DOE/PC/89866--T1
1

DOE/PC/89866--T1

DE91 000820

DIRECT CONVERSION OF LIGHT HYDROCARBON
GASES TO LIQUID FUEL

Report No. 4

Quarterly Technical Status Report
for
First Quarter F.Y. 1990

Project Manager: R. D. Kaplan

Principal Investigator: M. J. Foral

Work performed under Contract No. DE-AC22-89PC89866

For

U. S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By

Amoco Oil Company
Research & Development Department
Post Office Box 3011
Naperville, IL 60566

MASTER

JMP

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

FINAL QUARTERLY PROGRESS REPORT SUBMITTED TO:

1. George Cinquegrane (2 copies)
Contracting Officer's Representative
U.S. DOE/PETC
P.O. Box 10940
Pittsburgh, PA 15236
2. Dona G. Sheehan
Contract Specialist
U.S. DOE/PETC
P.O. Box 10940
Pittsburgh, PA 15236
3. Robert M. Hamilton
FE-231, E-155/GTN
U.S. Department of Energy
Washington, DC 20545
4. Gilbert V. McGurl
Program Manager
U.S. DOE/PETC, MS 922-H
P.O. Box 10940
Pittsburgh, PA 15236

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TABLE OF CONTENTS

	<u>Page</u>
BACKGROUND	7
PROGRAM OBJECTIVES	8
PROJECT DESCRIPTION	8
RESULTS AND DISCUSSION	9
Task 1: Management Plan	9
Task 2: Modification of Existing Pilot Plant	10
Task 3.1: Evaluation of Los Alamos Computer Model	10
Task 3.2: Process Variable Studies	10
CONCLUSIONS AND FUTURE WORK	10
ACKNOWLEDGEMENT	11

Figure 1
PROGRAM SCHEDULE AND TIMETABLE

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TECHNICAL STATUS

delete
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 the direct conversion of light hydrocarbon gases to liquid fuels via partial oxidation. This report describes work completed in the first quarter of the two-year project (first quarter FY 1990). Task 1 of the work, preparation of the Project Management Plan, has been completed. Work was started and progress made on three other tasks during this quarter:

Task 2. Modification of an existing Amoco pilot plant to handle the conditions of this project. Minor modifications were made to increase the maximum operating pressure to 1500 psig. Other more extensive modifications are being designed, including addition of an oxygen compressor and recycle system.

Task 3.1. Evaluation of a Los Alamos National Laboratory methane oxidation kinetic model for suitability in guiding the experimental portions of this project. Contact was made with Los Alamos and collaboration will begin as soon as legal negotiations on a secrecy agreement are completed.

Task 3.2. Process variable (e.g. temperature, pressure, residence time) studies to determine optimal partial oxidation conditions. The plant was calibrated, and flow-and pressure-tests were successfully completed. Experimental runs will begin in January 1990.

The direction of future work will depend in large part on the results from the computer modelling work (Task 3.1). Discussions with DOE personnel will be held to ensure agreement on project direction at this major decision point.

BACKGROUND

Fischer-Tropsch synthesis, gasification processes like Lurgi dry bottom gas, direct coal liquefaction, and remote natural gas all represent sources of substantial quantities of light hydrocarbon gases. Methane is the major and most stable component of all these gases. Steam reforming methane to produce synthesis gas is capital-intensive because it is highly endothermic and requires severe reaction conditions. A process for direct conversion of light gases, especially methane, to methanol, gasoline, or other liquid fuels could be far superior.

Steam reforming is the first stage in traditional commercial methods for the production of liquid fuels. This first step produces synthesis gas:

The synthesis gas is then converted into methanol via a catalytic process.

Reaction 1 produces more hydrogen than required by Reaction 2. The excess can either be utilized elsewhere in the case of a domestic refinery or, in the case of a remote operation, is lost. A third step could be the catalytic condensation of methanol to gasoline.

A more efficient route of converting light hydrocarbons would be to directly form methanol by partial oxidation.

Such a process could substantially reduce capital and energy requirements for methanol production. The methanol could be used as a fuel or a fuel blending component, as in the case of M80 fuels (80% methanol, 20% gasoline), or else converted into gasoline through well-known processes, such as MTG. A plant based on Reactions 1 and 2 followed by methanol condensation to gasoline has been built and is operating in New Zealand. However, the process is uneconomical if it were not for New Zealand Government support. If a process for the direct conversion of light hydrocarbons to methanol is feasible, thereby eliminating the process steps shown by Reactions 1 and 2, then a gas-to-gasoline process could become economically viable.

A proposed process for converting light hydrocarbon gases directly to hydrocarbon liquids, e.g., methanol or formaldehyde, is not new. In 1932 Newitt and Haffner reported the formation of methanol, along with smaller amounts of formaldehyde and formic acid, in the high-pressure oxidation of methane.⁽¹⁾ The reaction was carried out in a static system at 360°-393°C and 50-150 atm. The maximum methanol selectivity was ca. 22%; however, CH₄ conversion was only a few percent. More recently, Gesser, Hunter and co-workers have reported methanol selectivities up to 81% and yields of around 7%.⁽²⁾ However, other workers have been unable to reproduce these results.

- (1) D. M. Newitt, A. E. Haffner, Proc. R. Soc. London, 1932, Ser. A, 134, p. 591.
- (2) H. D. Gesser, N. R. Hunter, Chem. Rev., 1985, 85(4), p. 235,
H. D. Gesser, U. S. Patent 4,618,732, issued 10/21/86.

PROGRAM OBJECTIVES

The objective of this program is to investigate the direct conversion of light gaseous hydrocarbons, such as those produced during Fischer-Tropsch synthesis or as a product of gasification, to liquid transportation fuels via a partial oxidation process. The process will be tested in an existing pilot plant to obtain credible mass balances. Specific objectives to be met include determination of optimal process conditions, investigation of various processing options (e.g. feed injection, product quench, and recycle systems), and evaluation of an enhanced yield thermal/catalytic system. Economic evaluation of the various options will be performed as experimental data become available.

PROJECT DESCRIPTION

The project is of two years' duration and contains three major tasks. The third task (Pilot Plant Experiments) contains seven subtasks, corresponding to the project objectives outlined above. The tasks and subtasks foreseen when the project began are described below.

Task 1 --Project Management Plan: A plan will be prepared describing the work to be done, milestones, and manpower requirements and costs.

Task 2 --Pilot Plant Modification: An existing pilot plant dedicated to investigation of light hydrocarbon conversion will be modified to provide it with the capability to handle the processes and conditions of this program. These modifications will include construction of a new reactor, construction and installation of reactant injection and product quench systems, and, possibly, addition of a product recycle loop to the unit.

Task 3.1 --Comparison of Preliminary Data with Los Alamos Model: We will determine if the kinetic model developed by Los Alamos National Laboratory can be used to guide our experimental effort. Results from this task will be carefully analyzed and will determine the direction of the subsequent experimental program. This is a major decision point in the project.

Task 3.2 --Pressure/Temperature/Reaction Time Effects: The methane conversion data base will be extended over the following range of conditions:

Temperature:	600 to 1100 F
Pressure:	200 to 1300 psig
Reaction Time:	3 to 90 seconds

These experiments will be guided by the results of Task 3.1 to those process regimes which appear most promising.

Task 3.3.--Study of Different Injection Systems: Different schemes for introducing and mixing reactants before or within the reactor will be evaluated theoretically and/or experimentally. The goal will be to maximize methanol yield.

Task 3.4.--Study of Different Quench Systems: The efficacy of different product cooling techniques will be investigated to determine the effect of quenching on product composition and methanol yield. Both gas and liquid quench options will be investigated.

Task 3.5.--Effect of Reactor Geometry: The effect of reactor geometry, particularly aspect (i.e. length/diameter) ratio, will be investigated to determine mass transfer and mixing effects on product composition and methanol yield.

Task 3.6.--Effect of Reactor Recycle: The effect of recycling unreacted hydrocarbons to the reactor inlet will be evaluated first by appropriately blending the feed stream to simulate reactor recycle. If these results are promising relative to methanol production, a recycle compressor and recycle line will be added to the pilot plant for more detailed tests.

Task 3.7.--Enhanced-Yield Catalyst Study: An attempt will be made to develop a combined thermal/catalytic process in which byproduct carbon monoxide and hydrogen from the thermal process are converted to methanol over a heterogeneous catalyst. Such a combined process may provide higher methanol yields than the thermal process alone.

Reporting will be done periodically throughout the duration of the project according to DOE guidelines. The projected timetable for completion of these tasks is given in Figure 1.

RESULTS AND DISCUSSION

During this quarter, a draft of the Management Plan (Task 1) was sent to the U.S. Department of Energy for review. Minor modifications were made to the pilot plant (Task 2) to extend its operability range, while more extensive modifications are in the planning and design stages. Los Alamos personnel were contacted regarding use of their model (Task 3.1). They are agreeable to collaboration on the project, but model runs have been delayed, pending acceptable legal (secrecy) arrangements.

Task 1: Project Management Plan

The Project Management Plan was prepared and submitted in draft form to the U.S. Department of Energy on November 28, 1989. The Plan included sections on Project Management, Milestone Schedule/Manpower, and Costs. Submission of the Plan completes work on this task (barring revisions), which was completed on schedule and \$11M under budget.

Task 2: Pilot Plant Modification

Minor modifications were made to the pilot plant in order to extend its range of operability. In preparation for high-pressure process variable studies (under Task 3.2), higher pressure (1500 psi vs 1000 psi) rupture disks were installed on the unit. Discussions were also held with a representative of Pressure Products Industries regarding purchase of an oxygen-service compressor for the reactor feed section. This compressor will be necessary if numerous high-pressure (i.e. above 1000 psi) runs are desirable, since it will allow us to use a greater fraction of the oxygen cylinder contents. A suitable compressor has been identified, and will be ordered if process variable (Task 3.2) and computer modelling (Task 3.1) data indicate it will be needed. Delivery time on the compressor is 4-6 weeks.

Task 3.1: Evaluation of Los Alamos Kinetic Model

Since proprietary Amoco information will have to be divulged to Los Alamos personnel to effectively evaluate their computer model, Amoco has drafted a secrecy agreement between Los Alamos and Amoco personnel. Signing of this agreement has been delayed pending negotiation of various provisions in the agreement. The points being negotiated include contract duration and protection against release of Amoco data and conditions to outside parties. In the course of our discussions with Los Alamos, we have learned that their model can only handle pure methane feeds. In contrast, all of our preliminary data was obtained with natural gas feeds (containing up to 8% ethane and propane). Since the model cannot be easily modified to handle ethane and propane in the feed, several of our most promising experimental runs using natural gas feed will be replicated using pure methane. Comparison with Los Alamos predictions will then be made to check model accuracy and provide data on effects of other light hydrocarbons. These runs are currently being made on the pilot plant.

Task 3.2: Process Variable Studies

Work on this task began on-schedule in December. All flow meters and analytical instruments on the unit were calibrated and the plant was successfully flow- and pressure-tested. Experimental runs began in the first week of January 1990.

CONCLUSIONS AND FUTURE WORK

Work set for the next quarter will include runs on Los Alamos' computer model. These will begin as soon as legal matters are clarified. The results of these runs will determine in large part the direction of the rest of the project during the coming quarter. If use of the model corroborates our data and:

- (1) Predicts higher methanol yields in a particular operating regime, pilot plant runs will be made to confirm the predictions.

(2) If the model can locate no operating regimes with higher yields, then the extent of the process variable studies (Task 3.2) may be curtailed and other avenues explored, pending discussion with DOE personnel.

If model results do not corroborate our data, then a broader range of process variable conditions will be studied, using an evolutionary operations approach. Discussions with DOE personnel will be held to ensure agreement on project direction at this decision point.

Meanwhile, design of the more extensive pilot plant modifications will continue. These will include work on a new reactor with different aspect ratio (for Task 3.5), installation of an oxygen-service compressor in the feed section (if needed), and consideration of options for feed injection (Task 3.3) and product quench (Task 3.4).

ACKNOWLEDGEMENT

This work was supported by the United States Department of Energy under Contract DE-AC22-89PC89866.

NOTICE

This report was prepared by the organization(s) named below as an account of work sponsored by the United States Department of Energy (DOE). Neither DOE, members of DOE, the organization(s) named below, nor any person acting on behalf of any of them: (a) makes any warranty, express or implied, with respect to the use of any information, apparatus, method, or process disclosed in this report or that such use may not infringe privately owned rights; or (b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

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

/MJF/RDK/jmb/9002

- END -

DATE FILMED

11 / 05 / 90