

## Evaluation of OH Radicals in Aqueous Solution Produced by In-line Plasma Treatment Device

インラインのプラズマ処理装置により生成される水溶液中のOHラジカル評価

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In-liquid and gas-liquid interface plasma are expected as a new liquid treatment technique due to its high production rate of chemically reactive species (OH, O, etc.). We suggested a microwave plasma device using Venturi effect to treat a liquid, and have reported on the solution processing performance of organic decomposition by this plasma source. In this study, OH radicals generated in aqueous solution by the plasma is investigated using chemical probe method as well as using an optical emission spectroscopy. As high flow speed, it was suggested that the reaction efficiency with OH radical produced by the plasma became higher.

### 1. Introduction

Recently, plasmas generated under liquid, and at a gas-liquid interface are attracting much attention because of their industrial applications which utilize chemically reactive species in plasma. For example, these plasmas have been investigated for decomposition of organic compound, sterilization, inactivation of alga<sup>[1]</sup>. Recently, we suggested a microwave plasma device using Venturi effect to treat a liquid, and we have reported processing performance of organic decomposition by this plasma source<sup>[2]</sup>, showing that decomposition rate increased with increasing liquid flow speed. However, mechanism of the efficiency enhancement due to flow rate increase is still not clear. In this study, OH radicals in aqueous solution are investigated using chemical probe method as well as using an optical emission spectroscopy.

### 2. Experimental

In the experiment, a tube with a nozzle is installed inside a rectangular waveguide as shown in Fig. 1. Top and bottom parts of the nozzle are separated and are surrounded with a quartz tube to seal the liquid and the vacuum. A pulsed 2.45GHz microwave (peak power: 1120W, pulse repetition frequency: 10 kHz, duty ratio: 50%) is introduced into a waveguide and the plasma is produced inside a gap between the top and bottom part of the nozzle. During the plasma treatment, a solution was continuously supplied to the nozzle at a flow speed of 10.5~22.0 m/s and reduced-pressure condition is realized inside the gap, i.e., the plasma production region. Before the nozzle installation to the waveguide, pressure at the plasma production

region is measured using a pressure sensor. Optical emission from the plasma is observed by an optical multichannel analyzer with a CCD-array detector (Ocean Optics, HR4000-UV-NIR) through a quartz window on the sidewall of the waveguide.

In order to evaluate OH radicals dissolved in the liquid, chemical probe method based on terephthalic acid (TA) is used. TA is a well-known OH scavenger. OH radical can convert TA to 2-hydroxyterephthalic acid (HTA) though the reaction. It has low chemical reactivity with other radicals, such as O<sub>2</sub>·, HOO· and H<sub>2</sub>O<sub>2</sub>. Sample water after the plasma treatment is irradiated with UV light ( $\lambda = 315$  nm) from a LED UV light source and fluorescence light at  $\lambda = 425$  nm<sup>[3]</sup> is monitored and the HTA concentration is evaluated.

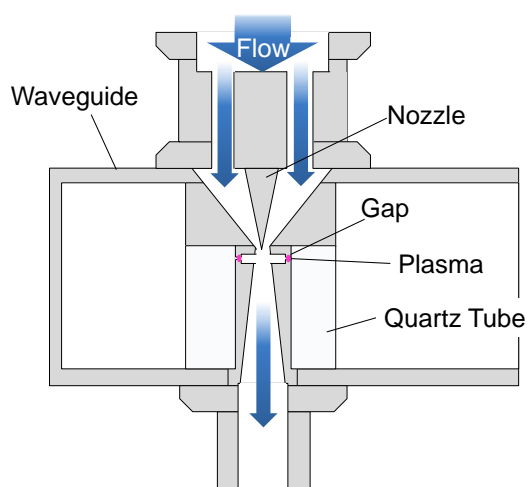


Fig. 1 Cross sectional view of the in-line plasma treatment device.

### 3. Results

Figure 2 shows HTA concentration as a function of the flow rate. The HTA concentration monotonically increases with increasing the flow speed and HTA concentration as high as 1.6  $\mu\text{M}$  was obtained at a flow rate of 22 m/s. This result indicates that the chemical reaction rate of OH with TA is enhanced by increasing the flow speed.

There are various possibilities of the reaction rate enhancement. One of the important points is the change in the plasma condition due to the flow speed. As was mentioned, the reduced pressure condition is realized by the liquid flow in this device. Accordingly, the plasma might be changed by the pressure variation due to the flow speed. To give an insight into the mechanism of the reaction enhancement by increasing the flow rate, pressure inside the plasma production region was measured by a pressure gauge. Figure 3 shows pressure of the plasma production region as a function of the liquid flow rate. At flow rates less

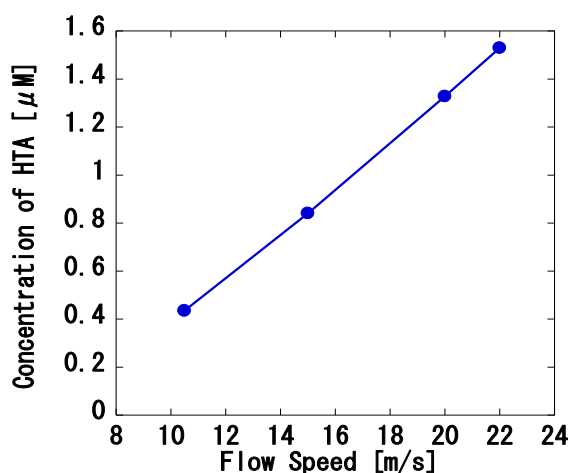


Fig. 2 HTA concentration as a function of the flow speed.

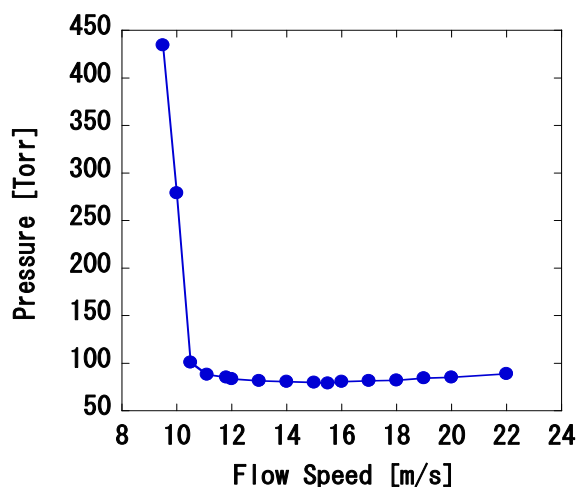


Fig. 3 Pressure of the plasma production region as a function of flow speed.

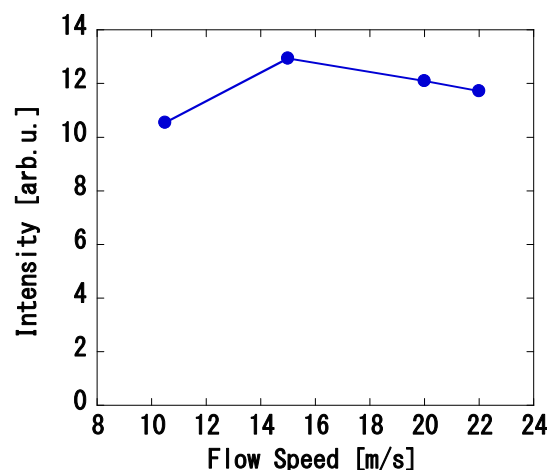


Fig. 4 OH emission intensity as a function of the flow speed.

than 10.5 m/s, the pressure was more than 100 Torr. At high flow rates more than 10.5 m/s, the pressure was kept below 100 Torr and the pressure was almost constant even changing the flow rate.

To investigate the influence of the plasma condition, OH emission intensity from the plasma was monitored as a function of the flow speed, as shown in fig. 4. The OH emission intensity was almost constant irrespective of the flow speed, suggesting that the plasma condition is not influenced at the flow speeds more than 10.5 m/s. The results strongly suggest that the reaction rate enhancement by the increase of the flow speed is not due to the increase in the concentration of OH radical but due to the enhancement of the reaction efficiency.

### 4. Summary

In summary, a pulsed microwave plasma device utilizing Venturi effect was investigated focusing on the liquid flow speed through a nozzle in the vicinity of the plasma region. Chemical reaction of terephthalic acid (TA) to produce 2-hydroxyterephthalic acid (HTA) was enhanced by increasing the liquid flow speed. Both pressure and OH emission intensity at the plasma production region was measured as a function of the flow speed and these parameters were almost constant at flow speeds more than 10.5 m/s, although the HTA production rate was increased at these flow speed region. These results strongly suggest that the reaction efficiency with OH radical produced by the plasma became higher at high flow speed.

### References

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