DIRECT CONVERSION OF LIGHT HYDROCARBON GASES TO LIQUID FUELS
Process Variable Studies

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OBJECTIVE

The objective of this project is to investigate the direct conversion of light hydrocarbon gases to liquid transportation fuels via a partial oxidation process. The process is being tested in a small pilot-scale unit to obtain credible mass balances.

INTRODUCTION

Coal gasification, Fischer-Tropsch synthesis, and, to a lesser extent, direct coal liquefaction technologies all produce substantial quantities of light hydrocarbon gases. Methane is the major and most stable component of these gas products, and much study has been directed to converting methane to more valuable or more useful products. Conventional methane conversion processes utilize steam reforming to produce synthesis gas (a mixture of CO and H_2), which is subsequently converted to desired products. This reforming process is very capital intensive because it is highly endothermic and requires severe reaction conditions. An efficient process for <u>direct</u> conversion of light hydrocarbon gases, especially methane, to methanol or other liquid fuels would be far superior.

In conventional methanol synthesis technologies, the first step is conversion of the methane to synthesis gas via steam reforming:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \quad (1)$$

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

$$CO + 2H_2 \longrightarrow CH_3OH \quad (2)$$

Reaction (1) produces more hydrogen than is required by reaction (2). This excess hydrogen can be utilized elsewhere if there is local demand, or is lost in the case of a remote operation. The methanol produced in reaction (2) can either be an end product or can be catalytically reacted to gasoline using commercial technology [1]. A plant based on reactions (1) and (2) followed by methanol reaction to gasoline has been built and is operating in New Zealand. However, the process itself is not economical and has remained in operation only with the financial support of the New Zealand government.

A more efficient route for conversion of methane to methanol would be direct conversion through partial oxidation:

$CH_4 + 1/2\ O_2 \dashrightarrow CH_3OH$(3)

Such a process could substantially reduce capital and energy requirements for methanol production, possibly rendering a gas-to-gasoline process economically attractive. This project was undertaken to assess the technical feasibility of such a direct partial oxidation system for converting light hydrocarbon gases to methanol. This paper reports results from process variable studies carried out in a small pilot-scale reactor. Numerous mass- and element-balanced runs were made to study the effects of hydrocarbon feed composition, oxygen concentration, temperature, and pressure on feed conversion and product selectivity. Feeds were pure methane, mixed hydrocarbons (99-94 vol% methane and 1-6 vol% C_{2+}), and pure oxygen.

PREVIOUS WORK

Direct conversion of methane to methanol is not a new approach. In 1932 Newitt and Haffner reported the formation of methanol, formaldehyde and formic acid in the high-pressure oxidation of methane [2]. The reaction was carried out in a static system at temperatures of 680-740°F and pressures of 725-2200 psig. The maximum methanol selectivity was ca. 22% at only a few percent methane conversion. The partial oxidation of methane and other hydrocarbons was the focus of a study by Wiezevich and Frolich in 1934 [3]. They found that methanol selectivity increased with increasing pressure up to 135 atmospheres. The presence of higher hydrocarbons (ethane and propane) significantly lowered the temperature at which the reaction first occurred. Partial oxidation of the higher hydrocarbons resulted in scission of C-C bonds, leading to the formation of lower derivatives.

In 1937 Boomer et al. [4-6] reported a series of high-pressure methane partial oxidation experiments using both copper and silver catalysts. With an empty copper-lined reactor [4], methanol selectivity decreased with decreasing pressure between 185 and 120 atm. A maximum in methanol selectivity with pressure was observed at 185 atmospheres in a reactor filled with copper catalyst [6]. In this system [5] they also found that lower oxygen concentrations increased methanol selectivity, but decreased methane conversion. A maximum in methanol yield (near 3%) was observed at 10 vol% O_2 in the feed. The effect of temperature seemed to depend on the concentration of oxygen in the feed. At higher oxygen concentrations (12.7 vol%) higher temperatures significantly decreased methanol selectivity [5], but at lower oxygen levels (3.7 vol%) temperature had little effect on selectivity. Like many other methane partial oxidation studies, these results were plagued by poor oxygen balance closures (generally between 60-90%) [4-6].

More recently, Gesser et al. [7-12] have reported methane partial oxidation experiments in which methanol selectivities as high as 90% were observed at methane conversions of up to 10% [7], giving an overall methanol yield of 9%. These results were obtained in the absence of catalyst at 50 atm. and 350°C with a glass-lined reactor and 5.7 vol% oxygen in the feed. This yield is significantly higher than reported by other workers [3-6,13]. Both pre-mixed feed [11] and dual-flow [7,8,10] systems gave similar results, provided that the gases in the dual-flow system were thoroughly mixed [9,12]. Like Boomer et al. [5,6], they found that lower oxygen levels increased methanol selectivity but decreased methane conversion. The effect of temperature on the system depended on both pressure and oxygen level in a complex manner [8]. Wall composition did not affect methanol selectivity [7], but the presence of catalysts in the reactor did. Of the catalysts studied, Cu/SiO_2 and SnO_2 showed the highest activity for methanol formation.

Burch et al. [13] recently attempted to reproduce the results of Gesser et al. by studying the effect of temperature, pressure, reactor type, residence time, oxygen concentration and gas mixing on the partial oxidation of methane in a dual-feed flow system. They found that glass-lined reactors were best for maximizing methanol production. At high pressures (40-50 atm), none of the experimental parameters had a significant influence on the selectivity to methanol. Methanol selectivities were generally around 40%, significantly lower than those reported by Gesser et al. [7]. Burch et al. suggested that there may be something unique about the design of Gesser's reactor which allows high methanol selectivity at high methane conversion.

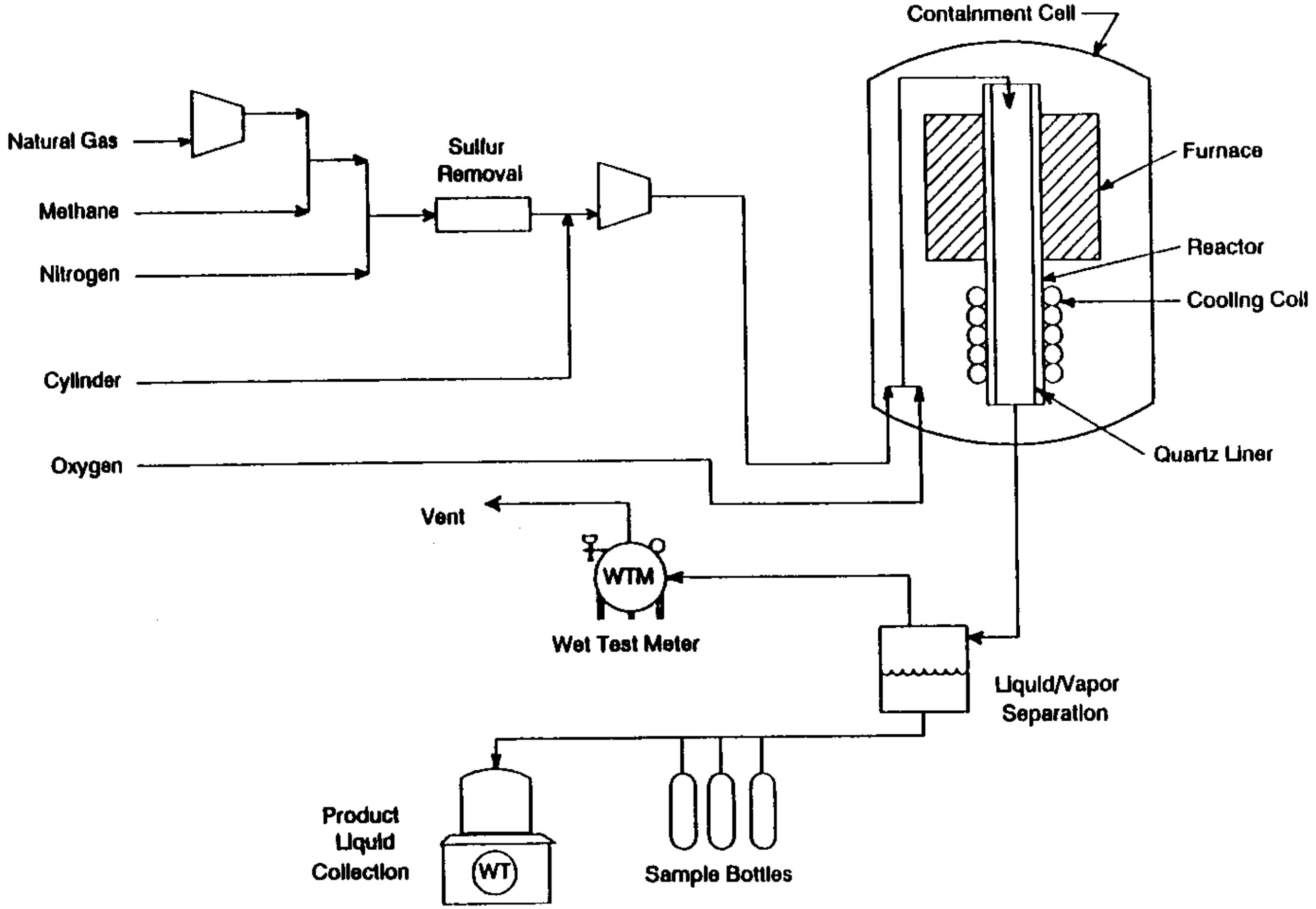
EXPERIMENTAL EQUIPMENT AND PROCEDURES

The present experiments were carried out in a small pilot plant designed for studying the direct conversion of light hydrocarbon gases into products such as methanol, gasoline, ethylene, and synthesis gas. A schematic diagram of the plant is shown in Figure 1. The reactor was located in a Fluitron containment cell to allow safe operation over a wide range of hydrocarbon to oxygen ratios at temperatures up to 1600°F and pressures to 1300 psig (at 1000°F). The unit was fully instrumented to allow unattended (24-hour) operation. Process conditions were monitored and controlled by computer, with additional monitoring and emergency shutdown procedures provided by two separate and redundant computers.

The feed section of the plant was used to meter, mix, and deliver the hydrocarbon and oxygen feeds. Flows were monitored and controlled with Brooks mass flow controllers. A compressor located in the hydrocarbon feed line allowed plant operation at pressures up to 1300 psig (88 atm.). Hydrocarbon feeds were CP grade methane or natural gas. The natural gas varied somewhat in composition, but averaged 93% methane, 4% ethane, 1% C_{3+}, 0.6% CO_2 and 1.4% N_2. Pure oxygen (Matheson Zero Gas) was used in all experiments.

Figure 1

Light Hydrocarbon Conversion Pilot Plant



The reactor was a 30-inch long, 1-inch ID, 2 1/4-inch OD Incolloy 800 pipe. The upper 13 inches of the reactor tube were heated with a three-zone electric furnace. The lower 10 inches of the reactor were wrapped with a cooling water coil to rapidly quench the product gases. An inert quartz tube inserted into the reactor served as the reactor liner. Internal temperatures were monitored by a 1/8-inch OD, 316 stainless steel-sheathed, four-junction thermocouple. A quartz sleeve covered the thermocouple to maintained all internal reactor surfaces inert.

The product gases were further cooled in the product recovery section and the liquid and gas phases were separated. The liquid phase was directed to a product receiver where product accumulation was continuously monitored. The gas-phase pressure was reduced through a back pressure regulator valve, and the offgases passed through a wet test meter to measure flow rate. The entire product recovery section was enclosed in a 1/4-inch thick steel plate explosion cage for safety.

Slipstreams from both the hydrocarbon feed and the product gas were analyzed with a 5580 Hewlett-Packard gas chromatograph refinery gas analyzer. This chromatograph allowed resolution of C_1 - C_5 hydrocarbons (paraffins and olefins), as well as H_2, O_2, N_2, CO and CO_2. Liquid samples were analyzed off-stream on a 5790 Hewlett-Packard gas chromatograph with a Porapak-QS column and thermal conductivity detector. This chromatograph could resolve water and C_1 - C_4 alcohols, but could not detect formaldehyde. Formaldehyde concentration in the aqueous product was determined colorimetrically, but was never found to be significant (i.e. less than 1% selectivity). In a typical test, conditions were set in the morning and the plant was allowed to reach steady state (usually 4-5 hours) before the test was begun. Tests generally lasted 16-17 hours.

Using these procedures, accurate mass and element balances were obtained. Mass balances were closed within 3%, as were carbon and hydrogen atom balances. Oxygen balances were somewhat less accurate, but were always within 10%, and usually within 5%.

In this paper, selectivity is defined as the moles of carbon in the product divided by the total moles of carbon present in all products detected. Methane conversion is calculated using the formula

$$CH_4\ Conversion = \frac{(moles\ CH_4\ in) - (moles\ CH_4\ out)}{(moles\ CH_4\ in)}$$

Hydrocarbon (HC) conversion (methane plus other hydrocarbons) is calculated based on carbon atom conversion:

$$HC\ Conv. = \frac{(moles\ C\ in\ feed) - (moles\ unreacted\ C\ in\ product)}{(moles\ C\ in\ feed)}$$

The unreacted moles of carbon in the product gas were defined as those contained in methane, ethane, propane, butanes, and pentanes. Other carbon-containing compounds were considered to be products. Methanol yield is defined as the product of methanol selectivity and hydrocarbon conversion.

The data reported below were statistically adjusted to better than 99% closure on the mass, carbon, hydrogen, and oxygen balances with a data adjustment program (see appendix). Otherwise, plus-or-minus 3% carbon balance closures translated to absolute differences of +/-3% in methane conversion and methanol yield. This is significant, since methane conversions and methanol yields were themselves on the order of 5% and 4%, respectively. The adjustment significantly improved the reproducibility of the data, especially in the low conversion cases.

RESULTS AND DISCUSSION

The effects of hydrocarbon feed composition, oxygen concentration, temperature, and pressure on the partial oxidation of light hydrocarbons were studied. The goal of these studies was to determine the optimal conditions for methanol production and methane conversion. The reaction parameters of most interest include methanol selectivity and yield, per-pass conversion of methane, and per-pass conversion of the total hydrocarbon feed. The following sections describe the effects of process variables on these important system parameters.

Effect of Hydrocarbon Feed Composition

To investigate the effect of feed composition on the system, runs using both pure methane and natural gas feeds were made and compared at a number of temperatures and pressures. The natural gas contained about 93% methane, 4% ethane, 1% C_{3+}, 0.6% CO_2, and 1.4% nitrogen. The major impurity in the "pure" methane was ethane at 0.02%. The effect of feed type on methanol yield, methanol selectivity, and methane conversion are shown in Figures 2, 3 and 4, respectively. In all cases the residence time was near 35 seconds and hydrocarbon/oxygen was 10.

These data show a number of significant trends. It is apparent that methanol yields are significantly higher with natural gas feeds than with pure methane. This increase in methanol yield is primarily due to increased hydrocarbon conversion. Methanol selectivity is slightly higher with natural gas feeds, except at higher pressures and temperatures, where is becomes slightly lower (Figure 3). Methane conversion with natural gas feeds is only about half the 6-8% observed in the pure methane runs (Figure 4). This can be attributed to limited oxygen availability in these experiments. The higher hydrocarbons in the natural gas react more easily than methane, consuming much of the oxygen and leaving little to combine with the less-reactive methane.

To further study the effect of higher hydrocarbons on the system, pure methane was spiked with 1-5 vol% ethane before being fed to the reactor. The effects of ethane level on hydrocarbon and methane conversion, product selectivity and product yield were studied. In these runs temperature was constant at 800°F, pressure was 1300 psig, and

Figure 2

EFFECT OF FEED COMPOSITION ON METHANOL YIELD

Natural Gas Compared to Pure Methane Feed

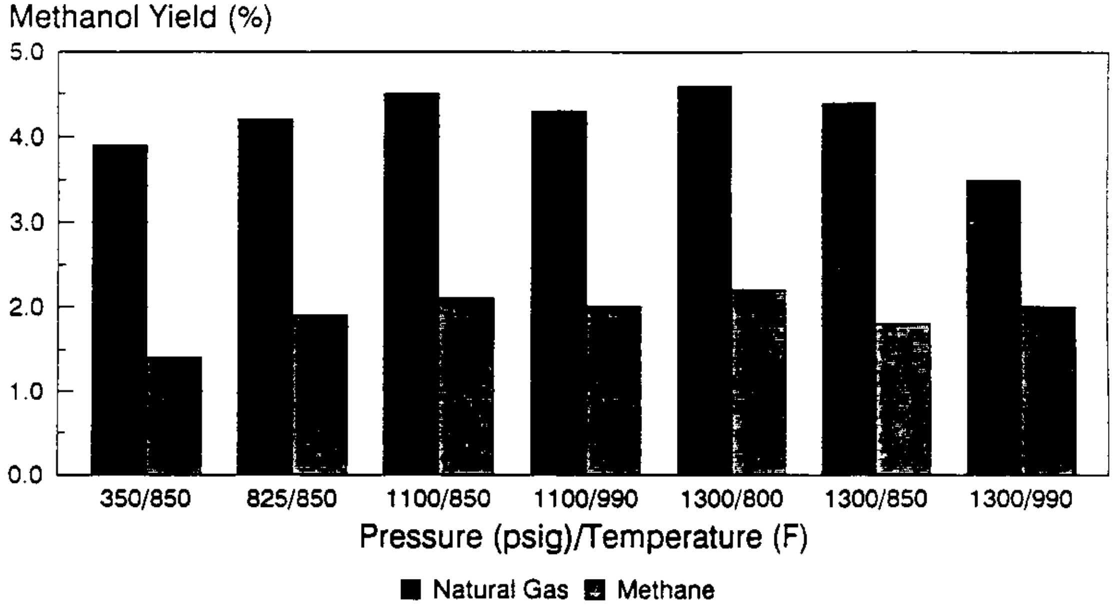


Figure 3

EFFECT OF FEED COMPOSITION ON MeOH SELECTIVITY

Natural Gas Compared to Pure Methane Feed

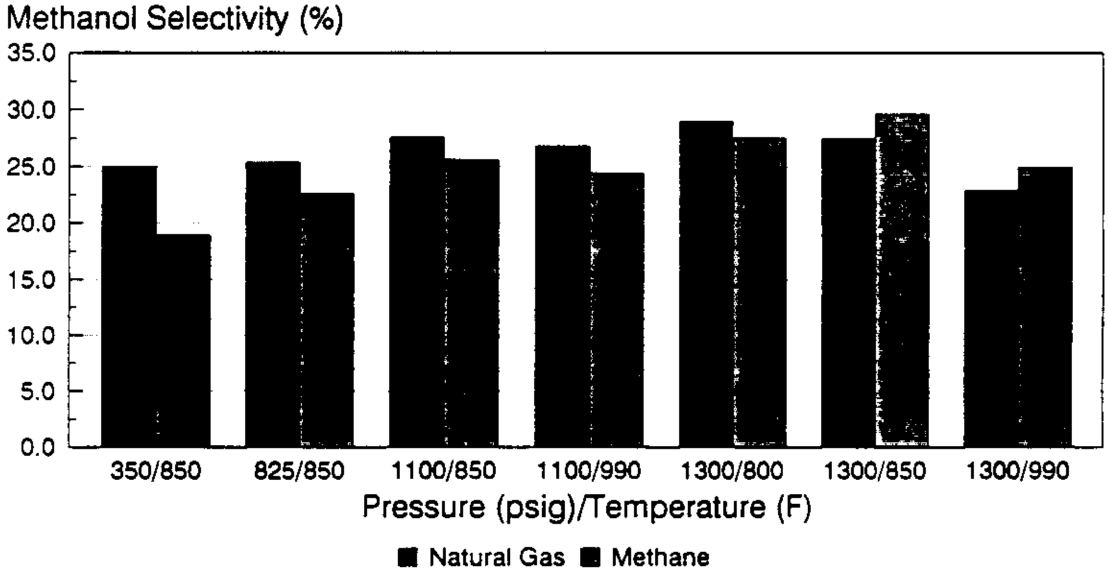
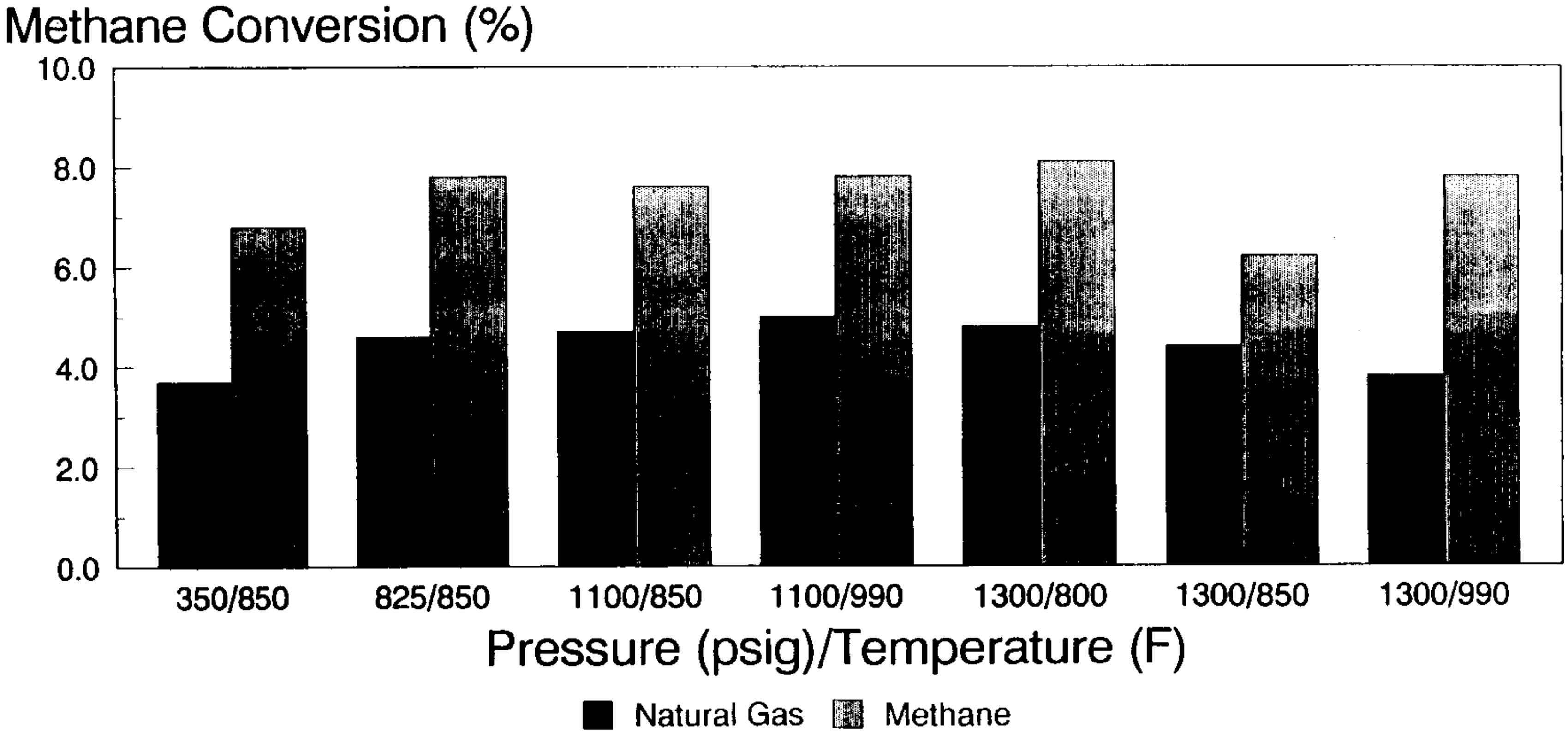


Figure 4

EFFECT OF FEED COMPOSITION ON METHANE CONVERSION

Natural Gas Compared to Pure Methane Feed



hydrocarbon/oxygen was 10. These conditions had been found to maximize methanol production, as described in later sections.

Figure 5 shows that hydrocarbon conversion increases linearly with increasing ethane content of the feed. As in the natural gas runs, this increase occurs because the ethane reacts more easily with oxygen than the methane. Ethane conversion in the reactor was 40%, independent of ethane concentration. Hydrocarbon conversion with natural gas feed falls on about the same line as conversion with ethane-spiked methane feeds (Figure 5).

Methane conversion decreases with increasing ethane concentration (see Figure 6). This is also similar to the natural gas runs and occurs because the more reactive ethane preferentially consumes the oxygen, leaving less to react with methane. Figure 6 also shows that natural gas feeds give lower methane conversions than feeds with equivalent amounts of ethane. This is probably due to the even higher reactivity of propane and butanes in the natural gas (present in sum at the 1.0 vol% level).

That methane conversion is lower in the presence of higher hydrocarbons (such as ethane) could have a significant impact on the economics of this process. Since a lower per-pass methane conversion translates to a larger recycle loop for the process (and therefore higher equipment cost), any effect that lowers the methane conversion significantly will probably be detrimental to process economics. We would expect this effect to be less significant at higher oxygen feed levels, since more oxygen would be available to react with methane. Runs related to the effect of oxygen level are presented in the following section.

Surprisingly, methanol selectivity is practically independent of ethane concentration, even at ethane concentrations of up to 5 vol% (Figure 7). At this ethane concentration, nearly 40% of the carbon in the products comes from ethane conversion. Since selectivity does not change over this range of ethane concentrations, it appears that the partial oxidation of ethane takes place with a selectivity pattern similar to that of methane. This result is supported by the early work of Wiezevich and Frolich [3] who found that carbon-carbon bond scission is an important step in the partial oxidation of higher hydrocarbons. One possible explanation is that both methane and ethane oxidation have the same rate-limiting step (and therefore a common reaction intermediate).

Methanol yield increases steadily with increasing ethane concentration (Figure 8), since hydrocarbon conversion increases and selectivity remains unchanged.

These results indicate that the level of C_{2+} hydrocarbons in the feed significantly influences per-pass conversion and methanol yield, but not methanol selectivity. This demonstrates the importance of using the proper feed in methane partial oxidation studies. Specifically, feeds containing higher hydrocarbons should be used, since any commercial operation will probably contain higher hydrocarbons in the feed.

Figure 5

EFFECT OF ETHANE LEVEL ON HYDROCARBON CONVERSION

P=1300 psig/ T=800 F / Res. Time=35 sec.

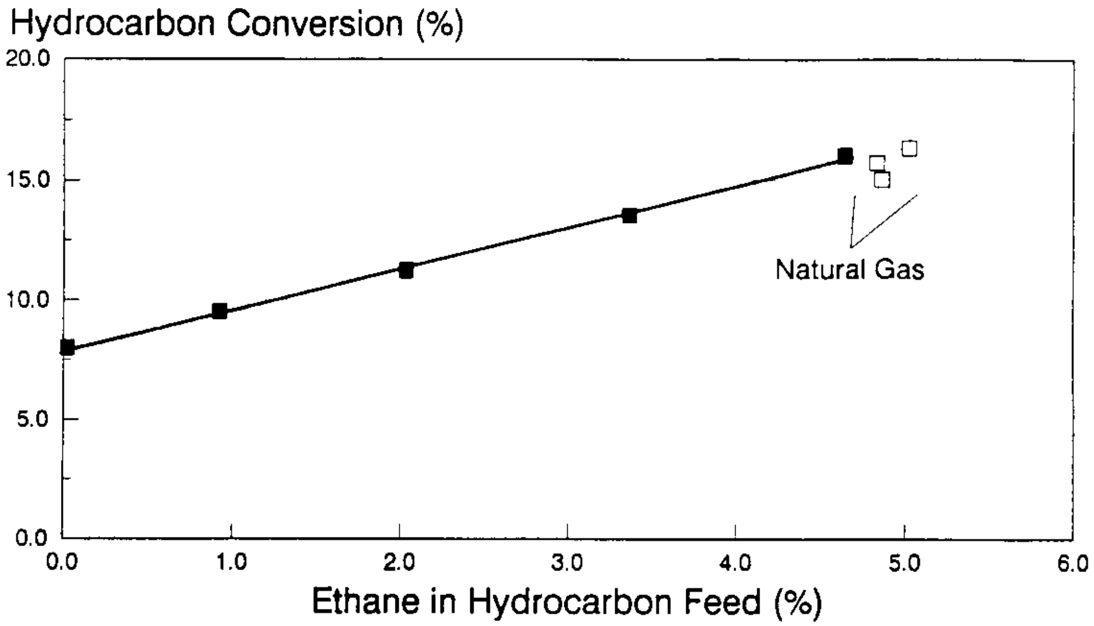


Figure 6

EFFECT OF ETHANE LEVEL ON METHANE CONVERSION

P=1300 psig/ T=800 F/ Res. Time=35 sec.

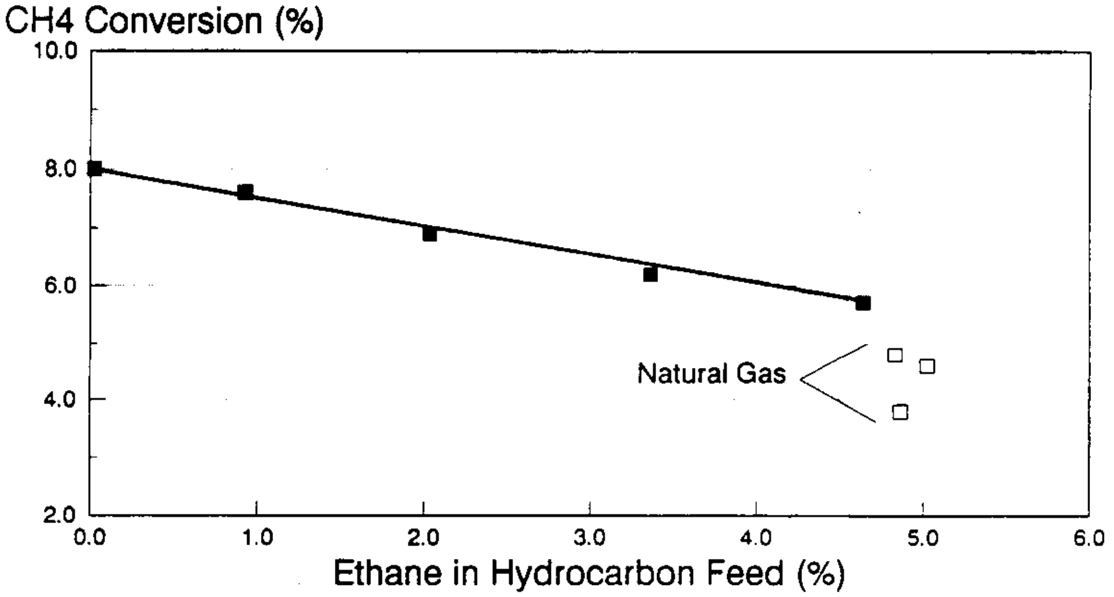


Figure 7

EFFECT OF ETHANE LEVEL ON C-BASED SELECTIVITY

P=1300 psig/ T=800 F/ Res. Time=35 sec.

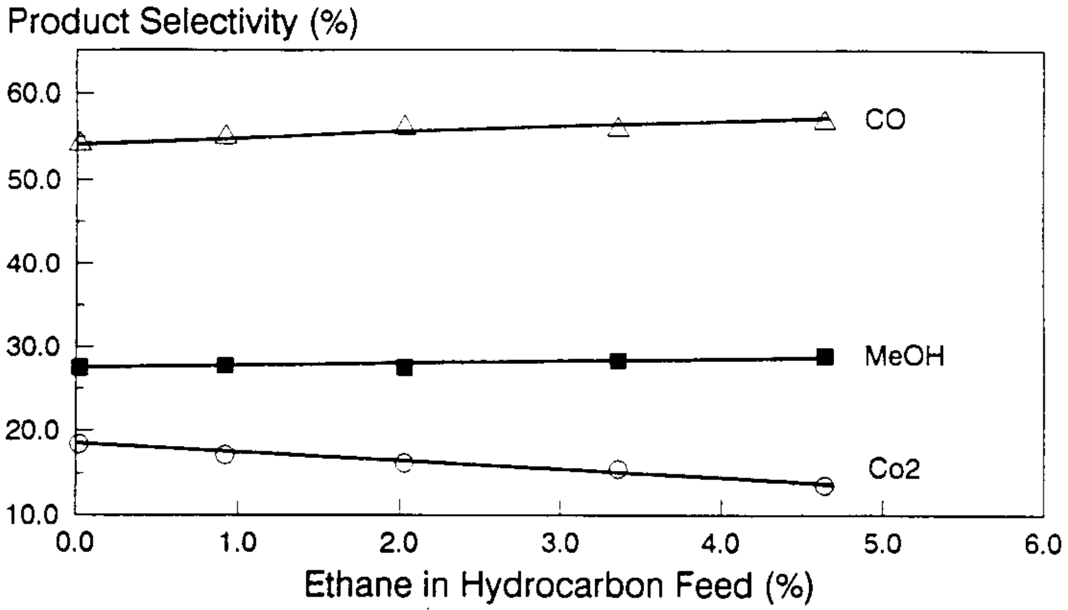
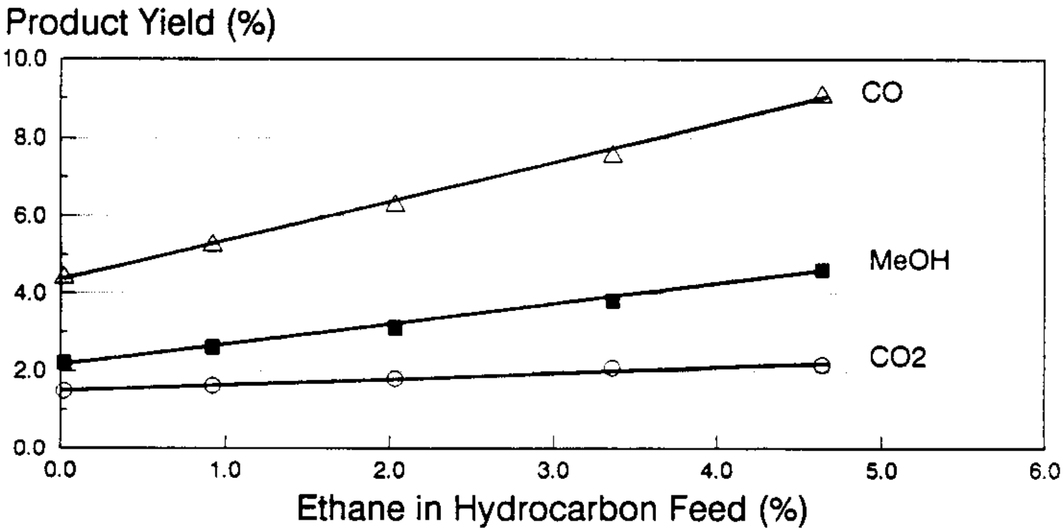


Figure 8

EFFECT OF ETHANE LEVEL ON PRODUCT YIELD

P=1300 psig/ T=800 F/ Res. Time=35 sec.



Consequently, all subsequent runs were made with a mixed hydrocarbon (natural gas) feed.

Effect of oxygen concentration:

In order to study the effect of oxygen on the system, a number of runs were made in which oxygen concentration varied between 1.5 and 12.5 vol% of the total feed. The feed in all cases was natural gas containing around 4 vol% ethane and 1 vol% C_{3+}. Other parameters were held constant at T=800°F, P=1300 psig and a 35 second residence time. Figures 9-12 show the effect of oxygen concentration on product selectivity, hydrocarbon conversion, product yield, and methane conversion, respectively.

The data presented in this and following sections are corrected for the amount of ethane in the natural gas feed. The natural gas was not a standard mixture; it was taken from the city supply line and compressed for use in these experiments. Therefore, the composition of the hydrocarbon feed varied slightly over time, primarily in the amount of ethane present. Since the level of higher hydrocarbons can significantly affect both methane and hydrocarbon conversion (see previous section), it was necessary to adjust the methane and hydrocarbon conversion levels in each run to an arbitrary standard ethane concentration (4.9 vol% ethane). The correction factors for this standardization were derived from the slopes of Figures 5 and 6.

Methanol selectivity increases with decreasing oxygen concentration (Figure 9). Selectivity to CO stays relatively constant, while selectivity to CO_2 decreases with decreasing oxygen concentration. The highest methanol selectivity observed was 46% at 1.5 vol% O_2 in the feed, and the major product at all oxygen levels is CO, with a selectivity of around 55%. An increase in methanol selectivity with decreasing oxygen level has also been reported by Gesser et al. [8] and Boomer et al. [5,6].

Hydrocarbon conversion increases steadily with increasing oxygen concentration, as shown in Figure 10. However, the effect of oxygen concentration is not as large as might be expected: an 8-fold decrease in oxygen concentration translates to less than a 2-fold decrease in hydrocarbon conversion. That less-oxidized products are formed at lower oxygen levels means that equal amounts of hydrocarbon can be converted with less oxygen.

The effect of oxygen level on product yield (selectivity times hydrocarbon conversion) is shown in Figure 11. Methanol yield increases slightly with decreasing oxygen level, while the yields of carbon oxides (CO and CO_2) decrease. These trends (and the selectivity trends in Figure 9) are consistent with the methane oxidation mechanism proposed by workers at Los Alamos [14]. In this mechanism a methoxy radical ($CH_3O\cdot$) can combine with either gas-phase oxygen (to form carbon oxides), or gas phase methane (to form methanol). Higher oxygen

Figure 9

SELECTIVITY AS A FUNCTION OF OXYGEN LEVEL

T=800 F; P=1300 psig; Res. Time=35 sec.

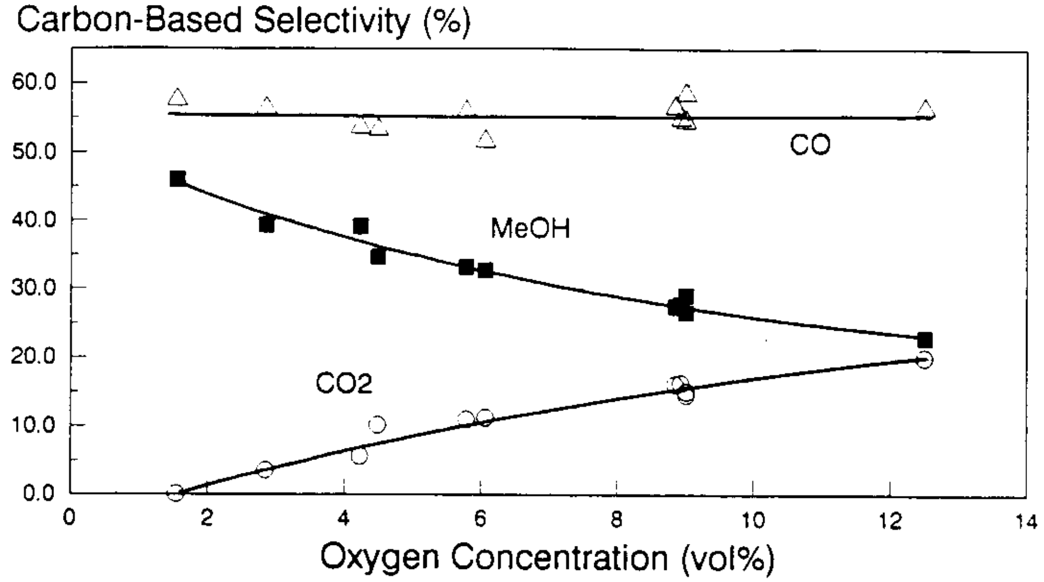


Figure 10

EFFECT OF OXYGEN LEVEL ON HYDROCARBON CONVERSION

T=800 F; P=1300 psig; Res. Time=35 sec

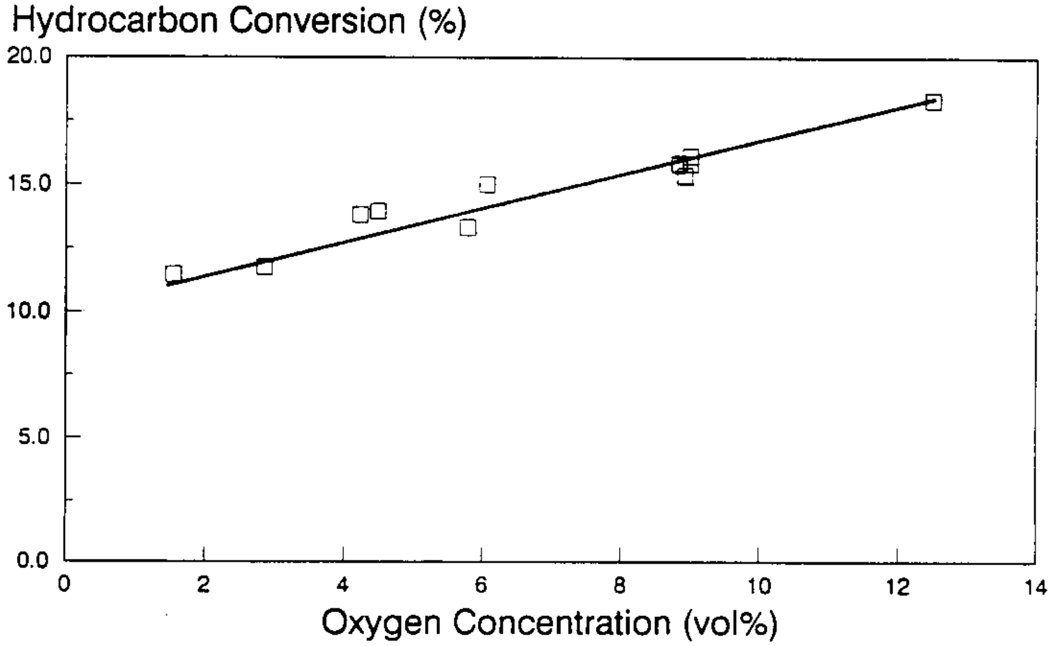


Figure 11

PRODUCT YIELDS AS A FUNCTION OF OXYGEN LEVEL

T=800 F; P=1300 psig; Res. Time=35 sec.

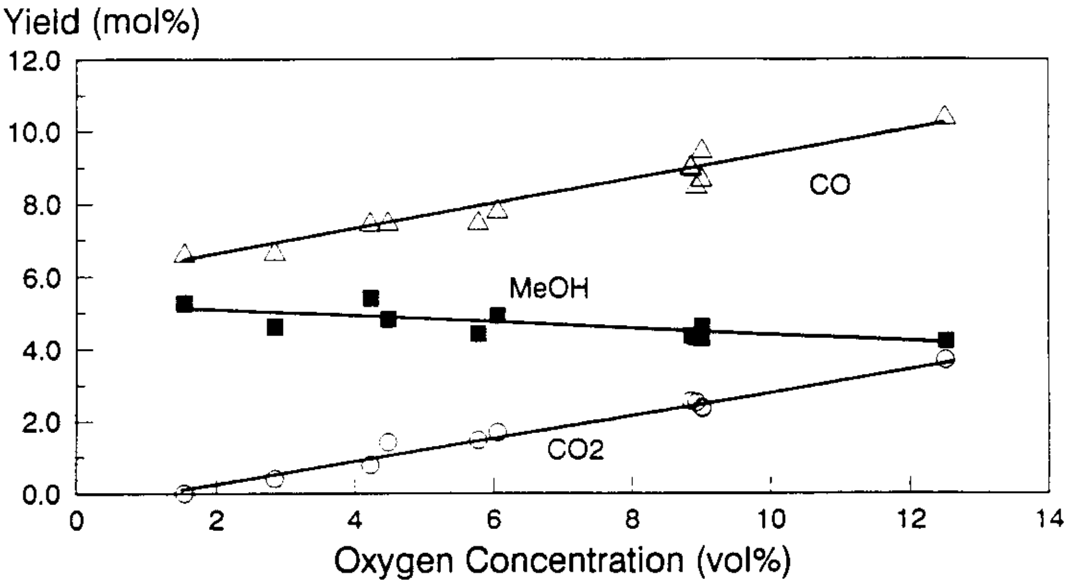
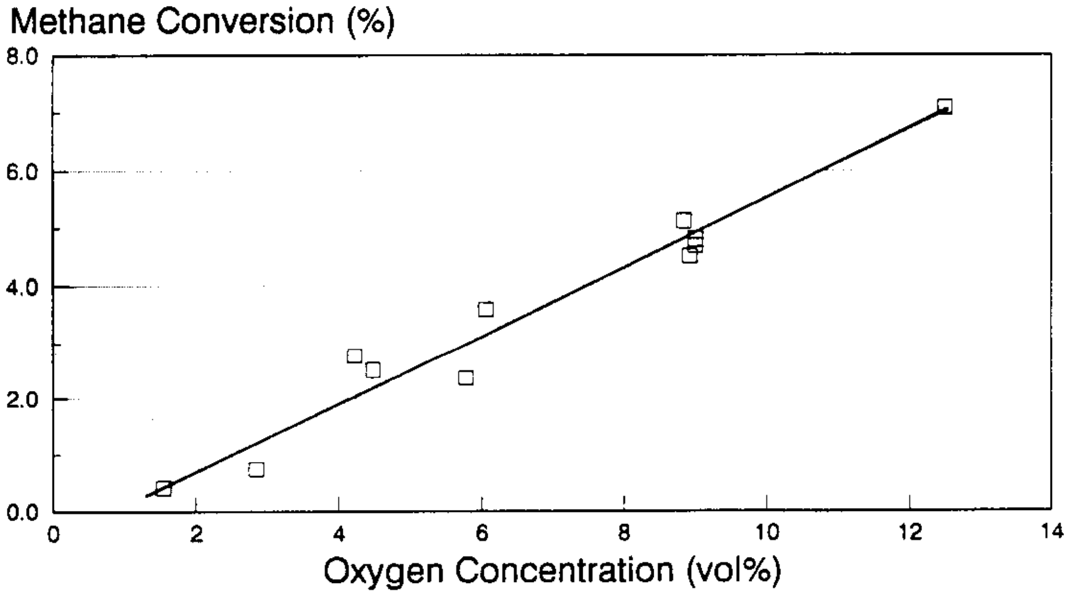


Figure 12

EFFECT OF OXYGEN LEVEL ON METHANE CONVERSION

T=800 F; P=1300 psig; Res. Time=35 sec



concentrations promote the carbon oxide formation branch at the expense of the methanol formation branch.

As expected, methane conversion increases steadily with increasing oxygen concentration (Figure 12). Methane conversion is more sensitive to oxygen concentration than is hydrocarbon conversion: at 1.5 vol% oxygen methane conversion is nearly zero, while hydrocarbon conversion is over 10%. This means that at the lower oxygen levels with a natural gas feed (where methanol selectivity is highest), almost all of the products result from partial oxidation of the higher (C_{2+}) hydrocarbons in the feed. At higher oxygen concentrations, more oxygen is left after reaction with higher hydrocarbons to react with methane.

These oxygen studies indicate that lower oxygen concentrations give higher methanol selectivity, while methanol yield is maximized at oxygen concentrations below 5 vol%. This suggests that, based on methanol yield, lower oxygen concentrations are desirable. As mentioned above, however, at these low oxygen levels methane conversion is almost zero: nearly all of the products result from conversion of C_{2+} species in the natural gas. Since the extent of methane conversion significantly impacts the economics of the process, higher oxygen concentrations are preferred. The optimal oxygen level will be intermediate between these extremes and would be fixed in a commercial operation by economic considerations. In this study, all subsequent runs used 9% oxygen (hydrocarbon/oxygen = 10) as the base concentration, since methane conversion is significant (nearly 5%) at this concentration and methanol yield is 4.5 mol%, only 0.3 mol% lower than the observed maximum.

Effect of Temperature

With the preferred hydrocarbon feed and oxygen level determined, experiments were run to determine the optimum temperature and pressure for methanol production and methane conversion. A series of runs was made in which temperatures were varied between 700-1000°F and pressures between 825-1300 psig. Hydrocarbon/oxygen was 10.0 and residence time was 35 seconds for all experiments. The temperature effects will be discussed in this section; pressure effects will be covered in the following section.

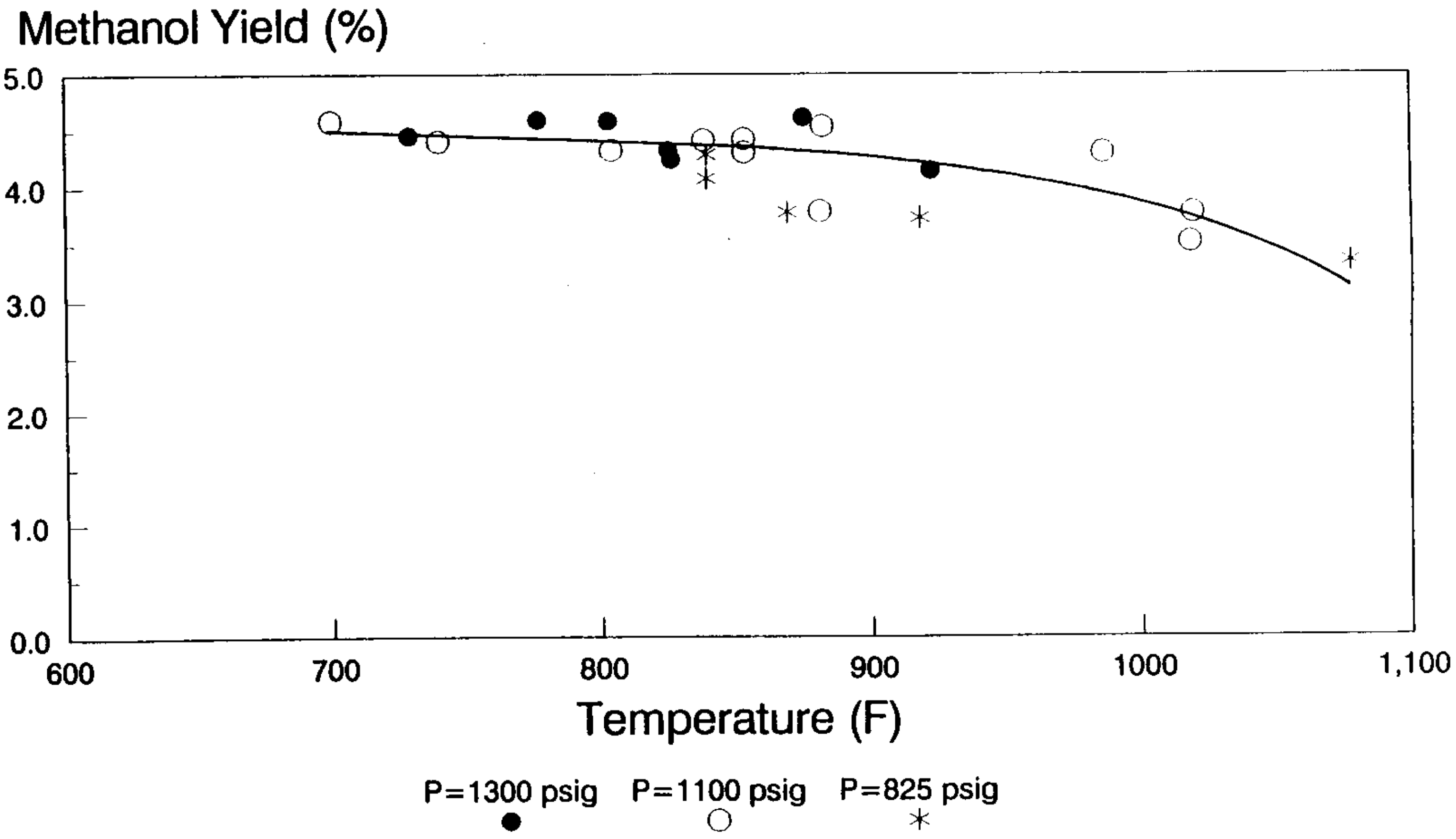
The temperatures indicated here correspond to <u>average</u> temperatures in the reaction zone. Even though the reactor heater was set for constant temperature, the size of the reactor (approximately 1 inch diameter) and the design of the furnace precluded isothermal operation. A significant temperature rise through the reactor (generally between 100 and 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.

The effect of temperature on methanol yield is shown in Figure 13. At every pressure, methanol yield decreased with increasing temperature. This suggests that lower temperatures are desirable for maximizing

Figure 13

EFFECT OF TEMPERATURE ON METHANOL YIELD

Res. Time=35 sec; HC/O2=10



methanol yield. The effect of temperature on product selectivity is shown in Figure 14. Temperature has little effect on product selectivity over the range between 700 and 1000°F. 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 H_2.

The effect of temperature on methane conversion is shown in Figure 15. The data contain some scatter, but the trend is for higher methane conversion with lower average temperature. Since higher methane conversions are desirable, this again suggests that lower temperatures are preferred. Temperature has no significant effect on hydrocarbon conversion in the range studied.

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. The literature is not consistent on the effect of temperature on this system, largely because different researchers use different sets of conditions (pressures, oxygen levels, residence times) at which to evaluate the effect of temperature. In this study, the trends with temperature are not large. This may indicate that in non-isothermal operation, tight temperature control might not be necessary in order to maximize methanol production. In any case, temperatures between 700 and 850°F appear to be optimal for methanol production and methane conversion in this system.

Effect of Pressure

The effects of pressure on methanol yield, product selectivity, methane conversion, and hydrocarbon conversion were studied between 825-1300 psig. At every temperature studied, methanol yield increases with increasing pressure between 800 and 1300 psig (Figure 16). This indicates that higher pressures are desirable for maximizing methanol production. The significantly lower methanol yield at 1000°F noted in the previous section is apparent in Figure 16.

The effect of pressure on product selectivity is shown in Figure 17. The trends are not large, but 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. Wiezevich and Frolich [3] also found higher methanol selectivity at higher pressures (up to 2000 psig). In addition Burch et al. [13] found that pressure had little effect on methanol selectivity in glass-lined reactors, but Boomer et al. [6] observed a maximum in methanol selectivity at 184 atmospheres. In this study, pressure has no discernable effect on either methane conversion or hydrocarbon (methane and C_{2+}) conversion.

Figure 14

EFFECT OF TEMPERATURE ON C-BASED SELECTIVITY

Res. Time=35 sec; HC/O2=10; 825-1300 psig

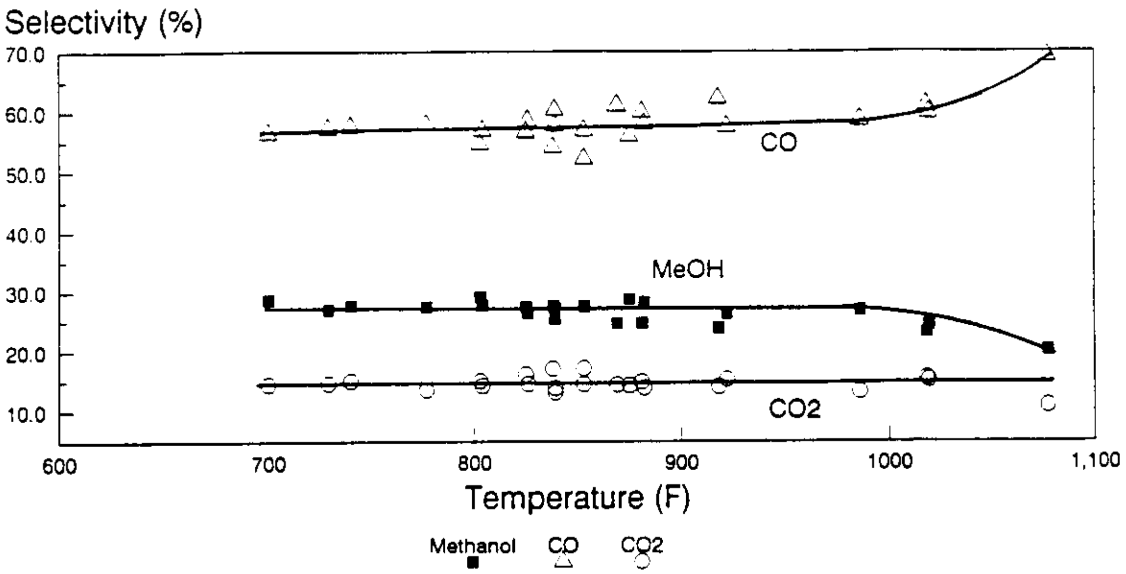


Figure 15

EFFECT OF TEMPERATURE ON METHANE CONVERSION

Res. Time=35 sec; HC/O2=10

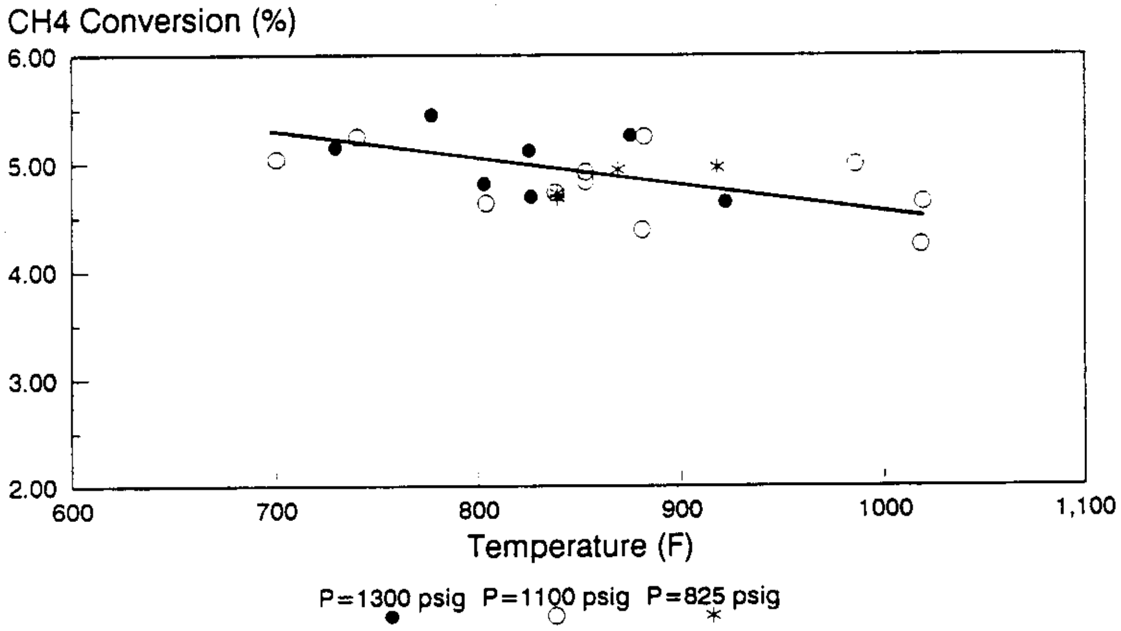


Figure 16

EFFECT OF PRESSURE ON METHANOL YIELD

Res. Time=35 sec; HC/O2=10

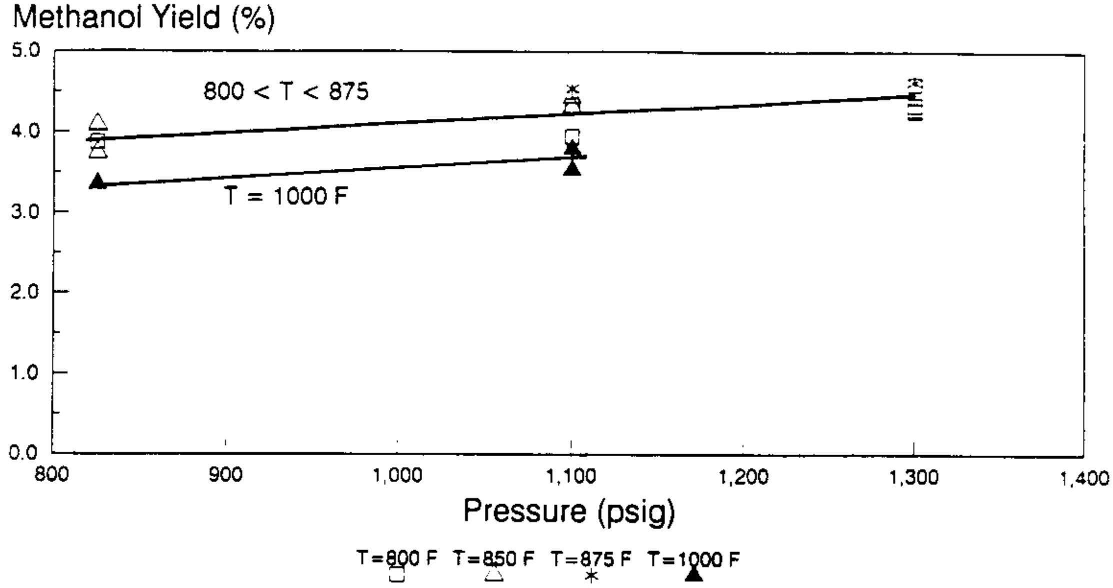
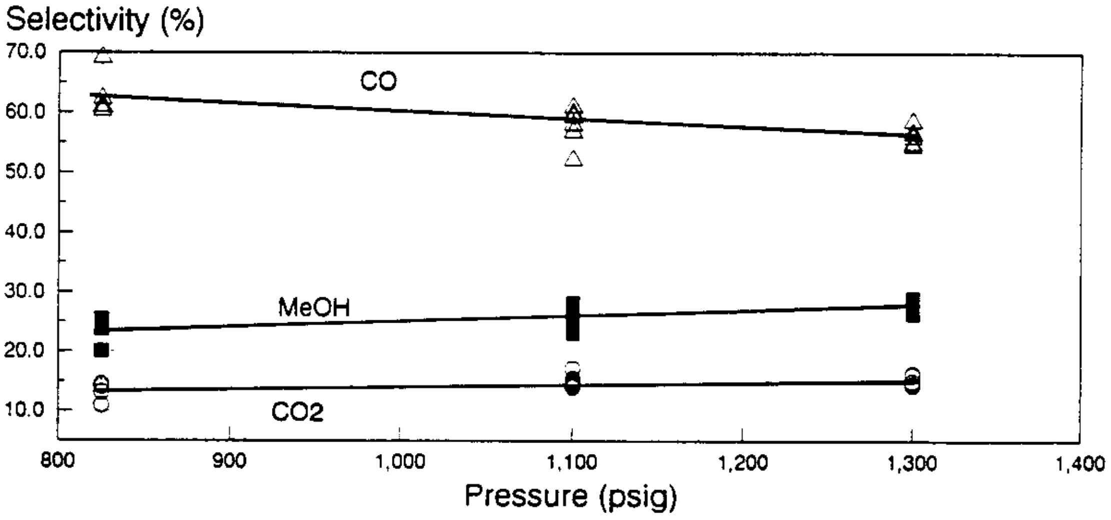


Figure 17

EFFECT OF PRESSURE ON C-BASED SELECTIVITY

Res. Time=35 sec; HC/O2=10; 800-1000 F



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

CONCLUSIONS

The process variable studies described in this paper form a basis for everal conclusions:

1. Higher (C_{2+}) hydrocarbons in the feed significantly affect both methane conversion and methanol yield. The effect on methane conversion is negative while the effect on methanol yield is positive. This behavior could impact the process economics, since lower per-pass methane conversions generally translate to poorer economics.

2. Lower oxygen concentrations improve methanol selectivity, but reduce per-pass methane conversion. Methanol yield is only slightly affected by oxygen level. The optimum oxygen level will be a compromise between higher methanol yield (low oxygen concentrations) and higher per-pass methane conversions (higher oxygen concentrations). In a commercial operation, the optimal oxygen level would be fixed by economic considerations.

3. Lower temperatures and higher pressures are desirable for maximizing both methanol yield and methane conversion. Average reactor temperatures of 700-850°F and a pressure of 1300 psig appear to be optimal within the ranges studied.

FUTURE WORK

Future work will concentrate on study of reactor and process design rather than further process variable studies. Work is currently underway to determine the effect of reactor geometry. Reactors of similar length but different diameters (i.e. different reactor surface-to-volume ratios) will be used to probe the importance of wall effects. Different feed mixing and injection systems will be studied in an effort to improve overall methanol yield. Finally, experiments will be carried out in which a catalyst bed will be placed after the thermal reaction zone. The goal of these experiments will be to determine if any of the carbon monoxide produced in the thermal zone can be subsequently converted to methanol, thereby increasing the overall selectivity of the process.

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APPENDIX

Statistical Data Adjustment Procedure

A Fortran program was written to adjust the input and outlet flow and composition data to achieve better than 99.99% mass, carbon and hydrogen balances while minimizing a chi-square objective function

$$\sum_{i=1}^{n} \frac{(Y_i - y_i)^2}{s_i^2}$$

In this function Y_i is the adjusted value, y_i is the original value, and s_i is the standard deviation of the measurement for each variable "i" ("n" total varibles). A non-linear iterative algorithm was employed which allowed simultaneous adjustment of both flow and composition data. Values for the standard deviations of the variables were either calculated using historical calibration data for the process instruments, or estimated from past experience with plant operation.

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