Production of Methanol from Methane by an Impulse Discharge on the Water Surface

Masato Mukawa¹, Takafumi Tanno¹ and Satoru Iizuka¹∗

¹Department of Electrical Engineering, Graduate School of Engineering, Tohoku University, Aza Aoba 6-6-05, Aramaki, Aoba, Sendai 980-8579, Japan.

ABSTRACT
Production of methanol from methane was investigated by a low pressure impulse discharge on the surface of the water without using catalysis. Methane was introduced above the water surface and mixed with steam generated by the heat supplied by the discharge. Discharge parameters were changed for optimizing the methanol production. Gaseous hydrocarbons such as ethane, ethylene and acetylene were produced except methanol. Carbon monoxide and carbon dioxide were also observed. The major product was carbon monoxide. Decomposition rate of methane, methanol selectivity, and energy efficiency for methanol production were 51.5%, 22%, and 0.14 L/kWh, respectively. The maximum of energy efficiency was 0.19 L/kWh at the methane flow rate of 10 sccm. The control of methane dissociation was a key factor for the methane conversion. Water surface discharge system developed here is quite effective for the methanol production.

Keywords: Methanol; methane; impulse discharge; water surface; steam.
1. INTRODUCTION

Methane (CH\textsubscript{4}), a main component of natural gas, is in a gas state at ordinary temperature and normal pressure. Methane is naturally emitted from the sea bottom as methane hydrate and also emitted as biomass gases. CH\textsubscript{4} is regarded as one of the greenhouse gases that cause global warming. The greenhouse effect of CH\textsubscript{4} is about 21 times as much as that of carbon dioxide (CO\textsubscript{2}). To transport methane by a vehicle, methane has to be liquefied at low temperature and high pressure. For this reason a conversion of methane to methanol has been proposed and studied [1]. Since methanol is in a liquid state unlike methane, it can be used in various ways such as alcohol fuel, hydrogen source, fuel cell, and raw material for chemical process industries. Methanol has a higher utility potential than methane.

In this work we intend to convert CH\textsubscript{4} to another reusable carbon materials such as methanol (CH\textsubscript{3}OH). Many works had been performed for converting CH\textsubscript{4} to methanol by using atmospheric barriers discharges [1-5]. Conversion from CH\textsubscript{4} to methanol with a mixed gas of steam and oxygen was usually discussed in a high-pressure barrier discharge with catalysts [6,7]. Modeling of CH\textsubscript{3}OH synthesis from CO\textsubscript{2} was also discussed and the vapor-liquid equilibrium was analyzed in the CH\textsubscript{3}OH, CO\textsubscript{2} and H\textsubscript{2} system [8]. Although several works were reported on the methanol production from methane by using atmospheric dielectric barrier discharge (DBD) with oxygen [9-14], only a few works was reported on the methanol synthesis from methane on the surface of the water under low pressure condition. In the discharge steam provides OH radical, which might give a different oxidation process for the methanol production.

Here, we employed a low-pressure glow discharge on the water surface for an investigation of the fundamental processes without using catalysts. The discharge took place inside a glass tube by changing the discharge parameters such as methane flow rate, and so on, where methane was dissociated and reacted with oxygen supplied from steam (H\textsubscript{2}O).

2. EXPERIMENTAL SETUP

Outline of the experimental device is shown in Fig. 1(a). An electrode, connected to a pulse generator, was a stainless pipe of 1/4 inch in diameter, which was set at a center port of the reactor consisting of a glass vessel of 90 mm in diameter and 185 mm in height with 3 ports at the top. Grounded electrode, which was floating in the water by polycarbonate float, was a copper plate with a needle that was used for suppressing the spread of the discharge. The distance between the copper electrode and the water surface was automatically maintained by the float, which was attached to the copper plate with a small glass tube for protecting the float from the discharge. The distance between the copper electrode and the water surface was automatically maintained by the float, which was attached to the copper plate with a small glass tube for protecting the float from the discharge. The discharge was generated between the pipe electrode and the water surface. Methane was supplied from a left port of the reactor vessel. In order that methane and steam definitely pass through the discharge plasma region, the pipe electrode was covered and shielded by a glass tube of 10 mm in diameter with a small hole of 1 mm in diameter at the end as shown in Fig. 1(b). By the heat of the discharge on the water surface, the water could be evaporated and mixed with CH\textsubscript{4}.

---

**Fig. 1 (a).** Entire view of the experimental apparatus and (b) a schematic of the discharge extended through a hole of the glass tube between a pipe electrode and the water surface with spacing distances $d_1$ (pipe tip to hole), $d_2$ (hole to water surface), and $d_3$ (water surface to needle electrode tip).
Then such mixed gas could enter the discharge region through the hole of the glass tube, and eventually evacuated passing through the discharge region and through the pipe electrode by a pump. The output gas was analyzed by Fourier Transform Infrared (FTIR) spectroscopy.

Spacing distances between the pipe electrode tip and glass tube hole, between glass tube hole and the water surface, and between the water surface and the top of the needle electrode are defined as \( d_1 \), \( d_2 \), and \( d_3 \), respectively, as shown in Fig. 1(b). An impulse voltage consisting of one sinusoidal waveform of a period of 10 \( \mu \text{s} \) with a repetition frequency of 10 kHz to 100 kHz was employed. The electric power was monitored by a watt meter of the impulse generator. In this study, we investigated conversion of methane to methanol by using an impulse discharge on the water surface at low pressure. The purpose of this study is to clarify efficient generation of methanol by controlling the discharge parameters.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Evaluation of the Results

The results were evaluated by the following quantities.

(i) CH\(_4\) decomposition ratio \( \alpha \):

\[
\alpha = 1 - \frac{[\text{CH}_4]}{[\text{CH}_4]} \quad (1)
\]

(ii) CH\(_3\)OH selectivity \( \beta \):

\[
\beta = \frac{[\text{CH}_3\text{OH}]}{[\text{all carbon species produced}]} \quad (2)
\]

(iii) Energy efficiency \( \gamma \) (L/kWh) for CH\(_3\)OH production:

\[
\gamma = \frac{[\text{CH}_3\text{OH} \text{ produced in litter}]}{[\text{electric energy consumed by the discharge}]} \quad (3)
\]

Here, [A] denotes amount of species A, and suffix 0 and 1 correspond to the values before and after the discharge, respectively. These quantities show how much carbon in CH\(_4\) has been converted to methanol. \( \gamma \) is an important factor to realize a suitable commercial system for producing methanol in high efficiency. Using \( \alpha \) and \( \beta \), \( \gamma \) can be expressed as follows.

\[
\gamma = \frac{\alpha \beta \Gamma}{[\text{electric power for the discharge (W)}] \times 60} \quad (4)
\]

where \( \Gamma \) is initial gas flow rate of CH\(_4\) [scc/min: standard cubic centimeter per minute]. The change of gas species measured by FTIR showed that main carbon products were CH\(_3\)OH, CO, C\(_2\)H\(_6\), C\(_2\)H\(_4\), and C\(_2\)H\(_2\) through the whole experiment. Therefore, in this case, the methanol selectivity \( \beta \) could be expressed by \( \beta = \frac{[\text{CH}_3\text{OH}]}{[\text{CH}_3\text{OH}] + [\text{CO}] + [\text{C}_2\text{H}_6] + [\text{C}_2\text{H}_4] + [\text{C}_2\text{H}_2]} \).

3.2 Methane Flow Rate Dependence

Fig. 2(a) shows variations of the yields of methanol, ethane, ethylene, acetylene and carbon monoxide as a function of methane flow rate. Methanol and CO were produced at methane flow rate of 1 sccm, where ethane, ethylene, and acetylene were not generated. With an increase in CH\(_4\) flow rate, the yield of methanol and CO were gradually decreased, and conversely ethane abruptly started to increase and was finally saturated for the CH\(_4\) flow rate larger than 10 sccm. Ethylene and acetylene also appeared and saturated for CH\(_4\) flow rate > 5 sccm, but their amounts were not so much compared to ethane.

![Fig. 2 (a). Selectivity of CH\(_3\)OH (\( \beta \)), CO, C\(_2\)H\(_6\), C\(_2\)H\(_4\), and C\(_2\)H\(_2\), and (b) CH\(_4\) decomposition ratio \( \alpha \), methanol selectivity \( \beta \), methanol yield \( \alpha \beta \), and energy efficiency \( \gamma \) as a function of CH\(_4\) flow rate. Input power = 50 W.](image-url)
In the range of low flow rate of CH₄, since the discharge power was fixed to 50 W, water vapor component, generated from the water surface by the heat of the discharge, was dominated in the discharge. Therefore, CH₄ was partially oxidized to become CH₃OH and further oxidized to CO via the following reactions.

\[
\begin{align*}
H₂O & \rightarrow H₂^* + O^* \quad (5) \\
CH₄ + O^* & \rightarrow CH₃OH \quad (6) \\
CH₃OH + 2O^* & \rightarrow CO + 2H₂O \quad (7)
\end{align*}
\]

On the contrary, when CH₄ flow rate was increased, the dissociation of CH₄ was enhanced and a polymerization reaction among dissociated CH₄ radicals exceeded the oxidation reaction among these radicals. Eventually, the following reaction would become dominant.

\[
\begin{align*}
CH₄ & \rightarrow CH₃ + H \quad (8) \\
CH₃ + CH₃ & \rightarrow C₂H₆ \quad (9)
\end{align*}
\]

Therefore, ethane production was dominated first as shown in Fig. 2(a). However, with an increase in CH₄ flow rate, CH₃ was further dissociated, which would result in a generation of ethylene and acetylene as follows.

\[
\begin{align*}
CH₃ & \rightarrow CH₂ + H \quad (10) \\
CH₂ & \rightarrow CH + H \quad (11) \\
CH₂ + CH₂ & \rightarrow C₂H₄ \quad (12) \\
CH + CH & \rightarrow C₂H₆ \quad (13)
\end{align*}
\]

From this experiment it was confirmed that CH₄ flow rate should be kept small for the generation of methanol. However, here it was also noted that the evaporation of water was related to the input discharge power and the resultant increase in the water temperature. If the water is heated additionally by an electric heater, for example, the optimum amount of CH₄ for methanol production will be shifted upward.

Fig. 2(b) shows variations of CH₄ decomposition ratio α, methanol selectivity β, yield of methanol γβ and energy efficiency γ, as a function of CH₄ flow rate. Conditions are as follows: input power = 50 W, total pressure = 5 kPa, and pulse repetition frequency = 10 kHz. When CH₄ flow rate is 1 sccm, 52% (= α) of CH₄ was decomposed, and 22% (= β) of the decomposed CH₄ was converted to methanol. Therefore, 11% (=γβ) of CH₄ was converted to methanol. In this case, the energy efficiency for methanol production was γ = 0.13 L/kWh. However, with an increase in CH₄ flow rate, both of α and β are lowered. On the other hand, energy efficiency γ is increased with CH₄ flow rate and saturated in the range that CH₄ flow rate > 20 sccm, since γ varies in proportion to CH₄ flow rate and γβ, as expressed in eq. (4).

### 3.3 Input Power Dependence

Variations of selectivity of methanol (β), ethane, ethylene, acetylene, and CO are shown in Fig. 3(a) as a function of input power. Conditions are as follows: CH₄ flow rate = 1 sccm, total pressure = 5 kPa, and pulse repetition frequency = 10 kHz. Ethane and ethylene except methane and CO were produced at the input power of 25 W. However, the production of ethane and ethylene were suppressed and only methanol and CO were generated at the power range above 50 W. When input power was further increased to 100 W, all species except CO were completely disappeared. This means that an perfect oxidization of CH₄ has been proceeded.

Fig. 3(b) shows variations of CH₄ decomposition ratio α, methanol selectivity β, yield of methanol γβ and energy efficiency γ, as a function of input power. α increased almost linearly with input power and α becomes 75% at input power of 100 W. On the other hand, β is 27% at input power of 25 W, and gradually decreases with input power until methanol was completely oxidized at 100 W. Consequently, methanol yield has a maximum γβ = 15% at 75 W.

From the power dependence the following reactions are considered. In the case of low power, the heat transferred to the water was less, therefore the evaporation is insufficient. However, the component of CH₄ exceeds H₂O, then CH₄ was dominantly dissociated, and then the reactions (8)-(13) were proceeded compared to the reactions (5)-(7). However, when input power is further increased, the heat from the discharge assists the water evaporation, therefore H₂O molecules are more contained in the mixed gas. Therefore, dissociation of H₂O starts to be enhanced as in the reaction (5), then oxidation due to O* would proceed to generate methanol and finally CO is generated. This heating effect was enhanced above 75 W, which resulted in a complete oxidization of CH₄. In this way, only CO was observed above this high power regime. The best condition in this case was α = 60%, β = 22%, γβ = 13%, and γ = 0.1 L/kWh at input power of 75 W.
3.4 Pulse Frequency Dependence

Fig. 4(a) shows variations of selectivity of methanol (β), ethane, ethylene, acetylene, and CO as a function of pulse repetition frequency. Conditions are as follows: CH₄ flow rate = 1 sccm, input power = 50 W, and total pressure = 5 kPa. Through the whole experiment ethane and ethylene were not generated, being independent of the frequency. Only methanol and CO were produced. As shown in Fig. 4(b), CH₄ decomposition ratio α, methanol selectivity β, yield αβ and energy efficiency γ were not so much changed by the repetition frequency. The favorable results were obtained at the frequency of 20 kHz, where α = 35%, β = 37%, αβ = 13%, and γ = 0.17 L/kWh were obtained.

3.5 Electrode Position d₁ and d₃ Dependences

Fig. 5(a) shows variations of selectivity of methanol (β), ethane, ethylene, acetylene, and CO as a function of electrode position d₁. Here, d₂ = 5 mm and d₃ = -2 mm. Through the whole experiment ethane, ethylene, and acetylene were not generated. Methanol selectivity β increase with d₁ from 28% to 33%, but the generation of methanol was extinguished at d₁ = 10 mm. As shown in Fig. 5(b) the decomposition of CH₄ was α = 45%, that was not much changed with an increase of d₁ in the range 2 to 5 mm, but α was decreased to 35% at d₁ = 10 mm. The yield of methanol αβ attained to the maximum of 12% at d₁ = 5 mm.

It was considered that methanol was further oxidized by O* due to an enlargement of oxidation reaction space when d₁ was increased. In our case d₁ = 5 mm was a best position of the methanol synthesis.

Variations of selectivity of methanol (β), ethane, ethylene, acetylene, and CO are shown in Fig. 6(a) as a function of needle electrode tip position d₃ relative to the water level. Here, d₁ = 5 mm and d₂ = 5 mm. Ethane was observed except methanol and CO at d₃ = -6 mm, but ethylene
and acetylene were not generated. However, ethylene was not generated with diminishing the water depth. In the range $d_3 > -2$ mm, methanol selectivity was increased with $d_3$ and attained to $\beta = 35\%$ at $d_3 = +2$ mm above the water surface as shown in Fig. 6(b). However, $\alpha$ was reduced from 47% to 37% with an increase of $d_3$ from -2 mm to +2 mm. The methanol yield was $\alpha \beta = 12\%$ which was not much changed by the change of the position $d_3$ from -2 mm to +2 mm.

In the case of $d_3 = -6$ mm, the discharge extended on the water surface broadly and the discharge volume was increased on the water surface. Since the heating energy density is reduced by this expansion, the water evaporation diminished and the volume ratio of CH$_4$ in the discharge seemed to be relatively increased. Then, the decomposition of CH$_4$ was enhanced, resulting in an appearance of the reactions in (8) and (9). But, the energy seemed to be not enough for the further reactions in (10) – (13). On the other hand, as the water depth was decreased to -2 mm, the discharge could be concentrated to a narrow water surface region just above the needle electrode position. Then, the energy density was increased, which resulted in an evaporation of water. Therefore, the polymerization reaction for ethane productions in (8) and (9) were suppressed. Then, oxidization reaction in (5)-(7) was dominated and methanol was selectively produced with carbon monoxide.

Fig. 5 (a). Selectivity of CH$_3$OH ($\beta$), CO, C$_2$H$_6$, C$_2$H$_4$, and C$_2$H$_2$, and (b) CH$_4$ decomposition ratio $\alpha$, methanol selectivity $\beta$, yield $\alpha \beta$, and energy efficiency $\gamma$ as a function of upper electrode position $d_1$. Input power = 50 W

Fig. 6 (a). Selectivity of CH$_3$OH ($\beta$), CO, C$_2$H$_6$, C$_2$H$_4$, and C$_2$H$_2$, and (b) CH$_4$ decomposition ratio $\alpha$, methanol selectivity $\beta$, yield $\alpha \beta$, and energy efficiency $\gamma$ as a function of needle electrode position $d_3$ against the water surface. Input power = 50 W
4. DISCUSSION

In this method, H₂O was supplied from the water surface by evaporation due to the heat supplied from the discharge, while methane was independently fed into the reaction space. Therefore, with an increase in the discharge power, the mixing ratio H₂O/CH₄ increases with a raise of water surface temperature, and as a result, oxygen atom radical density increases in the reaction space. In this way, the oxidation proceeded with an increase in power, and in the case of the power higher than 50 W, methane was oxidized and methanol was synthesized. As a byproduct, only carbon monoxide was observed, as shown in Fig. 3. On the other hand, in the case of the power below 50 W, oxidation proceeded insufficiently, where higher order hydrocarbons, such as ethane and ethylene, were generated together with methanol. This phenomenon corresponds to the case that methane flow rate is increased under a fixed power. Actually, higher order hydrocarbons were generated when methane flow rate was higher than 5 sccm, as shown in Fig. 2. The change of pulse repetition frequency did not give an effect to the methanol generation, since the gas mixing ratio seemed not to be changed under fixed power condition, as shown in Fig. 4. Here, it is noted that the power included a loss such as electrode heating and decay of impulse waveform in the external circuit.

The length of the discharge column d₁ was also an important factor for a generation of methanol. When d₁ is increased, the oxidation reaction space is enhanced. Therefore, the generated methanol itself was further oxidized to become CO₂ as shown in Fig. 5 as in the case of d₁ = 10 mm. The position of the lower needle electrode below the water surface was also important for proceeding a concentrated mild discharge. The depth of 2 mm was optimum for the methanol generation. When the tip of the needle was placed above the water surface, the discharge became more active, resulting in a further dissociation of methane as well as a production of higher order hydrocarbons, as shown in Fig. 6. Therefore, surface discharge with an electrode that sunk below the water surface is effective for the methanol generation.

5. CONCLUSION

Methanol was produced by a pulse discharge above the water surface with a needle electrode below the water surface. The needle electrode concentrated the discharge to a narrow region on the water surface above the needle. Methane supplied was mixed with the water molecule evaporated by the heat from the discharge. When CH₄ flow rate was 1 sccm, decomposition rate of methane, selectivity of methanol, and energy efficiency were 51.5%, 22%, and 0.14 L/kWh, respectively. The maximum value of energy efficiency was 0.19 L/kWh at CH₄ flow rate of 10 sccm.

Water surface discharge system developed here is quite effective for the methanol production.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Zhou LM, Xue B, Kogelschatz U, Eliasson B. Partial oxidation of methane to methanol with oxygen or air in a nonequilibrium discharge plasma. Plasma Chem. Plasma Process. 1988;18:375.
2. Eliasson B, Liu C-J, Kogelsschatz U. Direct conversion of methane and carbon dioxide to higher hydrocarbons using catalytic dielectric-barrier discharges with zeolites. Ind. Eng. Chem. Res. 2000;39:1221.
3. Zang K, Eliasson B, Kogelschatz U. Direct conversion of greenhouse gases to synthesis gas and C4 hydrocarbons over zeolite HY promoted by a dielectric-barrier discharge. Ind. Eng. Chem. Res. 2002;41:1462.
4. Nair SA, Nozaki T, Okazaki K. In situ Fourier transform infrared (FTIR) study of nonthermal-plasma-assisted methane oxidative conversion. Ind. Eng. Chem. Res. 2007;46:34886.
5. Tsuchiya T, Iizuka S. Conversion of methane to methanol by a low-pressure steam plasma. J. Environ. Eng. Technol. 2013;2:35.
6. Lodeng R, Lindvag OA, Soraker P, Rotenrud PT, Onsager OT. Experimental and modeling study of the selective homogeneous gas phase oxidation of methane to methanol. Ind. Eng. Chem. Res. 1995;34:1044.
7. Casey PS, Macallister T, Foger K. Selective oxidation of methane to methanol at high pressures. Ind. Eng. Chem. Res. 1994;33:1120.
8. R-Struckmann LK, Peschel A, H-Rausehenbach R, Sundmacher K. Assessment of methanol synthesis utilizing exhaust CO$_2$ for chemical storage of electric energy. Ind. Eng. Chem. Res. 2010;49:11073.

9. Yao SL, Takemoto T, Outang F, Nakayama A, Suzuki E, Mizuno A, Okamoto M. Selective oxidation of methane using a non-thermal pulsed plasma. Energy Fuels. 2000;14:459.

10. Larkin DW, Lobban L, Mallinson RG. Production of organic oxygenates in the partial oxidation of methane in a silent electric discharge reactor. Ind. Eng. Chem. Res. 2001;40:1594.

11. Indarto A, Yang DR, Palgunadi J, Choi JW, Lee H, Song HK. Partial oxidation of methane with Cu-Zn-Al catalyst in a dielectric barrier discharge. Chem. Eng. Process. 2008;47:780.

12. Tsai CH, Hsieh TH. New approach for methane conversion using rf discharge reactor. 1. Influences of operating conditions on syngas production. Ind. Eng. Chem. Res. 2004;43:4043.

13. Kano M, Satoh G, Iizuka S. Reforming of carbon dioxide to methane and methanol by electric impulse low-pressure discharge with hydrogen. Plasma Chem. Plasma Process; 2011. DOI: 10.1007/s11090-011-9333-0

14. Eliasson B, Kogelschatz U, Xue B, Zhou LM. Hydrogeneration of carbon dioxide to methanol with a discharge-activated catalyst. Ind. Eng. Chem. Res. 1998;37:3350.