Behavior of Sonochemical Reaction in Small Tube

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1. Introduction

Microreactors have high reaction performance due to their large specific surface area. However, because of the laminar flow in the tube, vertical mixing with respect to the flow is weak, and clogging by solid materials is a problem. To solve these problems, a combination of microreactors and ultrasound has been studied[1-2].

Ultrasonic irradiation to water causes mechanical and chemical effects due to ultrasonic cavitation. However, it is unclear whether the latter, sonochemical reaction, occurs in small tubes whose diameter is smaller than the wavelength of ultrasound. Furthermore, little has been reported on the effects of apparatus conditions on the sonochemical reaction performance in tubes.

In this study, sonochemical reaction rates were measured under the circulation of an aqueous solution of potassium iodide (KI) in the small tube. The effects of varying the tube position, liquid surface conditions and flow velocity on the reaction rate were studied.

2. Experimental

Fig. 1 shows the outline of experimental apparatus. The transducer was disk-type one (Honda Electronics) with a 50 mm diameter at a frequency of 213 kHz. The transducer was driven by a power amplifier (AP400B, ENI), which amplified a continuous sine wave generated by a signal generator (WF1946B, NF). A matching circuit was inserted in between the power amplifier and the transducer. An effective electric power applied to the transducer was calculated from the voltage and the electric current supplied to the transducer, which were measured by an oscilloscope (MDO3014, Tektronix) and a current probe (TCP202, Tektronix). To keep the effective electric power constant, an electrical control system (Honda Electronics) was used. The system on the personal computer read the value of the effective electric power from the oscilloscope to the personal computer via the general-purpose interface bus (GPIB), and adjusted the optimum signal generator output voltage via GPIB.

The water tank outside the vessel was filled with degassed water below a dissolved oxygen concentration of 4 mg·L^{-1} at 298 K. A stainless steel pipe with an outer diameter of 6.0 mm and inner diameter of 5.0 mm was placed in the water tank, and 50 mL of the KI solution was circulated between a beaker and the pipe using a pump. The pipe position was defined as a distance from the liquid surface to the bottom of the pipe, and was varied at a 0.25 mm interval using a vertical translation (z-axis) stage. The liquid surface was either free or covered with a reflection plate made of SUS304 stainless steel.

The KI method[3] was used to determine the sonochemical reaction rate. When an aqueous solution of KI is irradiated with ultrasound, I^- ions are oxidized to form I_2. When excessive I^- ions exist in the solution, an I_2 molecule reacts with an excessive I^- ion to produce a I_3^- ion as follows:

$$I_2 + I^- \rightleftarrows I_3^-, \tag{1}$$

The KI aqueous solution of an I^- ion concentration of 0.1 mol L^{-1} was prepared using KI (Fujifilm Wako Pure Chemicals) and ultrapure water. The I_3^- concentration was measured from the optical absorbance at 352 nm using a UV-Vis spectrometer (UV-1850, Shimadzu Corporation). The reaction rate k [mol·s^{-1}] was calculated as follows:

$$k = \frac{AV}{\varepsilon l t} \quad , \tag{2}$$

where A is the absorbance of I_3^- [−], V is the solution volume [L], ε is the molar extinction coefficient of I_3^- [L·mol^{-1}·cm^{-1}], l is the cuvette path length [cm], and t is the sonication time [s]. In this experiment, ε, l, and t were 26,303 L·mol^{-1}·cm^{-1}, 1 cm, and 300−600 s, respectively.

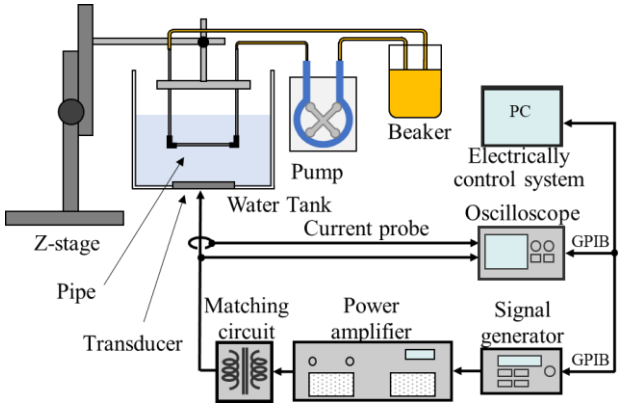

Fig. 1 Outline of experimental apparatus

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3. Results and discussion

Fig. 2 shows the effect of the effective electric power applied to the transducer on the reaction rate. This result indicates that the sonochemical reaction occurs in a small tube whose diameter is smaller than the wavelength of ultrasound (7.04 mm). The reaction rate initially increased with the electric power. However, at a certain electric power, the reaction rate reached a maximum value and then decreased. This phenomenon is called quenching of sonochemical reactions[4].

Fig. 3 shows the effect of the liquid flow velocity on the reaction rate. The reaction rate increased with the liquid flow velocity. Since the reaction rate decreases as cavitation bubbles aggregate, the increase in the reaction rate can be ascribed to that the liquid flow prevents the aggregation of cavitation bubbles[5]. We consider another mechanism in which the liquid flow provides the reaction field with bubble nuclei and reactants.

Fig. 4 shows the effect of the pipe position on the reaction rate with and without a reflection plate. In the absence of the reflection plate, the reaction rate periodically changed as the pipe position increased, and it exhibited minimum and maximum values at 12.00 mm and 13.25 mm, respectively. The positional difference between the minimum and maximum was 1.25 mm, which is close to the quarter of the wavelength of ultrasound (1.76 mm). The deviation from 1.76 mm might be attributed to the significant disturbance of the liquid surface due to acoustic radiation forces. In the presence of the reflection plate, the reaction rate also periodically changed as the pipe position increased, and they had maximum and minimum values at 11.25 mm and 13.50 mm, respectively. The liquid surface with and without the reflection plate corresponded to the fixed end and the free end, respectively. Therefore, the pipe position at which the reaction rate was maximized was different. The maximum reaction rate with the reflection plate was much higher than that without the plate. This is because the disturbance of the liquid surface was suppressed by the plate, and the stable standing wave was formed.

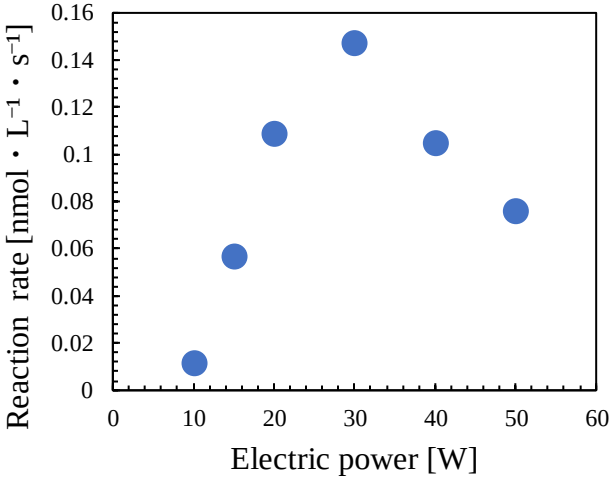

Fig. 2 Effect of the effective electric power applied to the transducer on the reaction rate

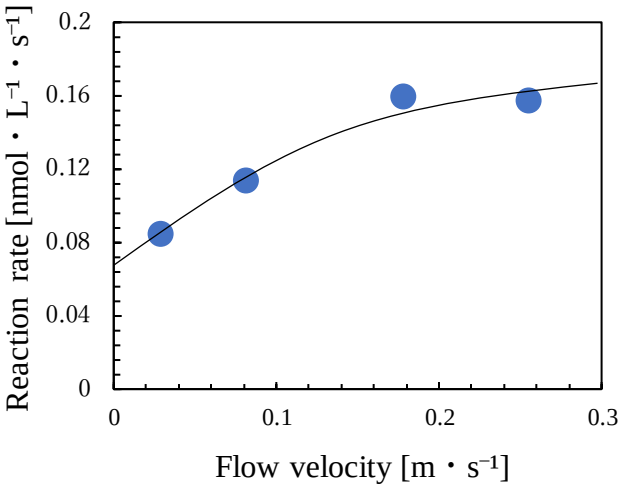

Fig. 3 Effect of the liquid flow velocity on the reaction rate

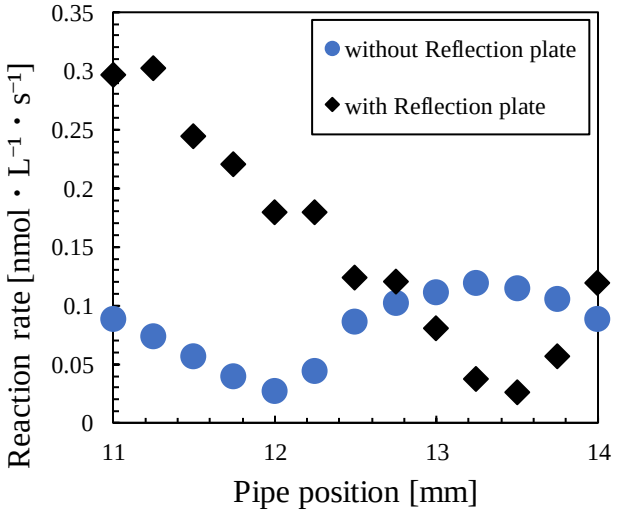

Fig. 4 Effect of the pipe position on the reaction rate with or without a reflection plate

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