

Methane Partial Oxidation in Alternating Electric Fields

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ABSTRACT

In this work, methane and oxygen mixtures have been oxidized to form methanol and smaller amounts of formaldehyde, methyl formate, formic acid and ethanol. Substantial amounts of water are also produced, as well as a small amount of ethane. The oxidation takes place at ambient conditions of temperature and pressure in an alternating electric field which is generated between cylindrical plates with a gap of 0.060 inches. Conversions were linearly dependent on the RMS voltage in experiments using up to 10 kV RMS. Among square, triangular, and sinusoidal wave forms, only small differences in performance were observed over the range of frequencies studied, from 25 to 200 Hertz. The effects of oxygen concentration, space time, frequency, and field plate area have also been examined on a limited basis. The power consumption to the power supply has been measured to determine the efficiency of this system, in which substantial heat is released. The yield of methanol is from seven to nine percent of the methane converted in which methane conversions of five to ten percent are obtained when an oxygen limited feed is used. Substantial amounts of the methane converted appear as carbon monoxide and carbon dioxide, both of which are somewhat inhibited by operation with the oxygen limited feed, although product inhibition during recycle experiments was not observed.

INTRODUCTION

There is currently a great deal of interest in the production of organic oxygenates via partial oxidation. Of particular interest is the conversion of methane to liquid fuels such as methanol, as well as the synthesis of other single and multiple carbon products such as formaldehyde, ethanol and acetic acid. Most current research involves the use of heterogeneous catalysts (1), although there has been some effort in examining thermal routes (2). It is only in the relatively old literature that the partial oxidation of methane in the presence of electric fields appears.

EXPERIMENTAL

The experimental reaction system was operated in three different configurations, however most of the results of this paper were obtained in the single pass mode. Figure 1 illustrates this configuration. Oxygen and methane are fed through individual rotameters and mixed and then flow to the reacto inlet. The reactor is the reaction vessel from an OREC model 03V5-0 ozone generator. The outer shell is a stainless steel cylinder with an outlet at the bottom. This shell serves as one electrode. The inside diameter of this outer shell is 77 millimeters. Within this shell, a glass tube is fitted which has a sealed bottom and the inner electrode which covers the inside surface of the glass tube. The gap between the outer wall of the glass tube and the inner wall of the shell is nominally 1.5 mm. Thus the

"active" reactor volume is in the shape of an annulus with an axial length of 332 mm. No analysis of the mixing characteristics was conducted, but it may be expected that there is some degree of backmixing. The volume of the reactor, between the electrodes, is about 118 cc, and the electrode area about 787 square centimeters. (The last experiment was conducted with one half of this plate area.) The outer shell has a water jacket made of PVC for control of the temperature by use of a water recirculation system or tap water.

After the gases have passed through the reactor, they pass through a dry ice/acetone trap to remove any condensable products. Following this, a small portion of the stream is diverted to a paramagnetic oxygen analyzer and, for later experiments, to a Carle gas chromatograph for analysis of the gaseous reactants and products. The thermal responses for all species detected were calibrated with known standards.

Power to the electrodes is provided by an Elgar AC power supply and a Wavetek function generator is used to generate the triangular wave used in the experiments discussed here. An oscilloscope is used to monitor the waveform, voltage level and frequency. A digital voltmeter is also used to monitor the RMS voltage.

A few experiments were run in a recycle configuration, illustrated in Figure 2. Mass flow controllers were used to add methane and oxygen to the system in a make-up gas stream. A Cole-Parmer diaphragm pump was used to recirculate the gas stream, with a bypass valve to maintain pressures slightly above atmospheric in all parts of the system.

RESULTS AND DISCUSSION

Initial runs were conducted at conditions previously established as optimal for a standard set of conditions (3). The feed flow rate was 566 cc/min at 71 ° F with a composition of 24.4 volume percent oxygen and 75.7 percent methane at a pressure of 12 inches of water. The reactor was maintained at 155 ° F. The electric field was maintained at 8 kV RMS at a frequency of 200 Hz using a triangular waveform. Under the standard conditions, the conversion of methane was about 15 percent and that of oxygen about 24 percent. Replicate experiments showed that the conversions of methane and oxygen varied ± 15 percent and ± 10 percent, respectively. The fractional yields of the primary liquid products under these conditions, water and methanol, were about .07 for methanol and .33 for water. The fractional yield is defined as the moles of a product produced per mole of methane reacted. This is used for water even though it is not a carbon based product. Thus about 7 percent of the methane converted formed methanol. Although methanol was the primary product, smaller amounts of other one and two carbon oxygenates were also formed. These products include formaldehyde, ethanol, methyl formate and formic acid. Qualitative GC/MS data showed the presence of numerous other compounds in minute quantities.

Run 4 was conducted to determine the variation on the oxygen conversion with changes in the field voltage. The oxygen concentration in the exit stream was used as an indicator of reactivity before more detailed analyses were made with later runs. In this experiment, the field was increased in increments from zero volts and allowed to equilibrate for several minutes. No decrease in the exit gas oxygen concentration was observed below 5 kV. At and above 5 kV the steady state oxygen concentration in the exit gas stream decreased linearly with increasing voltage. The system could attain a maximum RMS voltage of about 8kV at a frequency of 200 Hz. At 8 kV, the exit oxygen concentration was about 19.5 percent, or a conversion of 22 percent. A later run, run 25, was made to assess the effect of the frequency on the conversion and this, too, was found to be linear with decreased conversions at lower frequencies. In this run, the line power to the power supply was monitored and at a frequency of 50 Hz, the power consumed was approximately 30 percent of that at 200 Hz. The power used at 200 Hz was 350 Watts. There did appear to be some selectivity enhancement under these

conditions, as the methanol produced had decreased to about 43 percent of its amount at 200 Hz. However, the decrease in conversion would have a significant influence on the optimal frequency for operation.

Because significant amounts of carbon dioxide and water were produced, as well as the desired organic oxygenates, it was desirable to see if these might be inhibited by introduction of these species to the inlet stream of the reactor. Depending on the kinetics, it might be expected that significant quantities of these two species might drive the equilibrium in a favorable direction. In run 19, the inlet mole fraction of oxygen was reduced to .188 and a mole fraction of carbon dioxide of .085 was added, with the balance methane and the total inlet flow rate 485 cc/min. No differences could be detected in the results compared to runs at standard conditions, thus indicating that no equilibrium constraint appears to be limiting for carbon dioxide.

Run 20 was similar to run 19 except that an inlet mole fraction of water of .021 was used instead of the carbon dioxide. The water was added by saturating the inlet gas stream through a bubbler assembly. As with run 19, no remarkable results were observed here.

Although the reactor was being heated to 155 ° F, no work had previously been done to determine the effect of temperature on the reactions. Run 14 was made at ambient temperature, and it was observed that no effects due to the lower temperature were present. All runs subsequent to run 14 were, therefore, made at ambient temperature. It was noted that, in fact, significant quantities of heat were generated and a stream of cooling water was passed through the reactor water jacket to maintain ambient conditions. Measurements of the temperature rise of the cooling water through the jacket and its flow rate were made on several occasions. Although the accuracy may be considered poor, it appears that a significant fraction of the input power to the system may be dissipated as heat.

Because of the complete oxidation of a fraction of the methane to carbon dioxide, several experiments at lower increments of inlet oxygen concentration were made. The lowest concentration examined was about 1 percent oxygen. In run 23, the inlet mole fraction of oxygen was .012. The power required to maintain the 8 kV field increased somewhat, to 377 Watts. The conversion of the methane decreased substantially to .059, and the small amount of oxygen was about 49 percent converted. The yield of methanol remained near the standard value, about .073. The yield of water was substantially reduced, to .125, as might be expected with significantly less oxygen available. Interestingly, ethane now became a significant product from the methane. This would certainly indicate active methyl species participating in the reaction sequence. Another reactor configuration was used for one run, in which only the oxygen was passed through the reactor. This stream was then immediately mixed with methane to determine whether only active oxygen species, primarily ozone, might be the primary locus of the reactions. No reaction at all was observed in this case, and the literature on ozone chemistry agrees with the inability of ozone to significantly attack methane. Clearly the observed reactions indicate direct participation of active methane species.

A last standard experiment was made with one half of the inner electrode plate area. The results indicated that, while conversions tracked the decrease in the area, the power did not decrease by 50 percent. Thus, the inverse extrapolation for scale up would be that a 100 percent increase in the plate area, suitably configured, would result in a doubling of the quantities converted, but at less than a doubling of the power requirement, which is a favorable conclusion. The quantity of power used as "over-head" in the power supply was not determined. Attempts to measure the actual power used in the reactor field were unsuccessful, but it has already been mentioned that substantial heat was generated.

In the recycle configuration, two experiments were made. The only difference between them was the recycle flow rate. The carbon dioxide absorber shown in Figure 2, was not used for these runs. For run 29, the recycle flow rate, including make up gas, was 2.1 l/min, and for run 30, 1.0 l/min was used. The composition of gas entering the reactor was .005 mole fraction oxygen, once the reaction

had been underway for a short time. A material balance on the carbon and oxygen was made at the end of each run. The condensed products could only be removed after the system was shut down. The carbon balance was able to account for 73 percent of the carbon in the methane cumulatively provided to the system, initially and during the run. At the end of a ninety minute run, for run 30, about 112 millimoles of carbon, as methane, had been fed to the system, of which about 55 remained in the system or was lost in the GC bleed stream. About 2.6 millimoles of carbon went to produce ethane, about 4.7 as carbon dioxide and 5 as carbon monoxide. 15 millimoles of methanol were produced, but other organic compounds were not quantified and could be approximately 5 more millimoles. Thus, in this initial system configuration, approximately 13 to 17 percent of the methane used was converted to useful products. It may be that better material balances will enhance that figure to some extent.

On line GC analysis of the gases showed that ethane increased to a maximum of 1.2 and 1.4 millimoles in the system for the two runs, with the lower recycle rate having the higher maximum. Both maxima occurred about 40 minutes into the run, after which the concentrations both decreased by about 0.2 millimoles at the end of the 90 minute runs. Ethane, therefore appears to exhibit an equilibrium behavior. The carbon monoxide produced showed an induction period for the first 20 minutes, then continued increasing until the end of the run. Both experiments had virtually the same amount of carbon monoxide. Carbon dioxide increased linearly with time after also showing some induction during the first 20 minutes of the runs. However, the carbon dioxide produced at the higher recycle rate was significantly higher. At the end of the runs, the 2.1 l/min recycle rate had produced 6 millimoles of carbon dioxide, while the lower recycle rate had produced 4.7. One might think that the shorter contact time of the higher recycle rate would serve to minimize larger extents of oxidation.

The oxygen balance was able to account for 87 percent of the oxygen fed to the system. It might be noted that the oxygen conversion per pass was essentially 100 percent, and that higher inlet concentrations might alter the results obtained. Of the 40 millimoles of oxygen provided during the run, 5 appeared as carbon monoxide, 9.4 as carbon dioxide and 12 as water. Methanol accounted for 7.5 millimoles of the total.

The most significant result of the recycle experiments was that the percent methanol in the liquid product increased from one percent in the single pass runs to 12 percent for the recycle runs. Water concentration also increased, however.

Lastly, mention should be made that a number of other single pass experiments were conducted, both in search of other interesting reactions and in attempting to elucidate the reaction pathways of the methane-oxygen system. These runs were made at the standard conditions except that the species of the feed mixtures were altered. Mixtures examined were: carbon dioxide-methane, carbon monoxide-methane, hydrogen-nitrogen and carbon monoxide-hydrogen. Except for a trace amount of material produced from the carbon dioxide-methane mixture, no reactions were detected.

SUMMARY

The results from a number of scoping runs examining a number of variables have been presented for the oxidation of methane in an alternating electric field. Several features of these results point the way to further needed experiments to determine the possibilities for production of light organic oxygenates from this process. Fundamental studies to determine the mechanistic paths would also be useful to help focus further research on the optimal conditions for maximizing the yields of desirable products and for determining the economic potential of the process.

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REFERENCES

- (1) Pitchai, R. and K. Klier; *Catal. Rev.-Sci. Eng.*, **28**, 13 (1986).
- (2) Lockett, G. A. and B. Mile; *Combustion and Flame*, **26**, 299 (1976).
- (3) Rusek, S. and J. Wintgens, unpublished results (1985).

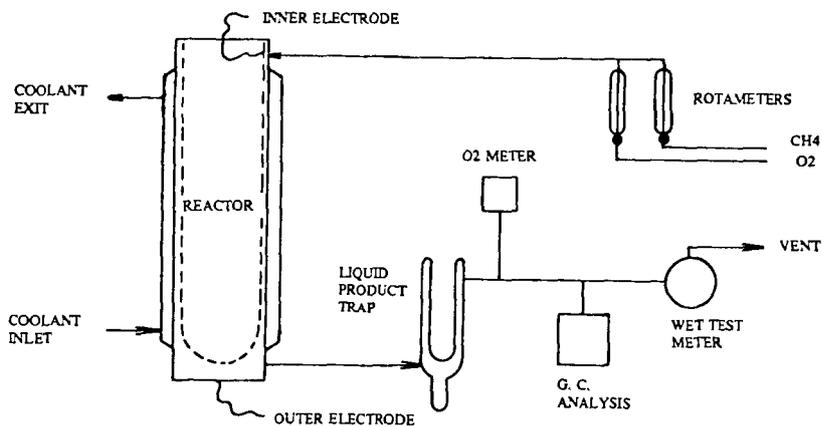


Figure 1. Single pass reactor system.

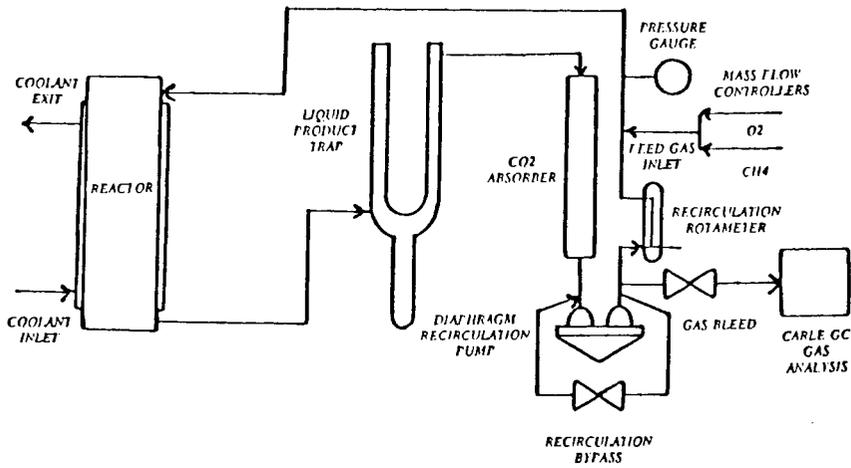


Figure 2. Recycle Reactor System.