DOE/PC/89866-T4

DOE/PC/89866--T4

DE92 015591

DIRECT CONVERSION OF LIGHT HYDROCARBON GASES TO LIQUID FUEL

Report No. 15

Quarterly Technical Status Report
for
Fourth 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

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.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MAY 07 1992

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

JUN 17 1992

ADDITIONAL CIRCULATION FOR DRAFT REPORTS TO:

Amoco Corporation
Suite 600
305 East Shuman Boulevard
Naperville, IL 60563-8408
J. A. Mahoney

Amoco Oil Company
P.O. Box 3011
Naperville, IL 50566
R. D. Kaplan, H-4
M. J. Foral, H-4
A. R. LaPuma, H-4
D. W. Washecheck, H-2
D. B. Lerman, H-1
E. G. Wollaston, H-3
A. S. Couper, H-1

TABLE OF CONTENTS

LIST OF FIGURES

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

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 fourth quarter of the two-year project. Task 1 of the work, preparation of the Project Management Plan, was completed in the first quarter. Work continued and progress was made on four other tasks during this quarter:

Task 2. Modification of an existing Amoco pilot plant to handle the conditions of this project. Construction was completed on a new reactor for Task 3.5 (Effect of Reactor Geometry) and it was installed on the pilot plant. Various forms of mixers have been selected and purchased for use in the Task 3.3 (Effect of Feed Injection) experiments. They will be installed in the beginning of November.

Task 3.2. Process variable (e.g. temperature, pressure, residence time) studies to determine optimal partial oxidation conditions. All experimentation for this Task has been completed. The effects of temperature, pressure and residence time are described in this report. Low temperatures (T < 850°F) and high pressure (P = 1300 psig) were found to be optimal for both methanol yield and methane conversion in this system. Residence time had little effect on methanol yield except when very short (less than 10 seconds), where methanol yield dropped sharply. Hydrocarbon conversion correlated well with gas flow rate in all experiments, suggesting that mass or heat transfer may be a controlling factor in this system. The highest methanol yield observed in any run was 5.5%, far below that needed for economic viability.

Task 3.3. Studies of different reactant gas mixing and injection systems. In August we visited the laboratories of Dr. Hyman Gesser at the University of Manitoba. Dr. Gesser has reported particularly high methane conversions and methanol selectivities for homogeneous methane partial oxidation. He claims that proper mixing of the reactant gases is very important to achieving high methanol yields. He discussed his mixing method with us, and we will try to verify his high methane conversions and methanol selectivities.

Task 3.5. Studies to determine the effect of reactor geometry. Two reactors of different diameter were used to probe the effect of reactor aspect (length/diameter) ratio on the system parameters. Methanol yields from the smaller-diameter reactor were consistently lower than those from the larger-diameter reactor. This was especially true at higher temperatures (T > 900°F) due to methanol decomposition on the reactor walls.

Because of operability problems with a natural gas flow controller and a plant computer, the project is proceeding about 3-4 weeks behind schedule. The total cost of the project in Fiscal 1990 was $293M. This is $123M below the budget plan of $416M. In the next quarter we will continue studying the effect of reactor geometry (Task 3.5). Work will also begin on the effect of feed pre-mixing and injection (Task 3.3).

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 syntheses gas:

$$CH_4 + H_2O \text{ ----> } CO + 3H_2 \qquad \Delta H = 49.3 \text{ kcal} \qquad (1)$$

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

$$CO + 2H_2 \text{ ----> } CH_3OH \qquad \Delta H = -21.7 \text{ kcal} \qquad (2)$$

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.

$$CH_4 + \tfrac{1}{2} O_2 \text{ ----> } CH_3OH \qquad \Delta H = -30.7 \text{ kcal} \qquad (3)$$

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 the 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, CH_4 conversion was only a few percent. More recently, Gesser, Hunter and co-workers have reported methanol selectivities up to 89% and yields of around 7%.(2) However, other workers have in general been unable to reproduce these results.

(1) D. M. Newitt, A. E. Haffner, Proc. R. Soc. London, Ser. A, 134, p. 591

(2) H. D. Gesser, N. R. Hunter, Chem. Rev.,(^T 15(4), p. 235 (1985); 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 is 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.

RESULTS AND DISCUSSION

During this quarter, pilot plant runs (Task 3.2) demonstrated that lower temperatures and higher pressures are desirable for increasing both methanol yield and methane conversion. These experiments have also indicated that gas flow rate in the pilot plant can affect the level of hydrocarbon conversion in the reactor. Experiments with two reactors of different length/diameter ratio indicated that larger-diameter reactors may be desirable for increasing methanol yield. A new, larger-diameter reactor has been installed and studies are underway to test this conclusion.

Task 2: Pilot Plant Modification

A new reactor with a 30 mm diameter reaction zone has been constructed and installed in the pilot plant. The reactor is capable of withstanding temperatures of up to 1250°F at pressures of 1700 psig and will allow further study of the effect of reactor geometry (Task 3.5). A commercial in-line static mixer has been selected and purchased for the mixing studies (Task 3.3 - Effect of Feed Injection Systems). It is currently being cleaned for oxygen service and should be installed by the beginning of November. For additional mixing studies, two oxygen-cleaned needle valves have been purchased. These will also be installed during the next quarter.

Task 3.2: Process Variable Studies:

During this quarter, data analysis was completed for the process variable studies (Task 3.5). Results are presented here for the effects of temperature, pressure and residence time on the partial oxidation of methane to methanol.

Effect of Temperature

Figures 1-4 summarize the effect of temperature on methanol yield, product selectivity, methane conversion, and hydrocarbon conversion, respectively. In all experiments the hydrocarbon feed was natural gas, the hydrocarbon/oxygen was 10 and the residence time was 35 seconds. Pressures of 1300 psig, 1100 psig and 825 psig were studied and are included on the figures. It should be noted that the temperatures shown in the figures correspond to average temperatures in the reaction zone. Even though the reactor heater was set for constant temperature, the size of the reactor (approximately 1 inch diameter) and the design of the furnace preclude isothermal operation. A significant temperature rise through the reactor (generally between 100-200°F) was observed in all runs. External thermocouples measured temperatures at three different points on the reactor (corresponding to the beginning, middle, and end of the reaction zone), and the temperatures reported below are averages of these three readings. This averaging method is sufficiently accurate to reveal temperature trends in the data, but given the large temperature rise through the reactor, it should not be used in any kinetic analysis. It was found that the average temperature corresponded reasonably well with the heater setpoint temperature in all cases, generally being 10-50°F higher.

The data presented in the figures are corrected for the amount of ethane in the natural gas feed. The natural gas feed was not a standard mixture; it was taken from the city supply line and compressed for use in these experiments. Because of this, the composition of the natural gas varied slightly over time, primarily in the amount of ethane present. Ethane levels in the natural gas ranged from 2.5-5.0 vol%. Since the level of higher hydrocarbons can significantly affect both methane and hydrocarbon conversion (see the May monthly report), it was necessary to adjust each run to a standard ethane concentration (in this case, 4.9 vol% ethane). The correction factors for this standardization were derived from the slopes of Figures 1 and 2 in the May report.

The effect of temperature on methanol yield is shown in Figure 1. At each pressure, methanol yield decreased with increasing temperature. These results indicate that lower temperatures are desirable for maximizing methanol yield. There is little difference between the pressures, so all of the data were combined into a single curve. It should be noted that the yields at 825 psig are all slightly lower than the curve. This will be discussed in the following section.

Figure 1

Effect of Temperature on Methanol Yield
Res. Time=35 sec; HC/O2=10

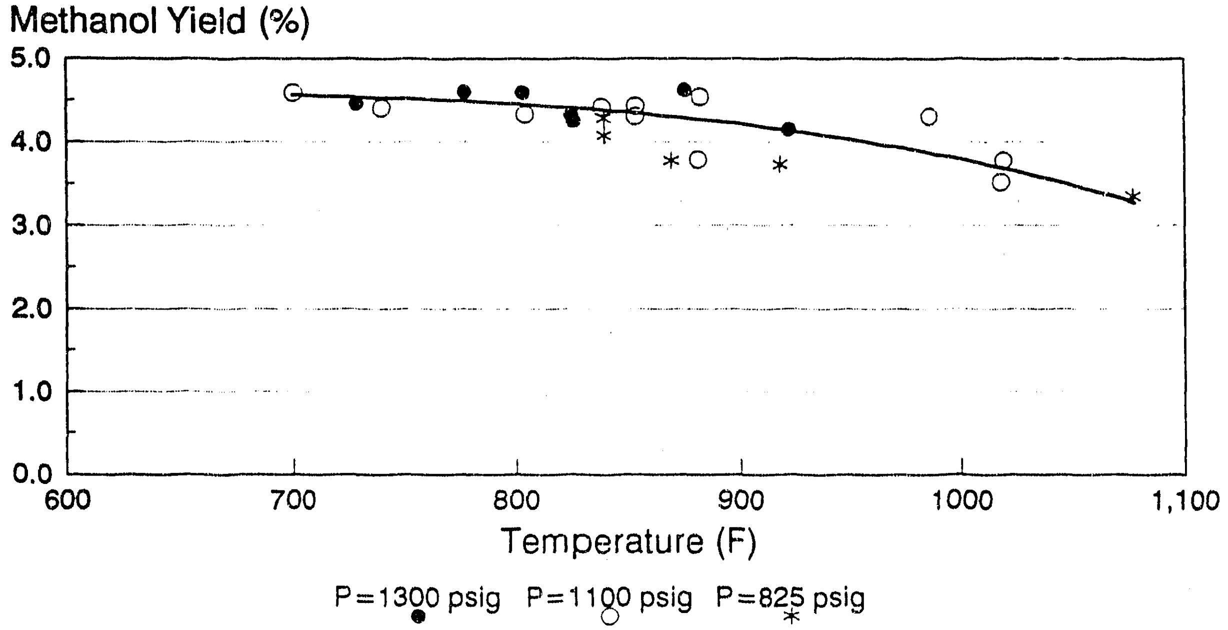


Figure 2

Effect of Temperature on C-based Selectivity
Res. Time=35 sec; HC/O2=10; 825-1300 psig

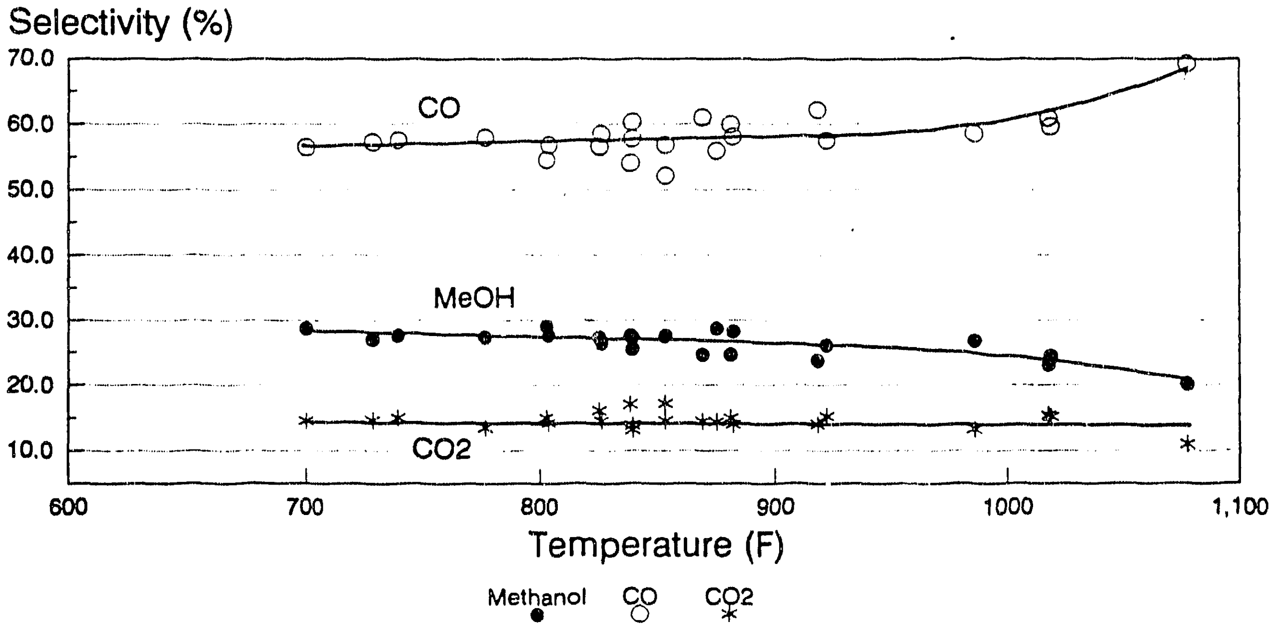


Figure 3

Effect of Temperature on CH4 Conversion
Res. Time=35 sec; HC/O2=10

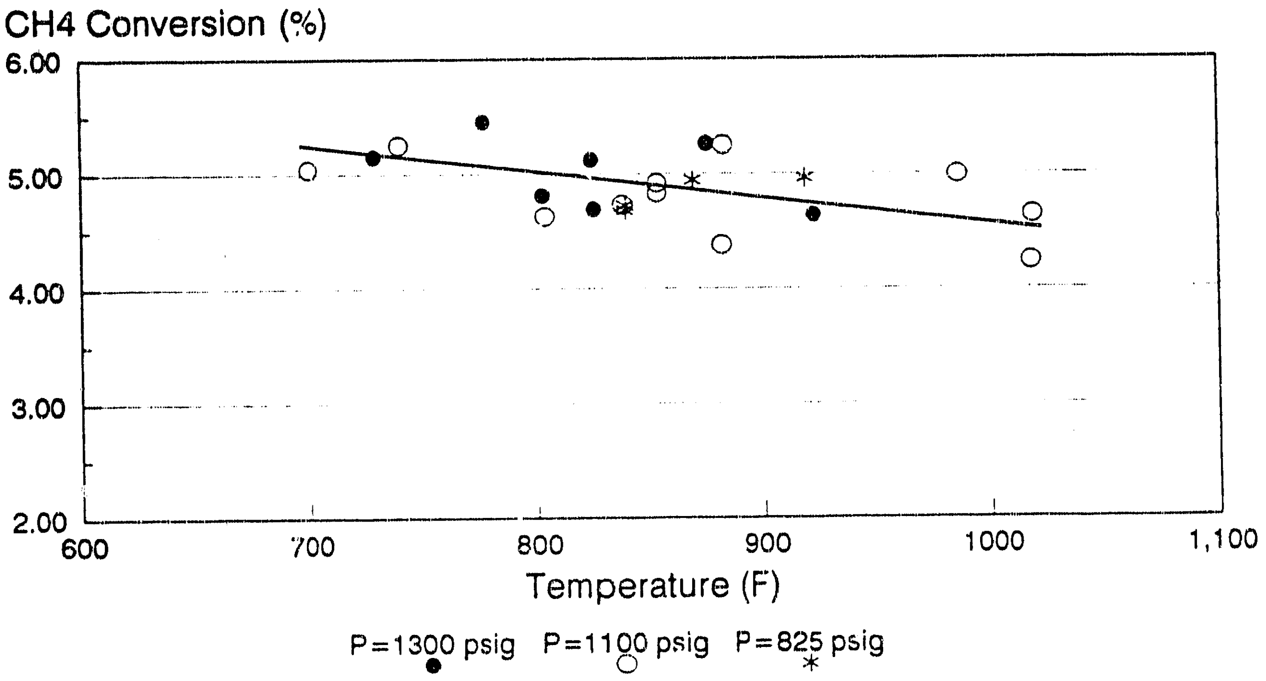
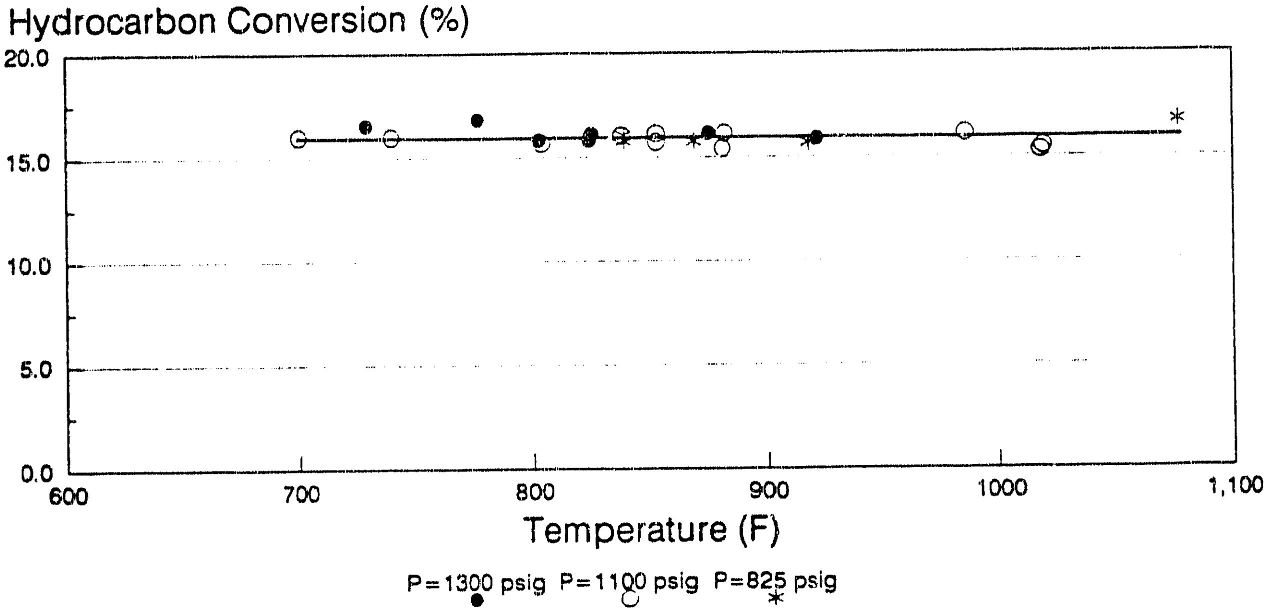


Figure 4

Effect of Temperature on Hydrocarbon Conversion
Res. Time=35 sec; HC/O2=10;



The effect of temperature on product selectivity is shown in Figure 2. It appears that temperature has little effect on product selectivity over the 700 and 1000°F range. Above 1000°F methanol selectivity drops and CO selectivity rises. Carbon dioxide selectivity is unchanged over the entire range. The decrease in methanol selectivity at the highest temperatures (and resulting increase in CO selectivity) may mark the onset of thermal methanol decomposition to CO and hydrogen.

The effect of temperature on methane conversion is shown in Figure 3. The general trend is for higher methane conversions at lower temperatures. This trend is supported by the data at 1300 and 1100 psig, but the data at 825 psig show the opposite trend. Given the relatively small amount of 825 psig data, its limited temperature range, and the small change in conversion found, the apparent reversal in trend at 825 psig may be fictitious. Since higher methane conversions are desirable, the data in Figure 3 suggest that lower temperatures are preferred.

As seen in Figure 4, temperature has no discernable effect on hydrocarbon (methane and C_{2+}) conversion. The slight decrease in methane conversion observed in Figure 3 is masked in this Figure by significant conversion of the higher carbon number hydrocarbons. The conversion of these higher hydrocarbons is apparently not affected by temperature.

The primary conclusion that can be drawn from the temperature studies is that lower temperatures appear to be desirable for both methanol yield and methane conversion. Burch et al. (J. Chem. Soc., Faraday Trans. 1, 85(10), 3561-3568 (1989)) also found that methanol selectivity increased as temperatures decreased. They used an isothermal reactor at a lower oxygen concentration (2.5 vol%) and lower pressure (150-750 psig). At higher oxygen levels (8-9 vol%) but lower pressures (300-500 psig) in an isothermal reactor, Gesser et al. (Ind. Eng. Chem. Res. 27, 252-256 (1988)) observed a maximum in methanol selectivity at around 825°F. The trends with temperature are not large in the present study. This may indicate that in non-isothermal operation, tight temperature control might not be necessary to maximize methanol production.

Effect of Pressure

The effects of pressure on methanol yield, product selectivity, methane conversion, and hydrocarbon conversion are summarized in Figures 5-8. In these runs other conditions were held constant at a residence time=35 seconds and hydrocarbon/oxygen=10 (9.1 vol% oxygen in feed). Setpoint temperatures of 800, 850, 875 and 1000°F are shown in the figures.

At every temperature studied methanol yield increases with increasing pressure between 800-1300 psig, as shown in Figure 5. This indicates that higher pressures are desirable for maximizing methanol production. This agrees with the 825 psig data shown in Figure 1 and discussed in the previous section. The significantly lower methanol yield at 1000°F noted in the previous section is apparent in Figure 5.

The effect of pressure on product selectivity is shown in Figure 6. The

Figure 5

Effect of Pressure on Methanol Yield
Res. Time=35 sec; HC/O2=10

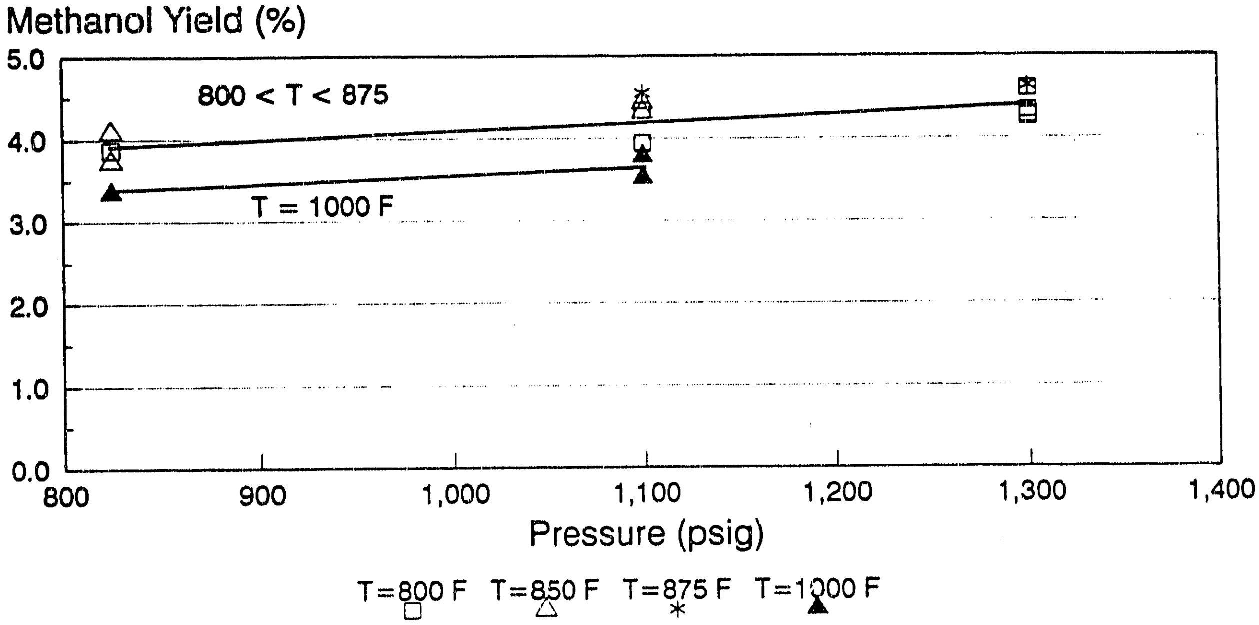


Figure 6

Effect of Pressure on C-based Selectivity
Res. Time=35 sec; HC/O2=10; 800-1000 F

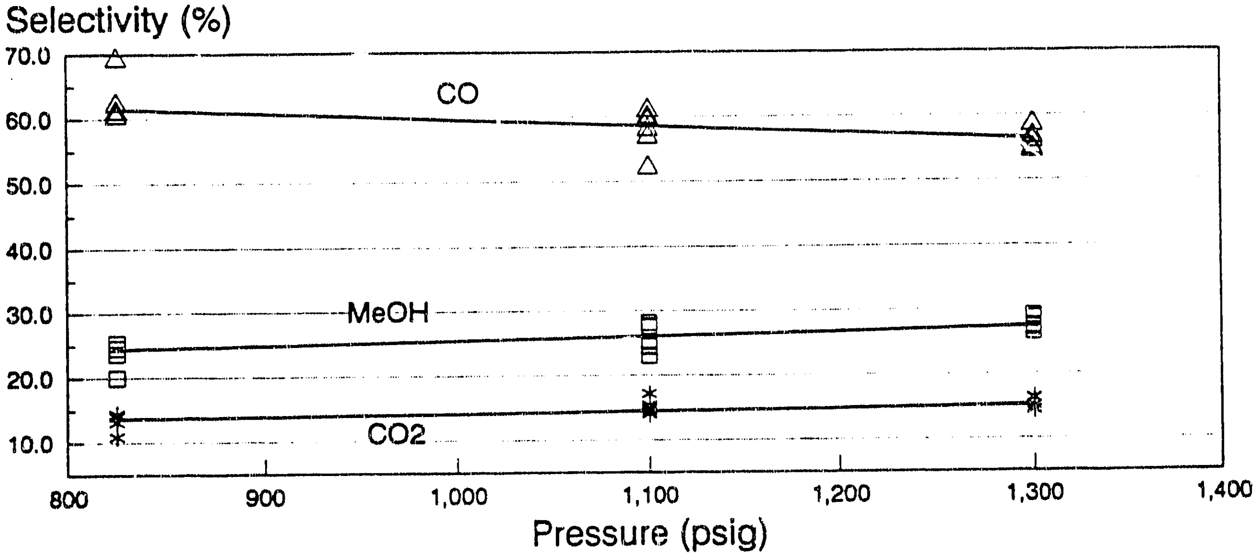


Figure 7

Effect of Pressure on Methane Conversion
Res. Time=35 sec; HC/O2=10

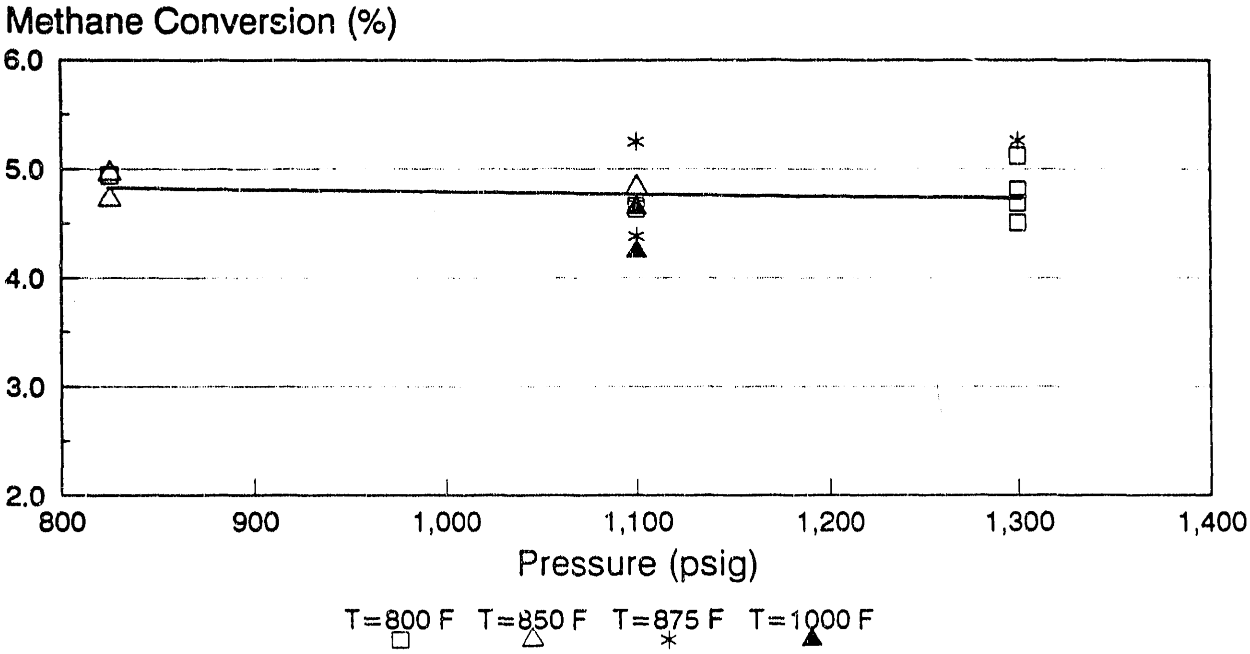
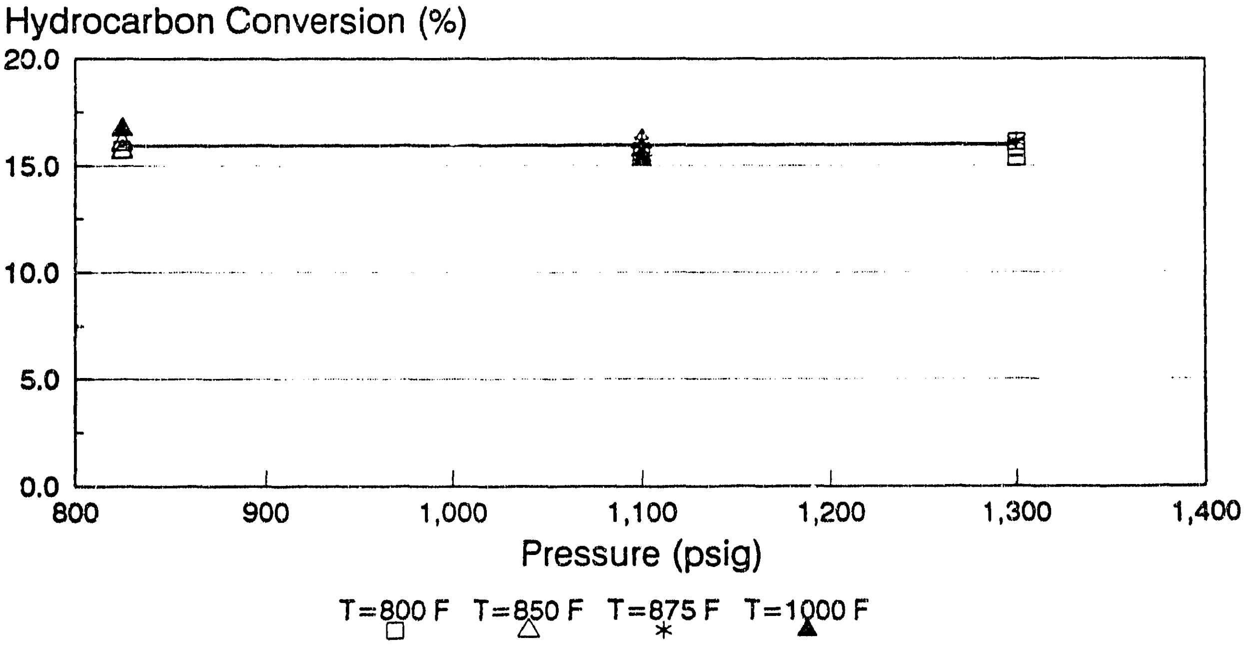


Figure 8

Effect of Pressure on Hydrocarbon Conversion
Res. Time=35 sec; HC/O2=10



trends are not large, but it appears that methanol selectivity increases slightly with increasing pressure, while CO selectivity decreases with increasing pressure. Carbon dioxide selectivity is relatively constant over the range of pressures studied. Frohlich et al. (Ind. Eng. Chem., 26(3), 267-276 (1934)) also found higher methanol selectivity at higher pressures (up to 2000 psig). Both Gesser et al. and Burch et al. found that methanol selectivity remained relatively unchanged in isothermal reactors at somewhat lower pressures (150-1000 psig).

Pressure has no discernable effect on either methane conversion or hydrocarbon (methane and C_{2+}) conversion, as shown in Figures 7 and 8, respectively.

Like the temperature trends, the trends with pressure are quite small. They indicate, however, that higher pressures are marginally better for increasing methanol yield.

The above experiments allow us to define more closely the base conditions for further natural gas conversion experiments. In earlier reports, we found that using a natural gas feed with 9 vol% oxygen (hydrocarbon/oxygen=10) was desirable. The above results helped define the base temperature and pressure at 800°F and 1300 psig, respectively.

Effects of Residence Time

The effects of residence time on methanol yield, product selectivity, methane conversion and hydrocarbon conversion were studied. All experiments were carried out at P=1300 psig, T=800°F and hydrocarbon/oxygen=10.0. Two different sizes of reactor liner were used in these residence time studies: a "large" 19 mm diameter tube (for the longer residence times) and a "small" 10.5 mm diameter tube (for the shorter residence times). Both reactors utilized the same 13-inch long furnace.

Figure 9 shows the effect of residence time on methanol yield. There is a striking difference between the results from the large- and small-diameter reactors. The large diameter reactor gave very consistent and reproducible results, and showed little effect of residence time on methanol yield. The data from the smaller diameter reactor were much more scattered and showed no clear trend with residence time, other than a possible maximum in methanol yield at around 10 seconds residence time. The small tube data seems to consistently fall below the large tube data. There was not much overlap between the residence time regimes studied with the different reactors, so it is possible that reactor size effects came into play. The lower yields in the small tube and decrease in methanol yield at short residence times may result from reactor size effects rather than residence time effects.

Figure 10 presents the effect of residence time on methanol selectivity. It has the same characteristics as the methanol yield plot. This is to be expected at relatively constant hydrocarbon conversions, since methanol yield is the product of methanol selectivity and hydrocarbon conversion.

Figure 11 shows the effect of residence time on methane conversion. Once

Figure 9

Effect of Residence Time on Methanol Yield
T=800 F; P=1300 psig; HC/O2=10

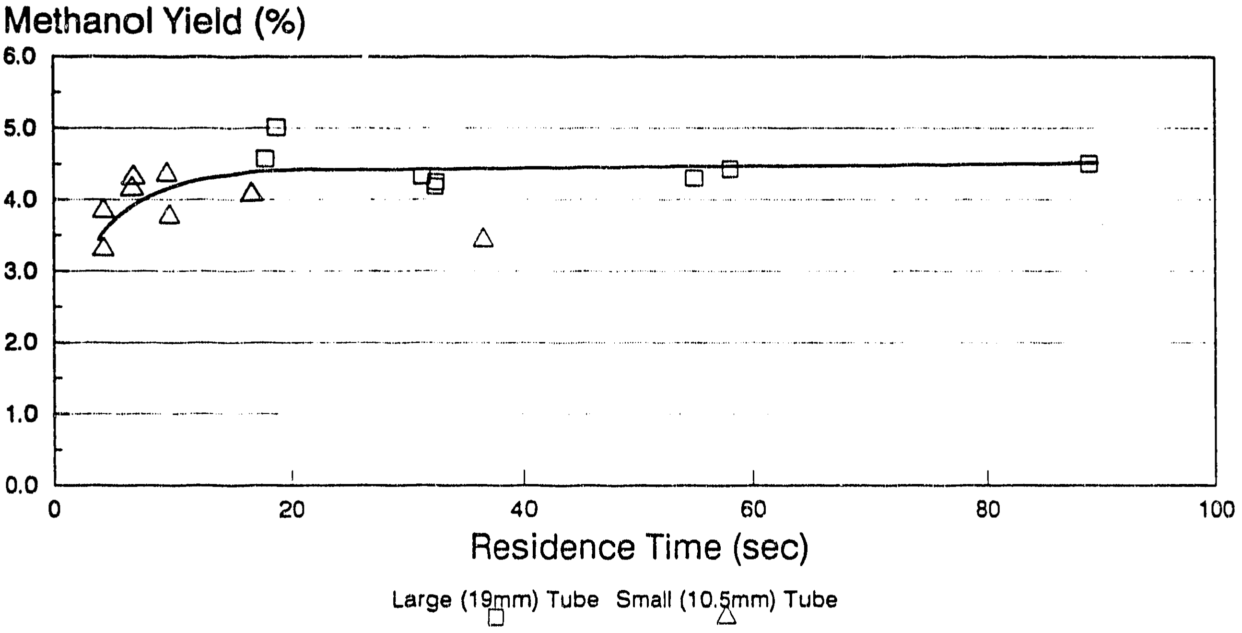


Figure 10

Effect of Residence Time on Methanol Selectivity
T=800 F; P=1300 psig; HC/O2=10

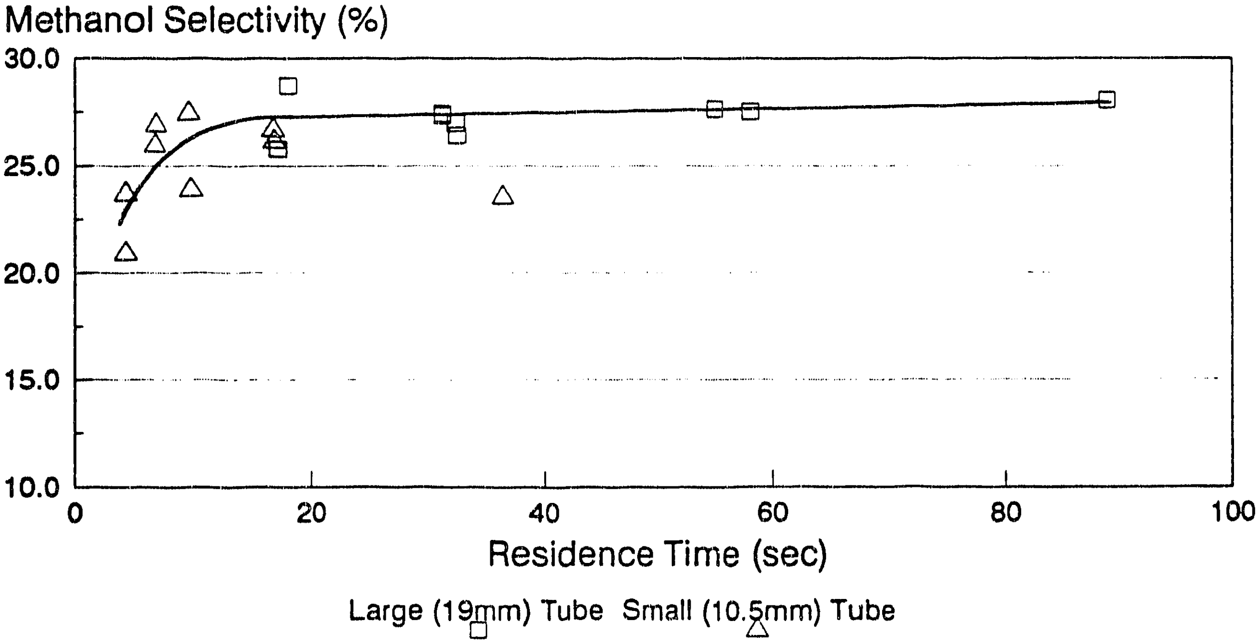


Figure 11

Effect of Residence Time on Methane Conversion

T=800 F; P=1300 psig; HC/O2=10

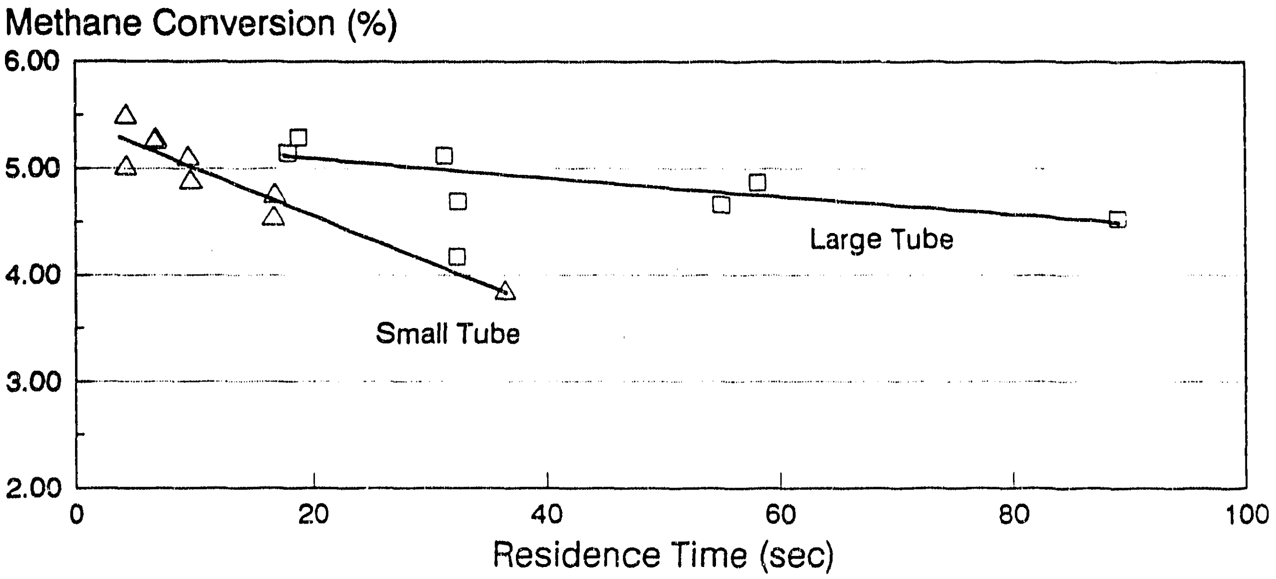
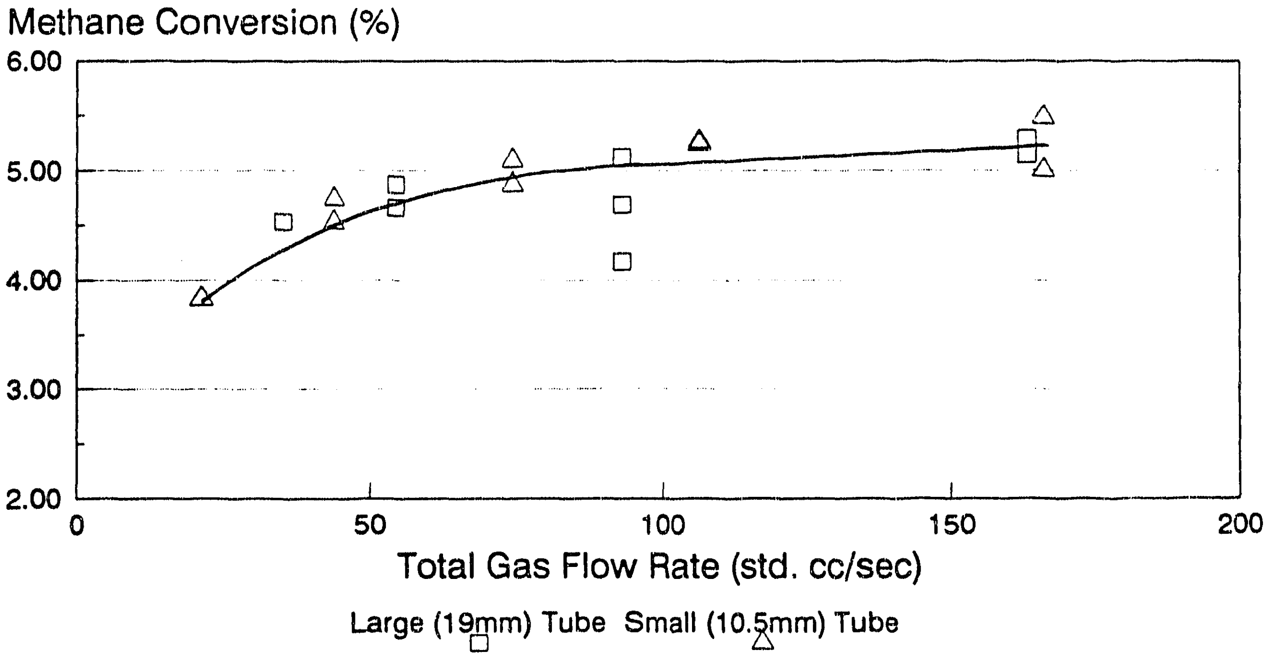


Figure 12

Effect of Gas Flow Rate on Methane Conversion

T=800 F; P=1300 psig; HC/O2=10



again there is a definite distinction between the large and small diameter tube data. This time, however, they both show a clear decrease in methane conversion with increasing residence time. Again, the small tube data appear to fall below the large tube data. The two distinct lines in Figure 11 can be made to converge into a single curve (see Figure 12) by plotting methane conversion as a function of total gas flow rate, rather than residence time. This suggests that gas flow rate, rather than residence time, is a key parameter in this system.

Two reasons for this behavior are proposed. First, mixing of the gases prior to reaction may be important. At the higher flow rates, better mixing occurs and methane conversion is higher. Calculations show that in the 1/4" transfer lines present in the pilot plant, laminar flow conditions (and resulting poor mixing) prevail at total (oxygen + natural gas) flow rates below about 85 sccs, while turbulent flow (better mixing) begins to occur above about 95 sccs. Turbulent flow is defined as flow where $N_{Re}>2000$. The wide scatter in the data at around 90 sccs could be due to this being within the transition region between laminar and turbulent flow, producing erratic flow conditions and mixing. Another potential reason for the single curve in Figure 12 is that there is some mass or heat transfer operation in the reactor itself that strongly affects methane conversion. In either case, the fact that methane conversion varies with flow rate rather than residence time suggests that a heat or mass transfer effect, rather than a kinetic effect, is controlling methane conversion in this system.

The effect of residence time on hydrocarbon (methane and C_{2+} conversion) is shown in Figure 13. Once again there appear to be two distinct lines, one for the large diameter tube and one for the smaller diameter tube. When hydrocarbon conversion is plotted against total gas flow rate (as in Figure 12), the two lines converge to form one curve (Figure 14). This again suggests that gas flow rate, rather than residence time in the reactor, is an important variable in this system.

Effect of Reactor Geometry (Task 3.5):

Methane partial oxidation experiments have been completed using reactors with two different aspect (length/diameter) ratios. We again utilized two different sizes of quartz reactor liner: a "large" 19 mm diameter tube and a "small" 10.5 mm diameter tube. In all cases the feeds were natural gas and pure oxygen, and HC/O_2 was 10.

Except for the cases presented below, trends in the data from the small diameter reactor mirrored data trends from the larger reactor. Under almost all conditions, however, methanol yields in the small reactor were slightly lower than methanol yields at similar temperatures and pressures in the larger reactor. This may have been caused by the lower gas flow rates used in the small-diameter reactor experiments. Data presented in the previous section indicate that lower gas flow rates in this system lead to lower hydrocarbon conversions (and therefore to lower methanol yields).

Figure 15 indicates that selectivity to methanol is much more sensitive to high temperatures in the small diameter reactor than in the larger diameter

Figure 13

Effect of Residence Time on HC Conversion
T=800 F; P=1300 psig; HC/O2=10

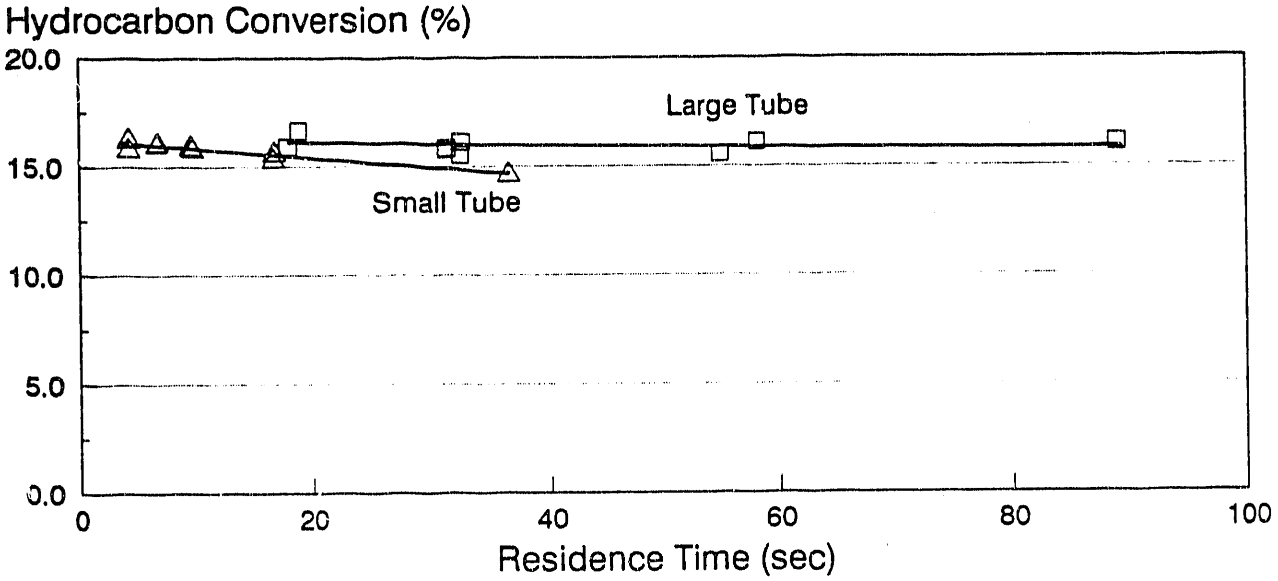


Figure 14

Effect of Flow Rate on Hydrocarbon Conversion
T=800 F; P=1300 psig; HC/O2=10

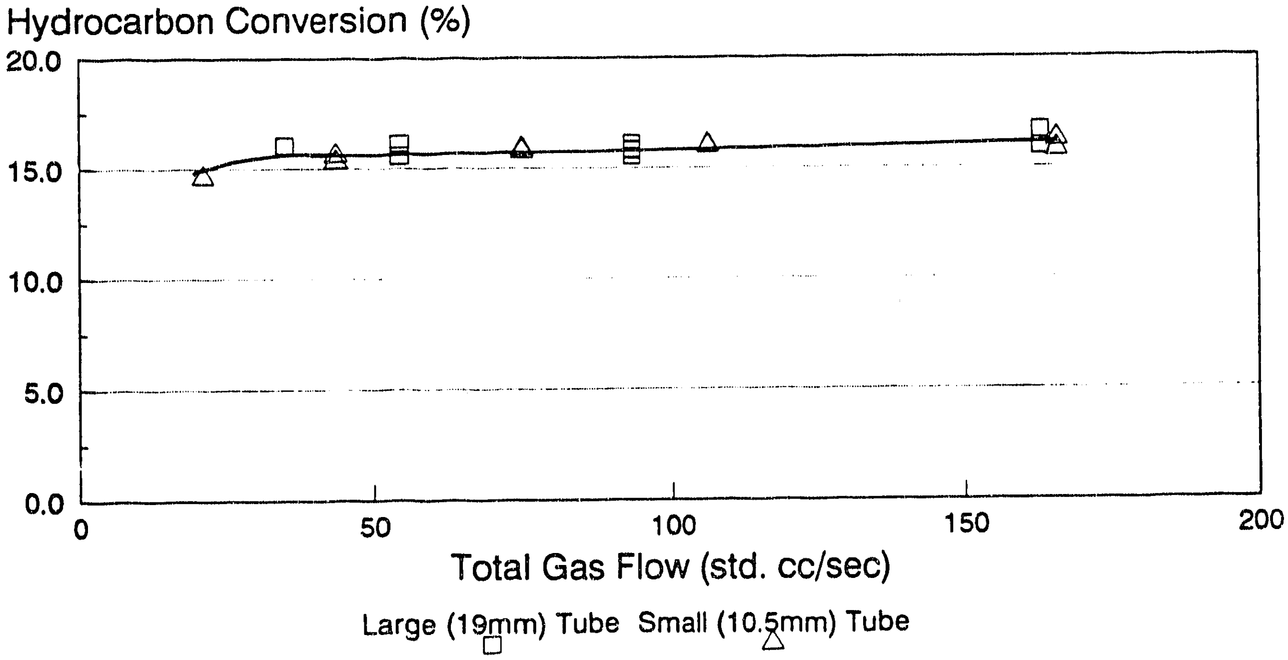


Figure 15

Effect of Temperature on MeOH Selectivity

P=1100-1300 psig; HC/O2=10

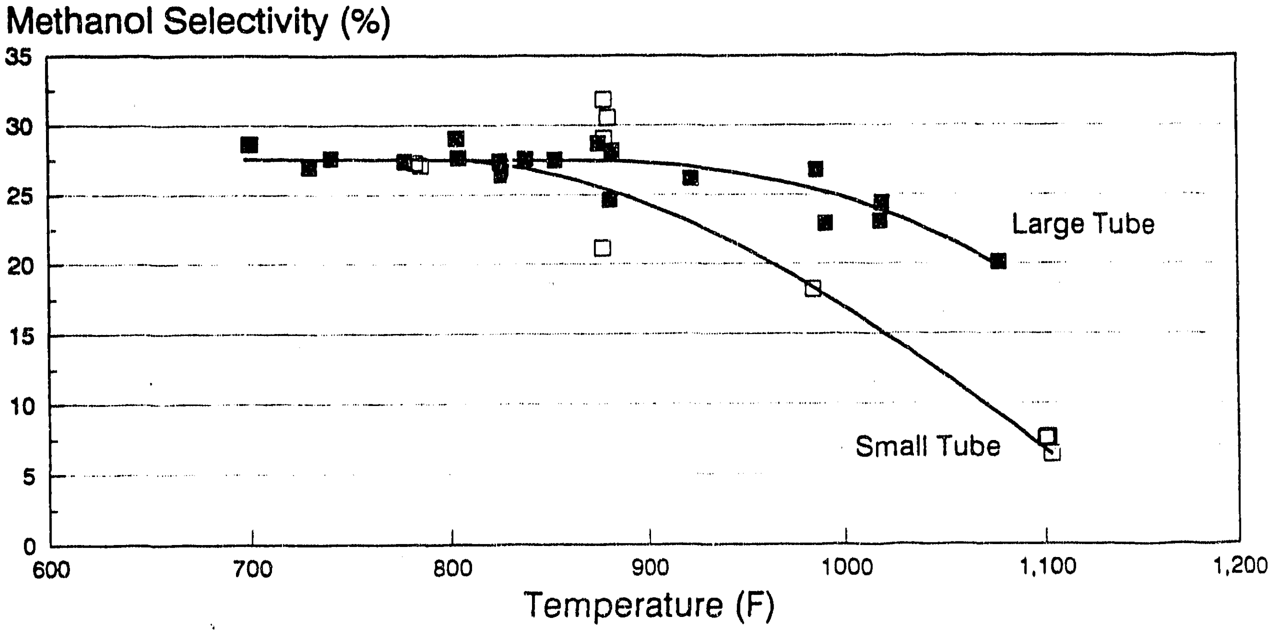
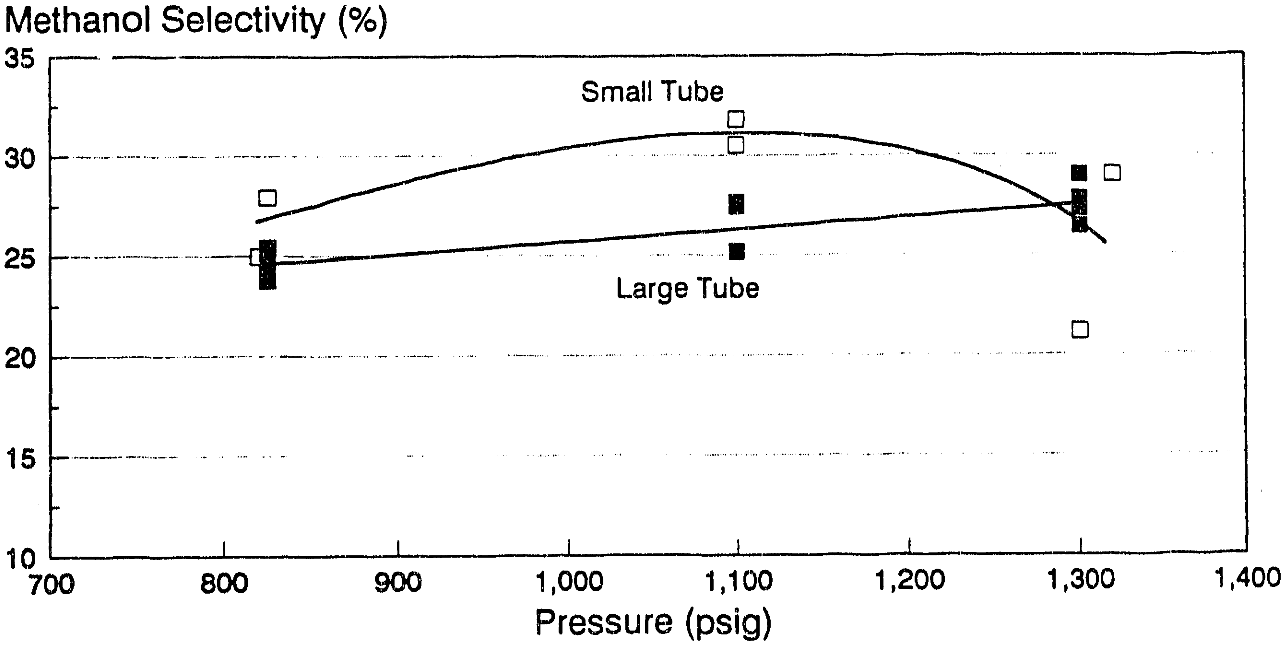


Figure 16

Effect of Pressure on Methanol Selectivity

T=800-850 F; HC/O2=10



reactor. This is expected, since methanol decomposition (to CO and eventually CO_2) can occur on the hot reactor walls at higher temperatures. The smaller reactor has a higher surface-to-volume ratio than the larger reactor, making these wall reactions more significant.

The data show that there may be a maximum in methanol selectivity at around P-1100 psig when the small diameter reactor is used (Figure 16). This differs from results with the large diameter reactor, which show a steady increase in methanol selectivity with increasing pressure. The scatter in the small tube data at 1300 psig makes this conclusion tentative.

There is also significant scatter in the small tube data with respect to the effect of oxygen concentration on the system. Figure 17 indicates that methanol selectivity in both reactors decreases with increasing oxygen concentration, but the selectivity with the small diameter reactor is consistently lower than that with the large diameter reactor. The effect of oxygen concentration on methanol yield is shown in Figure 18. For both reactors the trend is for slightly higher methanol yields to occur at lower oxygen concentrations, but again methanol yield in the small reactor falls consistently below that of the larger reactor. As mentioned above, this is probably an effect of the lower overall flow rate in the small diameter reactor experiments.

We are currently studying the effects of an even larger diameter reactor (30 mm) on the system. Coupled with the above results, these data should allow us to assess the importance of reactor geometry and provide guidance for further reactor design.

Study of Different Feed Injection Systems (Task 3.3):

This task is scheduled to begin in October, and preparations are on schedule. We plan to first study the effect of reactant mixing on the process. On August 14 we visited the laboratories of Professor Hyman Gesser at the University of Manitoba Professor Gesser claims to have achieved much better selectivities and conversions than we have; up to 80% methanol selectivity at 8% methane conversions. According to Prof. Gesser, mixing of the reactant gases is extremely important in achieving high selectivities and conversions. This would support our results presented above. He showed and described his experimental apparatus, and how he achieved good mixing. We are currently attempting to improve mixing in our system by adding both a commercial in-line static mixer and a needle valve in the feed line before the reactor. Dr. Gesser uses the needle valve to produce turbulence and high shear mixing conditions in his apparatus. These pieces of equipment have been ordered and will be cleaned for oxygen service and installed in the beginning of November.

CONCLUSIONS

The above results indicate that lower temperatures and higher pressures are desirable for maximizing methanol yield. Residence time appears to have little effect on methanol yield in the range of 10 to 90 seconds. As a result, future studies will use 800°F and 1300 psig as the base temperature and pressure, and residence time will be maintained between 15 and 60 seconds.

Figure 17

Effect of Oxygen Conc. on Methanol Selectivity

T=800-850; P=1300

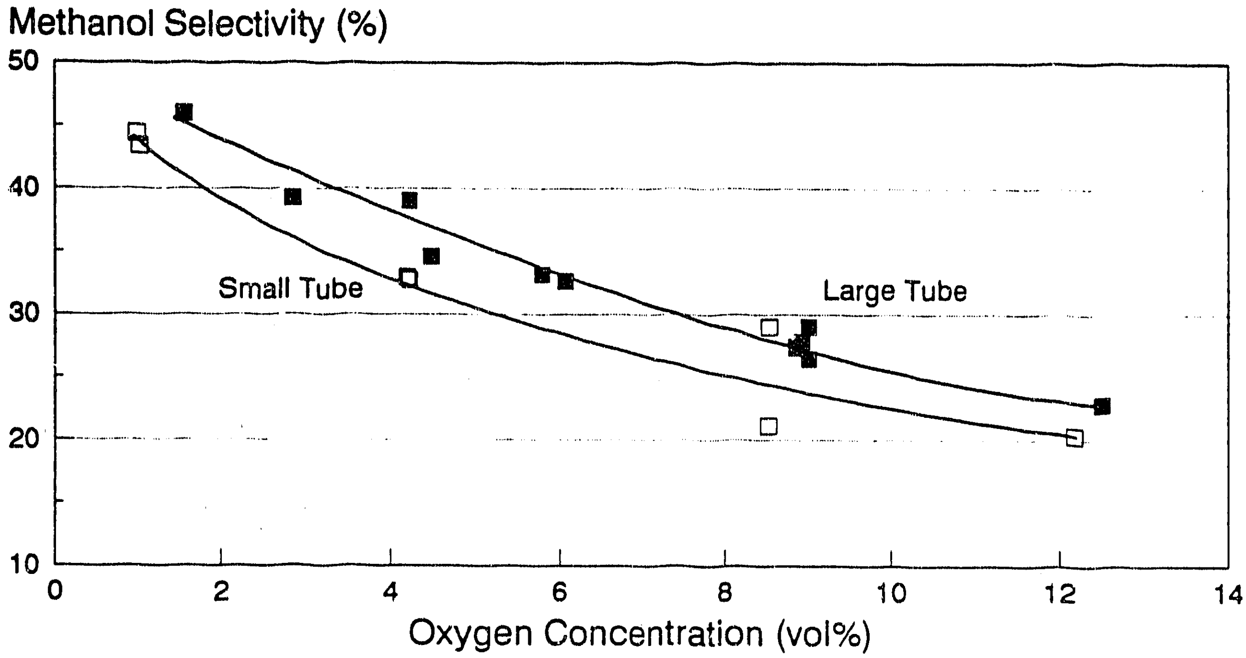
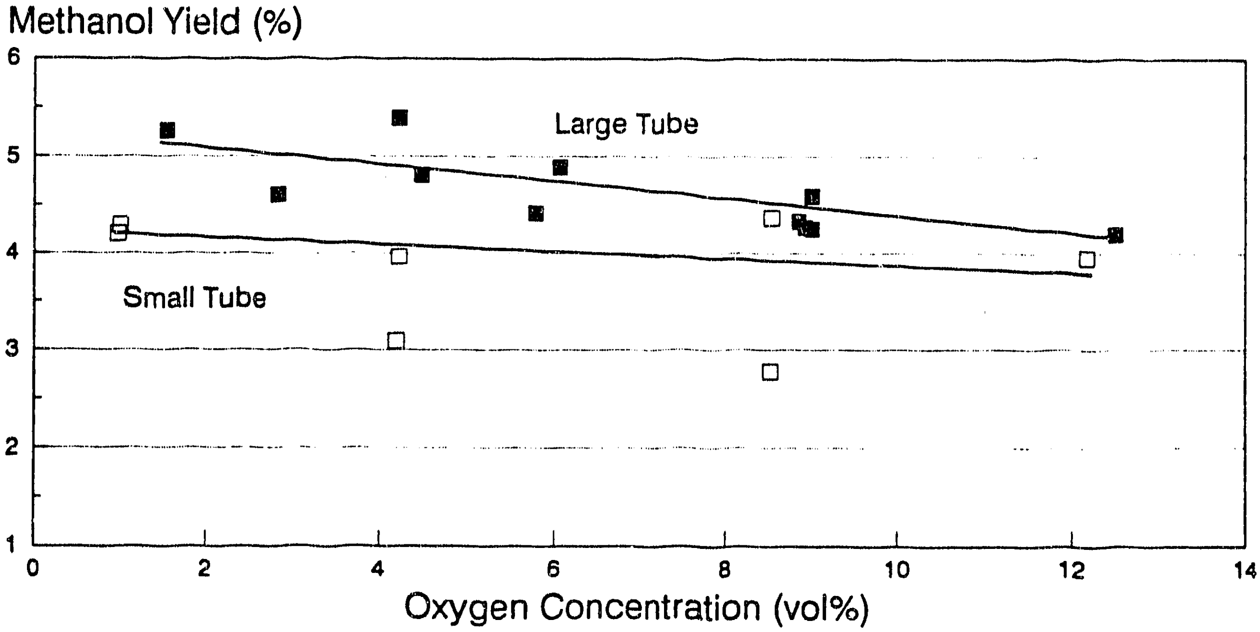


Figure 18

Effect of Oxygen Concentration on MeOH Yield

T=800-850; P=1300



Methanol yields in the smaller diameter reactor were lower than those in the larger diameter reactor in nearly all cases. Part of this difference may be attributable to the lower flow rates used in the small reactor experiments. We have found that hydrocarbon conversion is affected by the gas flow rate in the pilot plant, with lower conversions occurring at lower gas flow rates. This suggests that hydrocarbon conversion in this system might be controlled by mass or heat transfer effects, rather than kinetic effects. Experiments will begin shortly to study the effect of reactant mixing on hydrocarbon conversion and methanol yield.

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/jmb/doe9037

DATE FILMED

8/18/92