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

REPORT NO. 23

QUARTERLY TECHNICAL PROGRESS REPORT

FOR.

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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 naphtha and wax fractions to high value transportation fuels. This report describes the work in the third quarter, fiscal year, 1992, the fourth 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 C4- gas (high in propylene and  $C_4$  olefins) and naphtha ( $C_5$ -430°F). Three different types of zeolite catalysts and one amorphous cracking catalyst show wide variations of product yields as a function of wax feedstock conversion. The Beta and HZSM-5 zeolite catalysts have higher target light olefin (isobutylene and isoamylenes) yields than the Y zeolite sample. The HSZM-5 sample also produces the highest yields of propylene. Work this Quarter centers on the study of various types of HZSM-5 and Y zeolite catalysts. The overall activity (wax conversion) and product selectivities of two commercial HZSM-5 FCC catalysts are similar. Another HZSM-5 sample with a low acid site density is less active, as expected. A series of Y zeolite catalysts with variable rare earth exchange levels shows a decrease in olefin production with an increase in rare earth content. These variations in product yields will form the basis for economic calculations of the various process and catalyst options that will follow in the later stages of this project.

The catalytic cracking tests of a sample of Fischer-Tropsch light naphtha show lower conversion levels than the wax feedstock. This is due primarily to the light hydrocarbon  $(C_6-C_{12})$  composition of this naphtha, which are difficult to convert.

Task 4, Pilot Plant Tests. The wax cracking tests on the pilot plant unit were completed last Quarter. The initial product yields have now been corrected for gas and liquid component distribution. Several additional product quality measurements have been completed. The distillate product fraction, boiling between  $430-650^{\circ}F$ , obtained from the Y zeolite catalyst run, has a high quality Cetane Index of 59. These test results also show high conversion (85%+) of the wax feedstock to light gases and gasoline. The ranking of the three zeolite catalyst types for  $C_4-C_5$  iso-olefin production is similar to the findings of the small scale screening test program. It is not possible to obtain test results at a wide variety of conversion levels on the pilot plant due to operating constraints.

#### 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, C18+, 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 values. 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 alcehol 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 4 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.

The Fischer-Tropsch synthesis process also produces a light naphtha fraction in addition to the heavy wax materials that have been studied thus far in this project. This naphtha product is a complex mixture of  $C_5 - C_{12}$  linear paraffins, olefins and oxygenates. Table I illustrates the qualitative GC-MS analysis of this naphtha. The catalytic cracking studies of the Fischer-Tropsch product naphtha, obtained from UOP, show lower overall conversion compared to the F-T wax feedstock. (Technical Status Report, No.12, March, 1992) This is due primarily to the light hydrocarbon  $(C_6-C_{12})$  composition of the gasoline. These materials are more difficult to crack than the larger wax paraffins. The severity of the catalytic cracking of the F-T naphtha fraction can be increased by changes in several process and catalyst variables. The simplest variable to change is the reaction temperature. Table II shows the small scale catalytic cracking test results for the Fischer-Tropsch naphtha at 970°F. The overall naphtha conversion increases substantially at the higher reaction temperature. Figure 1 illustrates the naphtha conversion (C5products) results for the three catalysts in this study, at the two reaction temperatures. At these test conditions, the HZSM-5 catalyst has the highest gasoline conversion. In addition, this catalyst also has the highest yields of the target isobutylene and isoamylenes products, Figures 2 and 3. This increased yields of the desirable olefins by the HZSM-5 catalyst are a function of its higher conversion, rather than an improved selectivity. The solid curves in Figures 2 and 3 are a best fit of all points with correlation coefficients of 0.90 and 0.95. This constant selectivity behavior of the three tested catalysts for F-T naphtha conversion is different from the results for F-T wax conversion. Selectivity differences among the three zeolite catalysts are clearly evident in the wax conversion studies. The octane number ratings of the remaining gasoline range products from catalytic cracking of the F-T naphtha are relatively low, (RON - 74-76, MON - 68-70), Table II. The naphtha products from catalytic cracking of the Fischer-Tropsch wax are significantly higher, ( RON = 84-86, MON = 74-76). The low octane ratings of the naphtha products are due to the high normal paraffin content, low

aromatics level and high linear olefin content. The compositions (paraffins, isoparaffins, aromatics, naphthenes, olefins) of these naphtha products, Figure 4, are not very sensitive to changes in catalyst type or reaction temperature. The naphthas from catalytic cracking over both zeolite Beta and zeolite HZSM-5 have higher olefin contents than the products from the zeolite Y tests. The zeolite Y sample produces slightly more aromatics than the other catalysts.

These test results for the catalytic cracking of the Fischer-Tropsch gasoline suggest that more severe conditions will be required to upgrade these products to gasolines with satisfactory octane ratings.

A better understanding of the complex catalytic cracking chemistry of the Fischer-Tropsch wax conversion process is desirable for a number of reasons. Such studies could produce simple process models and more selective catalysts. The formation of gasoline range aromatics from wax cracking is one area of considerable importance. These aromatics products determine to a large extent the octane quality of the gasoline. In addition, governmental regulations may limit the amount of such compounds blended into gasolines. For the wax feedstock in these studies, the product aromatics must come from cyclization of olefin intermediates. Both catalyst and process parameters should influence this aromatics formation reaction. Figure 5 shows the behavior of three zeolite catalysts for aromatics formation as a function of wax feedstock conversion. Some of the scatter in these results arises from the lack of precision of the GC method for compound identification. However, qualitative trends are apparent. The aromatics yields for the three catalysts rise very slowly up to about 85% conversion. The aromatics formation for the HZSM-5 catalyst, initially lower than the other larger pore zeolite catalysts, then increases dramatically. Further changes in the aromatics yields for the other catalysts also occur to a lesser extent. Increases in reaction temperature and catalyst contact time (cat/oil ratio) also cause increases in aromatics yields. Further studies will be required to elucidate the mechanism of formation of these gasoline range aromatics.

The catalytic cracking results from both the small scale test unit (MYU) and the pilot plant indicate that the wax feedstock readily converts to product gas (C4-) and naphtha. The HZSM-5 zeolite catalyst has the highest isobutylene and isoamylenes yields among the catalysts tested to date. However, the production of propylene is also high. These results are from one sample of Intercat Corp.'s ZCATPLUS commercial FCC additive material. Further catalyst screening studies now center on various types of HZSM-5 catalysts. Another commercial HZSM-5 catalyst sample from Davison Chemical Co., Additive OH-S, and a sample of Intercat's ISOCAT material are under study with the small scale test unit. A standard steam pre-treatment, 100% steam, 1450°F, five hours, of these samples precedes the wax cracking tests. Table III lists the descriptions of these catalysts. Table IV presents the results of the initial tests of these catalysts at one set of process conditions, (880°F, 0.2 catalyst/oil ratio). There is considerable variability in the test results. However, a tentative conclusion is that the activity (overall conversion) and selectivity of the two conventional HZSM-5 samples, ZCATPLUS and OH-S are similar. The ISOCAT sample clearly has a lower activity than the other materials. This is consistent with the description of the ISOCAT zeolite sample as a high silica to alumina zeolite. The acid site density. zeolite framework alumina, is much lower and consequently the activity is

lower than the other conventional HZSM-5 samples. However, there are no major selectivity differences between the ISOCAT and the other HZSM-5 catalysts. The ratio of propylene to isobutylene yields and the gasoline composition are similar for all samples.

Further work will continue on the evaluation of these samples at other test conditions.

A series of HZSM-5 samples with added rare earth oxide levels are under study. The rare earth oxide is added to the base HZSM-5 catalyst (ZCAT PLUS) by standard impregnation techniques. Table V describes these catalysts. The initial wax cracking catalytic results at one test condition of 0.2 catalyst to oil ratio and 880°F are found in Table VI. The data are too limited for firm conclusions. However, it is clear that the addition of rare earth oxides lowers the overall activity of the HZSM-5 catalyst. The results for the base catalyst (Table IV) show a conversion level of between 85-90%. This contrasts with the present results for the rare earth catalysts of conversion levels of about 80%. There are no major selectivity changes with rare earth addition. The propylene to isobutylene weight ratio is about 1.0 - 1.3 for all samples of base and rare earth HZSM-5 samples. Further work on these samples will continue at various process conditions to obtain a wider conversion range. This will allow more accurate selectivity estimates.

A series of Y faujasite FCC catalyst samples with variable amounts of rare earth is also under study. In general, the addition of rare earth to conventional Y faujasite FCC catalysts raises the activity level, increases the gasoline selectivity and lowers the olefin yields and gasoline octane values. This series of rare earth Y FCC samples are described in Table VII. The matrix and zeolite levels are constant with only the 'are earth level varying. The steam treatments should yield samples of comparable activity. The last sample of high rare earth content (1.49%) was steamed at two different conditions to produce catalysts of two different activity levels (No. 1705,1706). The preliminary catalytic test results in Table VIII show some interesting trends.

The non rare earth sample, CCC-1701, has the highest gas  $(C_3+C_4)$  yields and the lowest  $C_5-430^{\circ}$ F naphtha yields and highest octane ratings. Two of the high rare earth samples, (No. 1704, 1705), show the expected "rare earth effect" of higher naphtha and lower olefin yields and octane ratings. The other high rare earth sample, No. 1706, appears to have a different product selectivity, more like the non-rare earth sample. More wax cracking test runs will be needed to fully define the product selectivities of these catalysts.

TASK 4. Pilot Plant Tests.

The initial screening tests on the pilot plant unit (AU-2L) were completed last Quarter. (see Quarterly Technical Status Report, Second Quarter, Fiscal Year, 1992, Report No. 13) The product distribution results from these runs require some recalculations to redistribute the gas and liquid components. Table IX presents these results. The yield structure of these runs has also been further analyzed, Table X, to show the reactive  $C_5$  and  $C_6$  isoolefins (an olefin that contains a tertiary carbon next to the double bond) that will be converted to gasoline range ethers in Task 5 of this program.

The liquid product from one run, No. 939-05, has been fractionated by an atmospheric distillation procedure (ASTM D-2892) to yield 430°F and 430°F fractions. The naphtha fraction has been analyzed for its octane rating. These results are found in the last Quarterly Report, Quarterly Technical Status Report, Second Quarter, 1992, Report No. 13. The 430°F fraction was then distilled under vacuum (10mmHg) to separate a 430-650°F distillate product. Table XI list several properties of this fraction. The cetane index rating is the major property of interest for distillate fractions. This property is calculated from the API gravity and the 50% distillation point. The cetane index of 59.2 for this distillate fraction is an excellent value. The high paraffin and low aromatic content of this distillate is the reason for this high quality distillate.

### 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 Task 4 (pilot plant scale) of the contract are underway. The catalytic cracking results of both the small scale test unit (MYU) and the pilot plant indicate that the wax feedstock readily converts (>85%) to product gas  $(C_4-)$  and naphtha  $(C_5-430^{\circ}F)$ . The HZSM-5 zeolite catalyst produces the highest yields of the target isoolefins, isobutylene and The overall wax conversion (activity) and product isoamylenes. selectivities of two different commercial HZSM-5 catalysts are similar. Another HZSM-5 sample with a lower acid site density has a lower wax conversion level than the other tested samples. The addition of rare earth ions to the HZSM-5 sample lowers the overall wax conversion of the base catalyst. A series of Y zeolite catalysts with variable rare earth ion contents show significant changes in olefin, gasoline and light gas yields. The catalysts with high rare earth levels have lower olefin production.

Some preliminary experiments with the catalytic cracking of a Fischer-Tropsch light naphtha fraction show that this feedstock is much more difficult to convert than the wax feedstock.

These variations in product yields will form the basis for economic evaluations of the various process and catalyst options that will follow in later stages of this project.

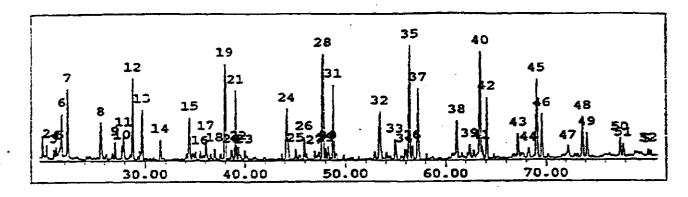
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Prepared by Amoco Oil Company (Amoco Corporation) Naperville, Illinois



Summary report from ADAM for F-TGAS1.D Sample =UOP FISCHER-TROPSCH PRODUCT - Bill Reagan

		A
Peak	Assignment	Confidence
1 (19.74)	1-Propanol	90
2 (20.16)	Ethene, 1,2-dichloro-, (E)-	96
3 (20.89)	Butanal	80
4 (21.09)	2-Butanone	78
5 (21.54)	Acetic acid	50
6 (21.69)	1-Hexene	91
7 (22.27)	Hexane	78
8 (25.63)	1-Butano1	90
9 (27.02)	2-Pentanone	64
10 (27.72)	Pentanal	64
11 (27.88)	Cyclohexene	90
12 (28.77)	1-Heptene	91
13 (29.71)	Heptane	. 91
14 (31.50)	Ethane, 1,1-diethoxy-	78
15 (34.40)	Pentane, 1-chloro-	83
16 (35.49)	2-Propenoic acid, 6-methylheptyl e	78
17 (36.06)	2-Hexanone	80
18 (36.96)	Hexanal	95
19 (37.99)	1-Octene	95
20 (38.66)	Acetic acid, butyl ester	72
21 (39.06)	Octane	94
22 (39.35)	Propane, 1,1-diethoxy-	74
23 (40.00)	Propane, 1-(1-ethoxyethoxy)-	<b>72</b> -
24 (44.20)	1-Hexanol	· 83
25 (45.08)	6-METHYL-1-OCTENE	47
26 (45.94)	2-Heptanone	91
27 (46.95)	Heptanal	87
28 (47.78)	1-Nonene	94
29 (48.00)	Ethanol, 2,2-diethoxy-	43
30 (48.25)	Acetic acid, pentyl ester	74
31 (48.78)	Nonane	95
32 (53.39)	Heptanol	90
33 (54.91)	2-Octanone	91
34 (55.90)	Cyclohexanamine	53
35 (56.36)	1-Decene	95
36 (56.67)	Acetic acid, hexyl ester	83
37 (57.21)	Decane	<del>9</del> 5
38 (61.11)	1-Octanol	86
39 (62.39)	2-Nonanone	91
(/		

Framery of Arrests O2 Company Proprietry ~ To Be Maintained in Confidence

# Summary report from ADAM for F-TGAS1.D Sample =UOP FISCHZR-TROPSCH PRODUCT - Bill Reagan

Peak	Assignment	Confidence
40 (63.42)	5-Undecene	93
41 (63.62)	Acetic acid, heptyl ester	56
	Undecane	94
	<del></del>	78
43 (67.19)	Nonanol	94 ·
44 (68.27)	2-Decanone	96
45 (69.01)	1-Dodecene	
46 (69.55)	Dodecane	94
47 (72.25)	1-Decanol	91
48 (73.72)	1-iridecene	98
49 (74.16)	Tridecane	94
	Cyclododecane	94
		94
51 (77.79)	Tetradecane	86
52 (80.36)	11-Tricosene	93
53 (80.61)	Pentadecane	73

TABLE II

CATALYTIC CRACKING RESULTS OF UOP F-T GASOLINE

MYU TEST RESULTS AT 970°F

Catalyst Type	Zeo	lite Y	Zeolite Beta	Zeolite	HZSM-5
Run No.	068	069	070	071	072
Cat/Oil Ratio	0.2	0.2	0.2	0.2	0.1
Product Yields, Wt%: Hydrocarbon Water	85 15	83 17	85 15	84 16	86 14
Product Yields, Hydrocarbon Only, Wt%: H2 C1 C2 C2° C3° C3° C4° C4° C5° C5° C5+ Coke Isobutylene Isoamylenes	0.02 0.18 4.76 0.43 4.28 0.12 5.88 0.25 8.81 0.72 74.6 0.2 1.22 3.04	0.03 0.17 4.41 0.43 4.13 0.12 6.33 0.26 9.54 0.76 73.8 0.23 1.31 3.32	0.04 0.16 4.66 0.46 6.44 0.13 9.06 0.28 12.13 0.87 65.8 0.18 3.15 5.84	0.03 0.14 5.55 0.28 11.75 0.11 14.02 0.14 14.91 0.74 52.3 0.12 5.61 8.93	0.04 0.14 4.74 0.36 8.80 0.1 11.92 0.25 14.06 0.75 58.8 0.19 3.93 7.63
Ron Mon	76.2 69.0	70.3	74.6 68.3	75.9 69.4	74.4 68.6

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TABLE III
DESCRIPTIONS OF BESH-5 FOR CANALTSES

Catalyst I.D.	Catalyst Description	MIU Test Bo's.
CCC-1891	Intercat ZCat Plus® large steamer, 5,000 g., 1450°P, 5	054,055 (April, 1992)
	hrs., 100% steem	087,088,089
14040-45-1	Intercat ZCat Plus® small steamar, 25 g., 1450°F, 5 hrs, 100% steam	090,094
L4G40-43-3	Interest Isocar® small steamer, 25g., 1450°F, 5 hrs., 100% steam	086,093
14040-43-1	Davison Additive CH-S <sup>®</sup> small steamer, 25 g., 1450°F, 4 hrs., 100% steam	084,091
14040-43-2	Repeat of above	085,092

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TABLE IV

NEU TEST RESULTS - FISCHER-TROPSCH MAX CRACKING VARIOUS BESM-5 CATALYSIS

(TEST COMMITTORS: 880°F, 0.187 CATALYSI/OIL RATIO)

Run No.	054	055	087	880	089	090	094	084	091	085	092	086	093
Catalyst Description	•	ZCat Pl				ZCat	-1891 Plus Steamer	14040 OE Small		14040 OE Small			040-43-3 Isocat Steamer
Conversion WtI	90.2	91.9	92.5	86.5	86.9	78.5	90.5	84.7	87.8	83.9	89.8	65.9	69_4
Product Yields WtI C <sub>2</sub> C <sub>3</sub> + C <sub>4</sub> C <sub>5</sub> - 30"F A30"F+ Coke	1.6 49,5 40.0 8.8 0.1	1.5 50.3 38.0 10.0	2.8 49.4 39.8 7.5 0.5	1.6 42.4 41.2 13.5 1.3	2.2 48.9 35.6 13.1 0.2	1.2 37.3 39.9 21.1 0.1	2-1 47-7 40-6 9-5 0-1	1.9 41.5 42.1 15.6 0.2	1.7 45.1 40.9 12.2 0.1	1.7 39.9 42.2 16.1 0.1	3.0 47.2 39.4 9.3 0.2	0.9 30.1 34.8 34.1 0.1	0.8 32.0 36.5 30.6 0.1
c," 1c," 1c,"	16.6 12.2 10.8	17.4 12.1 10.9	13.8 12.5 9.5	12.5 10.7 12.0	14.5 11.8 11.5	12.8 9.7 12.5	14.4 12.4 15.5	10.7 11.5 13.6	14.5 10.6 11.0	11.0 10.7 12.1	15.9 10.6 9.8	9.5 8.9 12.6	11.9 8.6 13.9
C <sub>5</sub> -430°F BOR MOR	85.4 76.4	84.4 76.0	80.9 74.2	84.3 75.1	82.5 74.8	84.3 74.9	83.5 75.2	84.4 75.0	81.7 74.2	86.2 75.7	85.0 76.5	83.6 74.3	84.8 75.3

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TABLE V

DESCRIPTION OF BARE EARTH OXIDE/ZSN-5 CATALYSTS

Catalyst I.D.	Description, Treatment
14040-42-1	1t ReO/Zcat Pluse, 1450°F, 5 hrs. 100t steam
14040-42-2	2% ReO/Zcat Pluse, 1450°F, 5 hrs. 100% steam
14040-42-3	3% ReO/Zcat Pluse, 1450°F, 5 hrs, 100% steam

TABLE VI

MYU TEST RESULTS - FISCHER-TROPSCH WAX CRACKING

ReO/ZSM-5 Catalysts
Test Conditions, 880°F, 0.187 Catalyst/Oil Ratio

Run No.	096	097	098	
Catalyst	14040-42-1	14040-42-2	14040-42-3	
Description	1% ReO	2% Re0	3% ReO	
Conversion Wt%	80.3	80.5	76.7	
Product Yields Wt%				
C <sub>2</sub> -	1.2	1.3	1.1	
C3+C4	39.5	39.0	36.6	
C <sub>5</sub> -430°F	39.5	40.1	38.9 23.3	
430°F <sup>-1</sup>	19.7	19.5		
Coke	0.1	0.1	0.1	
C <sub>3</sub> -	13.3	12.7	11.8	
iC,-	9.9	9.5	9.5	
1C <sub>5</sub> -	10.1	10.8	10.1	
C <sub>5</sub> -430°F				
RON	83.3	83.7	83.3	
MON	74.7	75.0	74.8	

TABLE VII

# DESCRIPTION OF RARE EARTH OXIDE/FAUJASITE CATALYSTS

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

# TABLE VIII

# HYU TEST RESULTS - FISCHER-TROPSCH WAX CRACKING

Rare Earth Oxide/Faujasite Catalysts
Test Conditions: 880°F, 0.75 Catalyst/Oil Ratio

				<u> </u>		
Rum No.	099	100	101	102	103	104
Catalyst Description	CCC-1710	CCC-1702	CCC-1703	CCC-1704	CCC-1705	CCC-1706
Conversion Wt%	92.4	87.8	85.5	91.5	87.3	91.9
			·			•
Product Yields Wtt			<u> </u>			<u> </u>
C <sub>2</sub> -	0.8	0.6	0.6	0.8	0.7	0.5
C <sub>3</sub> +C <sub>4</sub>	28.7	23.4	20.8	23.2	11.3	26.6
C <sub>5</sub> -430°F	62.1	63_0	63.2	66.5	66.5	63.9
430°F+	7.6	12.2	14.5	8.5	12.7	8.9
Coke	0.8	0_8	0.9	0.9	.8	0.1
C -	7.6	6.6	5.8	6.5	5.3	7.2
C <sub>3</sub> -	5.9	4.5	4.1	4.3	3.8	6.0
iC <sub>5</sub> =	7.8	6.4	5.6	6.4	5.9	8.3
C <sub>5</sub> -430°F						<del></del>
RON	89.7	88.7	87.4	88.0	86.5	88.8
MON	78.0	76.3	74.5	76.0	74.0	76.6

TABLE IX

PISCHER-TROPSCH WAX CATALYTIC CRACKING PILOT PLANT BONS

(Adjusted Liquid Yields)

	9:	ex Feedstock	
RUN NO.	939-1	939-2	939-4
RUN CONDITIONS			
Reaction Temp., *F	944	932	882
C/O Ratio	5.16	4.06	2.29
WESV (br')	21.0	20.4	38.2
Catalyst	eq. USY	eq. USY	eq. USY
Conversion, wil	93.5	93.7	83.0
Product Yields, wtX:			
E,S	0.00	8.00	0.90
<b>E</b> ,	0.84	0.04	0.03
5	0.36	0.33	0.18
c,=	0.48	0.42	0.26
с,	0.26	0.23	0.16
C <sub>3</sub> =	9.26	8.20	7.28
<b>G</b>	1.86	1.67	1.07
104	7.93	7.23	4.15
26,	2.08	1.84	1.21
1C,= + 1 - C,=	7.38	6.70	7.68
tC,=	4.19	3.74	3.69
eC_=	3.12	2.77	2.67
1C <sub>1</sub>	8,49	8.65	3.38
aC,	1.25	1.42	0.77
€C <sub>4</sub> =	7.37	9.50	6,30
C <sub>4</sub> /430	37.11	38.98	43.89
430+	6.47	6.27	16.69
Coke	2.34	2.61	0.61

WJR/11cm/93125 3/15/93

TABLE IX (continued)

# FISCHER-TROPSCH WAX CATALITIC GRACTING FILOT FLANT HURS (Adjusted Liquid Yields)

		Was	Feedstock		,
RUN RO.	939-05	940-1	940-2	941-1	942-2
RUN CONDITIONS					
Reaction Temp., *F	879	934	910	965	937
C/O Ratio	2.25	5.08	3.35	2.84	1.57
WESV (bz*1)	42.2	43.8	61.5	54.61	33.51
Catalyst	Steamed eq. USY	Steamed Bets	Steamed Bets	Steamed Steamed eq. USY HZSM-5 (75%) (25%)	50% eq. USY 50% Diluent
Conversion, whi	85.0	96.6	96.5	89.0	90.0
Product Yields, wtI:		<u> </u>		<u> </u>	<del></del>
В,	0.02	0.02	0.81	0.02	.02
с,	0.14	0.10	0.07	0.09	0.16
C <sub>2</sub> -	0.21	0.66	0.50	1.01	0.34
c,	0.14	0.11	0.08	0.10	0.15
G-	6.28	13.93	13.68	16.03	8.94
G,	0.90	2.11	1.81	2.47	1.25
10,	3.40	9.04	7.66	3.40	5.02
BC,	0.99	2.58	2.09	1.92	1.30
1C <sub>4</sub> = + 1 C <sub>4</sub> =	6.75	12.46	12.99	12.95	7.67
£C'+ TO'- + 7 O'-	3.19	3.65	5.44	5.33	3.72
CC.=	2.31	4.26	3.98	3.76	2.68
	3.35	5.11	3.73	2.16	3.97
16,	0.96	1.73	1.51	1.40	0.85
eC <sub>3</sub>	10.54	10.15	10.24	12.47	7.27
Total C.=	46.08	27.34	31.53	24.81	45.36
C430°F		3.59	3.57	11.60	10.42
430°F+	0.68	1.20	1.00	0.47	0.88

WJR/1kv/93125 3/15/93

TABLE X

FILET PLANT RUNS PISCHER-TROPEGH WAX CATALTIC CRACKING DETAILED C.-C. OLEFIH AMALYSIS

		N Regards-was	A CATALITIC CRACKING DETAILED		GG. OLEP'IR AMALYSIS	818		
RUN NO.	939-1	1	939-4	939-5	940-1	940-2	1-170	942-2
CATALYST				þ	RETA	BETTA	70477	5
CONVERSION, WT&	93.5	93.7	e E	S S	9.96	96.5	1463+x	1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
COMPONENT, WT. *								•
HYDROGEN	0.04	0.04	0.03	0.02	0.02	0.01	0.02	0
METHANR	ij	0.33	0.18	0.14	0.1	0.07	60.0	0.16
ETHYLENE	7	0.45	0.26	•	99.0	0.5	1.01	
KTHANE	7	0.23	0.16	0.14	0.11	0.08	, t	7
PROPYLENE	ç	8.2	7.28		13.93	13.68	16.03	
PROPANE	₩.	1.67	1.07	6.0	N	-	2.47	
1-BUTANE	•	. 7.23	4.15	3.4	9.04	7.66	4.6	1 9
n-BUTANE	2.08	1.84	1.21	•	2.58	2.09	1.92	
1-BUTENE	1.47	1.32	1.4	•	2.22	2.24	2.2	7
1-BUTYLENE	5.91	5.38	6.28	5.53	•	10.75	10.75	
C-Z-BOTENE	4.19	3.74	3,69	•	5.65	5.44	5,33	-
G-2-BUTENE	3.12	2.77	2.67	•	•	3.98	3.76	
1-PENTANE	8.49	8.65	3.38	•	5.11	3.73	2.16	5
n-PENTANE	_		O.	•	•	1.51	1.4	Ψ.
3M-1-BUTENE	•	0.166	0.092	7	0.187	0.214	0.279	12
2H-1-BUTENE	0.993	1.47	•	ស	1.68	1.77	2,3	1
2H-2-BUTENE	S.	4.57	2.99	9	5.03	•	5.94	
1-PENTENE	0.297	0.47	0.312	ເນ	0.476	•	0.62	6
t-z-pentene		1.8	•	•	•	•	2,145	7
C-2-PENTENE	0.806	-	~	ij	<b>ત</b>	•	1.18	-
Z, 3-DM-1-BUTENE	•	•	0	e.	•	•	0.085	
ZH-I-PENTENE	C	-		8	•	•	0.266	w.,
ZM-Z-PENTENE	•	0.919	1.287	1.419	ø	1.078	0.682	
C-3M-2-PENTENE	0.812	•	•	4.	0	•	0.84	
C-3M-2-PENTENE	ο.	•	•	ę,	.6	•	7	-
C6-4300F	Ş	r 2	<u> </u>	41.16	23.74	27.94	22.4	7
430~650oF	4.97	5.12	10.08	8.95	2.72	2.96	4	
650oF+		۲.	ø	5.1	•		4.13	•
SUBTOTAL	97.642	97.976	99.4046	30	~	98.99	99. K14	90,111
COKB	2.34	2.01	0.61	99.0	1.2		0.4	0.8
GRAND TOTAL	99,982	986 66	100.0146	99.988	99.931	66.66	. 00	00 00
		•		ļ.	) )	•	•	•

4C, fraction centains paraffins and non-ather-forming olefins.

### TABLE XI

# PROPERTIES OF DISTILLATE (#30-650°F) FRACTION PILOT PLANT CATALYTIC CRACKING OF FISCHER-TROPSCH WAX

# Rum No. 939-05

API Gravity (6 60°F) = 39.5

(ASDM) D-1160 50% distillation point = 553.1°F

(ASTM) D-2887 50% distillation point = 550°F (GC simulated distillation)

Cetane Index (ASTM D-976) = 59.2

WB/11cv/93125 3/15/93

FIGURE 1
CATALYTIC CRACKING OF FISCHER-TROPSCH GASOLINE
MYU TEST RESULTS

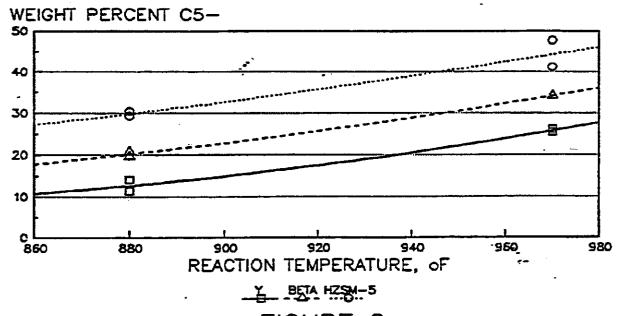
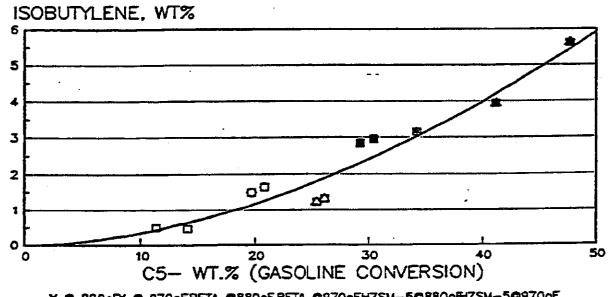
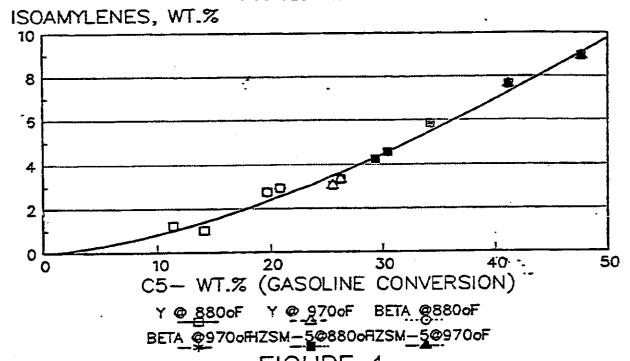


FIGURE 2
CATALYTIC CRACKING OF FISCHER-TROPSCH GASOLINE
MYU TEST RESULTS

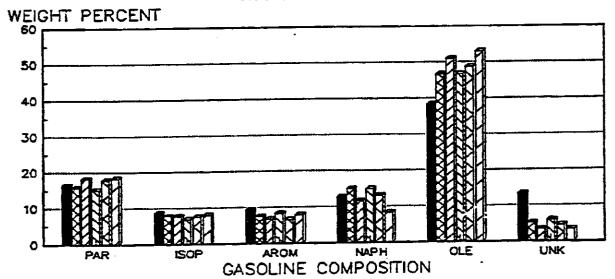


Y @ 8800FY @ 9700FBETA @8800FBETA @9700FHZSM-5@8800FHZSM-5@9700F

FIGURE 3
CATALYTIC CRACKING OF FISCHER-TROPSCH GASOLINE
MYU TEST RESULTS



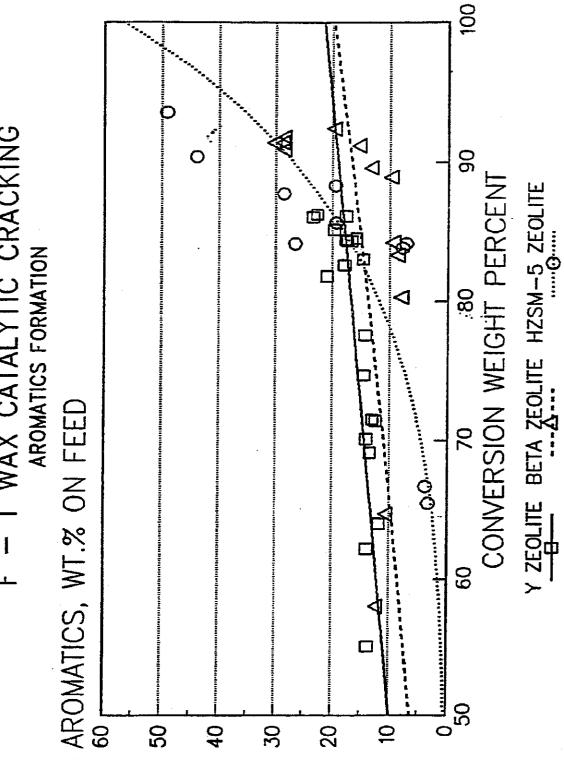
CATALYTIC CRACKING OF FISCHER—TROPSCH GASOLINE
MYU TEST RESULTS



■ Y@880oF & BETA@880oF Ø HZSM-5@880o® Y@970oF @ BETA@970oF D HZSM-5@970oF

FIGURE 5

T WAX CATALYTIC CRACKING



## QUARTERLY MANPOWER REPORT

## For THIRD QUARTER FISCAL YEAR, 1992

(April 1, 1992 - June 30, 1992)

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

IDENTIFICATION NUMBER: DE-AC22-91PC90057

START DATE: April 1, 1992 COMPLETION DATE: May 31, 1992

## 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	٥	0	190	98	0	0	0	288
D. M. Washecheck	` 0	0	81	25	0	0	0	106
G. G. Glasrud	0	0	0	0	0	0	0	0
Other Professionals	0	0	0	0	0	0	0	0
Technical Support	0	0	289	43	0	0	Ó	332
Secretarial	0	0	11	6	0	0	0	17
Total Hours	0	0	571	172	0	0	0	743