Direct Conversion from Methane to Methanol by a Pulsed Silent Discharge Plasma

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Abstract

A direct conversion of methane to methanol with a minimum required energy consumption could be one of the key technologies in the highly efficient utilization of fossil fuel energies, because low quality or low temperature energy sources corresponding to 100 ℃ can be used and regenerated through reforming of methanol to hydrogen. For this purpose, a new technique of synthesizing methanol directly from methane/oxygen mixture has been developed by use of a highly nonequilibrium pulsed silent discharge plasma at atmospheric pressure and temperature, and various effects of oxygen concentration, reaction time and discharge parameters on the conversion efficiency and reaction selectivity have been clarified. Further, reaction mechanisms in this type of plasma have been discussed by time-dependent optical emission measurements of CH radicals during the period of streamer current just after the sharp rise of pulsed voltage. Rather high values of 2.4 % and 32.6 % for methanol yield and selectivity, respectively, have been successfully obtained in one-path experiment and they could be largely enhanced by optimizing the reacting conditions, combining this technique with catalytic reactions and introducing a multi-recirculating reaction system.

1. Introduction

Fossil fuels possess, in general, a very high exergy up to 95% of the heat value as chemical energy and more efficient sophisticated system of utilizing them than just burnt directly to form thermal energy should be established to save fossil resources and to protect the global environment. It is proposed that the exergy loss through the combustion process could be largely reduced by introducing a reforming process from hydrocarbon fuels to hydrogen before combustion. Especially, a direct conversion from hydrocarbons such as methane to methanol with a minimum required energy consumption could be one of the key technologies in this highly efficient utilization of fossil fuel energies, because low quality or low temperature energy sources corresponding to the temperature level of 100 ℃, in principle, can be used and regenerated in the reforming process from methanol to hydrogen, whose exergy loss through the combustion process is the minimum among various hydrocarbon fuels. In other words, this direct conversion technology could have a significant contribution to realize a new energy system of exergy regeneration [1].

The conventional method of methanol synthesis consists of successive two processes, reforming of hydrocarbon fuel to synthetic gases ($CO+H_2$ or CO_2+H_2) and then synthesis of methanol from them usually with the aid of catalytic reactions at high pressures [2],[3],[4],[5]. The former process is a strong endo-thermic reaction and needs large external energy supply. So, the conventional process of methanol synthesis is not applicable in the system of highly efficient energy utilization. On the contrary, a direct conversion from methane to methanol with minimum energy consumption is a very attractive process. Although this direct conversion from methane to methanol has been investigated for many years mainly by use of catalytic reactions [6],[7],[8], a good success has not been attained yet from the engineering stand point of view due to a low conversion ratio and degradation of catalysis. In this study, a new technique of synthesizing methanol directly from methane/oxygen mixture has been developed by use of a highly nonequilibrium pulsed corona silent discharge plasma at atmospheric pressure, and various effects on the conversion efficiency and reaction selectivity have been clarified. Here, the partial oxidation of methane to methanol can be realized by an effective formation of radical species by high energy electron impacts keeping a room temperature of reacting gases, and the square-pulsed high voltages with sharp voltage rising and falling have made it possible to ralize much higher energy input efficiency into a reacting plasma field than that in the conventional silent discarge. Although we have already confirmed that the conversion ratio can be much improved by a simultaneous use of catalysis [9], this study aims at the improvement of methanol yield, reaction selectivity and reaction rate only by the control of plasma chemical reactions.

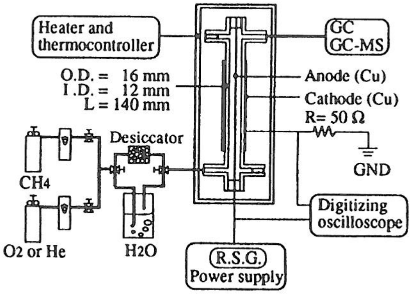

Fig. 1 Experimental system

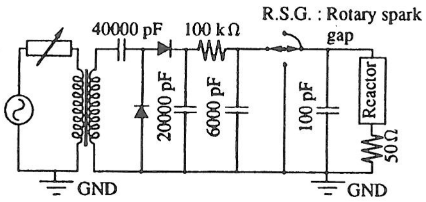

Fig.2 Electric power source circuit for pulse generation

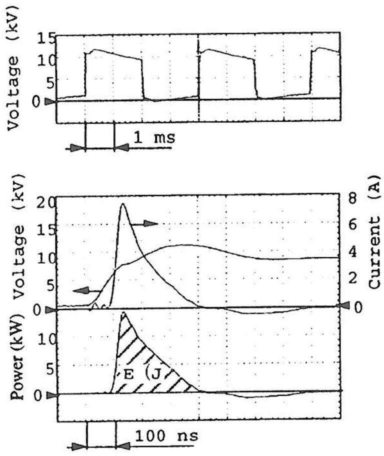

Fig. 3 Waveforms of voltage, current and input power (the lower figure shows the waveforms just after the sharp rise of pulsed voltage)

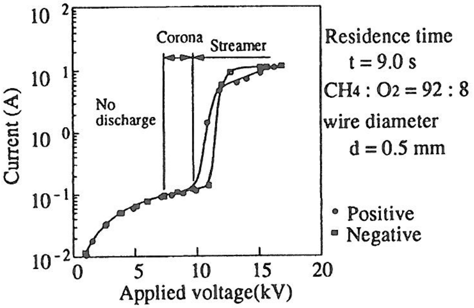

Fig. 4 V-I characteristics of square-pulsed silent discharge

2. Experimental System and Procedure

The experimental system used in this study is shown in Fig. 1. The cylindrical reactor is made of a pyrex or quartz glass tube of 140 mm in length, 16 mm and 12 mm in outer and inner diameter, respectively, and a thin wire electrode of positive high voltage at the center of the cylinder to form a corona discharge. As the effect of electrode material of this wire is not so significant [10], a copper wire of 0.5 mm in diameter is used in this experiment. The glass tube surrounded by copper sheet works as a dielectric layer to form a silent discharge. The temperatures of the reactor and gas lines are kept to be 100 ℃ to avoid condensation of water vapor and other products. The electric power source of a square-pulsed high voltages is formed using a rotary spark gap (R.S.G.) method [11] as shown in Fig. 2. The pulse frequency and voltage range are 250 Hz and 3 - 17 kV, respectively. Gaseous products synthesized through the plasma chemical reactions and their concentrations are quantitatively measured by a gas chromatograph and a quadrapole mass spectrometer. Voltage and current waveforms and input power are simultaneously measured by a fast digitizing oscilloscope. Representative waveforms of voltage, current and input power thus obtained are shown in Fig. 3, and the relation between the peak values of current and voltage is shown in Fig.4. Effective plasma chemical reactions actually ocurred in the streamer type discharge regime, and so applied voltages of around 15 kV are used in most experiments keeping the input power to be 0.5 W.

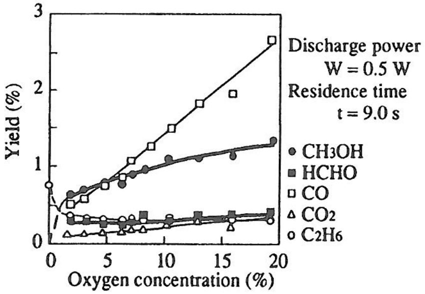

Fig. 5 Effect of initial oxygen concentration on products yield

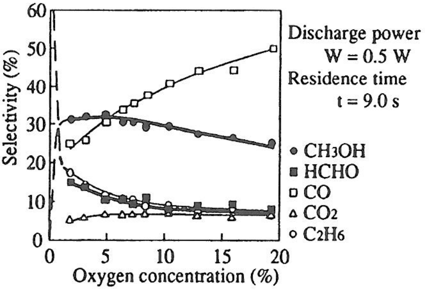

Fig. 6 Effects of initial oxygen concentration on products selectivity

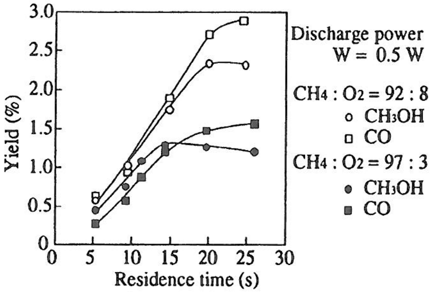

Fig. 7 Effect of residence time on methanol yield

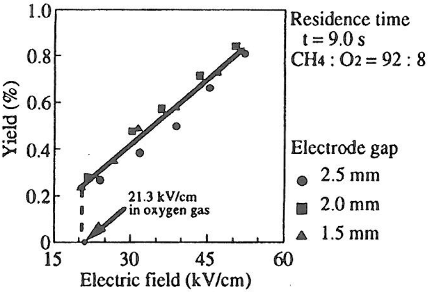

Fig. 8 Effective electric field for methanol formation

3. Results and Discussions

3.1 Effects of Various Factors on Methanol Yield and Selectivity

(a) Effect of Oxygen Concentration

Changes of yield and selectivity of various products with the oxygen concentration are shown in Figs. 5 and 6, respectively, for the residence time of 9.0 s. Major products are methanol and carbon monoxide. Even with the small amount of oxygen, methanol is effectively formed, and maximum value of methanol selectivity of 32.6 % has been obtained at the oxygen concentration of around 5 %. For higher oxygen concentrations, selectivity of carbon monoxide becomes larger than that of methanol. The partial oxidation of methane to methanol needs the low concentration of oxygen in the source gas mixture.

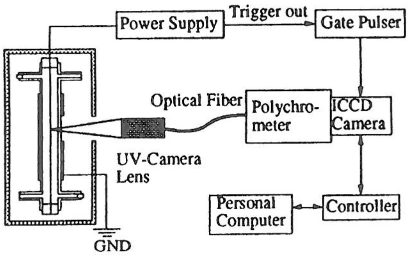

Fig. 9 Measurement system for optical emission intensity

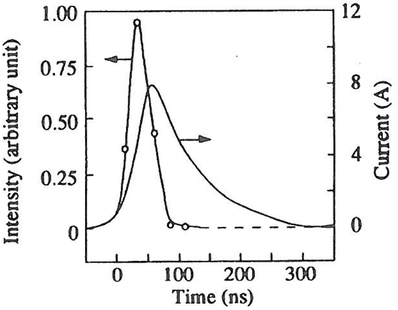

Fig. 10 Time-dependent changes of optical emission intensity from CH radicals

(b) Effect of Residence Time

The methanol yield increases with the increase of residence time as shown in Fig. 7, although it is becoming saturated after the residence time of 20 s. This is due to that more than 80 % of oxygen should have been consumed. Although the maximum methanol yield is 2.4 % in this one-path experiment, its value could be largely enhanced by using a multi-recirculating reaction system with adding a small amount of oxygen at each reaction path.

(c) Effect of Electric Field

The reactor system shown in Fig. 1 with a thin wire electrode at the center has a strongly non-uniform electric field and is not suitable to examine the pure effect of electric field. By use of a thick cylindrical center electrode which is a little smaller than the outer glass tube, a almost uniform electric field in the reaction zone has been realized. The electrode gap was changed to be 1.5, 2.0 and 2.5 mm. The effect of electric field on methanol yield thus obtained is shown in Fig. 8. All data clearly coincide almost on the one linear line for various different combinations of applied voltage and electrode gap. Below the electric field of 21.3 kV/cm, which corresponds to that of breakdown in pure oxygen gas, almost no methanol yield has been observed. This result implies the importance of dissociation of oxygen molecules forming oxygen atoms and ions for the effective methanol synthesis.

3.2 Time-Dependent Optical Emissin Measurement of CH Radicals

The time-dependent change of optical emission from CH radicals (wave length : 314.4 nm) near the center electrode has been measured by use of an optical measurement system as shown in Fig. 9. The result is shown in Fig. 10 with the current waveform just after the sharp rise of pulsed voltage. The CH emission is observed only at the first part of the pulse current and then sharply diminishes at the latter part where the electron energy is not enough to dissociate methane to form CH radicals. In other words, the sharp rise of squared pulse voltage itself should have played an important role in the effective formation of key radical species and actually realized a rather high performance in the direct conversion of methane to methanol.

4. Conclusions

1) A direct conversion from methane to methanol at atmospheric pressure and temperature has been successfully realized by a newly developed technique using a highly nonequilibrium plasma obtained by a square-pulsed corona silent discharge.
2) Various effects of oxygen concentration, reaction time and discharge parameters on the conversion efficiency and reaction selectivity have been clarified and rather high values of 2.4 % and 32.6 % for methanol yield and selectivity, respectively, have been obtained in one-path experiment.
3) Oxygen atoms or ions are the most important radical species to control the reaction process and selectivity of methanol synthesis.
4) The sharp rise of squared pulse voltage itself plays an important role in the effective formation of key radical species and actually realizes a rather high performance in the direct conversion of methane to methanol.

Acknowledgement

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