Discharge characteristics of water thermal plasma for D-glucose decomposition

T. Watanabe, J. Kohara, T. Matsuo and M. Tanaka

Department of Chemical Engineering, Kyushu University, Fukuoka, Japan

Abstract: Discharge characteristics of water plasma generation were examined by synchronized arc image observation with voltage measurement. The dynamic behavior of the arc as a restrike mode has faster fluctuation than the decomposition process in the water plasma. Decomposition of aqueous D-glucose using the water plasma system produces the effluent gas containing H_2 (55–56%), CO_2 (9.4–11%), and CO (33–34%).

Keywords: Water plasma, Arc fluctuation, Biomass gasification

1. Introduction

Thermal plasmas have attracted extensive attention due to their unique advantages, and it is expected to be utilized for a number of innovative industrial applications such as decomposition of harmful materials, recovery of useful materials from wastes, and synthesis of high-quality and high-performance nanoparticles. The advantages of thermal plasmas including high enthalpy to enhance reaction kinetics, high chemical reactivity, and oxidation or reduction atmospheres in accordance with required chemical reactions are beneficial for innovative processing.

Water plasma waste treatment has attracted the most attention as a green technology for the utilization of organic wastes. Hrabovsky et al. [1] and Oost et al. [2] developed a hybrid plasma torch using a water vortex and gas flow for the biomass gasification. Watanabe et al. [3-5] developed a DC water plasma torch for treatment of organic waste. Since a large amount of H, O, and OH radicals are generated in the water plasma, decomposition and syngas production are accelerated in the treatment of water-soluble organic compounds [6-8].

D-glucose has been produced from hydration of cellulose in biomass processing, thereby its gasification method and new applications should be developed for utilization of biomass. In this study, high concentration of aqueous D-glucose, used as a model substance for water-soluble compounds, was decomposed using the water plasma torch at atmospheric pressure. The arc behavior was also studied to evaluate the fluctuation effect on the decomposition process. The effect of the arc current on D-glucose decomposition and the influence of active species such as O, H, and OH radicals on the decomposition process were discussed by analyzing the generation products.

2. Experimental set-ups

A schematic diagram of DC water plasma system for aqueous D-glucose decomposition is shown in Fig. 1. The system consists of a DC power supply, a plasma torch, a metering pump, and a reaction tube. The plasma torch

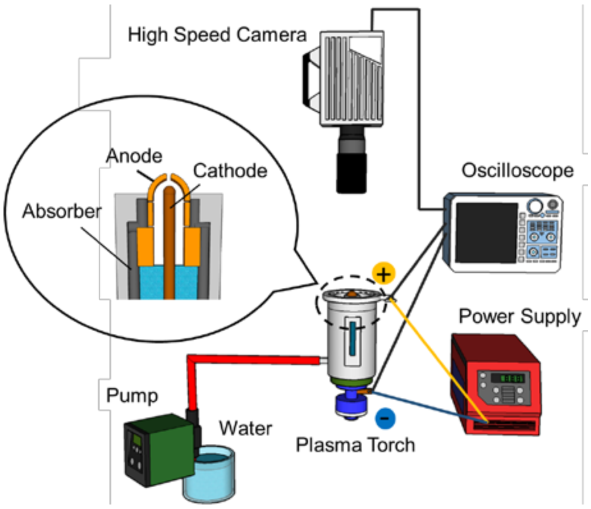

Fig. 1. Experimental set-ups for water plasma system for D-glucose decomposition.

was a DC non-transferred arc plasma generator of coaxial design with a cathode of hafnium embedded into a copper rod and a nozzle type copper anode. The diameter of hafnium was 1.0 mm. Using hafnium as a cathode material can prevent the erosion and perform a longer operating time in an oxidative atmosphere.

After the arc ignition, water plasmas were generated at discharge region by heating and ionization of steam that is produced by evaporation of water from the reservoirs. Simultaneously, the anode is cooled by the water evaporation, thus the torch can be operated in the absence of carrier gases or air injection, cooling-controlled system, and pressure-controlled devices. Therefore, the presented system is a portable light weight system that does not need gas supply system and has a high energy efficiency (> 90%) because of no-cooling system used, then leading to a low cost in contrast to conventional thermal plasma techniques. Moreover, the generated H, O, and OH radicals in water plasmas are useful for suppressing by-product formation.

D-glucose solution was introduced into the torch with a controlled feed rate after adjusting solution concentration to 1.0 mol% with analytical grade D-glucose (98%, Wako Pure Chemical Industries, Ltd.) and distilled water. The system was operated at an atmospheric pressure with arc currents of 6–9.5 A and the voltage from 100 to 140 V. Each run was operated for 10-30 min after a steady-state operation condition reached.

The instruments for gas analysis included a gas chromatograph equipped with a thermal conductivity detector, GC-TCD (GC-14B, Shimadzu) and a quadrupole mass spectrometer, QMS (Ametek, Dycor Proline). The GC-TCD was used for the quantitative analysis of gaseous products such as H_2, CO, CO_2, and CH_4. A high-performance liquid chromatograph, HPLC (pump: U-986, Jasco, column thermostat: CO-966, Jasco) with an ultraviolet detector (UV-975, Jasco) and ultraviolet-visible absorption spectroscope, UV-vis (V-550, Jasco) were used for analysis of the liquid effluent.

For the evaluation of the arc fluctuation, a high speed video camera (FASTCAM SQ-5, Photron Ltd.) was introduced to observe the moving arc from the top view at the nozzle exit with a high frame rate of 4.2×10^5 s^{-1} with the shutter speed of 1 μs. A digital oscilloscope (Scope Corder DL850, Yokogawa) was used to record the arc voltage at a 1 MHz synchronized with the high-speed camera.

3. Discharge Characteristics

The voltage waveform and the synchronized high-speed snapshots are shown in Fig. 2. A periodic saw tooth shape of the voltage waveform was clearly recorded by the oscilloscope. The arc voltages were fluctuated around the average voltage of 150 V with the standard deviation about 21 V. In addition, the arc frequency of 37 kHz was indicated in Fig. 3 through the Fast Fourier Transform, FFT, for the periodic voltage fluctuation. This frequency is sufficiently faster than the decomposition process, therefore the arc fluctuation is negligible in the water plasma decomposition process.

The axial movement of the arc was confirmed from Fig. 2 taken by the high-speed camera. The arc is bent in the axial direction and an anodic arc root appeared on the nozzle surface when the arc comes out from the water plasma torch. The spot of arc attachment on the anode surface is moved by the drag force lengthening the arc column and increasing the arc voltage in the water plasma torch. On the other hand, the anodic arc spot of the water plasma is fixed on the nozzle exit after the arc comes out from the inside chamber of the water plasma torch. Instead of the movement of the anodic arc spot, the arc column is more bent increasing its length and the arc voltage. According to these high-speed images, the water plasma has unique arc voltage fluctuation mechanism which is different from the conventional non-transferred plasma torch.

The relationship between the arc length and arc voltage was revealed by Fig. 2. The lowest arc voltage indicated

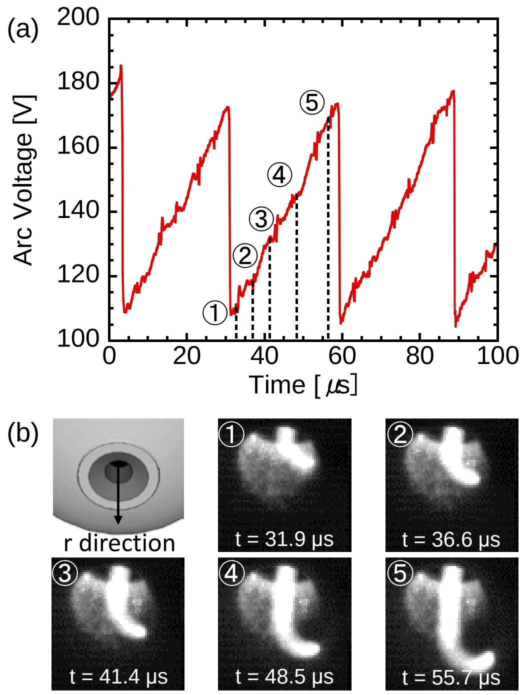

Fig. 2. Synchronized measurements of (a) waveform of arc voltage, and (b) high-speed snapshots of arc.

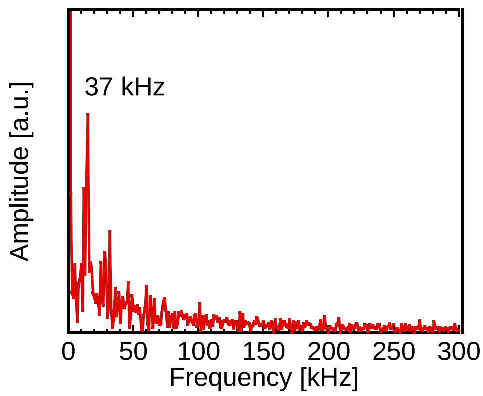

Fig. 3. Arc frequency from a periodic voltage fluctuation.

the anodic arc spot was closest to the cathode inside the water plasma torch when the shortest arc column was generated at 31.3 μs. The arc column with the arc voltage was grown by the drag force of steam flow in an axial direction toward the nozzle exit to reach the longest column. At the 58.8 μs, the arc column was longest resulting in the highest arc voltage. Importantly, a new shortest arc column was created when the electric field is higher than a critical field at the longest arc column. The arc reattached to the anode surface repeating the arc movement with the periodic voltage fluctuation. These results indicate that the arc fluctuation of the water plasma torch can be defined as a perfect restrike mode.

The arc movement is influenced by two forces; the gas drag force pulling the arc outside the torch is caused by the incoming gas flow, and the Lorentz force pushing the arc inside the torch is caused by the arc current density and self-induced magnetic field. However, the arc column has mainly operated by the drag force in the water plasma torch due to significantly small arc current than the typical DC plasma torch operated with several hundred amperes. Therefore, the arc voltage is increased until the maximum point without remarkably disturbing Lorentz force in a piece of the saw tooth.

4. Decomposition of D-glucose

The plasma and injected D-glucose solution were expected to undergo complex reactions in the high-temperature region. Therefore, the gaseous products can be quickly quenched in the reaction tube and separated into gaseous, liquid, and solid phases. Herein, quenching step is important to suppress by-product formation in the waste treatment process. In this torch, target compounds can pass though the discharge region and then injected into the high-temperature zone. Hence, the capable of obtaining high decomposition efficiency for organic waste is the unique characteristic of this torch.

The production rates of gaseous, liquid, and solid are shown in Fig. 4, where the solid production rate was calculated on the basis of the mass balance. Large production rates for liquid and gas was obtained at higher arc current because the water evaporation and dissociation were improved by increasing arc current. The feeding rate of D-glucose solution was 45.4-50.0 mg s^{-1} in which 92.7-93.1% was converted into liquid and 4.8-5.6% was converted into gas phase. Because the solid products was too small to measure, the produced gas and liquid were analyzed to investigate the decomposition characteristics.

The composition of the produced gas from 1.0 mol% D-glucose decomposition as a function of arc current is illustrated in Fig 5. The major compositions of the produced gas were H_2 (55.3–56.0%), CO_2 (9.49–11.0%), and CO (32.9–34.1%). With an increase of arc current, the concentrations of CO_2 increase while the concentrations of CH_4 decrease because a stronger oxidative environment was formed at higher arc current. As for the syngas of H_2 and CO, the mole fraction of 89% was obtained at arc current of 6-9.5 A.

Mass spectra of the gas produced from 1.0 mol% D-glucose decomposition are shown in Fig. 6. Production of H_2, C, CH_4, H_2O, CO, and CO_2 were observed from the intensity peaks of 2 (H_2^+), 12 (C^+), 16 (CH_4^+), 18 (H_2O^+), 28 (CO^+), and 44 (CO_2^+), respectively. In the case of decomposition of 10 mol% ethanol solution [9], the intensity peak of 26 ($C_2H_2^+$) was identified, however the peak 26 ($C_2H_2^+$) was not detected from the D-glucose decomposition. It is considered that the intermediates species generated from D-glucose decomposition were completely decomposed.

Measurement results of concentrations of organic compounds in the effluent liquid using HPLC are shown

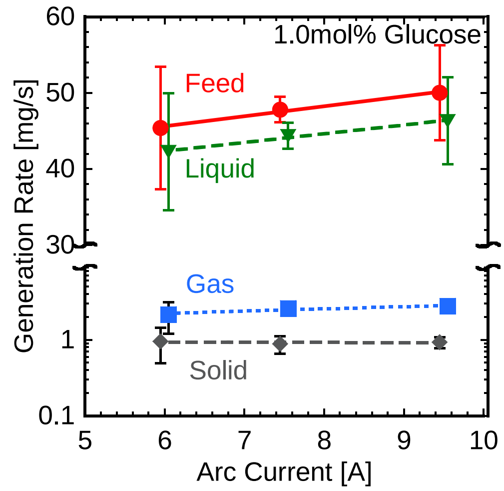

Fig. 4. Effect of arc current on mass balance generated from 1.0 mol% D-glucose.

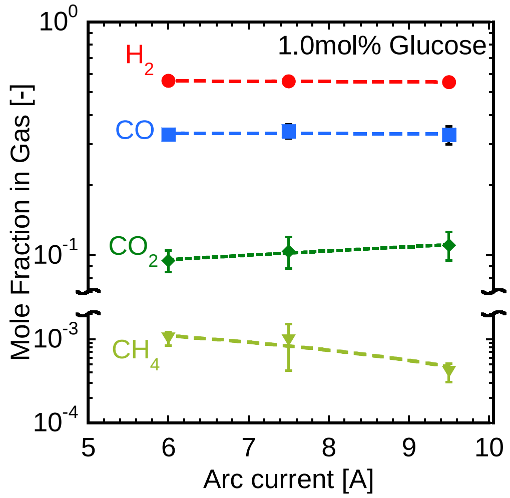

Fig. 5. Effect of arc current on gas composition generated from 1.0 mol% D-glucose.

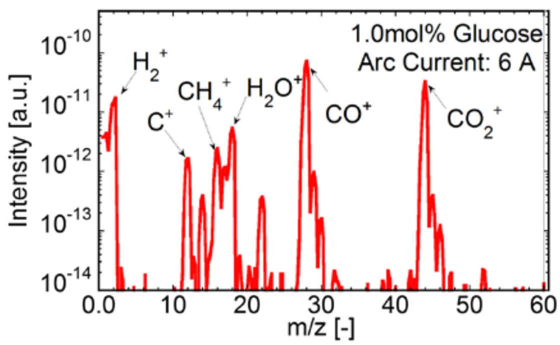

Fig. 6. Mass spectra of effluent gas from 1.0 mol% D-glucose by QMS at the arc current of 6A.

in Fig. 7. Undecomposed D-glucose as well as unwanted by-products of formaldehyde were detected. Note that other by-products for organic compound decomposition by water plasma technique [8], such as acetaldehyde were not observed in the effluent steam in all decomposition cases.

Carbon balance of decomposition products of 1.0 mol% D-glucose at different arc currents is presented in Fig. 8. The carbon balance is defined as the ratio of the total input carbon in D-glucose solution to the total amount of carbon in each product in unit time. To calculate the carbon balance, the solid products was estimated to be soot consisting of 53% carbon from the chemical analysis. Over 44 % of carbon in feeding D-glucose solution was converted into CO and CO_2, while the rest was converted into soot and water-soluble by-products in liquid. OH radical generated from D-glucose may enhance oxidation of intermediate species such as CH radicals.

Decomposition rate of D-glucose was estimated 94% because undecomposed D-glucose were not detected in gaseous and liquid products even at an arc current of 6 A. Higher decomposition rate was obtained at higher arc current in all decomposition cases, because stronger oxidative atmosphere formed due to acceleration of H_2O dissociation with increasing arc current.

5. Conclusions

An arc movement is periodically repeated from the inside to outside in an axial direction in the water plasma torch. Then the arc voltage waveform has a periodic saw tooth shape because of a restrike mode. The moving of the arc column is mainly influenced by the steam drag force in the water plasma torch for controlling operating parameter of the arc current. The arc fluctuation shows the frequency of 37 kHz, indicates that the fluctuation is negligible in the decomposition process.

Decomposition of D-glucose by water plasmas was investigated for the development of biomass utilization. At torch powers of 0.6-1.3 kW and organic compound concentration of 1.0 mol%, the decomposition rate obtained was over 94% and the major products were H_2, CO, and CO_2. The content of the synthesis gas, H_2 and CO, was about 89%, providing an incentive for liquid waste treatment by this technique.

6. References

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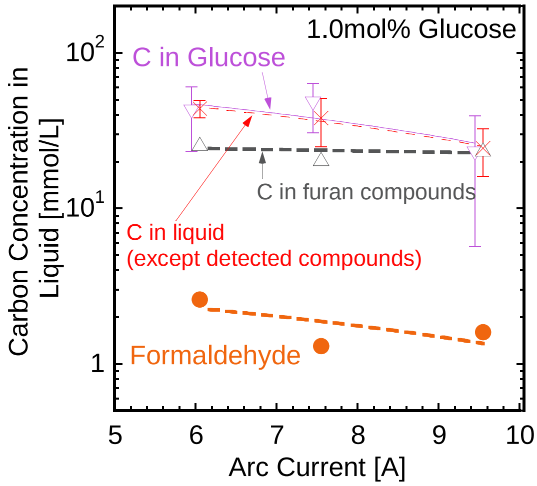

Fig. 7. Effect of arc current on liquid composition generated from 1.0mol% D-glucose.

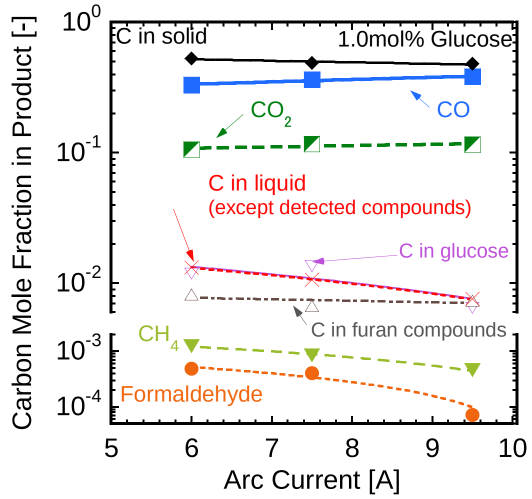

Fig. 8. Effect of arc current on carbon balance generated from 1.0mol% D-glucose.