SELECTIVE CATALYTIC CRACKING OF FISCHER-TROPSCH LIQUIDS TO HIGH VALUE TRANSPORTATION FUELS. REPORT NUMBER 38: QUARTERLY TECHNICAL STATUS REPORT FOR FOURTH QUARTER FISCAL YEAR 1993 (JULY 1--SEPTEMBER 30, 1993)

AMOCO RESEARCH CENTER, NAPERVILLE, IL.
RESEARCH AND DEVELOPMENT DEPT

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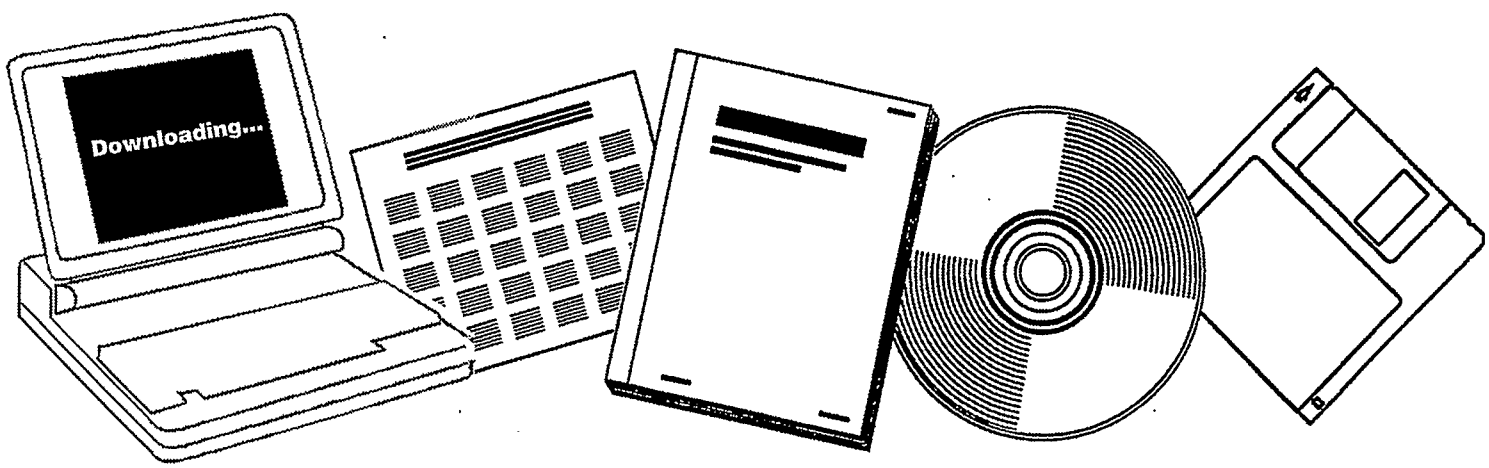

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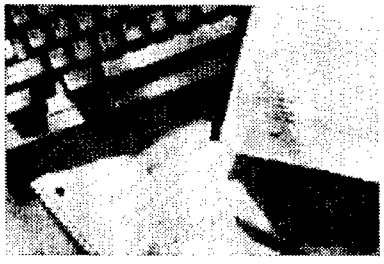

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THE SF ... CATALYTIC CRACKING OF FISCHER-TROPSCH LIQUIDS "I... VALUE TRANSPORTATION FUELS

REPORT NO. 38

QUARTERLY TECHNICAL STATUS REPORT

FOR

FOURTH QUARTER FISCAL YEAR, 1993

(July 1, 1993 - September 30, 1993)

PROJECT MANAGER: R. D. HUGHES

PRINCIPAL INVESTIGATOR: M. M. SCHWARTZ

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

FOR

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

BY

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DISCLAIMER

TECHNICAL STATUS

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

EXECUTIVE SUMMARY

Amoco Oil Company, under a contract with the United States Department of Energy, is investigating a selective catalytic cracking process to convert the Fischer-Tropsch gasoline and wax fractions to high value transportation fuels. This report describes the work in the Fourth Quarter, Fiscal Year, 1993, the eighth quarter of the two year project. The completion date of this contract has been extended (on the basis of no additional cost to DOE) until March 31, 1994.

Task 1, Project Management Plan. The plan has been accepted by the Project Manager DOE/PETC. Tasks 2, 4, 5, and 6 were modified. Preparation of alcohols was deleted from Task 5, and the blending of alcohols was deleted from Task 6. Characterization of LaPorte naphtha was added to Task 2, and additional pilot plant runs were added to Task 4. 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. Naphtha that was produced by the Liquid Phase F-T demonstration plant at LaPorte, Texas was received and characterized. It was later learned that this naphtha sample was a recombination of the aqueous and non-aqueous overhead fractions. The work in this area is now complete.

Task 3, Catalytic Cracking Catalyst Screening Program. The work in this area is complete.

Task 4, Pilot Plant Tests. Activities were performed under Task 3 during this reporting period. Three pilot plant runs were completed using Sasol wax as feedstock. The catalysts used were 10% steamed USY, 10% steamed Beta, and standard equilibrium USY. The 10% Beta catalyst gave much higher yields of propylene and butylenes than the USY-based catalysts, in agreement with our previous results. Characterization of the IBP-430, 430-650, and 650+ °F fractions of these runs is incomplete. The 10% Beta catalyst made 430-650 °F product with the highest cetane index (60.9), but the 430-650 °F product from all three runs would be excellent stock for blending into diesel fuel.

Task 5, Preparation of C_5-C_8 Ethers. The work in this area is complete.

Task 6, Evaluation of Gasoline Blending Properties of Ethers and Alcohol Products. The work in this area is complete.

Task 7, Scoping Economic Evaluation of the Proposed Processes. There was no activity in this area during this Quarter.

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. This is the primary focus of this project.

Fuel oxygenates, particularly alcohols and ethers, represent a potential solution to environmental concerns due to conventional automotive fuels. Governmental regulations, most recently in the Clean Air Act Amendments of November, 1990, have resulted in the phase-out of lead additives, lowering of the Reid vapor pressure of gasoline and in some geographical areas, the mandated use of oxygenates. Recent studies of methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME) suggest that these compounds may reduce automotive carbon monoxide emissions, have high blending gasoline octane ratings, R+M/2, (MTBE=108, TAME=102) and have low Reid vapor pressure. These ethers are produced commercially by the etherification of the appropriate olefin by methanol (MTBE, isobutylene; TAME, isoamylenes). These olefins are derived from conventional petroleum processes such as catalytic cracking or steam/thermal reforming.

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

PROGRAM OBJECTIVES

The objective of this program is to prepare high-value transportation fuels, including gasoline, distillate, and gasoline range ethers and alcohols from non-petroleum resources. A selective catalytic cracking process of Fischer-Tropsch liquids is proposed. The C_4-C_8 product olefins would then be etherified with methanol to prepare the target ethers. Alcohols will be produced by direct hydration of C_3-C_8 product olefins. The gasoline and distillate products are also expected to be superior to conventional fuels because of the unique combination catalysts to be used in this process.

PROJECT DESCRIPTION

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

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

Task 2. -- Preparation of Feedstocks and Equipment Calibration. Suitable mixtures of Fischer-Tropsch waxes (C_{18}+) and light olefin components (C_5-C_{12}) will be prepared to simulate full range F-T liquids without the premium distillate products. The necessary analytical equipment will be calibrated for the detailed identification of C_4-C_8 olefins and ethers and other paraffin, aromatic and naphthene gasoline range components.

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

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

Task 5. -- Preparation of C_5-C_8 Ethers and C_3-C_8 Alcohols. These products will be prepared from the pilot plant C_3-C_8 olefin products.

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

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

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

RESULTS AND DISCUSSION.

During this Quarter, project activities centered on Tasks 1, 2 and 4 of the contract.

TASK 1. Project Management Plan.

Modification of the draft Project Management Plan has been accepted by the Program Manager at DOE/PETC. Tasks 2, 4, 5, and 6 were modified.

Preparation of alcohols was deleted from Task 5, and the blending of alcohols was deleted from Task 6. Characterization of LaPorte naphtha was added to Task 2, and additional pilot plant runs were added to Task 4. 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 were performed during this reporting period. About 268 pounds of naphtha from the LaPorte, Texas slurry phase F-T plant, was received in a half-barrel container and given the Amoco identification of FHD-1468. Analysis of the oxygenate content of FHD-1468 was started, and the data we have obtained are presented next. We can not explain these results. But clearly, the material we received is not a material that is compatible with petroleum-derived naphtha.

The simulated distillation of FHD-1468, which is summarized in Table I, was reasonable, with 10, 50, and 90% temperatures of 73, 216, and 315 °F, respectively. However, elemental C, H, and O analyses of FHD-1468 were 5.82, 12.04, and 79.57 %, respectively. These elemental analyses indicated water containing a small amount of carbonaceous material, which suggested that we were not analyzing homogeneous samples of the naphtha because of separation of a water phase.

Table I

Simulated Distillation of LaPorte F-T Naphtha (FHD-1468)

Simulated Distillation, °F	
IBP	-64
5 %	59
10%	73
20 %	131
30 %	168
40 %	188
50 %	216
60 %	238
70 %	260
80 %	283
90 %	315
95 %	354
FBP	498

All the FHD-1468 (268 lbs) was distilled, in two batches because of equipment size limitations. The distillations are identified as 15586-37-1 (430- and 430+ °F fractions) fractions) and 15586-37-2 (430- and 430+ °F fractions). Table II, which gives the weights of each of the fractions, shows that FHD-1468 contained about 22% 430+ °F material. The water content of each fraction, which was determined by Karl Fischer titration, is also shown in Table II. These water analyses indicate that the barrel of material we received contained about 49% water. However, these water analyses are suspect because phase separation was later observed with the four distilled fractions -- so we might not have analyzed a homogeneous fraction.

Table II

Distillation Summary of FHD-1468

	# Recovered	% H_2O	# H_2O	# HC
15586-37-1, 430- °F cut	73.2	0.34	0.25	72.95
15586-37-1, 430+ °F cut	55.2	0.062	0.03	55.16
15586-37-2, 430- °F cut	135.4	96.1	130.12	5.28
15586-37-2, 430+ °F cut	4	0.13	0 01	3.99
Total:	267.8		130.41	137.38

The 430- °F fraction from distillation 15586-37-1 had a Reid vapor pressure of 1.60 mm. Octane numbers could not be obtained because the engine would not run on this material. A high temperature simulated distillation, which is summarized in Table III, showed the presence of material boiling above 1200 °F! One explanation for these simulated distillation data is that the 430- °F fraction contains unstable material which is polymerizing.

Table III

High Temperature Simulated Distillation 430- °F fraction of 15586-37-1

Simulated Distillation, °F	
IBP	200
5 %	203
10%	206
20 %	212
30 %	219
40 %	233
50 %	261
60 %	297
70 %	311
80 %	429
90 %	946
95 %	1067
FBP	1287

^{13}C NMR data were requested on the 430-°F fractions from both the 15586-37-1 and -37-2 distillations. Our NMR laboratory, after observing phase separation with both 430- °F fractions, separated each into "top" and "bottom" portions. While additional work will be required to definitively characterize these fractions, the initial analyses have given the following results. Each "top" contained as its major component a single (unidentified) α-olefin, with small amounts of mixed olefins and saturates (hexanes and heptanes). Each "bottom" contained mostly C_1-C_4 simple alcohols with ethanol dominant, plus a small amount of unknown C_4 or C_5 ester or acid; no olefins, aromatics, aldehydes, or ketones were observed.

It was later learned that this naphtha sample was a recombination of LaPorte's aqueous and non-aqueous overhead fractions. The analyses given above have limited value, and the work in this area is now complete.

TASK 4. Pilot Plant Tests. Activities were performed under Task 4 during this reporting period. Three pilot plant runs were completed using Sasol wax as feedstock. These were runs 943-1, 944-2, and 945-2, and the catalysts used were 10% steamed USY, 10% steamed Beta, and standard equilibrium USY, respectively. Table IV identifies the feedstocks, catalysts, process conditions used, and summarizes the conversions that

were obtained. The conversion to 430- °F product is based on atmospheric distillation of the total liquid product. The conversions to 430-650 light catalytic cycle oil (LCCO) and 650+ °F cycle oil are based on vacuum distillation of the 430+ °F fraction.

The 10% steamed USY and 10% steamed Beta catalysts, previously described[1] numbers 9669-154 and -155, were used because the objective of these runs was to use low activity catalysts and mild cracking severities to get yield data at lower conversions than were obtained in our previous runs.[2,3] Low catalyst activity was verified by microactivity tests. Standard MYU microactivity tests showed that the 10% USY catalyst had a RMA of 77 with a coke factor of 0.96, and the 10% Beta catalyst had a RMA of 60 with a coke factor of 1.18. The compositions of these catalysts were confirmed by x-ray crystallography. The catalysts also were screened to pass 100 mesh for proper fluidization in the pilot plant before evaluation.

Although the catalyst activities were low and the pilot plant conditions were as mild as possible, Table IV shows that the objective of low conversion was not fully met. By using mild cracking conditions in Run 945-2, the conversion with reference USY was lowered to about 85% from the 93% conversion with this catalyst that was previously obtained in Runs 939-1 and -2. The approximately 90% conversion that was obtained with the 10% steamed Beta catalyst in Run 944-2 was lower than the 96% previously obtained in Runs 940-1 and -2 with steamed Beta. But the 89% conversion with the 10% steamed USY catalyst in Run 943-1 was actually higher than the 85% previously obtained (Run 939-5) with steamed USY under mild conditions.

Mass balances with this unit are typically over 98% when gas oil feedstock is used with the standard feed rate of 13 g/m. However, the product condenser on this pilot plant floods when Fischer-Tropsch wax feedstock was added at the feed rates of 23-24 g/m that were used in our experiments. The consequence of the condenser flooding is low and erratic mass balance for the runs with wax feedstock. The mass balances for our nine previous runs with wax feed were typically 82-88%, with a low of 77% and a high of 93%. For the three experiments with wax feedstock that are described in this report, a 94 weight percent recovery was obtained with the 10% steamed USY catalyst in Run 943-1. However, the recoveries with the 10% steamed Beta and reference USY catalysts were 55 and 63%, respectively. These latter two runs were not repeated because the problem of condenser flooding, which is the reason for the poor mass balances with all the wax runs, could not be eliminated without extensive unit modifications. Fortunately, these low mass balances do not affect the measurements of product selectivity and quality with the different catalysts, which is the objective of this program; the total liquid products that were recovered are representative of the process.

As Table IV shows, the 10% Beta catalyst gave much higher yields of propylene and butylenes than the USY-based catalysts, in agreement with our previous results.[3]

The total liquid products from these runs were distilled into IBP-430, 430-650, and 650+ °F fractions, and each fraction is being extensively characterized. Tables V-VII give the characterizations that have been

obtained on the naphtha (IBP-430 °F), light catalytic cycle oil (LCCO; 430-650 °F), and 650+ °F cycle oil, respectively. Other analyses are in progress for each of these fractions.

Table VI shows that the 10% steamed Beta catalyst produced LCCO with the highest cetane index (60.9) of the three catalysts. The reference USY catalyst produced LCCO with the lowest cetane index (50.8), with LCCO from the 10% USY catalyst intermediate at 56.3 cetane index. Although the 10% steamed Beta catalyst made the highest cetane index product, the LCCOs from all three runs would be excellent stock for blending into diesel fuel.

CONCLUSIONS

Task 1 of the contract, the Project Management Plan, was modified. Tasks 2, 4, 5, and 6 were modified. Preparation of alcohols was deleted from Task 5, and the blending of alcohols was deleted from Task 6. Characterization of LaPorte naphtha was added to Task 2, and additional pilot plant runs were added to Task 4. This completes Task 1 of the contract.

Task 2, Preparation of Feedstocks and Equipment Calibration. Activities were performed under Task 2 during this reporting period. Naphtha that was produced by the Liquid Phase F-T demonstration plant at LaPorte, Texas was received and characterized. It was later learned that this naphtha sample was a recombination of the aqueous and non-aqueous overhead fractions, so the characterizations are of limited value. This completes Task 2 of the contract.

There was no activity under Task 3, Catalytic Cracking Catalyst Screening Program, during this Quarter. Task 3 of the contract is completed.

Task 4, Pilot Plant Tests. Activities were performed under Task 4 during this reporting period. Three pilot plant runs were completed using Sasol wax as feedstock. The catalysts used were 10% steamed USY, 10% steamed Beta, and standard equilibrium USY. Characterization of the IBP-430, 430-650, and 650+ °F fractions of these runs is in progress. The 10% Beta catalyst gave much higher yields of propylene and butylenes than the USY-based catalysts, in agreement with our previous results. The 10% Beta catalyst made 430-650 °F product with the highest cetane index (60.9), but the 430-650 °F product from all three runs would be excellent stock for blending into diesel fuel.

There was no activity under Task 5, Preparation of C_5-C_8 Ethers, during this Quarter. Task 5 of the contract is complete.

There was no activity under Task 6, Evaluation of Gasoline Blending Properties of Ethers and Alcohol Products, during this Quarter. Task 6 of the contract is complete.

There was no activity under Task 7, Scoping Economic Evaluation of the Proposed Processes, during this Quarter.

REFERENCES

(1) Quarterly Technical Progress Report for Fourth Quarter Fiscal Year 1992, July - September, 1992; Report No. 24 for Contract DE-AC22-91PC90057.

(2) Quarterly Technical Progress Report for First Quarter Fiscal Year 1992, October - December, 1991; Report No. 10 for Contract DE-AC22-91PC90057.

(3) Quarterly Technical Progress Report for Second Quarter Fiscal Year 1992, January - March, 1992; Report No. 13 for Contract DE-AC22-91PC90057.

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NOTICE

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

QUARTERLY MANPOWER REPORT

For FOURTH QUARTER FISCAL YEAR, 1993

(July 1, 1993 - September 30, 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: March 31, 1994

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	0	24	0	80	0	104
M. M. Schwartz	0	20	0	26	0	114	0	160
R. D. Hughes	0	0	0	1	0	31	0	32
Other Professionals	0	0	0	0	0	0	1	1
Technical Support	0	21	0	18	0	48	0	87
Secretarial	0	0	0	0	0	4	0	4
Total Hours	0	41	0	69	0	227	1	388

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