

Methanol Production in AC Dielectric Barrier Discharge

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Abstract

Non-equilibrium plasma was generated in a dielectric barrier discharge for conversion of methane to higher hydrocarbons and methanol. Experiments were carried out at atmospheric pressure and ambient temperatures. Activation of methane molecules led to the production of C₂ hydrocarbons and methanol. The effect of applied voltage, residence times, and feed mixtures such as helium and oxygen on methane conversion and product selectivity was studied. Our results show that conversion increases with increasing voltage and residence time while product selectivity is independent of the applied voltage. Methane conversion increases significantly by introduction of oxygen in the feed stream. Inclusion of oxygen leads to the formation of methanol.

Keywords:

methanol, methane conversion, DBD, plasma discharge, non-equilibrium

1. Introduction

Plasma processes have recently been utilized in many chemical reactions for the production of higher value hydrocarbons from natural gas [1-7]. The direct synthesis of hydrocarbons from methane is not feasible and the conventional methods of partial and total oxidation of methane have poor yields [8,9].

The catalytic reforming of methane has several drawbacks, including high temperature conditions and rapid oxidation, since the product is oxidized faster than methane itself over the catalyst [10], which leads ultimately to the deactivation of catalysts.

Plasmas are good sources for generating active species, including electrons, ions, and radicals. Plasmas have advantages over other processes in realizing unfavorable reactions and also overcome the problem of the high temperature required by catalytic process [11]. One important type of plasma is the non-equilibrium plasma in which the electron mean energies are considerably higher than those of the background gas. The energy efficiency in non-equilibrium plasma is high because the energetic electrons collide with background neutral atoms or molecules and result in high dissociation and ionization of background gas. We have conducted experiments using an ac and a dc corona discharge reactor to generate non-thermal plasma for the oxidative conversion of methane in an atmospheric pressure. In this technique, free radicals are formed by reaction of methane

with negatively charged oxygen, created in the corona discharge. To enhance the conversion of methane to other products, we have also used a dielectric barrier. In this scheme, the discharge plasma is generated through very short-lived successive micro arcs, which are randomly initiated through out the discharge region. The dielectric barrier discharge (DBD) provides a sufficiently high breakdown potential and thus electrons can reach to higher energies. In this article, we present the results of a DBD plasma methane conversion, which have been concentrated on determination of appropriate conditions for the production of light higher hydrocarbons and methanol.

2. Experimental set-up

The discharge reactor consists of a 10 mm inside diameter quartz tube, which also serves as a dielectric barrier. Two electrodes, one made of stainless steel and the other made of aluminum foil make the anode and the cathode of the discharge. The aluminum foil is tightly wrapped around the quartz tube, which has a 12 mm outer diameter. The 2 mm in diameter stainless steel rod placed on the symmetric axis of the tube. The active reaction volume of discharge is approximately 12 cm³. Figure 1 illustrates the discharge reactor. The plasma discharge is created either by a high voltage 70 kV dc power supply or by a 50 kV, 50 Hz ac power supply with a high voltage transformer. In this article, we

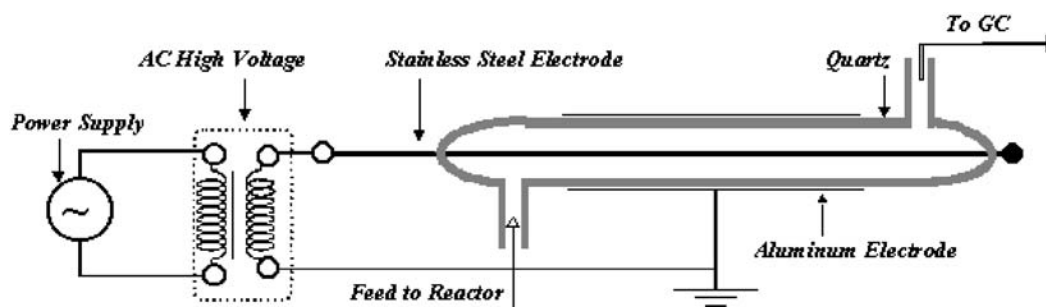


Fig. 1 DBD plasma reactor.

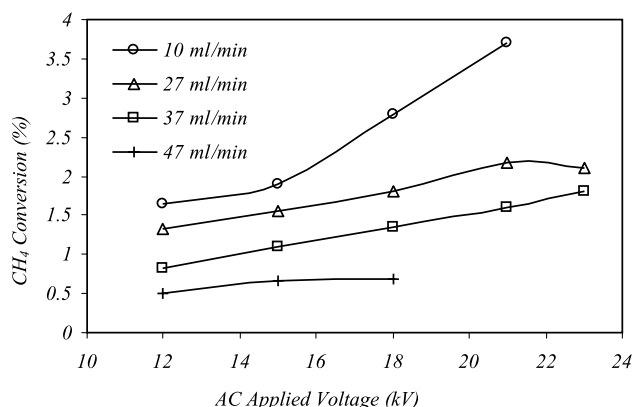


Fig. 2 Effect of applied voltage on methane conversion at different flow rates.

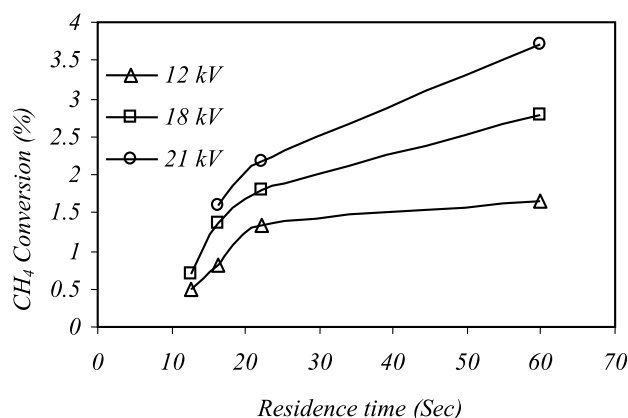


Fig. 3 Effect of residence time on the methane conversion at three different applied voltages.

report the results of experiments conducted only with the ac supply. The feed gases, methane, helium, and oxygen were introduced into the discharge system via three mass flow controllers. The feed gases were analyzed by an on line gas chromatography using a thermal conductivity detector (TCD).

The exhaust gases from the reactor were analyzed by the gas chromatograph using a pro-pack column in series with the molecular sieve.

3. Results and discussion

We first conducted a series of experiments using pure methane feed to determine the achievable degree of direct activation of methane. The effects of the applied voltage on selectivity (the percentage of methane converted to a specific product) as well as the methane conversion (the fraction of methane converted to other products) at different flow rates were investigated. The measurements of the product were taken at constant frequency of 50 Hz with applied voltages up to 23 kV. Figure 2 shows the effect of varying the applied voltage on methane conversion at different flow rates.

The conversion of methane increases with an increase in the applied voltage. As the external voltage increases, the internal electric field across the region between the anode and the cathode goes up. Therefore, the number of energetic electrons within the discharge gap gets larger. As the number density of high-energy electrons increases, more collisions

between methane molecules and those electrons take place. Thus the probability of breaking the bond between the carbon and hydrogen in the methane molecule becomes higher and the degree of dissociation and conversion increases. The effect of varying the flow rate on conversion at different voltages is best signified in Fig. 3, which is the plot of the conversion as a function of residence time. At higher flow rates, the methane conversion is lower. This is due to the lower residence time and the fact that each methane molecule has a lesser chance of having a successful interaction with energetic electrons. This can be clearly seen in Fig. 3, as the residence time increases, the conversion goes up especially at higher voltages.

In these series of experiments, we only observed the production of C₂ hydrocarbons. The absence of higher hydrocarbons may be attributed to the short residence times of the reactions. Figure 4 shows the distribution of the product selectivity as a function of the applied voltage at a methane flow rate of 10 mL/min. Ethane is the major product and the figure clearly shows that increasing the applied voltage has almost no effect on the selectivity.

In the second series of experiments, helium and oxygen were added to the feed to determine the effect of their presence on methane conversion and product selectivity. First helium alone was added to the methane feed. We then added oxygen to the feed and left helium as a diluent in the mixture.

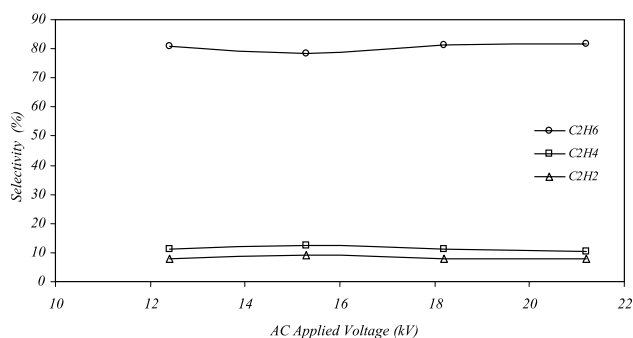


Fig. 4 Product selectivity as a function of the applied voltage.

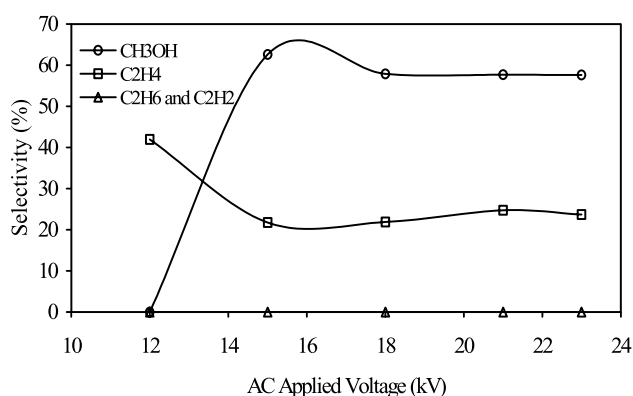


Fig. 5 Product selectivity as a function of applied voltage in the presence of oxygen.

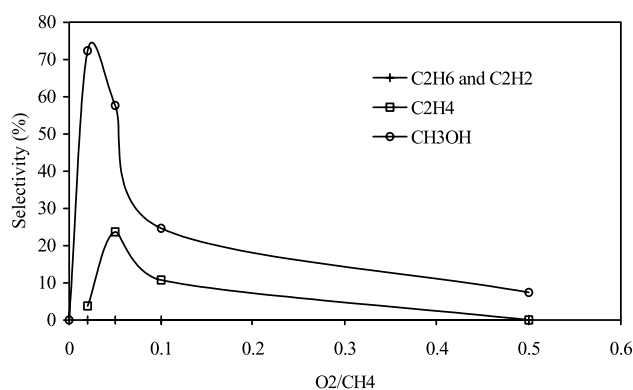


Fig. 6 Effect of oxygen to methane ratio on product selectivity.

The mixture consisted of different ratios of methane to helium and oxygen. Once again, the applied voltage varied up to 23 kV and the total flow rate was maintained at 100 mL/min.

The same experiments with similar conditions as previous series were performed. The effect of adding oxygen to the methane feed is depicted in Figs. 5 and 6.

Figure 5 shows the ethylene and methanol selectivity plots at various voltages. This figure indicates a decrease in the ethylene concentration as the voltage is increased from 12 to 15 kV and from which point it levels off. In contrast, as

the ethylene concentration decreases, methanol follows an increasing trend and peaks off around 15 kV from which point it reaches a saturation state.

As Fig. 6 shows inclusion of oxygen in the reaction system causes further activation of the methane molecule and also plays an important role in the oxidative coupling of methane. These results suggest that conversion of methane and oxygen on one hand and selectivity of ethylene and methanol on the other hand all increase with decreasing flow rate and increasing residence time. One can argue that interaction of energetic electrons with oxygen results in generation of O_2^- and O^- , which in turn activate methane by separating hydrogen to form methyl radicals. Coupling of the methyl radicals produces C_2 hydrocarbons. Reaction of methane with O^- also generates OH^- , which once again couples to the methyl radicals to form methanol.

4. Conclusions

The results of our experiments show that the dielectric barrier discharge plasma is an effective method to activate and convert methane to higher hydrocarbons. Conversion rate increases by increasing the applied voltage and decreasing the flow rate of the methane gas. This can be attributed to an increase in the number of energetic electrons and also an increase in the residence time. Presence of oxygen has a significant effect on conversion and product selectivity. Existence of oxygen in the gas mixture, above certain voltages leads to the production of methanol. Although ethylene is the major product of the plasma process, once methanol is formed ethylene concentration starts decreasing by increasing the applied voltage. Methanol will eventually replace ethylene as being the leading product as the applied voltage increases.

References

- [1] C.J. Liu, R.G. Mallinson and L.L. Lobban, *Appl. Catal. A* **178**, 17 (1999).
- [2] C.J. Liu, L.L. Lobban and R.G. Mallinson, *J. Catal.* **179**, 326 (1998).
- [3] M.A. Malik and X.Z. Jiang, *Plasma Chem. Plasma Process.* **19**, 505 (1999).
- [4] S. Yao, T. Takemoto, F. Ouyang and E. Suzuki, *Energy Fuels* **14**, 459 (2000).
- [5] B. Eliasson, C.J. Liu and U. Kogelschatz, *Ind. Eng. Chem. Res.* **39**, 1221 (2000).
- [6] H.D. Gesser and N.R. Hunter, *Catal. Today* **42**, 183 (1998).
- [7] D.W. Larkin, T.A. Caldwell, L.L. Lobban and R. Mallinson, *Energy Fuels* **12**, 740 (1998).
- [8] P.S. Yarlagadda, L.A. Morton, N.R. Hunter and H.D. Gesser, *Fuel Sci. and Tech. Inst.* **5**, 169 (1987).
- [9] H. Zanthoff and M. Baerns, *Ind. Eng. Chem. Res.* **29**, 2 (1990).
- [10] C.J. Liu, A. Marafee, B. Hill, G. Xu, R. Mallinson and L.L. Lobban, *Ind. Eng. Chem. Res.* **35**, 3295 (1996).
- [11] A. Huang, G. Xia, J. Wang, S.L. Suib, Y. Hayashi and H. Matsumoto, *J. Cat.* **189**, 349 (2000).