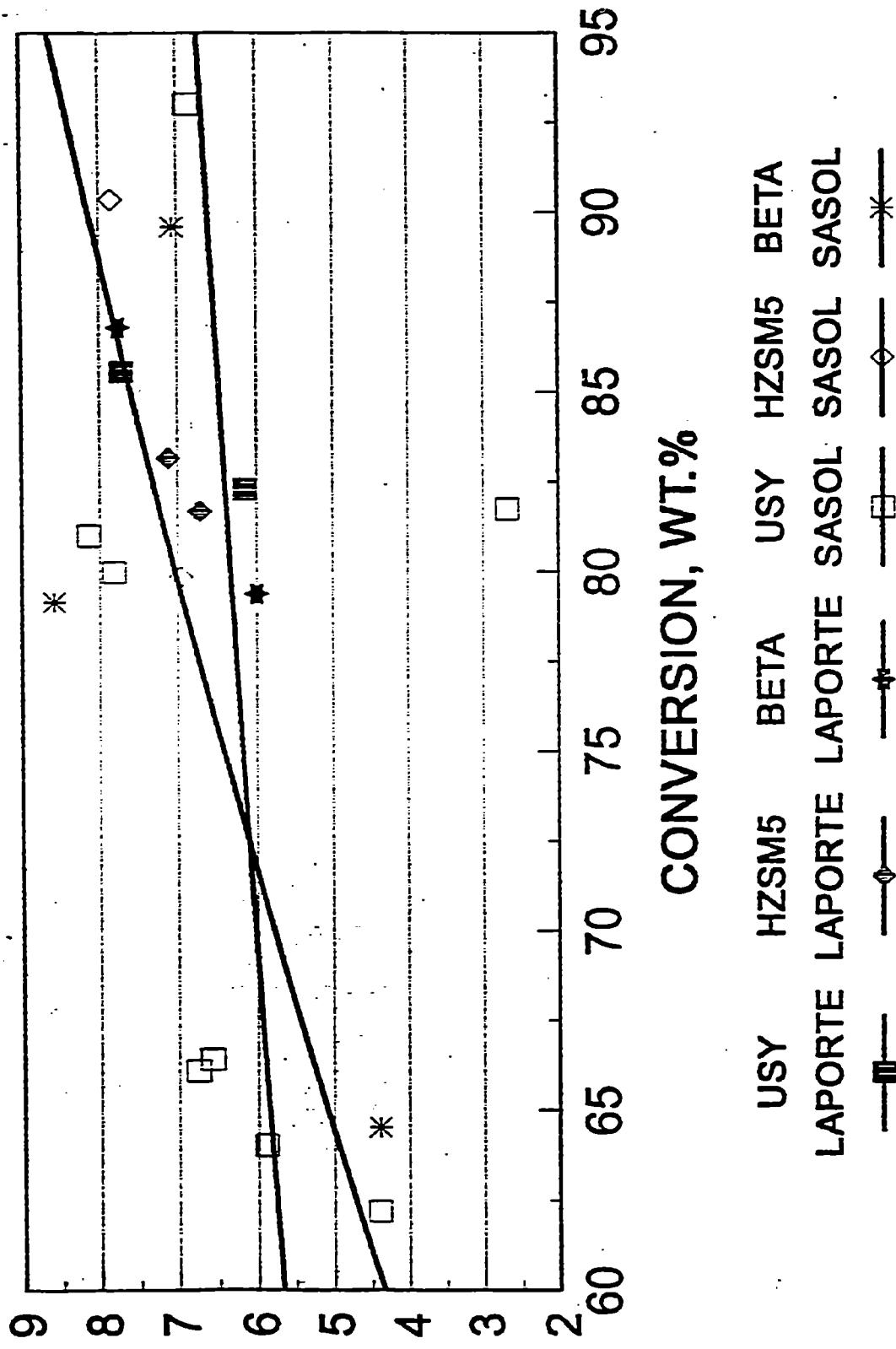


FIGURE 15

NAPHTHA SELECTIVITY SASOL AND LAPORTE WAX  
C5-4300F, NAPHTHA, WT. %

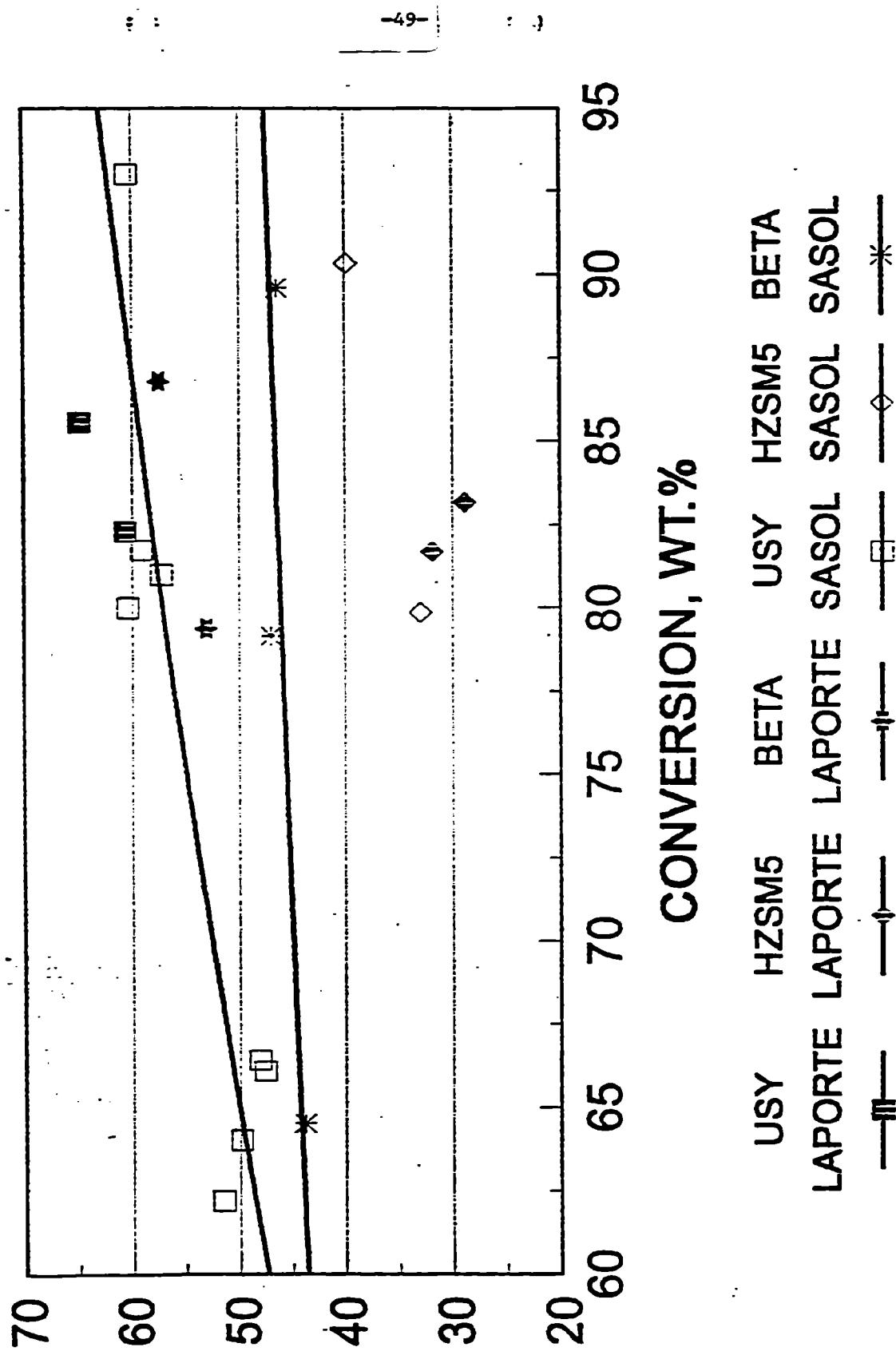


FIGURE 16

DISTILLATE SELECTIVITY SASOL AND LAPORTE WAX  
430-650°F, WT.%

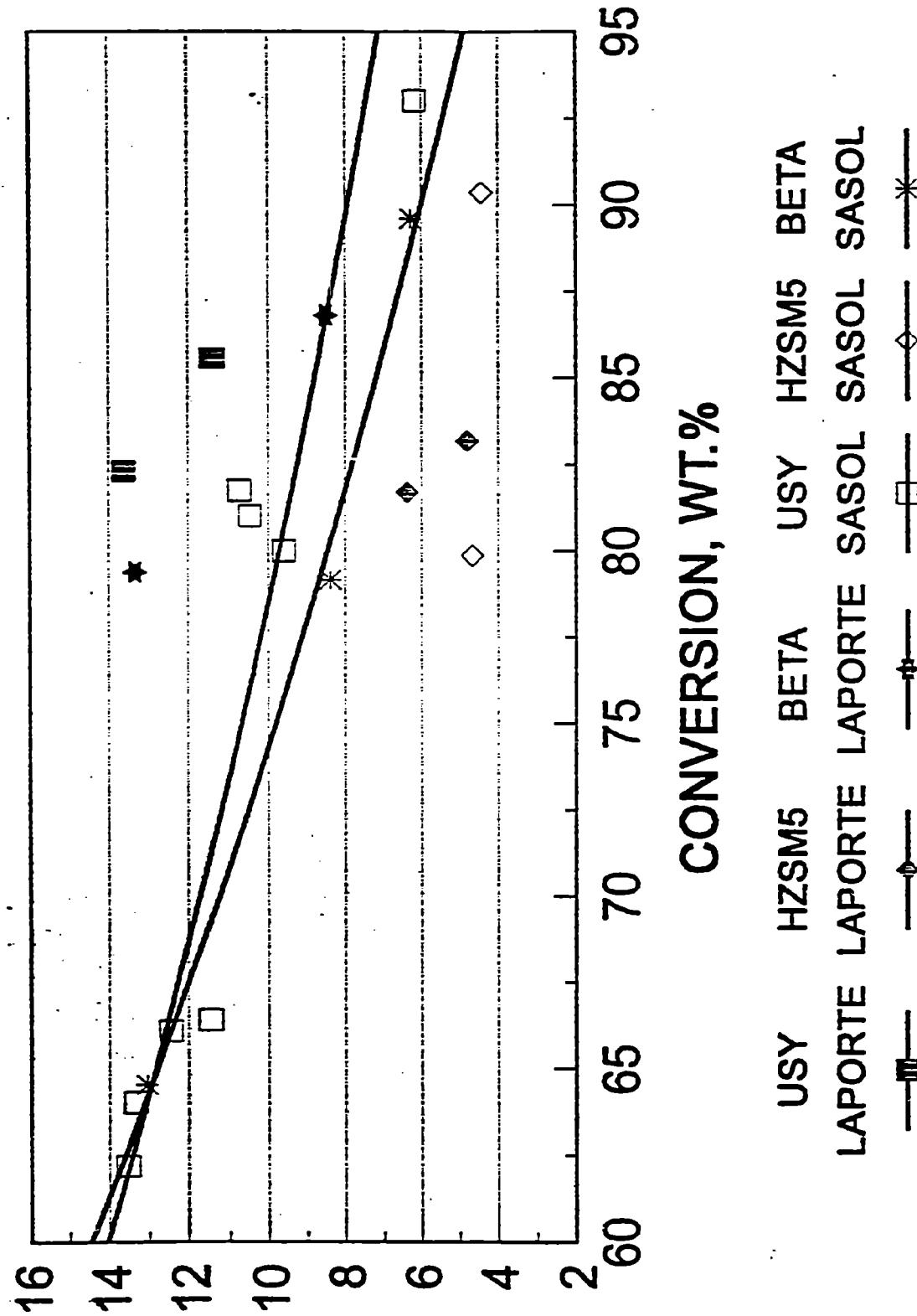


FIGURE 17

BOTTOMS SELECTIVITY SASOL AND LAPORTE WAX  
650-8000°F, WT. %

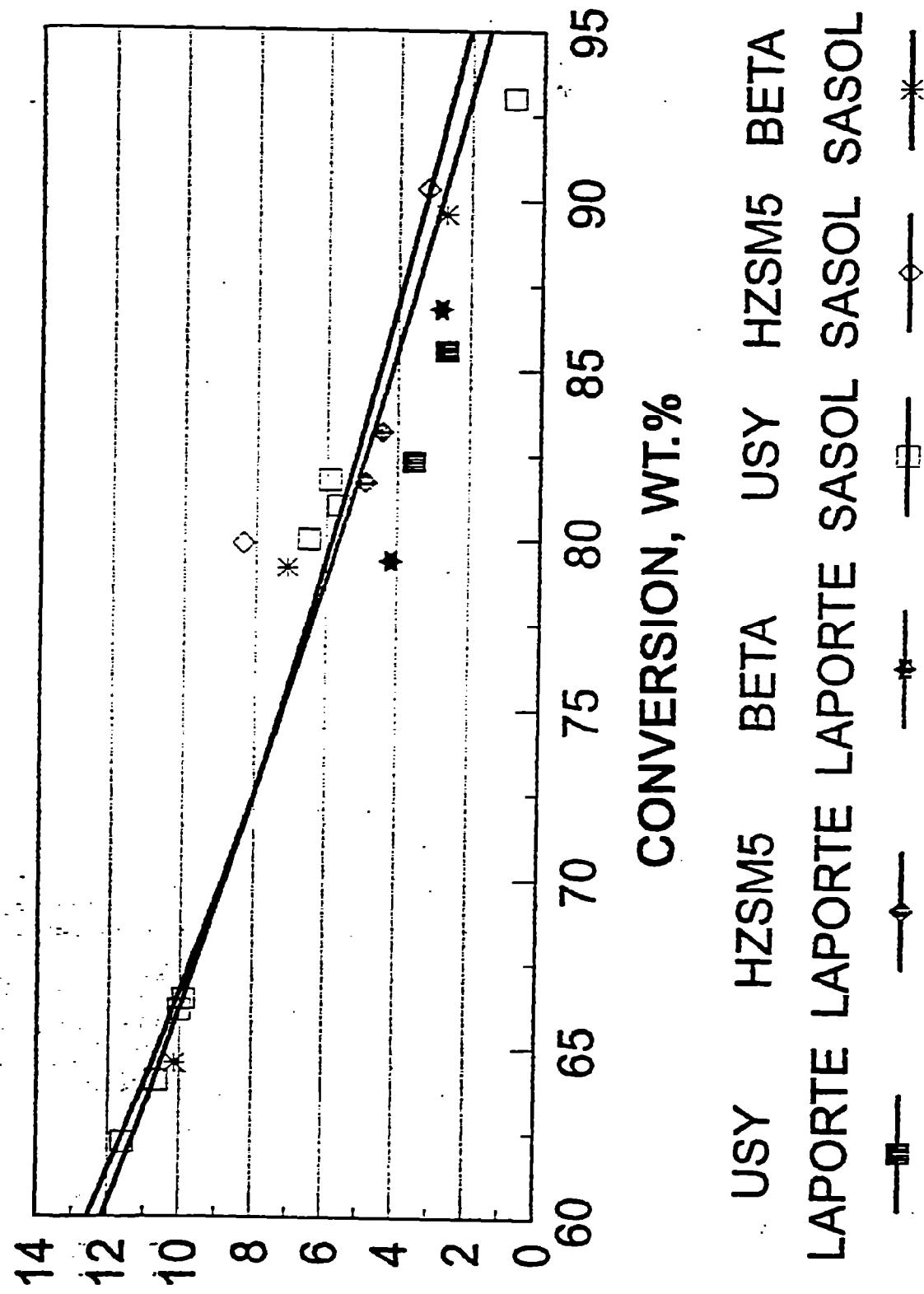


FIGURE 18

BOTTOMS SELECTIVITY SASOL AND LAPORTE WAX

800oF+, Wt.%

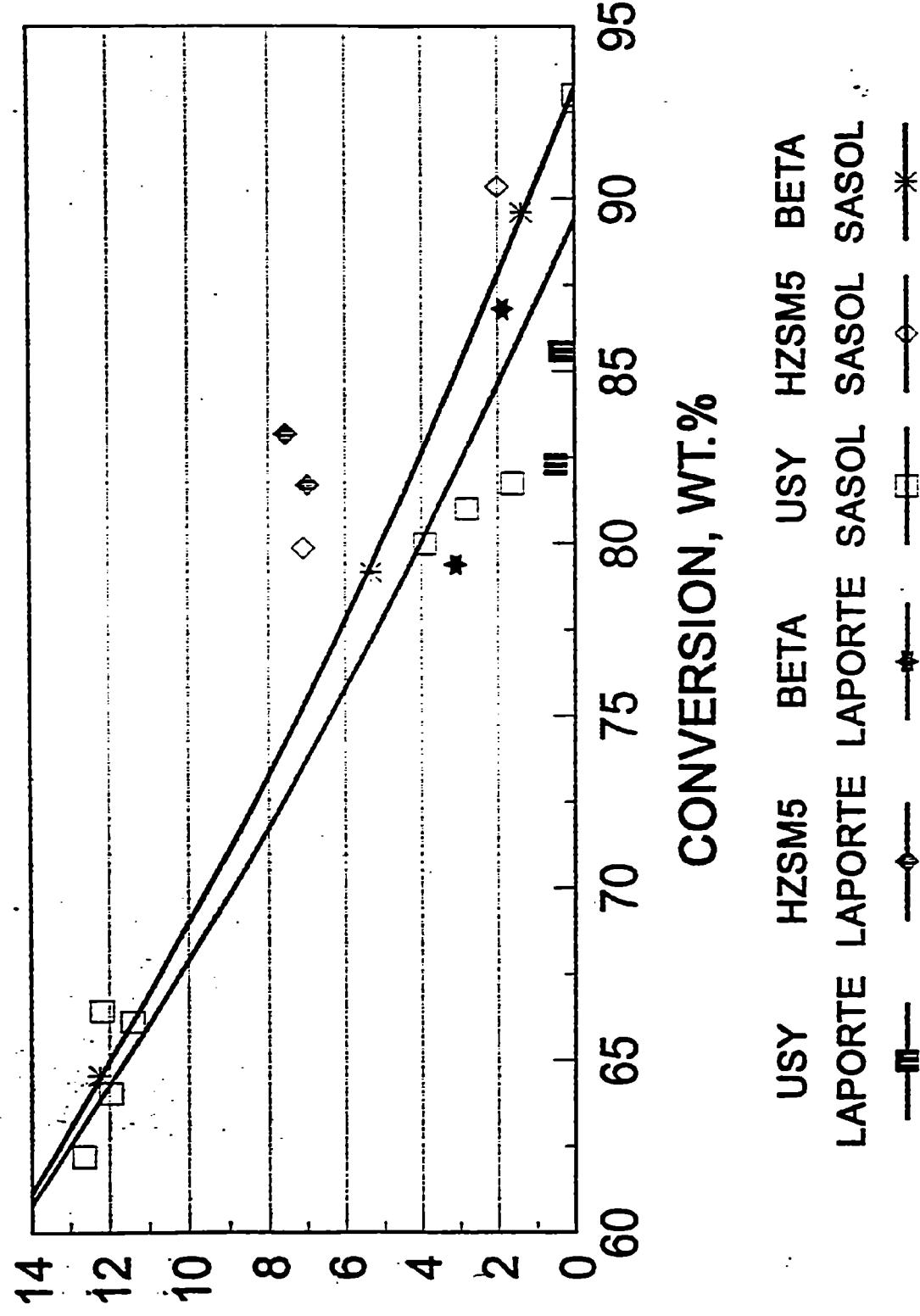


FIGURE 19

RESEARCH OCTANE NUMBER LAPORTE AND SASOL WAX  
C5-4300F RON

