Characteristics of water thermal plasma for biomass utilization system

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Abstract
The purpose of the present work is to visualize the temperature fluctuation of water thermal plasma for biomass gasification. Another purpose is to investigate D-glucose decomposition mechanism in water thermal plasma because D-glucose is one of the main components in general biomass products. Arc temperature distributions of water thermal plasma with and without D-glucose injection were successfully visualized by high-speed camera. Two synchronized arc images in different wavelengths of Hα and Hβ were observed owing to appropriate optical band-pass filters with negligible other emissions from the arc. The arc temperature was measured based on Boltzmann-plot method. Measured arc temperature without D-glucose was 9000 K, and that with D-glucose was 7500 K. These temperatures were sufficiently high to decompose D-glucose completely. Furthermore, frequency analysis of arc fluctuation revealed that the time period of arc fluctuation was sufficiently shorter than that of the time constant of D-glucose decomposition. These results implied that the influence of arc fluctuation on D-glucose decomposition was negligible. In addition, the decomposition mechanism of D-glucose was discussed on the basis of the analyses of the products in vapor, liquid, and solid phases. They were converted from D-glucose through the water thermal plasma. Decomposition rate of D-glucose reached 99%. Gaseous product contains more than 86% of syngas, H2 and CO. This ratio is much higher than that in conventional gasification device. From these characteristics, water plasma system is suitable device for biomass utilization.

Keywords: Thermal plasma, Water plasma, Arc fluctuation, D-glucose decomposition, Decomposition mechanism

1. Introduction
Thermal plasmas have attracted great attention due to their unique advantages. These advantages including high enthalpy to enhance reaction kinetics, high chemical reactivity, and oxidation or reduction atmospheres in accordance with required chemical reactions are beneficial for various industrial applications. In particular, thermal plasmas are expected to be utilized for decomposition of harmful materials and recovery of useful materials from the wastes.

Water plasma is one of the most attractive thermal plasmas for innovative green technology. This is because the water plasma has a strong benefit to possess large amount of H, O, and OH radicals. These radicals combine with decomposed components to inhibit the generation of by-products, and a large amount of syngas, H2 and CO, can be produced. Therefore, water plasma has been intensively explored for the purpose of the waste treatment and its gasification. Hybrid plasma torch using a water vortex and gas flow for the biomass gasification was developed (Hrabovsky et al., 2006; Oost et al., 2010). The results showed that the syngas ratio of gas products reached 90vol%.

DC water plasma torch for treatment of organic waste was also developed (Yuan et al., 2010; Narengerile et al., 2010; Choi and Watanabe, 2012). Non-transferred plasma torch system is used for water plasma system. Many kinds of water-soluble organic compounds such as fluorinated compounds had been successfully decomposed in water plasma system.

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. The experimental investigation of the decomposition of D-glucose using the water plasma torch has been investigated (Watanabe et al., 2015). Results
indicated the capability of the water plasma torch in biomass gasification processes. However, the fundamental phenomena in water plasma torch have not been clarified yet. One of them is the decomposition mechanism of D-glucose. Another is the fluctuation characteristics and its effect on the decomposition of organic compounds.

Arc fluctuation has strong effect on the properties of the processed object. In the conventional non-transferred DC torch for plasma spray process, the arc fluctuation effect on the in-flight particles and coating properties have been clarified (Bisson et al., 2003; Pfender, 1994). Due to the fluctuation of plasma arc, the particle velocity and temperature are not stabilized. Moreover, the coating property varies because of the above-mentioned particle behavior.

Arc fluctuation and temperature fluctuation in water plasma have not been understood well in spite of their importance on the organic waste decomposition. This mainly originated from the difficulty of the temperature measurement in the water thermal plasma due to rapid arc fluctuation at kHz order, resulting from restrike phenomena of the arc (Matsuo et al., 2016).

Temperature measurements of thermal plasmas using high-speed camera system have been developed in past years. Conventionally, optical emission spectroscopy (OES) was applied to measure the temperature distribution of thermal plasmas. However, time resolution of OES techniques was not sufficient to measure the temperature fluctuated on kHz order. Therefore, the high-speed camera techniques for temperature measurements have been developed. By high-speed camera, temperature can be measured in two dimensions at a high framerate more than 10^4fps. Observation with high-speed camera provides a more efficient approach as an imaging method. This imaging method was applied for the temperature distribution measurements of DC arc (Bachmann et al., 2013) and RF thermal plasma (Kodama et al., 2016).

The first purpose of this study is to investigate the fluctuation effect in water plasma torch on the decomposition of D-glucose. The high-speed camera combined with the appropriate band-pass filters was applied to visualize the arc temperature field and investigate its fluctuation characteristics. Second purpose is to investigate the decomposition mechanism of D-glucose in water plasma. 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.

2. Experiments
2.1. Experimental setup and condition

A schematic diagram of DC water plasma system for aqueous D-glucose decomposition is shown in Fig. 1. The system consisted of a DC power supply, a plasma torch, a metering pump, and a reaction tube. The plasma torch 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 plasma was generated at discharge region by heating and ionization of steam that was produced by evaporation of water from the reservoirs. Simultaneously, the anode was 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 system consisted of 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 were useful for suppressing by-product formation.

D-glucose solution was introduced into the torch after adjusting solution concentration to 1.0 mol% with analytical grade D-glucose (98%, Wako Pure Chemical Industries, Ltd.) and distilled water. Feed rate of the treated solution in water plasma was determined by the thermal balance of the plasma torch. D-glucose solution was directly fed into the high temperature region. Thus the D-glucose solution evaporated at the discharge region in an instant. All of solution fed into the arc was converted into gas during flash evaporation, therefore the liquid and gas composition was the same. The fed solution of D-glucose contributed to cool both anode and cathode for the protection of the electrodes from the thermal damage due to high temperature arc. 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.

2.2. High-speed imaging of arc temperature field

Measurement of arc temperature in water plasma was carried out by the high speed camera system (Phantom v...
An optical system (MSI-2, Photron Ltd.) including the band-pass filters (Andover Optical Inc.) was combined with the high-speed camera, as shown in Fig. 2. Conventionally, the visualization of fluctuated arc temperature field is difficult because of the requirement of high time resolution. In the present work, the high-speed camera combined with appropriate band-pass filters was applied to achieve the visualization of the temperature field in the water thermal plasma. The wavelength for the high-speed camera measurements of atomic emissions from hydrogen were selected as 486 nm and 656 nm. The sensitivity of whole system including the camera, filters, lenses, and the mirrors was calibrated for both wavelengths on the basis of the tungsten lamp. The synchronized images for different wavelength were observed by this system. Then, arc temperature was calculated based on the Boltzmann plot method.

Typical frame rate and shutter speed of the measurements were $2.0 \times 10^5$ s$^{-1}$ and 4.5 μs, respectively. The arc voltage fluctuation during arc operation were recorded at 1MHz by an oscilloscope (Scope Corder DL850, Yokogawa) synchronized with the high-speed camera.

### 2.3. Analyses of vapor and liquid products

A schematic diagram of analyses of gas and liquid phase produced through D-glucose decomposition is shown in Fig. 3. After decomposed by water thermal plasma, products were cooled and then separated into gas, liquid and solid phase. 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 (U-986, Jasco) with an ultraviolet detector (UV-975, Jasco), liquid chromatograph-mass spectrometer (LC-MS) (HPLC: nexera X2, Shimadzu, Mass: micrOTOF-QIII, Bruker), and ultraviolet-visible absorption spectroscope, UV-vis (V-550, Jasco) were used for analysis of the liquid effluent.

### 3. Results and discussion

#### 3.1 Temperature fluctuation

Arc temperatures of water thermal plasma with and without D-glucose were successfully visualized in microsecond time scale as shown in Fig. 4. Obtained temperature distributions revealed that the arc temperature reached to 9000 K in the case of pure water. The arc temperature with 1mol% D-glucose is about 7500 K, which was lower than that without D-glucose. This is because decomposition energy of D-glucose was required in the case of D-glucose solution. Although the temperature was decreased with injection of D-glucose solution, the arc temperature was sufficiently high.
to decompose the organic compounds.

The arc voltage waveforms synchronized with the high-speed visualization of the arc temperature are also presented in Fig. 4. A periodic saw tooth shapes of the voltage waveforms were clearly recorded at both D-glucose solution and the pure water. These waveforms originated in the restrike phenomena of the arc. The arc voltages were fluctuated from 105 V to 150 V with the standard deviation of 23 V at 1mol% D-glucose solution. When pure water was used, arc voltages were fluctuated from 108 to 170 V with the standard deviation of 31 V. The arc frequency was also indicated in Fig. 5 through the Fast Fourier Transform (FFT) for the periodic voltage fluctuation. The frequency was 28.1 kHz at 1mol% D-glucose solution, while the frequency was 39.0 kHz at pure water. This difference was also because of D-glucose decomposition in the region of arc.

The characteristics time of arc fluctuation was about 0.026 ms from Fig. 5. The time constant at D-glucose decomposition process was estimated to be on millisecond order (Narengerile, 2011). This estimation suggests that the influence of arc fluctuation on the D-glucose decomposition is negligible.

![Fig. 4 Synchronized measurements of arc temperature distribution and waveform of arc voltage with (a) D-glucose solution (b) pure water.](image)

![Fig. 5 Arc frequency from a periodic voltage fluctuation of (a) D-glucose solution (b) pure water.](image)

### 3.2 Decomposition of D-glucose

Injected D-glucose solution was decomposed with complex reaction in the high temperature region of water plasma. In order to reveal the decomposition mechanism, main products as well as by-products must be analyzed. D-glucose solution was decomposed through the high temperature region of the plasma, and converted into gaseous products at downstream of plasma where temperature was less than 1000 K. Then they can be quenched in the reaction tube and separated into gaseous phase, liquid phase, and solid phase.

The effect of the arc current on the generation rate of D-glucose solution is shown in Fig. 6. The solution feed rate increased from 46.8 to 52.6 mg/s with increasing arc current. This is owing to larger Joule heating at higher arc current. The generation rates of gas, liquid, and solid were also presented in Fig. 6. In this system, the solid production rate and feed rate were estimated on the basis of the mass balance and carbon balance because of the difficulty of direct measurement:
\[ F_{\text{feed}} = G_{\text{gas}} + G_{\text{liquid}} + G_{\text{solid}} \]  
\[ F_{\text{feed}} w_{\text{feed}} = G_{\text{gas}} w_{\text{gas}} + G_{\text{liquid}} w_{\text{liquid}} + G_{\text{solid}} w_{\text{solid}} \]

where \( G_i \) is the generation rate of \( i \) phase (gas, liquid, or solid), and \( F_{\text{feed}} \) is the feed rate. \( \omega_i \) is carbon containing rate in the \( i \) phase. Generation rates of liquid and gas increased with increasing the arc current. This is because the evaporation and decomposition of D-glucose solution was enhanced at higher arc current. About 93wt% of fed solution was converted into liquid and 4.4wt% of that was converted into gas. The liquid effluent contained more than 99.9mol% of water and less than 0.1mol% of undecomposed D-glucose and by-products. Estimated decomposition rate was more than 99% in all conditions conducted in the present work. More details of the liquid effluent will be discussed in the following paragraphs after the discussion about gaseous products.

Fig. 6  Mass balance generated from 1.0mol% D-glucose at different arc currents.

Gaseous products were qualitatively analyzed by QMS. Representative mass spectrum of the gaseous product are shown in Fig. 7. Production of \( \text{H}_2 \), \( \text{C} \), \( \text{CH}_4 \), \( \text{H}_2\text{O} \), \( \text{CO} \), and \( \text{CO}_2 \) were observed from the intensity peaks of 2(\( \text{H}_2^+ \)), 12(\( \text{C}^+ \)), 16(\( \text{CH}_4^+ \)), 18(\( \text{H}_2\text{O}^+ \)), 28(\( \text{CO}^+ \)), and 44(\( \text{CO}_2^+ \)), respectively. In the past study about decomposition of 10mol% ethanol solution by water plasma (Nishioka et al., 2009), the intensity peak of 26 (\( \text{C}_2\text{H}_2^+ \)) was identified. \( \text{C}_2\text{H}_2 \) was considered to be the intermediate product of the production of soot. However, the peak at 26 was not detected from the D-glucose decomposition. This result suggests that the products in solid phase are different from soot. Quantitative analysis of the gas products was carried out by GC-TCD. The composition of the produced gas from 1mol% D-glucose solution at different arc current is presented in Fig. 8. The major products in gas phase were \( \text{H}_2 \), \( \text{CO} \), and \( \text{CO}_2 \). The concentration of \( \text{CO}_2 \) increased at higher arc current because of stronger oxidative atmosphere due to enhanced dissociation of \( \text{H}_2\text{O} \) at higher arc current. Importantly, gaseous products contained more than 86vol% of syngas, \( \text{H}_2 \) and \( \text{CO} \), which was much higher than 35vol% of the syngas concentration in the conventional gasification device by thermal decomposition (Tuomi et al., 2015).

Fig. 7  Mass spectrum of gaseous products from 1.0mol% D-glucose by QMS at the arc current of 6 A.

Fig. 8  Gas composition generated from 1.0mol% D-glucose at different arc currents.
Undesired by-products of aldehydes (HCOH, CH_{2}COH, \((COH)_{2}\), CH_{3}COCOH) in the liquid phase were detected by LC-MS. Then, the quantitative analysis of the liquid effluent was conducted by HPLC. Measured concentration of aldehydes is shown in Fig. 9. These materials were considered to be the by-products of D-glucose decomposition. Thus, the decomposition mechanism was considered from the intermediate products of by-products. This decomposition mechanism is discussed in the following paragraph.

Carbon balance of decomposition products of 1mol% D-glucose at different arc currents is presented in Fig. 10. The carbon balance was defined as the ratio of the carbon amount in each product to the total carbon from D-glucose solution. More than 32% of carbon in fed D-glucose solution was converted into CO and CO_{2}, while the rest was converted into soot and by-products in liquid phase. Carbon mole fraction in solid decreased and mole fraction of CO and CO_{2} increased with higher arc current. Products in the solid phase were generated due to the incomplete decomposition of D-glucose by water plasma. Thus, decreasing carbon mole fraction in solid means larger amount of D-glucose was decomposed in water plasma. The reason of increase CO and CO_{2} is that OH radical from water plasma was generated more at higher electric power of plasma, and oxidation of intermediate species such as CH radicals is enhanced.

Decomposition mechanism of D-glucose in water plasma was considered from the results of gas and liquid analyses and its schematic diagram is indicated in Fig. 11. By-products were produced when hydrocarbon radicals as intermediate products react with H or OH radicals at around 1000 K. Therefore, intermediate products of D-glucose decomposition can be identified from the results of by-products in liquid phase. Two routes of by-products formation with one main decomposition route were considered from main products of gas (H_{2}, CO, CO_{2}) and aldehydes in liquid phase. The D-glucose was decomposed by dehydration and pyrolysis at around 7000 K, then H_{2}, CO, CO_{2} were finally produced. Aldehydes of by-products were produced by recombination at around 1000 K. These understandings of the decomposition mechanism will enable to find optimized conditions for biomass utilizations including the D-glucose.
4. Conclusion

The arc temperature of water thermal plasma was successfully visualized by high-speed camera with appropriate band-pass filters. Transmission wavelengths of filters corresponded to the atomic emissions from hydrogen at 656 and 486 nm. The measured arc temperature was 7500 K at D-glucose solution, and the arc fluctuation showed the frequency of 28 kHz. Obtained results showed that the arc temperature fluctuated at kHz order owing to arc restrike phenomena. This measurement reveals that the temperature fluctuation is negligible in the decomposition process of D-glucose due to the sufficiently short time period of the arc fluctuation.

Decomposition of D-glucose by water thermal plasma was investigated for biomass utilization. Decomposition rate of D-glucose was more than 99.9%. The major products were H$_2$, CO, and CO$_2$. The concentration of H$_2$ in generated gas was 56mol%. Decomposition mechanism was discussed based on by-products in the effluent liquid. From the obtained results, water plasma has a potential to be utilized for biomass utilization, especially as a gasification system.

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