

Liquid Waste Decomposition by DC Water Plasmas at Atmospheric Pressure

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Decomposition system of liquid waste by DC water plasmas generated at atmospheric pressure was developed. The developed water plasma torch is a DC thermal plasma generator of coaxial design with a cathode of hafnium embedded into the copper rod and a nozzle-type copper anode. The plasma torch can generate 100%-steam plasma without a commercially available steam generator. The water plasma system is a portable light-weight system that does not require any gas supply. The plasma system has high energy-efficiency since cooling water is not needed. Methanol or ethanol used as model substances of liquid waste was mixed with water for plasma supporting gas. Rapid and complete decomposition for these alcohols produce H_2 , CO , and CO_2 in the decomposed gas. The decomposition rate as well as the decomposition mechanism was determined by gas chromatography and mass spectrometry. The water plasma system can be used for industrial application of liquid waste decomposition.

Key words: water plasma, thermal plasma, atmospheric pressure plasma, hydrogen production, waste treatment

1. INTRODUCTION

Wastes of 450 million tons a year are discharged by economic activities of mass production, mass consumption, and mass disposal in Japan. Thermal plasmas provide the advanced technologies for environmental problem solution. Thermal plasmas have received many attentions due to its high chemical reactivity, easy and rapid generation of high temperature, high enthalpy to enhance the reaction kinetic, oxidation and reduction atmosphere in accordance with required chemical reaction as well as rapid quenching capability (10^5 - 10^6 K). Therefore, thermal plasmas have been widely applied to many fields because of these advantages, such as waste treatment, synthesis of nanoparticles, chemical vapor deposition and plasma spraying.

Waste decomposition using thermal plasmas have been reported, for example, polymer [1-3], hydrocarbon [4, 5], organic waste [6, 7], used tires [8], biomass [9-11]. When water plasmas are applied to waste treatments, the use of additional steam generator is unsuitable, because the steam generator requires complicated system including the heating-up of the steam feeding line for preventing from condensation.

The developed torch provides the generation of 100%-water plasma without commercially available steam generator. The features of the torch results from the simple steam generation; liquid water from the reservoir is heated up and evaporates at the anode region to form the plasma supporting gas. Simultaneously, the anode is cooled by the water evaporation, therefore the electrodes require no additional water-cooling. The distinctive steam generation method provides the portable light-weight plasma generation system that does not require the gas supply unit, thus the high energy-efficiency results from the nonnecessity of the additional water-cooling. These features of the proposed plasma generation method, which are not readily

achievable by other methods, allow for simple and effective water plasma generation system.

The purpose of this paper is to decompose liquid waste at atmospheric pressure. Methanol and ethanol solution were used as the model substances of liquid waste. Furthermore, wastes are converted into synthesis gas (mixture of H_2 and CO), which can be used as fuel gas or for productions of other chemicals.

2. EXPERIMENT

The schematic experimental apparatus used in this study is presented in Fig. 1. The experimental apparatus consists of a plasma torch, a reaction tube, a pump, and a DC power supply. The water plasma torch set below the reaction tube is a DC non-transferred plasma arc generator of coaxial design with a cathode of hafnium embedded into a copper rod and a nozzle-type copper anode. Methanol or ethanol solution was supplied into the torch with controlled feed rate. The alcohol solution was injected into the discharge region soon after the evaporation due to the extensive heat from the anode. In

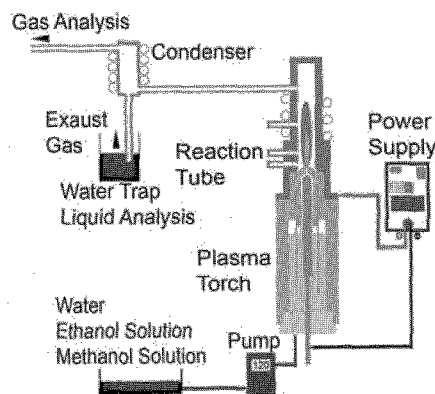


Fig. 1 Schematic of experimental apparatus.

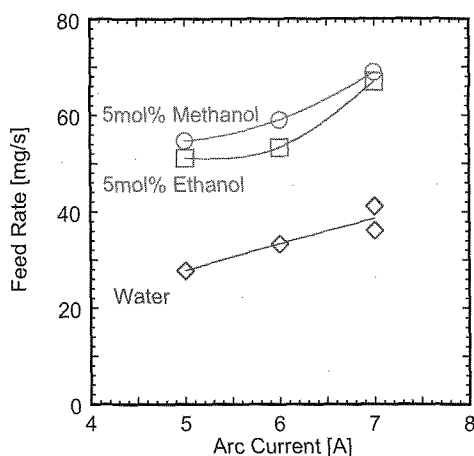


Fig. 2 Effect of arc current on feed rate of plasma supporting gas.

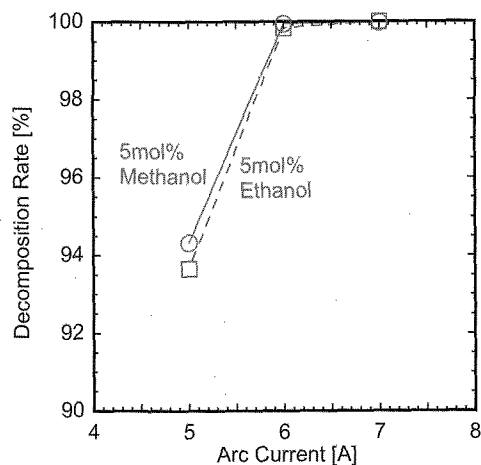


Fig. 3 Decomposition rate of 5mol% methanol solution and 5mol% ethanol solution.

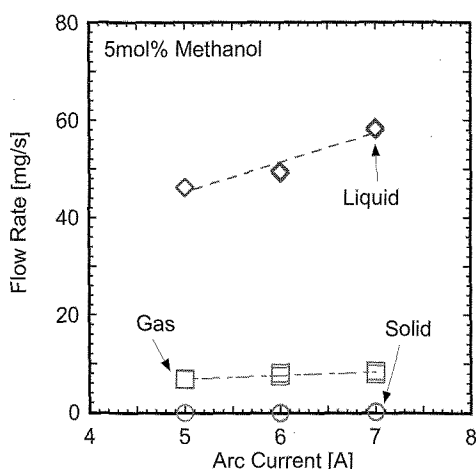


Fig. 4 Effect of arc current on flow rates of produced solid, liquid and gas for 5mol% methanol solution.

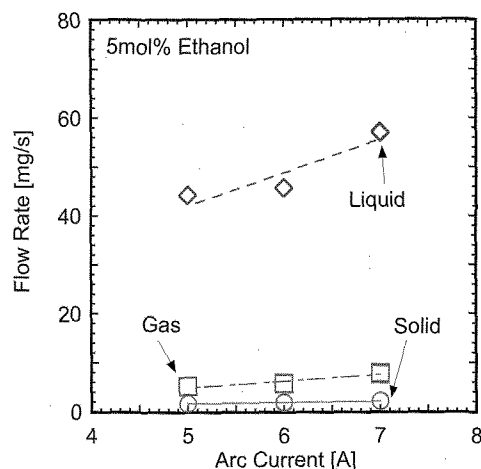


Fig. 5 Effect of arc current on flow rates of produced solid, liquid and gas for 5mol% ethanol solution.

the high-temperature region after the discharge zone, the alcohol vapor was decomposed by the water plasma.

The arc power was 0.65-1.05 kW with the arc current of 5.0-7.0 A. The measured feed rate for plasma gas from water, methanol solution, and ethanol solution are presented in Fig. 2. Plasma gas flow rate increases with increasing arc current because of stronger Joule heating for evaporation. Higher vapor pressure of the methanol solution causes larger feed rate of the plasma supporting gas evaporated from the methanol solution.

The produced gas and liquid were separated by cooling at the condenser. The produced gas was analyzed by gas chromatography (GC) equipped with a thermal conductivity detector (SHIMADZU, GC-8A) and a quadrupole mass spectrometer (QMS, AMETEK, Dycor Proline). The produced liquid was analyzed by GC and a total organic carbon analyzer (SHIMADZU, TOC-V CSN).

3. RESULTS AND DISCUSSION

The decomposition rates of methanol and ethanol are presented in Fig. 3. Higher decomposition rate was obtained at higher arc current, because of stronger oxidation due to higher H_2O dissociation. The decomposition rate was estimated from the undecomposed methanol or ethanol in the liquid,

because the undecomposed methanol or ethanol was negligible from the gas phase measurements. Higher H_2O dissociation at higher arc current is also indicated in Figs. 4 and 5 for methanol and ethanol decomposition, respectively. These figures show the higher arc current leads to larger amount of the produced gas containing H_2 as the main component. To determine the decomposition mechanism, the composition of the produced gas, liquid, and solid were analyzed.

The amount of solid product, which was assumed to be soot, was estimated from the total and species mass balance. The amount of soot as the solid product from ethanol decomposition was larger than that from methanol decomposition, indicating the different decomposition mechanism between methanol and ethanol decomposition by the water plasmas.

The gas phase composition was shown in Figs. 6 and 7 for methanol and ethanol decomposition, respectively, from the GC measurements to investigate the decomposed species. The mole fraction of H_2 in the produced gas was more than 67%. As the arc current increases, the concentration of H_2 and CO_2 increases while CO and CH_4 decreases. At higher arc current, the oxidation due to H_2O dissociation leads to increasing CO_2 . In addition, the concentration of H_2 of methanol is larger than that of ethanol.

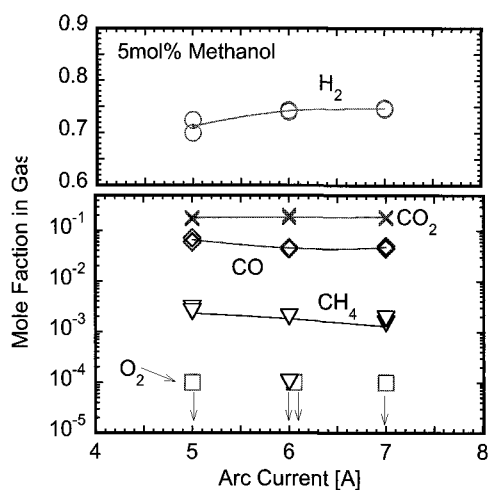


Fig. 6 Effect of arc current on gas composition generated from 5mol% methanol solution.

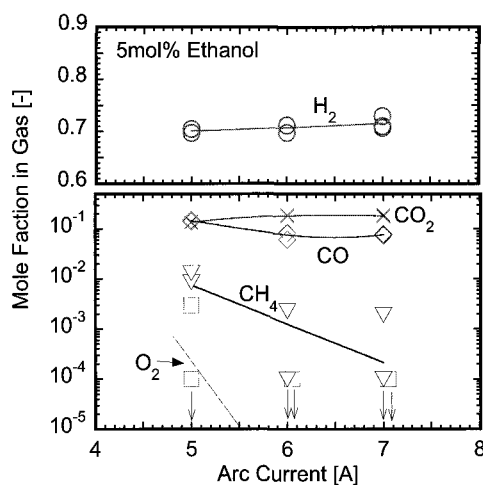


Fig. 7 Effect of arc current on gas composition generated from 5mol% ethanol solution.

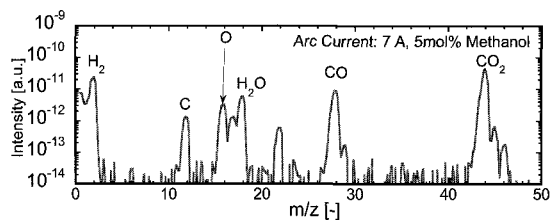


Fig. 8 Spectrum of produced gas of 5mol% methanol solution at 7 A.

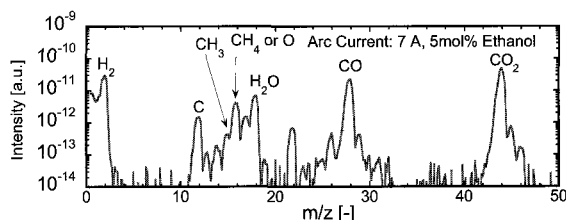


Fig. 9 Spectrum of produced gas of 5mol% ethanol solution at 7 A.

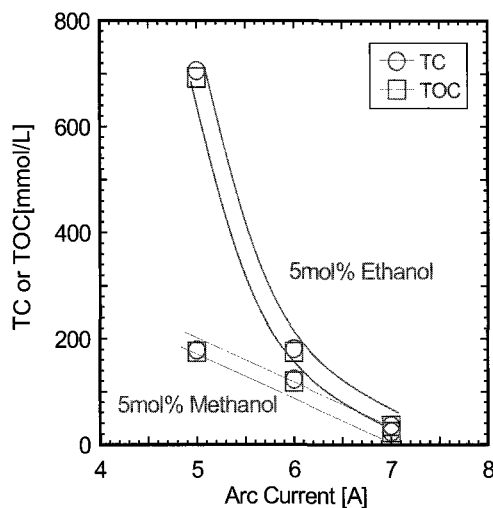


Fig. 10 Amount of carbon in produced liquid of 5mol% methanol solution and 5mol% ethanol solution.

The measured mole fraction of CH_4 from the GC measurements was unreliable because the detected concentration of CH_4 was near or below the detection limit of the GC measurements. Therefore, QMS measurement was used for quantitative discussion for CH_4 . Figs. 8 and 9 for methanol and ethanol decomposition, respectively, represent the detection of H_2 , O_2 , CO , CO_2 , and CH_4 . From the detection intensities, the ratios of CH_3/CO_2 from methanol and ethanol decomposition at 7 A were estimated to be 3.30×10^{-3} and 1.33×10^{-2} , respectively. The production of CH_3 indicates the main path of soot formation from the alcohol decomposition. Therefore, larger amount of soot

was produced from the ethanol decomposition.

The chemical analysis of the produced liquid was carried out to confirm the by-product from the alcohol decomposition. The amount of carbon in the liquid is presented in Fig. 10. Small difference between the total carbon (TC) and the total organic carbon (TOC) indicates that the dissolved carbon dioxide is negligible in the liquid. The value of TOC can be assumed to be the soot and undecomposed alcohol, thus larger TOC value for ethanol decomposition indicates larger amount of soot was produced from the ethanol decomposition.

The carbon balance of the product is presented in Figs. 11 and 12 for methanol and ethanol decomposition, respectively. The carbon balance was estimated from the total carbon in the gas phase (CO , CO_2 , and CH_4) and the liquid including traces of organics dissolved in the water, and soot formed during the experiments. It was assumed that gas components were H_2 , O_2 , CO , CH_4 , and CO_2 , because other species detection was negligible. Soot in Fig. 11 is assumed zero for methanol decomposition because the produced solid in Fig. 4 is almost zero. Fig. 12 indicates the 50wt% of carbon from ethanol was transformed into soot, while the soot formation from methanol was negligible. This would be explained by the difference of decomposition mechanism between ethanol and methanol. Dissociation of C-C bond of ethanol occurs at high-temperature region to form CH_3 and CH_2OH as shown in Fig. 13. Soot generated from CH_3 is the primary soot formation path. In contrast, CH_3 formation from the methanol decomposition is small owing to the stronger $\text{H}_3\text{C-OH}$ bond of methanol [12].

The residence time of the decomposition substances in the high-temperature region was estimated at 1 ms.

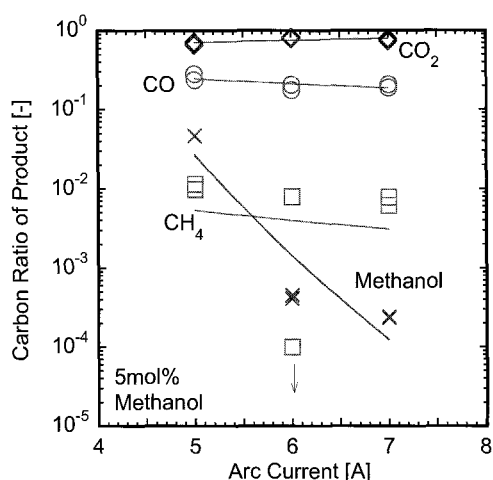


Fig. 11 Carbon ratio of decomposition product from 5mol% methanol solution.

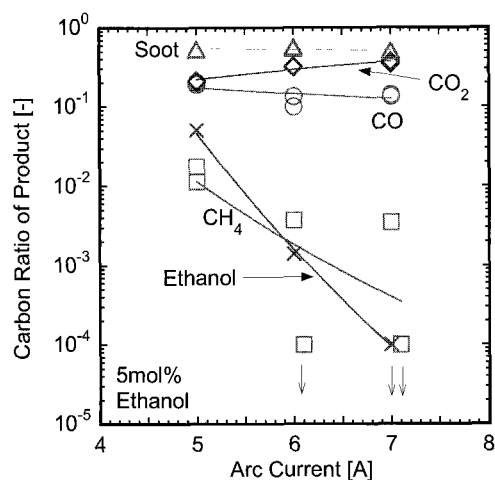


Fig. 12 Carbon ratio of decomposition product from 5mol% ethanol solution.

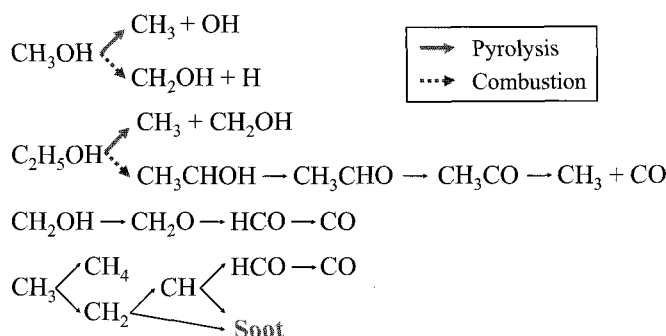


Fig. 13 Reaction mechanism of methanol and ethanol decomposition.

The short residence time leads to insufficient H_2O dissociation as well as ionization. Therefore the dissociation of methanol and ethanol was limited in the high-temperature region, followed by the lower-temperature region where methanol and ethanol was oxidized by oxygen from the H_2O dissociation. Therefore, it is considered that main decomposition path of methanol was combustion, while that of ethanol was pyrolysis by water plasma.

4. CONCLUSION

The water plasma system can be used for industrial application of liquid waste decomposition. The mole fraction of H_2 in produced gas was more than 67% suggests synthesis gas production from liquid wastes.

Ethanol decomposition produced large amount of soot; 50wt% of carbon from ethanol was transformed into soot. On the other hand, soot production from methanol decomposition was negligible. Therefore, the decomposition mechanism between methanol and ethanol is different in water plasmas.

References

- [1] A. Vaidyanathan, J. Mulholland, J. Ryu, M. S. Smith, and L. J. Circeo Jr, *J. Environ. Manage.*, **82**, 77-82 (2007).
- [2] H. S. Park, C. G. Kim, and S. J. Kim, *J. Ind. Eng. Chem.*, **12**, 216-223 (2006).
- [3] L. Tang, and H. Huang, *Fuel Process. Technol.*, **88**, 549-556 (2007).
- [4] K. S. Kim, J. H. Seo, J. S. Nam, W. T. Ju, and S. H. Hong, *IEEE Trans. Plasma Sci.*, **33**, 813-823 (2005).
- [5] S. Nakanishi and H. Sekiguchi, *J. Japan Petrol. Inst.*, **48**, 22-28 (2005).
- [6] L. Tang, and H. Huang, *Energy Conv. Manage.*, **48**, 1311-1337 (2007).
- [7] B. Lemmens, H. Elslander, I. Vanderreydt, K. Peys, L. Diels, M. Oosterlinck, and M. Joos, *Waste Manage.*, **27**, 1562-1569 (2007).
- [8] J. S. Chang, B. W. Gu, P. C. Looy, F. Y. Chu, and C. J. Simpton, *J. Environ. Sci. Health*, **A31**, 1781-1799 (1996).
- [9] R. Kezelis, V. Mecius, V. Valinciute, and V. Valincius, *High Technol. Plasma Process*, **8**, 273-282 (2004).
- [10] G. V. Oost, M. Hrabovsky, V. Kopecky, M. Konrad, M. Hlina, T. Kavka, A. Chumak, E. Beeckman, and J. Verstraeten, *Vacuum*, **80**, 1123-1137 (2006).
- [11] M. Hrabovsky, M. Konrad, V. Kopecky, M. Hlina, T. Kavka, G. V. Oost, E. Beeckman, and B. Defoort, *Czech. J. Phys.*, **56**, B1199-1206 (2006).
- [12] S. Singh, W. Grosshandler, P. C. Malte, and R. W. Grain, Jr., *17th Inter. Symp. Combust.*, 689-699 (1979).

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