

---

## **Oxidative Coupling of Methane with ac and dc Corona Discharges**

---

**Changjun Liu, Abdulathim Marafee, Bobby Hill, Genhui Xu,  
Richard Mallinson, and Lance Lobban**

Institute of Natural Gas Utilization, School of Chemical Engineering  
and Materials Science, University of Oklahoma,  
Norman, Oklahoma 73019

**INDUSTRIAL &  
ENGINEERING  
CHEMISTRY<sup>®</sup>  
RESEARCH**

Reprinted from  
Volume 35, Number 10, Pages 3295-3301

# Oxidative Coupling of Methane with ac and dc Corona Discharges

Changjun Liu,<sup>†</sup> Abdulathim Marafee, Bobby Hill, Genhui Xu,<sup>†</sup>  
Richard Mallinson, and Lance Lobban\*

*Institute of Natural Gas Utilization, School of Chemical Engineering and Materials Science,  
University of Oklahoma, Norman, Oklahoma 73019*

The oxidative coupling of methane (OCM) is being actively studied for the production of higher hydrocarbons from natural gas. The present study concentrated on the oxidative conversion of methane in an atmospheric pressure, nonthermal plasma formed by ac or dc corona discharges. Methyl radicals are formed by reaction with negatively-charged oxygen species created in the corona discharge. The selectivity to products ethane and ethylene is affected by electrode polarity, frequency, and oxygen partial pressure in the feed. Higher C<sub>2</sub> yields were obtained with the ac corona. All the ac corona discharges are initiated at room temperature (i.e., no oven or other heat source is used), and the temperature increases to 300–500 °C due to the exothermic reactions and the discharge itself. The largest C<sub>2</sub> yield is 21% with 43.3% methane conversion and 48.3% C<sub>2</sub> selectivity at a flowrate of 100 cm<sup>3</sup>/min when the ac corona is at 30 Hz, 5 kV (rms) input power was used. The methane conversion may be improved to more than 50% by increasing the residence time, but the C<sub>2</sub> selectivity decreases. A reaction mechanism including the oxidative dehydrogenation (OXD) of ethane to ethylene is presented to explain the observed phenomena. The results suggest that ac and/or dc gas discharge techniques have significant promise for improving the economics of OCM processes.

## Introduction

Natural gas is potentially the next least-cost energy resource as we make the transition into the twenty-first century. Its relative abundance and availability are convincing reasons to further develop this resource, particularly where strategic questions related to the security of stable energy and petrochemicals supplies are concerned. Demands for methanol and ethylene, two target products of natural gas conversion research, are large and increasing. In particular, the possibility of producing ethylene from methane (the primary component of natural gas) has attracted intense industrial and academic interest. However, even with the low cost of natural gas, current methane-to-methanol or methane-to-ethylene conversion technologies are in most cases simply too expensive. Despite numerous and intense research efforts to improve the selectivity and yield of the favored products, the partial oxidation of methane to methanol or the oxidative coupling of methane to ethane and ethylene is not yet economically competitive with syngas-based methane conversion methods, which first convert methane into syngas and then convert syngas to chemicals.

A large number of chemicals have been reported to be prepared by electrochemical synthesis methods, including via plasma reactions. The potential of clean, low cost, highly selective, and energy-efficient synthesis has been found to exist in those processes involving organic electrosynthesis and plasma catalytic synthesis techniques. In most of these plasma techniques, free radicals generated by excitation, dissociation, and ionization of gas molecules are essential for the subsequent free-radical reactions. Control of electron energy by appropriate design of discharge reactors improves the selectivity to the favorable products. We have constructed plasma systems for the oxidative coupling of

methane using ac and dc corona discharge reactors. The nonthermal corona discharge, which is characterized by low gas temperature and high electronic temperature, is usually generated by strong electric fields associated with a small-diameter rod, wire, or needle electrode and a second plate electrode at or near atmospheric pressure. Because the corona is particularly easy to establish, it has had wide application in a variety of processes, including synthesis of chemicals (Chang et al., 1991). In the presence of gaseous oxygen, the corona discharge provides a source of negatively charged oxygen ions (O<sup>-</sup> or O<sup>2-</sup>) formed via electron attachment to oxygen molecules in the gas phase (Chang et al., 1991; Grill, 1994; Lee and Grabowski, 1992). It is generally agreed that surface or lattice oxygen ions are responsible for activation of methane in heterogeneous catalytic reactions (Capitan et al., 1993; DeBoy and Hicks, 1988; Eng and Stoukides, 1991a,b; Gaffney et al., 1988; Imai and Tagawa, 1986; Lee and Oyama, 1988; Otsuka et al., 1987; Yamagata et al., 1993), hence, the same type of activity might be expected from gas phase oxygen ions. In this paper, the role of gas discharge in the oxidative coupling of methane is investigated. Under corona discharge conditions we have achieved good C<sub>2</sub> selectivities and yields at moderate temperatures. In a separate paper (Marafee et al., to be published), we will present our study of the role of gas discharge on the reactions occurring in a corona-packed bed reactor (in which the corona discharge occurs in the presence of a solid catalyst).

## Experimental Section

The corona discharge reactor is shown in Figure 1. The reactor was constructed of a 7 mm i.d. quartz tube and could be heated by a cylindrical furnace. A thermocouple in a small alumina tube was placed against the outside wall of the reactor to measure the reaction temperature, which is controlled by a temperature controller (Watlow Series 965). The temperature measured in this way has been calibrated with the reacting gas temperature inside the reactor as described in

\* To whom correspondence should be addressed. email address: lobban@mailhost.ecn.uoknor.edu.

<sup>†</sup> On leave from the State Key Laboratory of C<sub>1</sub> Chemical Techniques, Tianjin University, People's Republic of China.



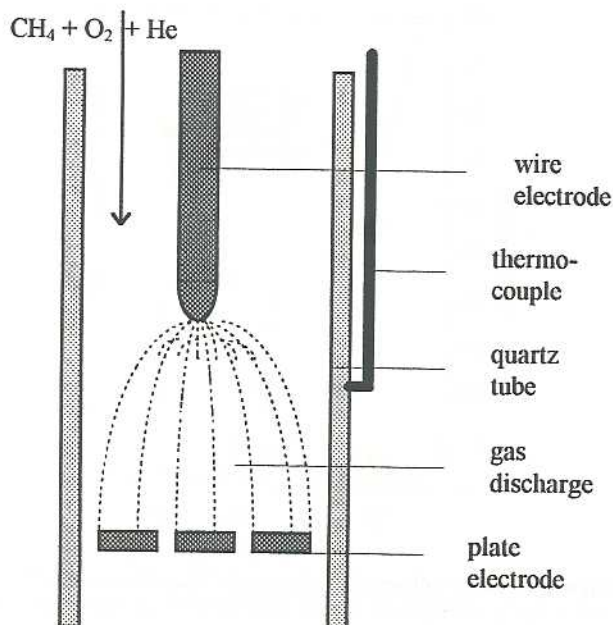


Figure 1. Corona discharge reactor.

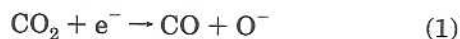
another paper (Marafee et al., to be published). The flowrates of reactants methane and oxygen and the dilution gas helium were regulated by Porter Instrument Co. Model 201 mass flow controllers. Methane and oxygen were mixed with helium and then introduced downward through the reactor for all experiments. A total flowrate of 100 cm<sup>3</sup>/min with 0.2 atm partial pressure of methane, 0.05 atm partial pressure of oxygen, and the balanced helium was applied for the dc corona experiments. The total flowrates of 50–200 cm<sup>3</sup>/min with the same partial pressures of methane, oxygen, and helium as the dc corona reactions (except for the experiments varying oxygen partial pressure) were also used for the ac corona experiments. The feed gases were analyzed by on-line gas chromatography (HP5890) using a thermal conductivity detector and equipped with a molecular sieve packed column (Alltech Associates, Inc., No. 123281L). The exhaust gas was introduced into a condenser, cooled by a mixture of dry ice and acetone which was used to remove the residual water. The effluent gas from the condenser was analyzed by the gas chromatograph. The condensate was analyzed by a GCD system (HP GCD G1800A) using an electronic ionization detector. The reaction products are mainly ethylene, ethane, carbon dioxide, carbon monoxide, and trace formaldehyde. All experiments were carried out at atmospheric pressure.

The ionized gases were formed in the gap between two stainless steel electrodes, as shown in Figure 1. The upper wire electrode was positioned with its tip 10 mm above the plate electrode. The discharge was created by means of a high-voltage dc power supply (Model 210-50R, Bertan Associates Inc.) or an ac power supply (Model 251B, Elgar Power System Co.) with a high-voltage transformer. When dc coronas were applied, the plate electrode was always grounded and the wire electrode was at either positive potential (referred to as the positive corona) or negative potential (referred to as the negative corona). In the discharge volume, the interaction between accelerated charged particles (i.e., electrons and ions) and other chemical species (i.e., molecules and radicals) takes place. This interaction leads to the synthesis of new chemical species, specifically the desired ethane and ethylene as well as undesired CO and CO<sub>2</sub>. The plasma-generated reactive

species probably persist for only a very short distance downstream of the plasma zone. The conversion and selectivity depended on the residence time, the dc polarity, the type and frequency of the ac waveform, and the methane to oxygen ratio in the feed. The results of the dc corona experiments are presented and discussed first.

## Results and Discussion

**1. dc Corona Discharge Characteristics.** We first conducted a temperature-programmed corona reaction (TPCR) experiment to investigate the temperature-related performance of corona reactions. The TPCR experiment utilizes the same apparatus as just described. During the TPCR, a record of the composition of effluents from the corona discharge OCM as a function of temperature or time in the course of temperature-programmed corona reaction may be referred to as a spectrum, which usually consists of one or more peaks. The shapes and positions of the peaks on a temperature scale are related in a fundamental way to the reaction and therefore provide us information on the manner in which corona discharge reactions occur. A temperature increase rate of 3 °C/min was applied for our TPCR experiments. In the absence of the corona discharge, no C<sub>2</sub> products were observed below 1000 °C. Only a small amount of carbon dioxide formed. However, the TPCR experiment showed the formation of ethane, ethylene, and CO<sub>2</sub> and CO at temperatures as low as 100 °C for both positive and negative corona discharges. At 100 °C, however, the electrodes were found to be covered by a thin layer of liquid carbon species presumably formed by polymerization of free radicals. The insulated liquid layer has a retarding effect on the corona discharge. At 300 °C, the carbon layer was found to be inhibited by the increasing temperature (this is thought to be that the increasing temperature promotes the radical reactions with carbon deposit, leading to oxidation of part of the carbon deposit), and corona discharges were apparently stable at this temperature. The rate of C<sub>2</sub> formation was still very low until the temperature was increased to 450 °C, at which temperature most of carbon species are removed from the electrodes, allowing a stable discharge environment for the oxidative conversion of methane. The amount of CO<sub>2</sub> produced increases rapidly for  $T > \sim 400$  °C with the positive corona and for  $T > \sim 500$  °C with the negative corona, as shown in the TPCR spectrum of Figure 2. The amount of CO<sub>2</sub> reaches a maximum value around 875 °C for the positive and negative corona discharges. These points correspond to the total consumption of oxygen. That the CO<sub>2</sub> subsequently decreases suggests CO<sub>2</sub> contributes one of its two oxygen atoms for the oxidative conversion of methane or other hydrocarbons by electronic dissociative attachment of CO<sub>2</sub>:



This will be discussed in more detail later.

Following the TPCR experiments, steady-state experiments under a variety of conditions were conducted. Table 1 shows the results of corona discharge reactions at different CH<sub>4</sub>/O<sub>2</sub> ratios and different polarities.

The positive corona shows the highest conversion of oxygen and methane and the highest yield of C<sub>2</sub> products, with these occurring at low CH<sub>4</sub>/O<sub>2</sub> ratio. Methane conversion decreases and oxygen conversion



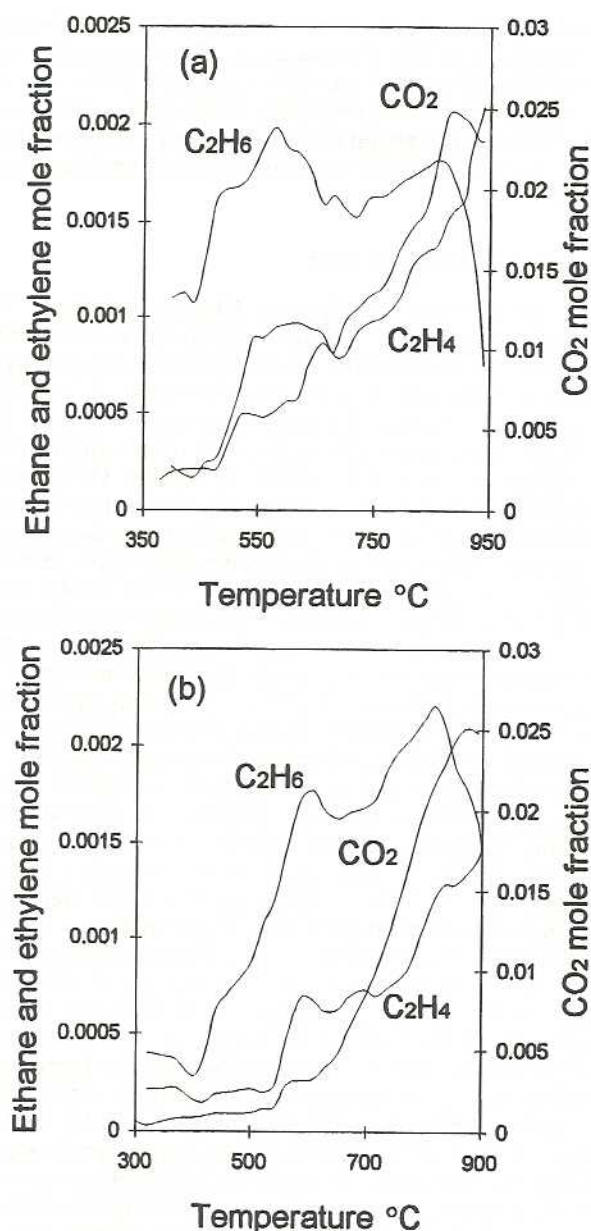


Figure 2. Temperature-programmed corona reactions: (a) positive corona; (b) negative corona. Flowrate: 100 cm<sup>3</sup>/min. CH<sub>4</sub>/O<sub>2</sub>: 4. Temperature increase rate: 3 °C/min.

Table 1. Comparison of Positive and Negative dc Corona Processes (100 cm<sup>3</sup>/min, 923 K)

CH <sub>4</sub> /O <sub>2</sub>	wire electrode potential, kV	selectivity for C <sub>2</sub> products, %	yield of C <sub>2</sub> products, %	conversion of methane, %	conversion of oxygen, %
10:1	+5	48.8	1.89	3.87	50.3
	-5	52.0	2.05	3.92	32.7
4:1	+5	59.2	6.25	10.60	17.2
	-5	54.9	3.69	6.71	12.0
2.5:1	+5	41.7	2.44	6.00	23.8
	-5	42.1	1.15	2.70	16.2

increases as the methane to oxygen ratio is increased. Generally, higher conversions of methane and oxygen were found with the positive coronas. The positive corona typically exhibits streamer or glow characteristics, while the negative corona exhibits Trichel pulse or pulseless characteristics (Chang et al., 1991). These results suggest that the streamer or glow corona is more helpful for production of the desired C<sub>2</sub> hydrocarbons. The positive streamer is generated when the density of positive ions is large enough to extend the corona

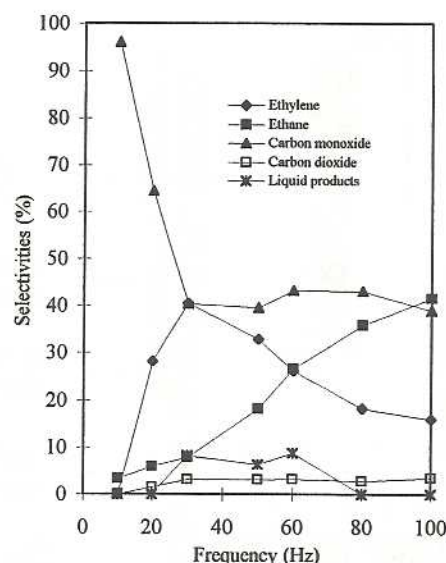


Figure 3. Effect of frequency on selectivities. Flowrate: 100 cm<sup>3</sup>/min. CH<sub>4</sub>/O<sub>2</sub>: 4. Applied voltage: 5 kV(rms). Sinusoidal waveform.

initiation zone into the interelectrode gap. The streamer corona thus possesses a much greater active volume than the other corona discharge forms, which are limited by their generation mechanisms to the near-electrode regions (Chang et al., 1991; Eliasson and Kogelschatz, 1991). According to the previous research (Eliasson and Kogelschatz, 1991), the positive streamer corona is characterized by higher electron concentrations and a more stable hydrodynamic performance, the characteristics of which are apparently more favorable for the OCM reaction. As the dc streamer corona discharge is more difficult to maintain than the ac corona discharge, we discuss the ac discharge reactions in a little more detail next.

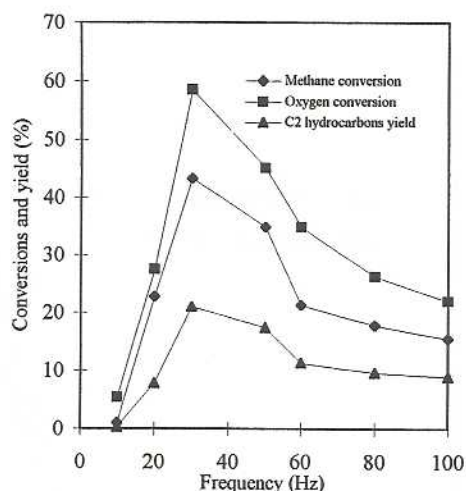
## 2. ac Corona Discharge Characteristics. a.

**Frequency Effect.** All the ac corona discharge experiments were started at room temperature, but high methane conversions were achieved and gas temperatures as high as 500 °C were observed due to the heat of reaction and the energy release from the discharge. As the ac discharge is applied, each electrode performs alternately as anode or cathode. The alternating behavior has proven effective to eliminate the contaminant accumulation on the electrodes, which shows that the system behavior is significantly different with ac discharge than with dc.

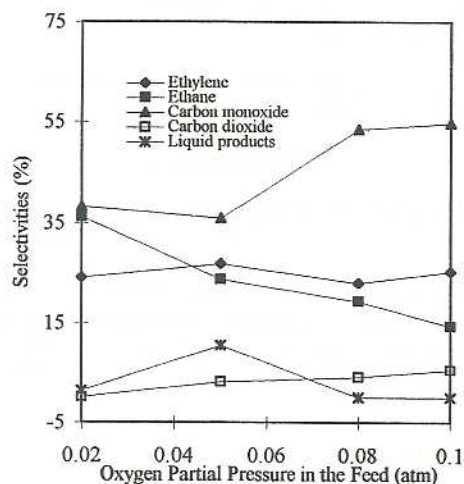
Figures 3 and 4 show the effect of frequency on methane conversion and C<sub>2</sub> selectivity. With the sinusoidal voltage waveform, the methane and oxygen conversions and the C<sub>2</sub> selectivity exhibit a maximum at a frequency of 30 Hz. High ratios of ethylene/ethane (5.14) and CO/CO<sub>2</sub> (12.7) were reached at this frequency. Lower or higher frequencies gave a lower ratio of ethylene/ethane, but CO/CO<sub>2</sub> did not change significantly. For example, ethylene/ethane of 1.8 and CO/CO<sub>2</sub> of 12.5 were obtained at a frequency of 50 Hz. As the frequency is further reduced from 30 Hz, the streamer corona will shift to a spark corona, which explains the maximum at 30 Hz for the methane and oxygen conversions.

**b. Oxygen Partial Pressure Effect.** For experiments to study the effect of oxygen partial pressure, the total feed flow rate was held at 100 cm<sup>3</sup>/min. Results are shown in Figures 5 and 6. Increasing oxygen partial pressure in the feed causes higher conversions of methane and oxygen. The yield of C<sub>2</sub> products increases

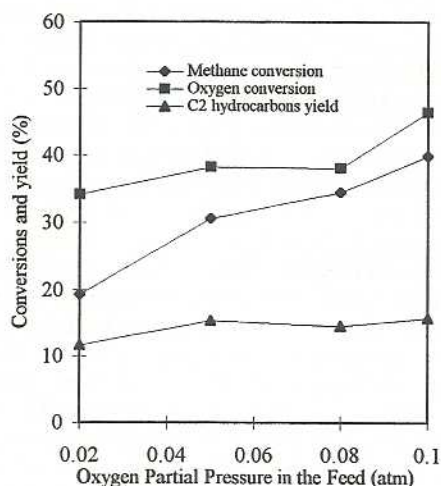




**Figure 4.** Effect of frequency on conversions and yield. Flowrate: 100 cm<sup>3</sup>/min. CH<sub>4</sub>/O<sub>2</sub>: 4. Applied voltage: 5 kV(rms). Sinusoidal waveform.

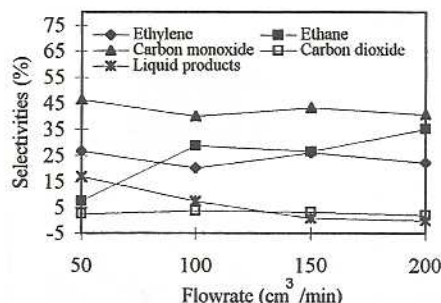


**Figure 5.** Effect of oxygen partial pressure on selectivities. Flowrate: 100 cm<sup>3</sup>/min. Applied voltage: 5 kV(rms). Sinusoidal waveform. Constant methane partial pressure in the feed: 0.2 atm. Frequency: 60 Hz.

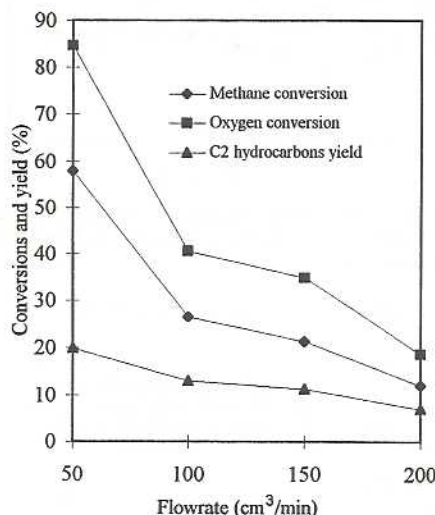


**Figure 6.** Effect of oxygen partial pressure on conversions and yield. Flowrate: 100 cm<sup>3</sup>/min. Applied voltage: 5 kV(rms). Sinusoidal waveform. Constant methane partial pressure in the feed: 0.2 atm. Frequency: 60 Hz.

only slightly, but the ethylene/ethane ratio is highest at the highest partial pressure of oxygen. In our experiments, there are some trace unidentified products in the liquid condensate but about 20% of the liquid product is formaldehyde. We refer to these products



**Figure 7.** Effect of flowrate on selectivities. CH<sub>4</sub>/O<sub>2</sub>: 4. Applied voltage: 5 kV (rms). Frequency: 60 Hz. Sinusoidal waveform.



**Figure 8.** Effect of flowrate on conversions and yield. CH<sub>4</sub>/O<sub>2</sub>: 4. Applied voltage: 5 kV (rms). Frequency: 60 Hz. Sinusoidal waveform.

(including formaldehyde) as C<sub>liq</sub>. The yield of C<sub>liq</sub> products is significant only at oxygen partial pressure of 0.05 atm, decreasing quickly with increasing oxygen partial pressure thereafter. These results suggest that oxygen plays an important role in the ac discharge OCM reactions and the ethylene formation.

**c. Effects of Flowrate (Residence Time).** Constant partial pressures of methane and oxygen were maintained in the feed gases (0.2 atm for methane and 0.05 atm for oxygen), while the total flowrate was varied. Results are shown in Figures 7 and 8. Methane conversion, oxygen conversion, ethane selectivity, and ethylene selectivity all increase significantly with decreasing flowrate or increasing residence time, although ethylene selectivity increases faster, suggesting that ethylene forms via the oxidative dehydrogenation of ethane. The decreasing trend of C<sub>liq</sub> product with increasing flowrate from 50 to 200 cm<sup>3</sup>/min suggests the C<sub>liq</sub> is a secondary product of the reactions. Figure 7 also indicates a very low CO<sub>2</sub> yield. The average CO/CO<sub>2</sub> ratio is 16.0. Compared to the CO<sub>2</sub> yield with dc corona discharges, it is clear that dc corona discharges will generate much more CO<sub>2</sub> product (more than 20 times higher than the CO<sub>2</sub> yield with ac corona). Two possible explanations are as follows: (i) in the ac corona, CO<sub>2</sub> is converted to CO by reaction (1); (ii) carbonaceous deposits formed on the electrodes during dc coronas may be an intermediate to CO<sub>2</sub>.

**d. Effect of Input Voltage on ac Corona Discharge Reactions.** Figure 9 shows the effect of input voltage on ac corona discharge OCM with a constant methane/oxygen ratio of 4 and a feed flowrate of 100 cm<sup>3</sup>/min. When the applied voltage reaches 3.5 kV, the gas discharge is initiated. The conversions of methane



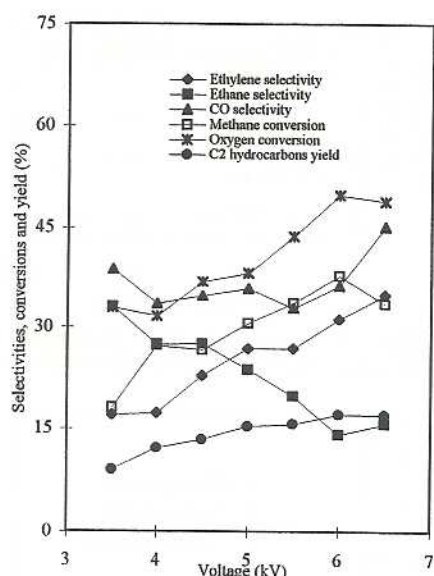


Figure 9. Effect of applied voltage on selectivities, conversions, and yield. Flowrate: 100 cm<sup>3</sup>/min. CH<sub>4</sub>/O<sub>2</sub>: 4. Frequency: 60 Hz. Sinusoidal waveform.

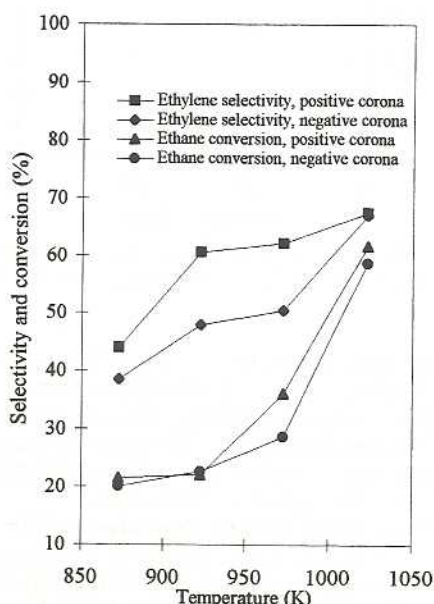


Figure 10. Effect of temperature on ethane conversion and ethylene selectivity. Flowrate: 100 cm<sup>3</sup>/min. C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub>: 1. Applied voltage: 5 kV.

and oxygen increase with increasing voltage. But, the yield of C<sub>2</sub> hydrocarbons increases slightly. Figure 9 shows that the selectivity of ethylene increases with increasing voltage, but the selectivity of ethane decreases. This also explains why ethylene is a secondary product. As the figure shows, methane conversion and C<sub>2</sub> yield increase gradually with voltage and appear to approach a "saturation" state.

3. Experimental Investigation of the Oxidative Dehydrogenation of Ethane. An experimental investigation of the oxidative dehydrogenation (OXD) of ethane was carried out to confirm that ethylene is produced from ethane. The dc corona discharge system used for the OCM experiments was used. The experiment was performed at atmospheric pressure with constant partial pressures of ethane (0.015 atm) and oxygen (0.015 atm) in the feed. The feed gases were diluted by helium, and the total flowrate was regulated to be 100 cm<sup>3</sup>/min. Figures 10 and 11 show the effect of temperature on the OXD of ethane. The ethane conversion and ethylene

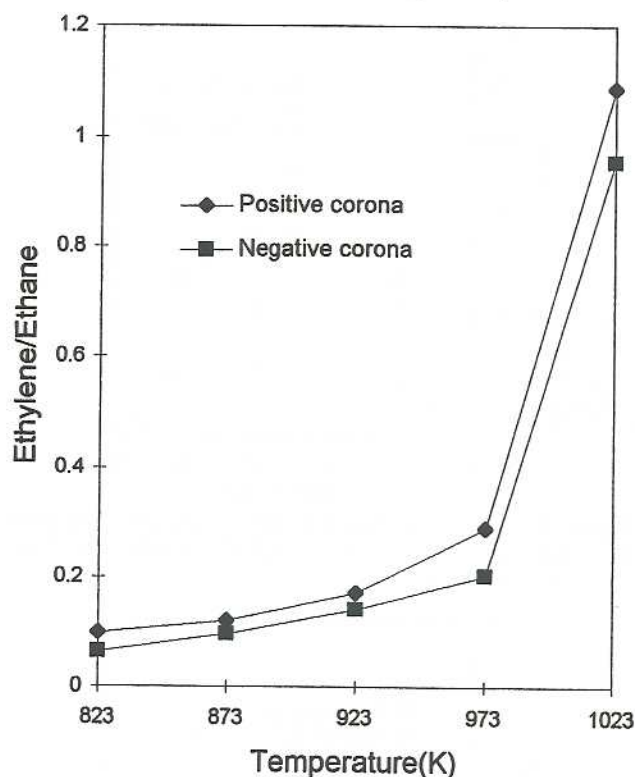


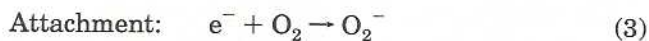
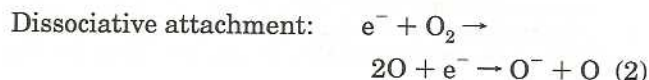
Figure 11. Effect of temperature on ethylene to ethane ratio. Flowrate: 100 cm<sup>3</sup>/min. C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub>: 1. Applied voltage: 5 kV.

selectivity increase quickly with increasing temperature for both positive and negative corona discharge reactions. The positive corona is a little more favorable for the OXD of ethane than is the negative corona.

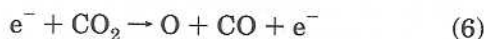
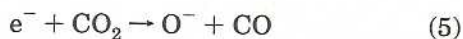
## Discussion

A heterogeneous OCM reaction is believed to include heterogeneous and homogeneous reaction steps. The catalyst with surface or lattice O<sup>-</sup> or O<sub>2</sub><sup>-</sup> is needed to activate methane by abstraction of hydrogen to form methyl radicals. Production of C<sub>2</sub> hydrocarbons is believed to occur primarily in the gas phase by coupling of the methyl radicals. In our system, we hypothesize that oxygen anions are formed by interaction of O<sub>2</sub> with electrons. These anions play a role similar to surface oxygen anions in the activation of methane. Research has previously demonstrated the important role of the oxygen anion in the synthesis of organic reactive intermediates, including methane and ethane radicals. As early as the 1960s, Bohme, Fehsenfeld, and Young (Bohme and Fehsenfeld, 1969; Bohme and Young, 1970) studied the reactions of methane and ethane molecules with atomic oxygen anion in the gas phase. It was also observed (Lindinger et al., 1975) that the H-atom transfer rate from CH<sub>4</sub> to O<sup>-</sup> increases with increasing O<sup>-</sup> kinetic energy. They also found that the ion signals between the consumed O<sup>-</sup> and the formed OH<sup>-</sup> are balanced and the reaction of methane with O<sup>-</sup> results in the formation of CH<sub>3</sub> and OH<sup>-</sup>. Tiernan (Tiernan, 1975) and Viggiana et al. (Viggiana et al., 1989, 1990) correlated the O<sup>-</sup> kinetic energy with the reaction kinetic parameters. Thus, there is more evidence to suggest that O<sup>-</sup> formed in the discharge will activate methane. The reaction efficiency of CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub> with O<sup>-</sup> in the gas phase is apparently related to the alkane C-H bond dissociation energy (Lee and Graboski, 1992). The gas discharge OCM reaction may occur as follows:

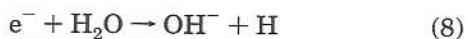
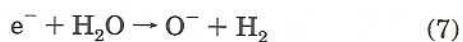


**(1) O<sup>-</sup> Formation and Initiation of Discharge Reactions.**

The dissociative attachment reaction requires the least energy and so is considered most likely (Eliasson and Kogelschatz, 1991; Grill, 1994). In our system, a corona gas discharge was applied to initiate the reactions. The corona discharge produces electrons with an average electron energy of about 6 eV (Eliasson and Kogelschatz, 1991). This energy is insufficient to activate a methane molecule because the appearance potentials of methane ions are greater than 12 eV (Sorensen et al., 1995), but the energy is sufficient for the dissociative attachment reaction of oxygen yielding negatively charged oxygen ions. Thus, we expect reactions involving CH<sub>4</sub> to occur after CH<sub>4</sub> activation by O<sup>-</sup>. Similarly, no evidence was reported (Lee and Grabowski, 1992) of associative attachment with methane, i.e., formation of CH<sub>4</sub> ions, which result is consistent with the research results using metal oxide catalysts. On the other hand, CO<sub>2</sub> and H<sub>2</sub>O are products of the gas discharge OCM reaction. The newly-formed products CO<sub>2</sub> and H<sub>2</sub>O are intrinsically already excited and require only a relatively low electron energy to dissociate these two molecules (Chantry, 1972; Lee and Grabowski, 1992; Orient and Strivastava, 1983):

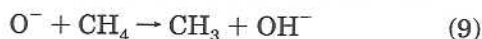


and



**(2) Homogeneous Reactions.** The O<sup>-</sup> formed by dissociative attachment reacts further as follows:

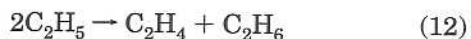
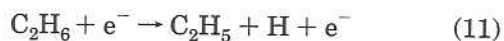
Methane radical formation:



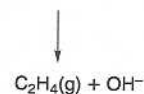
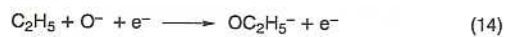
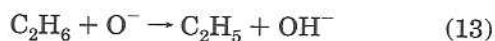
Ethane formation:



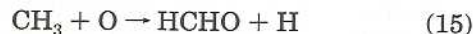
Ethylene formation:



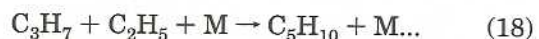
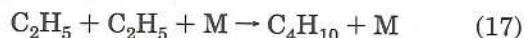
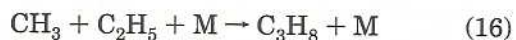
Oxidative dehydrogenation of ethane:



Formaldehyde formation:



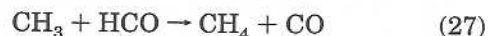
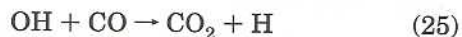
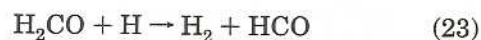
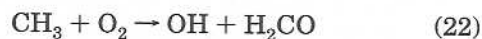
Possible higher hydrocarbons formation (higher hydrocarbons have not been isolated, but a small amount may be formed via the following reactions):



H<sub>2</sub>O formation:



CO<sub>x</sub> formation:



The formation of O<sup>-</sup> via reactions (2)–(4) would be the controlling step at the lower input voltages. At high voltages the concentration of O<sup>-</sup> species may be sufficiently great that the subsequent radical reactions control the rate of conversion. Additionally, there may exist a "saturation" ionization rate in the corona system, which ultimately limits the rate of conversion.

The rapid increase in the ethylene/ethane ratio above 973 K (Figure 11) may reflect the increasing importance of reactions (11) and (12) at higher temperature, while at low temperatures reactions (13) and (14) are responsible for conversion of ethane to ethylene. This suggests some possible thermally initiated reactions and is basically similar to the regular catalytic oxidative conversion of ethane to ethylene. The effects of temperature on the ethylene/ethane ratio suggest these ratios with OXD of ethane are very consistent with those attained during OCM reactions (with an ethylene/ethane ratio of 0–1.2). This similar ratio suggests that, in both cases, ethylene is formed from the ethane, probably via oxidative dehydrogenation.

The OCM reaction products include CO<sub>2</sub> and H<sub>2</sub>O, which probably absorb some energy from the discharge.



They are also probably active to react with methane to form syngas, which may react further to produce methanol and formaldehyde. These reactions may be catalyzed by the stainless steel electrode. As mentioned above, the electrode with dc corona discharge reactions will be covered by pollutant carbons, and the pollutant layer would inhibit the steam and CO<sub>2</sub> methane reforming reactions and stop the methanol and formaldehyde formations. In order to further our understanding of the corona discharge-initiated reactions, plasma characterization and kinetics analysis are necessary.

## Conclusions

The results demonstrate the following:

1. The corona discharge is an effective method to activate methane via negatively charged oxygen ions, leading to the oxidative coupling of methane in the gas phase at relatively low temperatures.

2. The positive dc corona discharge has a slightly larger yield of C<sub>2</sub> products than the negative dc corona discharge.

3. The ac corona discharge has a significantly larger yield of C<sub>2</sub> products than does the dc corona.

In general, the corona OCM reactions have reached the high methane conversion with large yields of CO and ethylene at temperatures less than 600 °C. Further improvements with this system may lead to economic and effective processes for methane conversion to more valuable hydrocarbons.

## Acknowledgment

Support from the U.S. Department of Energy (under Contract No. DE-FG21-94MC31170) is greatly appreciated. Support from the Kuwait Institute for Science and Technology for A.M. is gratefully acknowledged. Partial support for C.L. and G.X. from Tianjin University is also gratefully acknowledged.

## Literature Cited

- Bohme, D. K.; Fehsenfeld, F. C. Thermal Reactions of O<sup>-</sup> Ions with Saturated Hydrocarbon Molecules. *Can. J. Chem.* **1969**, *47*, 2717.
- Bohme, D. K.; Young, L. B. Gas-phase Reactions of Oxide Radical Ion and Hydroxide Ion with Simple Olefins and of Carbanions with Oxygen. *J. Am. Chem. Soc.* **1970**, *92*, 3301.
- Capitan, M. J.; Malet, P.; Centeno, M. A.; Munoz-Paez, A.; Carrizosa, I.; Odriozola, J. A. Sm<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> Catalysts for Methane Coupling. Influence of the Structure of Surface Sm-Al-O Phases on the Reactivity. *J. Phys. Chem.* **1993**, *97*, 9233.
- Chang, J.; Lawless, P. A.; Yamamoto, T. Corona Discharge Processes. *IEEE Trans. Plasma Sci.* **1991**, *19*, 1152.
- Chantry, P. J. Dissociative Attachment in Carbon Dioxide. *J. Chem. Phys.* **1972**, *57*, 3180.
- DeBoy, J. M.; Hicks, R. F. Kinetics of the Oxidative Coupling of Methane over 1 wt % Sr/La<sub>2</sub>O<sub>3</sub>. *J. Catal.* **1988**, *113*, 517.
- Eliasson, B.; Kogelschatz, U. Nonequilibrium Volume Plasma Chemical Processing. *IEEE Trans. Plasma Sci.* **1991**, *19*, 1063.
- Eng, D.; Stoukides, M. Catalytic and Electrocatalytic Methane Oxidation with Solid Oxide Membranes. *Catal. Rev., Sci. Eng.* **1991a**, *33*, 375.
- Eng, D.; Stoukides, M. Catalytic and Electrochemical Oxidation of Methane on Platinum. *J. Catal.* **1991b**, *130*, 306.
- Gaffney, A. M.; Jones, C. A.; Leonard, J. J.; Sofranko, J. A. Oxidative Coupling of Methane over Sodium Promoted Praseodymium Oxide. *J. Catal.* **1988**, *114*, 422.
- Grill, A. *Cold Plasma in Materials Fabrication: From fundamentals to applications*; IEEE Press: New York, 1994.
- Imai, H.; Tagawa, T. Oxidative Coupling of Methane over Lanthanum Aluminum Trioxide. *J. Chem. Soc., Chem. Commun.* **1986**, 52.
- Lee, J. S.; Oyama, S. T. Oxidative Coupling of Methane to Higher Hydrocarbons. *Catal. Rev., Sci. Eng.* **1988**, *30*, 249.
- Lee, J.; Grabowski, J. J. Reactions of the Atomic Oxygen Radical Anion and the Synthesis of Organic Reactive Intermediates. *Chem. Rev.* **1992**, *92*, 1611.
- Lindinger, W.; Albritton, D. L.; Fehsenfeld, F. C.; Ferguson, E. E. Reactions of O<sup>-</sup> with N<sub>2</sub>, N<sub>2</sub>O, SO<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> with O<sub>2</sub> from 300K to Relative Kinetic Energies of ~2eV. *J. Chem. Phys.* **1975**, *63*, 3238.
- Marafee, A.; Liu, C.-J.; Xu, G.-H.; Mallinson, R.; Lobban, L. An Experimental Study on the Oxidative Coupling of Methane in a Corona Discharge Reactor over Sr/La<sub>2</sub>O<sub>3</sub> Catalyst. To be published.
- Orient, O. J.; Strivastava, S. K. Production of O<sup>-</sup> from CO<sub>2</sub> by Dissociative Electron Attachment. *Chem. Phys. Lett.* **1983**, *96*, 681.
- Otsuka, K.; Shimizu, Y.; Komatsu, T. Ba Doped Cerium Oxides Active for Oxidative Coupling of Methane. *Chem. Lett.* **1987**, 1835.
- Sorensen, S. L.; Karawajczyk, A.; Stromholm, C.; Kirm, M. Dissociative Photoexcitation of CH<sub>4</sub> and CD<sub>4</sub>. *Chem. Phys. Lett.* **1995**, 232, 554 and references therein.
- Tiernan, T. O. In *Interactions between Ions and Molecules*; Ausloos, P., Ed.; Plenum Press: New York 1975; p 353.
- Viggiano, A. A.; Morris, R. A.; Paulson, J. F. Rotational Temperature Dependences of Gas Phase Ion-molecule Reactions. *J. Chem. Phys.* **1988**, *89*, 4848.
- Viggiano, A. A.; Morris, R. A.; Deakyne, C. A.; Dale, F.; Paulson, J. F. Effects of Hydrogen on Reactions of O<sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> (n = 0-2). *J. Phys. Chem.* **1990**, *94*, 8193.
- Yamagata, N.; Igarashi, K.; Saitoh, H.; Okazaki, S. Preparation of a Voluminous Composite Barium-Lanthanum Oxide of BaLa<sub>2</sub>O<sub>4</sub> and its Catalytic Performance for the Oxidative Coupling of Methane. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1799.

Received for review March 12, 1996

Revised manuscript received June 5, 1996

Accepted June 14, 1996<sup>®</sup>

IE960138J

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, August 15, 1996.