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

REPORT NO. 33

QUARTERLY TECHNICAL STATUS REPORT

FOR

THIRD QUARTER FISCAL YEAR, 1993

(April 1, 1993-June 30, 1993)

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PRINCIPAL INVESTIGATOR: M. M. SCHWARTZ

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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DISCLAIMER

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 is a commercial sample of Fischer-Tropsch product from Sasol. A second feedstock being used is a high melting point paraffinic wax that 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. The viscosity of LaPorte wax was found to be much higher than the viscosity of Sasol wax.

Task 3, Catalytic Cracking Catalyst Screening Program. Two new technicians were trained to run the MYU. Equipment problems encountered during the new operator training are being addressed.

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

Task 5, Preparation of C_5-C_8 Ethers. There was no activity in this area during this quarter.

Task 6, Evaluation of Gasoline Blending Properties of Ethers and Alcohol Products. Research octane numbers (RON) and Motor octane numbers (MON) were determined in engine tests using 10% blends of the mixed ether products (previously prepared under Task 5) with unleaded regular gasoline.

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_2-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 2, 3, and 6 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 in this contract is a sample from Sasol. Additional experiments were made using as feedstock Fischer-Tropsch wax that was produced during 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. The viscosities of these two wax feedstocks were determined, and the viscosity of LaPorte wax was found to be much higher than the viscosity of Sasol wax. The viscosity of each wax at 135 and 150°C is shown in Table I.

TABLE I

VISCOSITIES OF SASOL AND LAPORTE WAXES

	Sasol Wax	Laporte Wax
Viscosity @ 135°C, cSt	6.65	64.07
Viscosity @ 150°C, cSt	5.28	23.30

No further characterization of either wax is planned.

TASK 3. Screening Catalytic Cracking Tests.

Activities under Task 3 of the contract continue on the small scale test unit, the MYU (micro yields unit). Two new technicians were trained to run the MYU. During the new operator training, several problems with the equipment were encountered, all of which contributed to unacceptable repeatability of test runs. The problems all related to uneven delivery of feed from the syringe. In one case, the syringe broke, which required replacement and recalibration of a new syringe. But in general, the problem of irreproducible feed delivery appears to be caused by uneven and inadequate heating of the wax delivery lines. The problem is being addressed, but has not yet been resolved.

TASK 6. Evaluation of Gasoline Blending Properties of Ethers and Alcohol Products.

Activities under Task 6 were performed during this reporting period. It was previously reported that the methanol etherification of the light naphtha product (200°F- fraction) from the pilot plant catalytic cracking runs of Fischer-Tropsch wax feedstock yields a mixed ether product which consists of TAME (tertiary amyl methyl ether) and the three C_6 ethers, THME (tertiary hexyl methyl ethers), which are 2-methyl-2-methoxypentane, 2,3-dimethyl-2-methoxybutane, and 3-methyl-3-methoxypentane.[1]

Research octane numbers (RON) and Motor octane numbers (MON) were obtained on those mixed ethers products. The RON and MON were determined in engine tests using 10% blends of the mixed ether product with unleaded regular gasoline. The octane number of the ethers was calculated from the observed octane number of the blend by assuming that the volumes of ethers and unleaded regular gasoline blend linearly. These RON and MON data are given in Table II, which also gives the RON data that were calculated from gas chromatography analyses and reported previously.[1]

The calculated RON values for the products of the 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. However, as Figure 1 shows, there is only fair agreement between the measured blending RON and the RON calculated by gas chromatography, even after editing the data to exclude outliers from the engine tests. Although the measurement of octane numbers in engine tests is usually very accurate, the data we obtained on the mixed ether blends is extremely sensitive to small errors because only enough etherified product was available for a single evaluation as a 10% solution, and the octane numbers of the unleaded regular blend stock were very similar to those of the ether blends. Figure 1 excludes the data for additive 92-0490-1A because the MON was higher than the RON, which is impossible.

These measurements of blending octane values for the etherification products conclude this portion of the contract.

CONCLUSIONS

Task 1 of the contract, the Project Management Plan, is complete.

Task 2--Preparation of Feedstocks and Equipment Calibration. The work in this area is virtually complete. The viscosity of Laporte wax was found to be much higher than the viscosity of Sasol wax.

Task 3--Catalytic Cracking Catalyst Screening Program. Two new technicians were trained to run the MYU. Equipment problems encountered during the new operator training are being addressed.

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

There was no activity under Task 5--Preparation of C_5-C_8 Ethers, during this quarter.

Task 6--Evaluation of Gasoline Blending Properties of Ethers and Alcohol Products. Research octane numbers (RON) and Motor octane numbers (MON) were determined in engine tests using 10% blends of the mixed ether products (previously prepared under Task 5) with unleaded regular gasoline.

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

REFERENCES

(1) Report No. 30, Quarterly Report for Jan-Mar, 1993.

ACKNOWLEDGEMENT

This work is supported by the United States Department of Energy under Contract No. DE-AC22-91PC90057.

TABLE II

RON AND MON OF LIGHT NAPHTHA ETHERIFICATION RUNS

							Engine Test Measurements of RON and MON			
	Run No.	Reaction Temp.	Catalyst	Olefins	Oxygenates	GC Calculated Research Octane Number	Measured Blend Value RON	Measured Blend Value MON	Observed RON*	Observed MON*
Feed A	92-0190-01A			44.507	0.871	80.92	66.9	67.3	89.4	80.8
	15586-024-2	125°F	Amberlyst 15	33.762	12.406	82.09	77.9	74.3	90.5	81.5
	15586-024-6	150°F	Amberlyst 15	29.671	16.294	83.76	79.9	75.3	90.7	81.6
	15586-024-8	150°F	Amberlyst 15	29.58	16.436	83.88	–	–	–	–
Feed B	93-0024-01A			64.472	0.17	83.12	83.9	–	91.1	–
	15586-031-2	150°F	Amberlyst 15	41.847	21.815	87.43	87.9	78.3	91.5	81.9
	15586-033-1	150°F	Bayer K2634	41.716	22.445	87.48	85.9	79.3	91.3	82.0
	15586-033-3	150°F	Bayer K2634	45.889	17.277	85.78	84.9	74.3	91.2	81.5
Feed C	93-0024-01C			68.651	0.15	84.56	95.9	80.3	92.3	81.1
	15586-034-1	150°F	Bayer 112 K2634	35.369	17.332	79.47	88.9	81.3	91.4	81.2
	15586-034-3	150°F	Bayer no 112 K2634	43.51	21.192	85.78	95.9	85.3	92.3	81.6

*Observed Octane = (Volume Fraction Additive) (Blend Value Additive) + (Volume Fraction Unleaded Regular Gasoline) (Observed Octane Unleaded Regular Gasoline)

Volume fraction unleaded regular gasoline = 0.90
RON unleaded regular gasoline = 91.9
MON unleaded regular gasoline = 82.3

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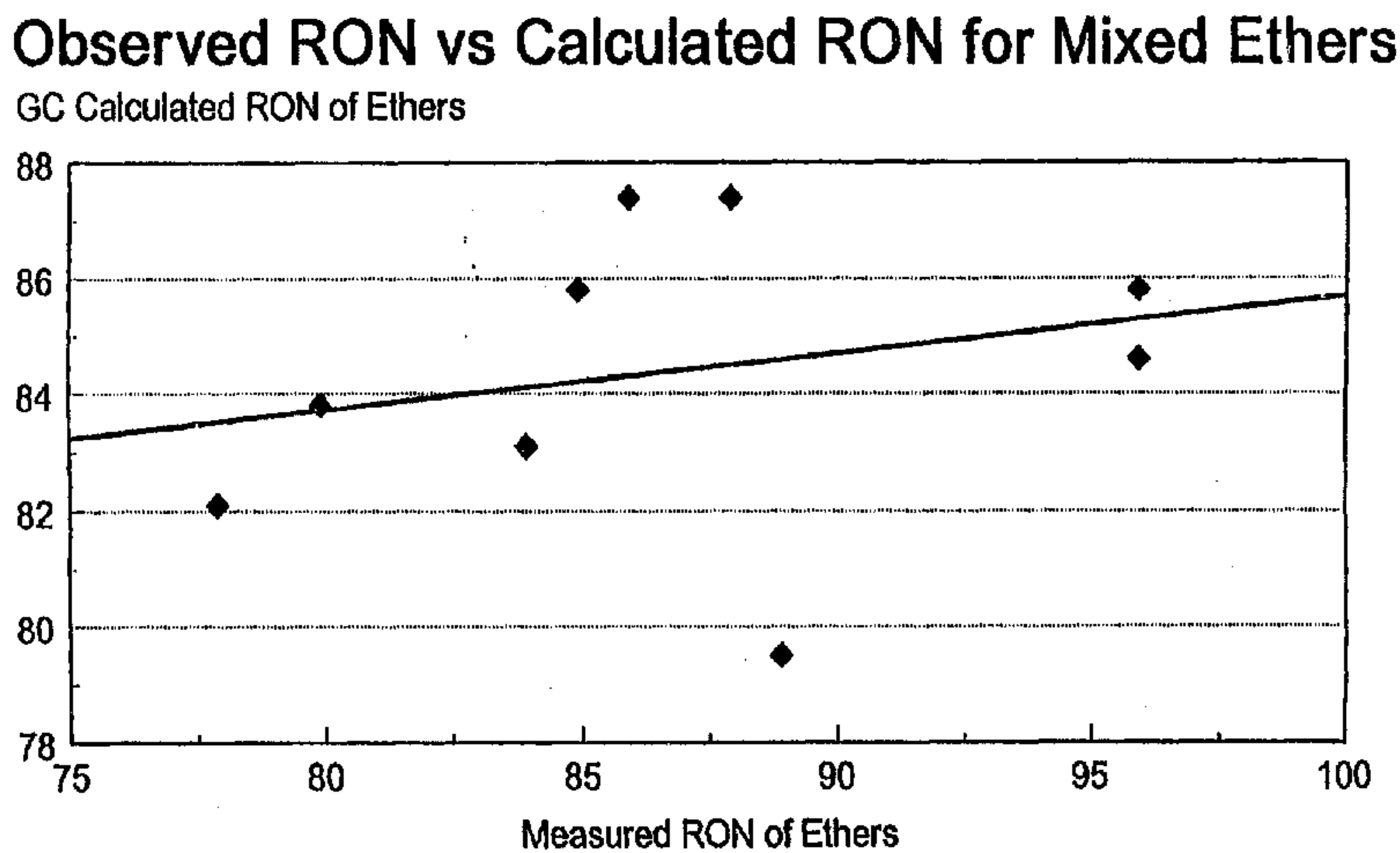
Figure 1

[redacted]



NOTICE

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

QUARTERLY MANPOWER REPORT

For THIRD QUARTER FISCAL YEAR, 1993

(April 1, 1993 - June 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: May 31, 1993

PARTICIPANT NAME AND ADDRESS:

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

	Manpower in Hours by Task							
	1	2	3	4	5	6	7	Total
W. J. Reagan	0	6	1	1	0	0	0	8
R. D. Hughes	0	2	2	6	0	36	0	46
M. M. Schwartz	0	17	20	20	0	86	0	143
Other Professionals	0	0		0	0	1	0	1
Technical Support	0	5.5	7	38	0	20	0	70.5
Secretarial	0	0	0	0	0	15.5	0	15.5
TOTAL HOURS	0	30.5	30	65	0	158.5	0	284