

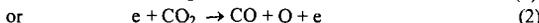
CO₂ UTILIZATION BY GAS DISCHARGES

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INTRODUCTION

Carbon dioxide is the end product to complete combustion of all fossil fuels. The generation of carbon dioxide is the primary cause for the greenhouse effect. However, carbon dioxide is a potential carbon source. To utilize such a plentiful carbon source, it has been considered carbon dioxide as a feedstock for organic synthesis of carbonyl- and carboxyl-containing compounds or as an oxidant for oxidative synthesis of more valuable organics (Krylov and Mamedov, 1995; Xu and Moulijn, 1996). The heterogeneous catalysis has been extensively thought to be the desirable technique for CO₂ utilization. Especially, for the oxidative synthesis, the radical reactions have been demonstrated (Nishiyama and Aika, 1990). But, a difficulty faced in the regular catalytic conversion of carbon dioxide to usable chemicals is the industrial CO₂ emissions containing "poisonous" gases, e.g., SO_x. Although gas "scrubbing" is usually conducted first to eliminate the poisonous gases from flue gases, trace SO_x can still remain in the gases. Regarding this, some alternative technology should be investigated. The previous researches on the oxidative conversion of methane have indicated that the plasma radical reactions are quite similar to the heterogeneous catalytic radical reactions (Oumghar *et al.*, 1995), but the plasma way has a higher efficiency in initiating radicals. Reduction of CO₂ from flue gases using a corona discharge at the same time with reduction of SO_x and NO_x has also been performed by Higashi *et al.* (1985) and Xie *et al.* (1991). Maezono and Chang (1990) tried to produce the commercial CO by reduction of CO₂ from combustion gases using dc corona torches. The plasma promoted catalytic reduction of CO₂ from flue gases has also been reported (Jogan *et al.*, 1993). The oxidative synthesis of aldehydes from methane and carbon dioxide by gas discharges has been reported as early as 1930s (Finlayson, 1935). A gas mixture containing 58% methane and about 33.3% carbon dioxide was used for such a synthesis in the temperature range of 25°C to 500°C. No further mechanism analysis was reported. Exactly, carbon dioxide can contribute one of its two oxygen atoms for oxidative synthesis by electronic dissociative attachment reactions:



The O⁻ and some metastable states of O have been well-known as active oxygen species for oxidative synthesis of organics (Oumghar, *et al.*, 1995). Gas discharge (glow, corona, arc and silence discharges) is an abundant resource of free radicals. The potential to develop a technique, in which oxidative synthesis of high-valued hydrocarbons together with removal of CO₂, NO_x and SO_x is very economically attractive. The by-product of such a technique is carbon monoxide, which can be also applied for organic synthesis, e.g., F-T synthesis. In this paper, the results of oxidative methane conversion to ethane and ethylene using CO₂ as an oxidant by streamer corona discharge is reported.

EXPERIMENTAL APPARATUS AND PROCEDURE

The quartz tube reactor (with an I.D. of 6 mm and a tube length of 600 mm) for the streamer corona discharge synthesis consists of two electrodes. The top wire electrode and the lower cylindrical hollow electrode with a diameter 1 mm less than the inner diameter of the quartz tube is shown in figure 1. The gap between the two stainless steel electrodes is 12 mm. The feed gas flow enters the upstream wire electrode and exits at the downstream one. The streamer corona discharge is generated between these two electrodes by an AC generator, with which a high voltage transformer is applied. The AC voltage provides an easy way to generate the streamer discharges, which takes place only when the voltage reaches a sufficiently high level during each half cycle, as shown in figure 2. 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 formation of new chemical species, like ethane, ethylene and carbon monoxide.

(Figures 1 and 2)

The feed gases CO₂, CH₄ and the dilution gas Helium are adjusted by controlling the flow rate. The effluent product gases run through a condenser to eliminate the moisture from the gas mixture. This gas mixture from condenser is then analyzed by an on line gas chromatography (HP5890) using a TCD detector. The gas pressure inside the reactor is slightly above the atmospheric pressure. All the experiments are initiated at room temperature (around 25°C). No attempt has been made to heat or cool the reactor externally. The gases from the gas cylinders

are mixed and then fed into the quartz reactor where a streamer corona discharge is generated. The input power to the high-voltage transformer is measured by recording the current and voltage.

With such an experimental device, the methane and carbon dioxide conversions are defined as:

Methane conversion = (moles of methane consumed/moles of methane introduced) * 100%

CO₂ conversion = (moles of CO₂ consumed/moles of CO₂ introduced) * 100%

The yield of C₂ hydrocarbons is as following:

Yield of ethane = 2 * (moles of ethane formed)/(moles of methane consumed) * 100%

Yield of ethylene = 2 * (moles of ethylene formed)/(moles of methane consumed) * 100%

RESULTS

All the corona discharge reactions are started at room temperature. The gas temperature reaches 200°C to 500°C depending on the different reaction conditions. The reaction temperature is measured by an insulated copper-constantan thermal couple situated upstream or downstream of reaction zone. The detail of such temperature measurements with plasma or electric field has been discussed elsewhere (Kingston and Jassie, 1988; Oumghar *et al.*, 1994).

The experimental results are shown in figure 3 to 6. Figure 3 shows the effect of applied voltage. When the applied voltage reaches 3.75kV, the gas discharge is initiated. The discharge reactions lead to the change in compositions. From figure 3, the reaction rate of methane and carbon dioxide have significant variations above 4.4 kV of the applied voltage. The composition of ethane increases with increasing in the applied voltage at the very beginning and then decreases, while the composition of ethylene increases slightly with increasing in the applied voltage. Figure 3 shows a significant increase in the composition of carbon monoxide. This suggests that part of C₂ products are destroyed to form CO by the increasing voltage. According to figure 3, it is not suggested that high voltage should be applied if the favorable C₂ products can not be moved out of the discharge reactor quickly.

(Figures 3, 4, 5 and 6)

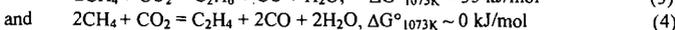
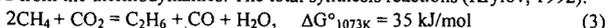
The effect of CO₂/CH₄ ratio is shown in figure 4. From reactions (1) and (2), more CO₂ in the feed will generate more active oxygen species for methane conversion. This has been demonstrated in figure 4. The conversion of CO₂ and CH₄ monotonically increase with increasing amount of carbon dioxide when the partial pressure of methane is kept constant. The yield of ethane decreases with increasing CO₂/CH₄ ratio. This means ethane has been converted to form some different species. The yield of ethylene shows a maximum when the CO₂/CH₄ ratio is equal to 2. The decrease in yield of ethylene suggests that an increase in the amount of the oxidant, CO₂, leads to the complete oxidation of hydrocarbons.

Figure 5 shows the effect of flowrate on the discharge reactions. The high flowrate results into a short residence time. The experimental results demonstrate that a higher yield of ethylene occurs at the lower flowrate or longer residence time. The conversion of CO₂ and CH₄ and the yield of ethylene decrease with the increase in the flowrate, but the yield of ethane increases. This suggests that ethane is a primary product and ethylene is the secondary product, which is formed by the oxidative of dehydrogenation of ethane. The same conclusion has also been drawn from figures 3 and 4, and can be further confirmed by the effect of frequency.

The streamer corona discharge generated by AC electric field is characterized with the temporary DC corona discharge, established within each half-cycle, as shown in figure 2. The effect of frequency is thought to be on the duration of each temporary DC corona discharge. Experimental results shown in figure 6 shows that the long duration (low frequency) is disfavorable for the yield of ethane and ethylene. The yield of ethane decreases with decreasing the frequency, but the yield of ethylene shows a maximum at frequency of 70Hz. This suggests that ethane is converted to ethylene at the lower frequencies, while at too low frequencies (less than 70 Hz) ethylene is also converted and complete oxidation occurs. The largest change in conversion of CO₂ and CH₄ is observed at the frequency of 70 Hz.

DISCUSSION

Here, we have experimentally confirmed that the streamer corona discharge oxidative coupling of methane using CO₂ as an oxidant is much more effective than the heterogeneous way, by which the yield of C₂ hydrocarbons was limited to less than 9% because of the difficulty in activation of catalysts (Nishiyama and Aika, 1990; Xu and Moulijn, 1996). This can be explained from the thermodynamics. The total synthesis reactions (Krylov, 1992):



Both these reactions are a little thermodynamically unfavorable, especially the first one. A high reaction temperature is expected for these two reactions with limited C₂ yield, if the regular catalytic way is employed. Other thermodynamically favorable reactions of CO₂ and CH₄, e.g., syngas (CO + H₂) formation, will compete with these C₂ formation reactions such regular catalytic techniques at sufficiently high temperatures. Considering this, the plasma can be

applied for enhancing the competitiveness of reactions (3) and (4). Also, from the thermodynamic point of view, the plasma will be useful for two classes of systems (Veprek, 1972): systems in which the reaction is allowed thermodynamically but hindered kinetically, and systems with which the reaction does not proceed due to an extreme chemical equilibrium constant in the absence of plasma. Reactions (3) and (4) would be covered by the first system. For this kind of reactions, a weak discharge, e.g., streamer discharge, can promote greatly the reactions. Such weak discharge promoted reactions are characterized themselves with low gaseous temperature and high electronic temperature. And, as the reaction temperature was experimentally measured to be less than 500°C, and according to researches on methane pyrolysis (Holmen *et al.*, 1995), no direct methane conversion was generated under 1000°C, therefore we may exclude the possibility of methane pyrolysis to higher hydrocarbons during our experiments. Basically, in our discharge system, a streamer corona discharge is applied to initiate the reactions. The streamer discharge, as mentioned before, has been known to produce electrons with electron energy of about 6eV (Eliasson and Kogelschatz, 1991), and such a low energy is insufficient to activate the kinetically inert methane molecule which possesses an appearance potentials of ions of around 12eV (Sorensen, 1995) although methane was passed directly through the discharge. The initiation reactions are thought to be the streamer corona-induced plasma decomposition of CO₂ as described in reactions (1) and (2). Such formed oxygen species, O[•] or O with some excited state or metastable state is very active for the coupling reactions and can lead to the products observed. The main reactions responsible for ethane, ethylene and carbon monoxide are as follow:

a. Methane Radical Formation:



b. Ethane Formation:



c. Ethylene Formation:



d. H₂O Formation:



e. CO Formation:



CONCLUSION

CO₂ formation is a significant cause of greenhouse effect. Methane contributes also to the greenhouse effect. The combination of conversion of methane and carbon dioxide to more useful chemicals has potential industrial applications. Regarding these, we presented a streamer discharge system to oxidatively convert methane to ethylene using CO₂ as an oxidant. The results achieved right now shows the following:

(1) Conversions of methane and carbon dioxide and yield of ethylene increase with increasing input voltage and increasing CO₂ amount in the feed. The increasing CO₂ composition, however, will reduce the yield of C₂ hydrocarbons.

(2) The low flowrate leads to large conversions of methane and carbon dioxide and high yield of ethylene.

(3) The low frequency results in large conversions of methane and carbon dioxide but the maximum yield of ethylene occurs at the frequency of 70 Hz.

(4) All the experiments right now come to an end that ethylene is a second product.

REFERENCES

- Eliasson B. and Kogelschatz U. Nonequilibrium volume plasma chemical processing. *IEEE Trans. on Plasma Sci.*, 19, 1063., 1991
- Finlayson D. Manufacture of aliphatic aldehydes. US Patent 1,986,885
- Higashi M., Sugaya M., Ueki K. and Fujii K. Plasma processing of exhaust gas from a diesel engine vehicle, in *Proc. Int. Conf. on Plasma Chem.*, 2, 366., 1985.
- Holmen A., Olsvik O. and Rokstad O.A. Pyrolysis of natural gas: chemistry and process concepts. *Fuel Processing Tech.* 42, 249.,1995
- Jogan K., Mizuno A., Yamamoto T. and Chang J.-S. The effect of residence time on the CO₂ reduction from combustion flue gases by an AC ferroelectric packed bed reactor. *IEEE Trans. on Industry Applications*, 29(5), 876., 1993.

Kingston H.M. and Jassie L.B. Monitoring and predicting parameters in microwave dissolution. In: *Introduction to Microwave Sample Preparation*. Kingston H.M. and Jassie L.B., ed., ACS, Washington, DC, 1988.

Krylov, O.V. Methods for increasing the efficiency of catalysts for the oxidative condensation of methane. *Russian Chem. Rev.*, 61, 851.,1992.

Krylov O.V. and Mamedov A.Kh. Heterogeneous catalytic reactions of carbon dioxide. *Russian Chemical Reviews*, 64(9), 877., 1995.

Lee J. and Grabowski J.J. Reactions of the atomic oxygen radical anion and the synthesis of organic reactive intermediates. *Chem. Rev.*, 92, 1611.,1992

Maezono I. and Chang J.-S. Reduction of CO₂ from combustion gases by dc corona torches. *IEEE Trans. on Industry Applications*, 26(4), 651., 1990.

Nishiyama T. and Aika K.-I. Mechanism of the oxidative coupling of methane using CO₂ as an oxidant over PbO-MgO. *J. of Catalysis*, 122, 346., 1990.

Oumghar A., Legrand J.C., Diamy A.M. and Turillon N. Methane conversion by an air microwave plasma. *Plasma Chemistry and Plasma Processing*, 15(1), 87., 1995.

Oumghar A., Legrand J.C., Diamy A.M., Turillon N. and Ben-Aim R.I. A kinetic study of methane conversion by a dinitrogen microwave plasma. *Plasma Chemistry and Plasma Processing*, 14, 229., 1994.

Sorensen S.L., Karawajczyk A., Stromholm C. and Kirm M. Dissociative Photoexcitation of CH₄ and CD₄. *Chem. Phys. Letter*, 232, 554.,1995

Veprek, S. Chemical Evaporation and Deposition of Solids in a non-Isothermal Plasma. *J. of Crystal Growth*, 17, 101., 1972

Xie Z., Jogan K. and Chang J.S. The effect of residential time on the reduction of CO₂ in combustion flue gases by a corona torch. in *Conf. Rec. of IEEE-IAS Meeting*, 814., 1991.

Xu X.-D. and Moulijn J.A. Mitigation of CO₂ by chemical conversion: Plausible chemical reactions products. *Energy & Fuels*, 10, 305., 1996.

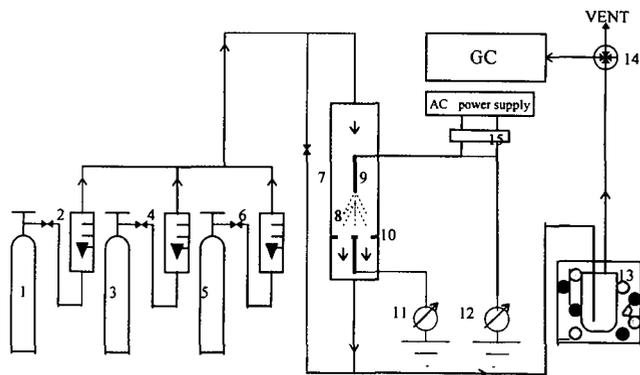


FIGURE 1 SCHEMATIC OF EXPERIMENTAL SETUP

- | | | | |
|----------------------------|--------------------------|--------------------|----------------------|
| 1,3,5 Gas Cylinders | 2,4,6 Flow Meter | 7 Reactor | 8 Streamer Discharge |
| 9 Wire Electrode | 10 Cylindrical Electrode | 11 Current Meter | 12 Voltage Meter |
| 13 Condenser(with dry ice) | 14 Multiway Value | 15 H.V.Transformer | |

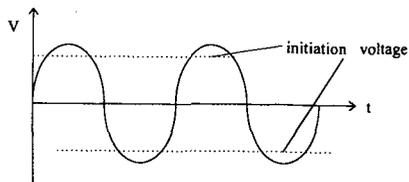


Figure 2 The AC Voltage

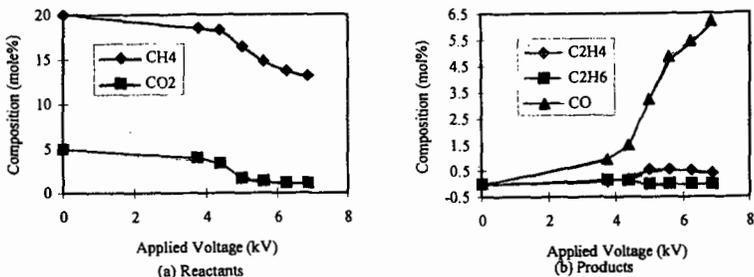


Figure 3 The effect of applied voltage

Flowrate : 100 ml/s Frequency: 60 Hz CO₂/CH₄: 4 (0.2 atm./0.05 atm.) Total Pressure: 1 atm

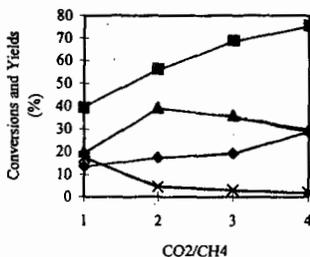


Figure 4 Effect of CO₂/CH₄

Flowrate : 100 ml/s Frequency: 60 Hz
 CH₄ Partial Pressure: 0.05 atm Total Pressure: 1 atm
 Applied Voltage: 5.6kV

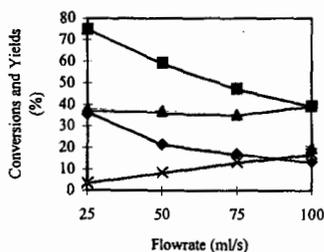


Figure 5 Effect of flowrate

Frequency: 60 Hz Applied Voltage: 5.6kV
 CO₂/CH₄: 4 (0.2 atm./0.05 atm.) Total Pressure: 1 atm

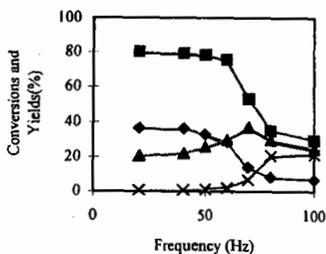


Figure 6 Effect of frequency

Flowrate : 100 ml/s Applied Voltage: 5.6kV
 CO₂/CH₄: 4 (0.2 atm./0.05 atm.) Total Pressure: 1 atm