Methane Conversion Using a High-Frequency Pulsed Plasma: Important Factors

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Factors influencing methane conversion in a high-frequency pulsed plasma were studied. Pulse frequency is the most important factor influencing acetylene selectivity and methane conversion rate that represents electric energy efficiency. The high pulse-frequency plasma promotes acetylene formation and improves methane conversion rate. With increasing pulse voltage, acetylene selectivity increases, but methane conversion rate decreases. The temperature of the background methane gas does not markedly influence methane conversion in a temperature range of 20 to 200°C. A co-axial cylindrical reactor with a fine central anode is favorable to practical use of methane conversion.

Introduction

Progress in plasma physics has been characterized in the last several decades by remarkable advances in knowledge of electrons, ions, atoms, molecules, and related chemical reactions. Much more attention has been paid to nonthermal pulsed plasma in chemistry due to its high-energy efficiency. Its application in environmental protection has specially expanded. Recent progress in plasma chemistry was reviewed (Chang et al., 1991; Eliasson and Kogelshatz, 1991). Methane plasma conversion was also summarized elsewhere (Bhatnagar and Mallinson, 1995; Thanyachotpaiboon et al., 1998; Zhou et al., 1998). The outline of methane conversion using a pulsed plasma as a kind of nonthermal plasma was given in this journal under the title "Methane Conversion Using a High-Frequency Pulsed Plasma: Discharge Features" (Yao et al., 2000a). This article will help readers to understand the pulsed discharge of methane at atmospheric pressure and room temperature.

In the present study, we focus on a pulsed plasma as a chemical process. For the practical use of a pulsed plasma in industry, we shall have to investigate experimentally factors influencing methane conversion, such as pulse voltage, pulse frequency, temperature of the background gas, and reactor configuration.

Experimental

Figure 1 shows the experimental setup that was described in detail elsewhere (Yao et al., 2000a). The pulse voltage was generated with a power supply and controlled by adjustment of the charging-system (CS) input voltage. Three co-axial cylindrical types of reactors were used (Table 1). Reactor A was used for investigating the influence of reaction temperature, pulse frequency, methane residence time, and pulse voltage on methane conversion. Reactors B and C were used especially for the investigation of the influence of reactor configuration and electrode arrangement on methane conversion. The temperature of the reactors was controlled with an electric heater with a heating zone of 30 cm and a uniformly heated zone of 20 cm. A thermocouple for temperature measurement was set at a central point of the outside surface of a quartz tube. After a 2-min plasma reaction, a 50–60-min halt

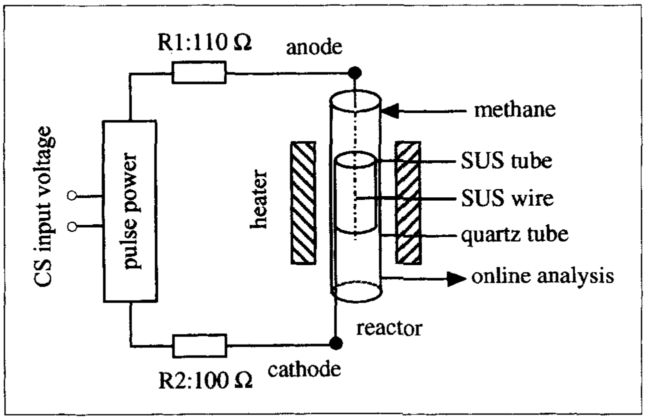

Figure 1. Pulsed plasma system.

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Table 1. Configuration of Each Reactor

Reactor	A	B	C
Cathode, stainless-steel tube (SUS 316) inner diameter (mm)	10	10	4
Anode, stainless-steel tube (SUS 316) diameter (mm)	0.5	2.9	0.5
Length (mm)	150	150	150

was required for analysis of the product, during which the reactor was reset at the initial temperature. All experiments were carried out at atmospheric pressure.

The energy injection rate, P_a in J/pps (pulses per second), into the background methane gas was calculated by Eq. 1 using pulse voltage V_i in volts and anode current I_{ai} in amperes at discharge time t in seconds:

$$P_a = \Sigma((V_i + V_{i+1})/2)((I_{ai} + I_{ai+1})/2)(t_{i+1} - t_i). \quad (1)$$

The methane conversion rate R (mol/J) that represents energy efficiency was calculated by Eq. 2.

$$R = \text{moles of methane converted in a minute}/(60\, F\, P_a) \quad (2)$$

Here, F is the pulse frequency in pps.

Results and Discussion

Influence of reaction temperature

The reaction temperature is an important factor for the gas-phase reaction. Therefore, its influence on both discharge and methane conversion was investigated first. Methane conversion increased when the reaction temperature increased up to 100°C and decreased obviously at a reaction temperature higher than 200°C (Figure 2). This decrease in methane conversion is due to the reduction in energy injection rate caused by a high reaction temperature (Figure 3). The pulsed plasma of air at a high temperature was reportedly easily broken down, resulting in the formation of pulsed streamer/spark discharge (Van Heesch et al., 1989). This implied that the resistance of background methane in the plasma zone decreases at a high reaction temperature. Our results showed that the resistance of background methane was at a level of 500–1000 Ω at room temperature, but dramatically dropped to a level of 50 Ω at 300°C. Most of energy is therefore consumed by resistors R1 (110 Ω) and R2 (100Ω) at 300°C. This also implied that there is a matching effect between pulse power supply and the load. Some basic studies on designs of pulse power supply and reactor in order to improve energy efficiency are now being undertaken.

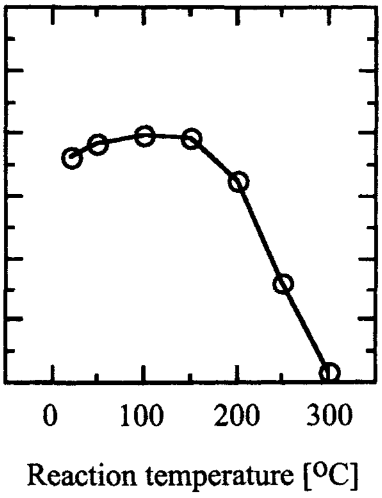

Figure 2. Methane conversion at various temperatures.

Methane conversion was carried out with reactor A at 6 kpps, 130 V CS input voltage, and 150 mL/min CH_4.

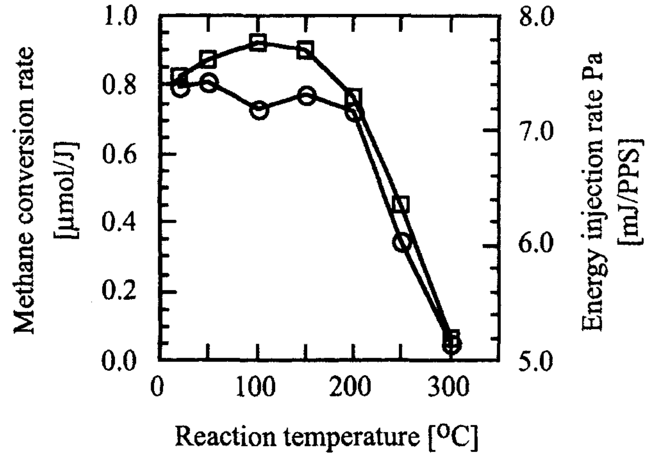

Figure 3. Methane conversion rate and energy injection rate as a faction of reaction temperature.

Conditions are the same as those in Figure 2. □ —Methane conversion rate: ○ —Energy injection rate.

The methane conversion rate peaked at 100°C and decreased remarkably when the reaction temperature increased from 200°C to 300°C (Figure 3), which suggested that a reaction temperature lower than 200°C is favorable for industrial methane conversion. Figure 4 shows the selectivity of each product at various reaction temperatures. The selectivity of each product didn't obviously change withing 20 to 200°C. The selectivity of acetylene decreased, but that of ethane and other high-carbon compounds such as propane increased when the reaction temperature was raised above 200°C. This result also explained that a reaction temperature lower than 200°C is advantageous to methane conversion.

Influence of pulse voltage

The electron energization that influences methane activation can be generally enhanced by increasing the strength of an electric field. Therefore, the relation of CS input voltage and methane conversion rate was investigated (Figure 5). The methane conversion rate was kept at a constant level in the input voltage range of 100–130 V, and decreased when the CS input voltage increased further. This indicated that a pulse power supply with a low pulse voltage yields high-energy efficiency. Since there is a minimum pulse voltage for the incep-

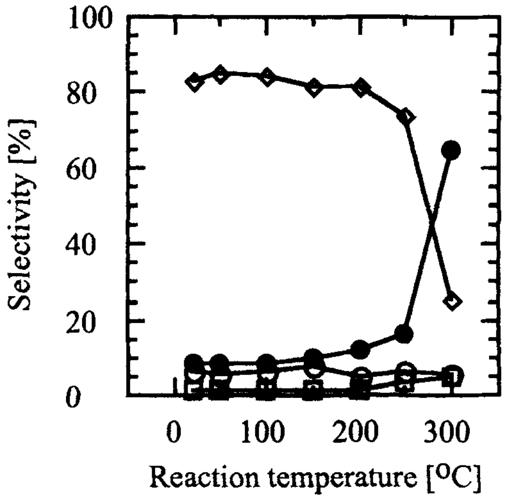

Figure 4. Selectivity of each product at various temperatures.

Conditions are the same as those in Figure 2. ◇—Acetylene; ○—ethylene; □—ethane; ●—other high-carbon compounds.

tion of the pulsed streamer or spark, the optimum pulse voltage is to be determined using these factors. Our results showed that the minimum CS input voltage at 6 kpps is 100 V, which corresponds to a peak pulse voltage of 6.9 kV under the condition without loads.

The selectivity of acetylene increased, but those of ethylene and ethane decreased with the increase in CS input voltage (Figure 6). This is because CH_4 could be activated to CH_2 or CH, rather than CH_3 at a high CS input voltage, since electrons energized by a high-strength electric field can activate CH_4 to CH_2 or CH, which contributes to the formation of acetylene.

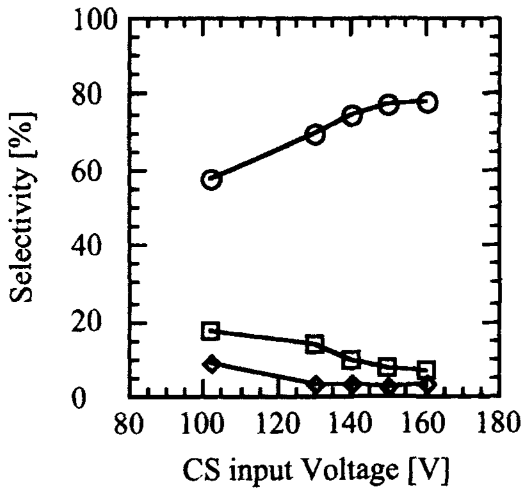

Figure 5. Selectivity of each product at various CS input voltages.

Methane conversion was carried out with reactor A at 4 kpps, 150 mL/min CH_4, and room temperature. ○—Acetylene; □—ethylene; ◇—ethane.

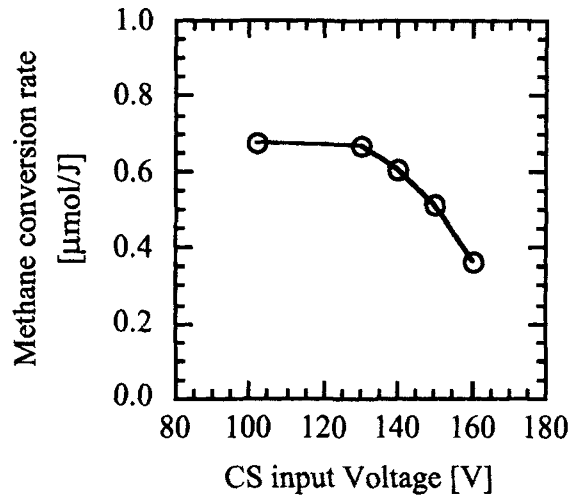

Figure 6. Methane conversion rate at various CS input voltages (conditions are the same as those in Figure 5).

Effect of pulse frequency

Methane conversion at a CS input voltage of 130 V was then investigated at various pulse frequencies. Acetylene selectivity increased dramatically to 92% at 8 kpps (Figure 7). Ethane selectivity decreased with increasing pulse frequency. Ethylene selectivity peaked at 4 kpps. The direction of the increase in acetylene selectivity and decrease in ethane selectivity implied that ethane is first formed and then dehydrogenated to acetylene and ethylene. Similarly, the decrease in ethylene selectivity also implied that ethylene is further dehydrogenated to acetylene. Methane conversion at a pulse frequency above 8 kpps yields carbon. This means that acetylene and CH radicals could be also further dehydrogenated.

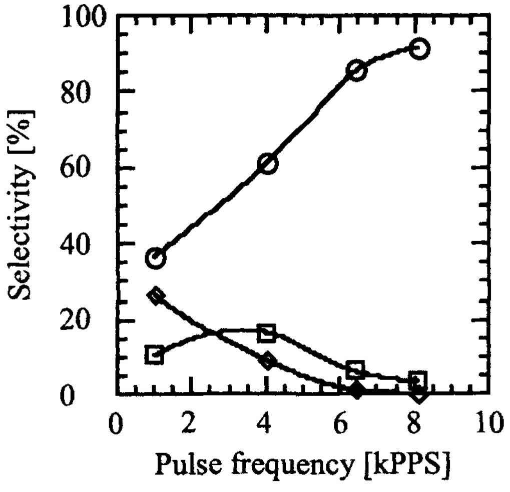

Figure 7. Selectivity of each product as a function of pulse frequency.

Methane conversion was carried out with reactor A at 130 V CS input voltage, 150 mL/min CH_4, and room temperature. ○—Acetylene; □—ethylene; ◇—ethane.

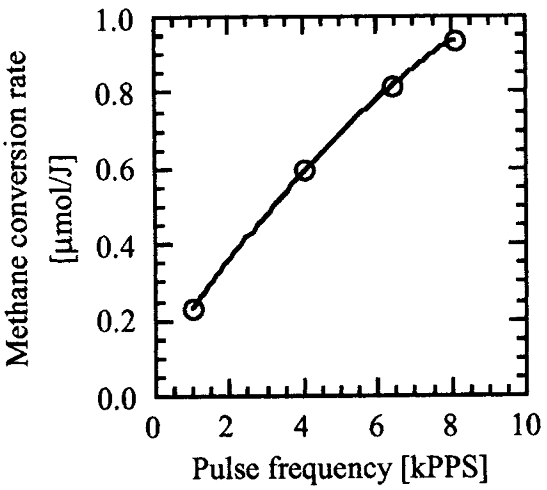

Figure 8. Methane conversion-rate improvement using a high pulse frequency (conditions are the same as those in Figure 7).

The methane conversion rate increased dramatically with increasing pulse frequency (Figure 8). The pulsed plasma consists of a pulsed corona and pulsed streamer or spark discharges. The energy used for ionization and stray capacitor charging in the pulsed corona discharge is about one-sixth to one-eighth of the total in a single pulse mode (Yao et al., 2000a). This energy would be decreased by the existence of ions at a high pulse frequency and used for methane conversion rather than methane ionization. This contributes to the methane conversion rate by a 17% increase at maximum. The methane conversion rate at 8 kpps was 4.2 times as high as that at 1 kpps (Figure 8), which suggested that some other factors, such as short discharge (pulsed streamer or spark) time and short rest time between two pulses, could promote methane conversion at a high pulse frequency.

Relation of residence time and methane conversion

The residence time is an important factor for a gas-phase reaction. Its influence on methane conversion was studied by changing the flow rate of methane. Acetylene selectivity decreased with the increase in methane flow rate, but the selectivities of ethane and ethylene increased (Figure 9). The methane conversion rate peaked at a flow rate of 200 mL/min (Figure 10). The gas residence time did not significantly influence methane conversion in comparison with the other factors, such as pulse frequency.

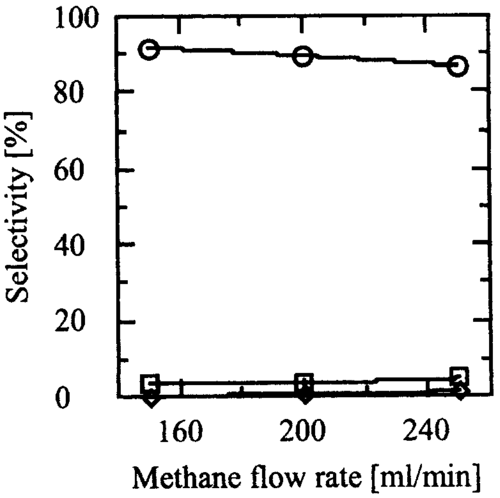

Figure 9. Influence of methane flow rate on selectivity of each product in methane conversion.

Methane conversion was carried out with reactor A at 8 kPPS, 130 V CS input voltages, and room temperature. ○ —Acetylene; □ —ethylene; ◇–ethane.

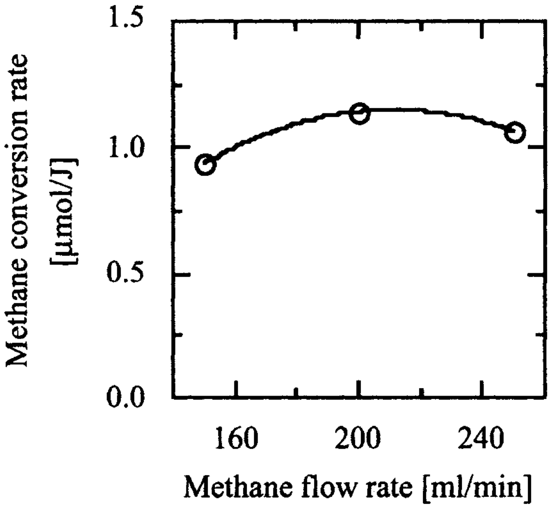

Figure 10. Methane conversion rate at various methane flow rates (conditions are the same as those in Figure 9).

Influence of reactor configuration and electrode arrangement

Finally, we used reactors A, B, and C to compare the influence of reactor configuration and electrode arrangement on methane conversion (Table 1). The results are shown in Figure 11. Methane conversion was carried out at various pulse frequencies and different CS input voltages due to the difference configurations. Methane conversion rate increased with increasing pulse frequency. Compared to reactor A, methane conversion rate using reactor B was higher at a pulse frequency below 6 kpps, but lower at a pulse frequency above 6 kpps. On the other hand, the streamer or spark-inception pulse voltage using reactor B was high than that using reactor A, since the anode diameter of reactor B was bigger than that of reactor A. The streamer or spark-inception pulse voltage could be reduced by using reactor C with a small cathode. The methane conversion rate using reactor C was, however, lower than when using reactor A.

The difference in methane conversion rate using these three reactors was due to the different configuration and electrode arrangements and different CS input voltages for different reactor configurations and electrode arrangements, since this difference has an influence on the methane conver-

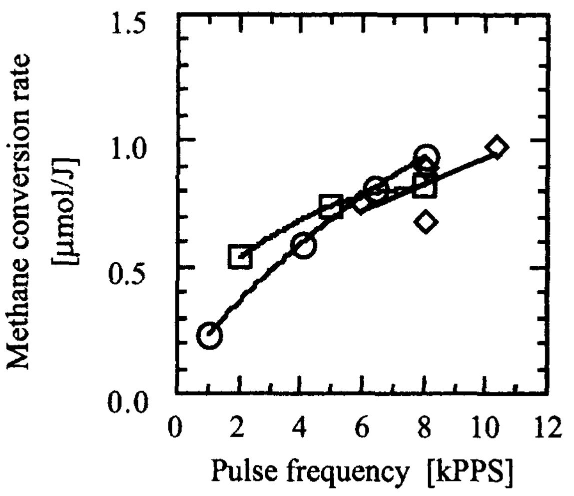

Figure 11. Methane conversion rates using reactors A, B and C as a function of pulse frequency.

Methane conversion was carried out at room temperature. ○—Reactor A: 130 V CS input voltage and 150 mL/min CH_4; □—reactor B: 170 V CS input voltage and 200 mL/min CH_4; ◇—reactor C: 100 V CS input voltage and 200 mL/min CH_4.

sion rate (Figure 5). Our findings generally suggested that a large-diameter reactor with a large-diameter anode, like reactor B, is not useful because of its low energy efficiency at a pulse frequency higher than 6 kpps. The co-axial cylindrical reactor with a cathode with an inner diameter of 4 mm used for reactor C or larger and a small central anode (such as 0.5 mm diameter) is appropriate for practical use in methane conversion.

Methane conversion in a pulsed plasma

As we reported, the anode current is almost the same as the cathode current in streamer or spark discharge (Yao et al., 2000a). This suggested that methane conversion enhanced by energized electrons in such a discharge is similar to pyrolysis. There are many discharge channels in the plasma zone. The methane temperature in the discharge channels reaches an order of 2500 K at maximum, as estimated with an equivalent single-channel model (Yao et al., 2000b).

In the discharge channels, the pyrolysis of CH_4 could be represented by sequential Reactions 3 to 6:

$$CH_4 + e \rightarrow CH_3 + H + e \tag{3}$$

$$CH_3 + e \rightarrow CH_2 + H + e \tag{4}$$

$$CH_2 + e \rightarrow CH + H + e \tag{5}$$

$$CH + e \rightarrow C + H + e \tag{6}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{7}$$

$$CH_2 + CH_3 \rightarrow C_2H_4 + H \tag{8}$$

$$CH + CH_3 \rightarrow C_2H_2 + H \tag{9}$$

$$CH_2 + CH_2 \rightarrow C_2H_2 + H_2 \tag{10}$$

$$C_2H_6 + H \rightarrow C_2H_5 + H_2 \tag{11}$$

$$C_2H_5 + H \rightarrow C_2H_4 + H_2 \tag{12}$$

$$C_2H_4 + H \rightarrow C_2H_3 + H_2 \tag{13}$$

$$C_2H_3 + H \rightarrow C_2H_2 + H_2 \tag{14}$$

$$C_2H_6 + e \rightarrow C_2H_5 + H. \tag{15}$$

Ethane is formed via reaction of CH_3 (Reaction 7). Ethylene is prepared from the reaction of CH_3 and CH_2 (Reaction 8) and dehydrogenations of ethane (Reactions 11 and 12). Acetylene can be produced directly from Reactions 9 and 10, in which CH_2 radicals play an important role in acetylene formation. On the other hand, as we described earlier, ethane and ethylene can be further dehydrogenated to ethylene and acetylene, respectively. This suggested that there are two paths for acetylene formation : one is C1 radical combination and the other is C2 dehydrogenation.

Since electrons play an important role in this kind of pulsed plasma, some dehydrogenation reactions of ethane, ethylene, and acetylene also may be electron-related reactions, such as Reactions 3 to 6 and 15.

Conclusions

Factors influencing methane conversion in a pulsed plasma were investigated. The pulse frequency is an important factor, significantly influencing methane conversion rate and acetylene selectivity. The methane conversion rate could be dramatically improved by using a high pulse frequency. The methane conversion rate also can be improved by using a low CS input voltage at which the pulsed plasma (pulsed streamer and spark discharges) could be developed. The co-axial cylindrical reactor of a cathode with an inside diameter larger than 4 mm and a small central anode would be suitable for practical use.

An arc plasma has a higher methane conversion rate (about 3.1 μmol/J) than the high-frequency plasma of this study, but its operation has difficulties, because the reaction temperature in the arc zone is higher than 5,000°C (Ibberson and Thring, 1969), at which the electrode would be unusable, and about several ten percentages of methane is converted to carbon black (Fey, 1979). The methane conversion rate using a high pulse frequency plasma is higher than other kinds of plasmas, such as microwave (Suib and Zerger, 1993) and silent plasma (Shepelev et al., 1993; Larkin et al., 2000). Methane conversion using our findings is practical, since it can be carried out at a high energy efficiency, room temperature, and atmospheric pressure.

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Literature Cited

Bhatnagar, R., and R. G. Mallinson, *Methane and Alkane Conversion Chemistry*, Plenum Press, New York (1995).

Chang, J. S., P. A. Lawless, and T. Yamamoto, "Corona Discharge Processes," *IEEE Trans. Plasma Sci.*, **19**, 1152 (1991).

Eliasson, B., and U. Kogelschatz, "Nonequilibrium Volume Plasma Chemical Processing," *IEEE Trans. Plasma Sci.*, **19**, 1063 (1991).

Fey, M. G., "Arc Heater Pyrolysis of Hydrocarbons," AIChE Meeting, Philadelphia (1979).

Ibberson, V. J., and M. W. Thring, "Plasma Chemical and Process Engineering," *Ind. Eng. Chem.*, **61**(11), 48 (1969).

Larkin, D. W., L. L. Lobban, and R. G. Mallinson, "Production of Organic Oxygenates in the Partial Oxidation of Methane in a Silent Electric Discharge Reactor," AIChE Meeting, Atlanta (2000).

Shepelev, S. S., H. D. Gesser, and N. R. Hunter, "Light Paraffin Oxidative Conversion in a Silent Electric Discharge," *Plasma Chem. Plasma Process.*, **13**, 479 (1993).

Suib, S. L., and R. P. Zerger, "A Direct, Continuous, Low-Power Catalytic Conversion of Methane to Higher Hydrocarbons via Microwave Plasmas," *J. Catal.*, **139**, 383 (1993).

Thanyachotpaiboon, K., S. Chavadej, T. A. Caldwell, L. L. Lobban, and R. G. Mallinson, "Conversion of Methane to Higher Hydrocarbons in AC Nonequilibrium Plasmas," *AIChE J.*, **44**(10), 2252 (1998).

Van Heesch, E. J. M., A. J. M. Pemen, and P. C. T. van der Laan, "Pulsed Corona Existence up to 850°C," Int. Symp. on High Voltage Engineering, New Orleans, LA (1989).

Yao, S. L., A. Nakayama, and E. Suzuki, "Methane Conversion Using a High-Frequency Pulsed Plasma: Discharge Features," *AIChE J.*, **47**(2), 419 (Feb. 2000a).

Yao, S. L., E. Suzuki, and A. Nakayama, "The Pyrolysis Property of a Pulsed Plasma of Methane," *Plasma Chem. Plasma Process.* (2000b).

Yao, S. L., F. Ouyang, A. Nakayama, E. Suzuki, M. Okumoto, and A. Mizuno, "Oxidative Coupling and Reforming of Methane with Carbon Dioxide Using a High Frequency Pulsed Plasma," *Energy Fuels* (2000c).

Zhou, L. M., B. Xue, U. Kogelshatz, and B. Eliasson, "Nonequilibrium Plasma Reforming of Greenhouse Gases to Synthesis Gas," *Energy Fuels*, **12**, 1191 (1998).

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