

## Sonochemical Production of H<sub>2</sub> using Water/alcohol Mixtures in a 300 kHz System

Seokho Yoon<sup>1,2†</sup>, Taehui Park<sup>1,2</sup>, Jongbok Choi<sup>1</sup> and Younggyu Son<sup>1,2\*</sup>  
 (<sup>1</sup>Dept. Environ. Eng., Kumoh Nat'l Inst. Technol.; <sup>2</sup>Dept. Energy Eng. Converg., Kumoh Nat'l Inst. Technol.)

### 1. Introduction

Ultrasonic cavitation technology can be applied in the field of environmental engineering due to its ability to control oxidation and reduction reactions for the degradation of various substances.<sup>1)</sup> The reactions are induced by chemical and physical effects that occur through cavitation phenomena.<sup>2)</sup> Chemical effects include thermal decomposition and radical reactions, and physical effects include shock waves and liquid-phase mixing.<sup>3)</sup>

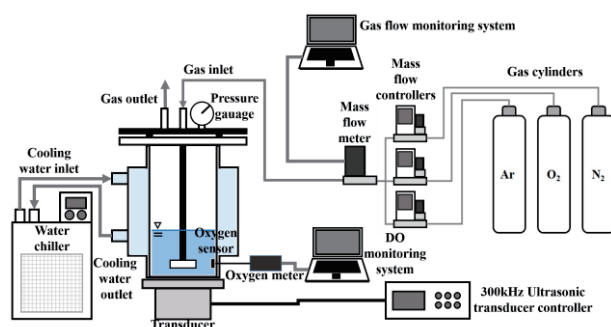
In recent times, researchers have actively explored the potential of sonochemical effects, including oxidation and reduction, such as hydrogen production and the decomposition of perfluorinated compounds.<sup>4-5)</sup>

This study focuses on optimizing hydrogen generation through sonochemical reduction reactions using a 300 kHz ultrasonic system. By evaluating hydrogen generation rates, the study optimizes the liquid phase conditions (0.1%, 0.5%, 1%, 5%, 10%, 20%) of three organic solvents (Methanol(MeOH), Ethanol(EtOH), n-propanol(n-PrOH)) under optimal dissolved gas conditions. Additionally, a comparison between hydrogen production and hydrogen peroxide production is conducted under various dissolved gas conditions known for their favorable sonochemical effects.

### 2. Materials and Methods

Chemicals used in this study were provided and sourced as follows: Methanol (CH<sub>3</sub>OH, 99.9%, HPLC grade) and Ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99.9%, HPLC grade) were supplied by Samchun Pure Chemical Co., Ltd. (KOR). n-Propanol (C<sub>3</sub>H<sub>7</sub>OH, 99.5%, extra pure) and Potassium biphthalate (C<sub>8</sub>H<sub>5</sub>KO<sub>4</sub>) were obtained from Daejung Chemicals & Metals Co., Ltd. (KOR). Ammonium molybdate [(NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>] and potassium iodide (KI) were procured from Junsei Chemical Co. Ltd. (JPN). All chemicals were used as received.

The ultrasonic system is schematically illustrated in Fig. 1. It comprised a double-walled pyrex reactor (D × H : 105 mm × 125 mm) equipped



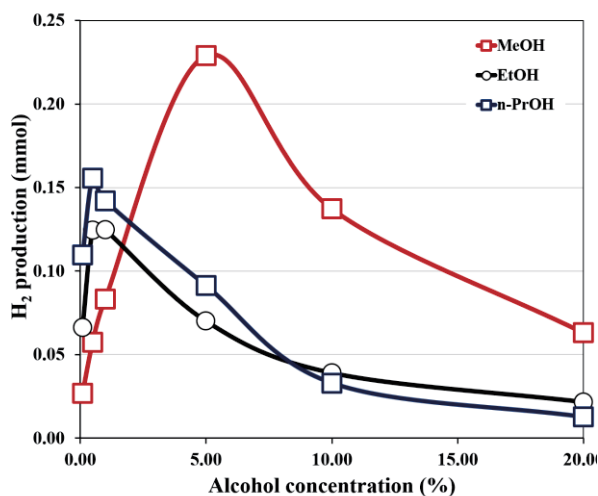
**Fig. 1** Schematic of the 300-kHz double-walled pyrex sonoreactor with the gas supply system, cooling system, and DO monitoring system.

with a 300 kHz ultrasonic transducer module (Mirae Ultrasonic Tech., KOR). A cooling water system was implemented to maintain the solution temperature at  $20 \pm 2.5$  °C by circulating water around the reactor. The volume of solution is 220 mL (5  $\lambda$ ,  $h_{\text{solution}} = 2.5$  cm), and the ultrasonic transducer operated at a electric power of  $80 \pm 2$  W.<sup>6)</sup> As shown in Fig. 1, a controlled mixture of argon and oxygen gases was introduced into the solution using a mass flow meter controllers. The gas sparger was positioned 1 cm above the reactor bottom, and a gas flow rate of 3 L/min was maintained.

Hydrogen analysis was conducted via gas chromatography with a thermal conductivity detector (GC-TCD, Agilent 8890, USA) on samples obtained through headspace sampling using a 500  $\mu$ L glass syringe (TRAJAN, AUS). The carrier gas is nitrogen (99.999 %). The analysis utilized a Packed column (G3591-80013, 6Ft 1/8 2mm propak Q 80/100 SS), and oven and detector temperatures were set at 40 °C and 250 °C, respectively.

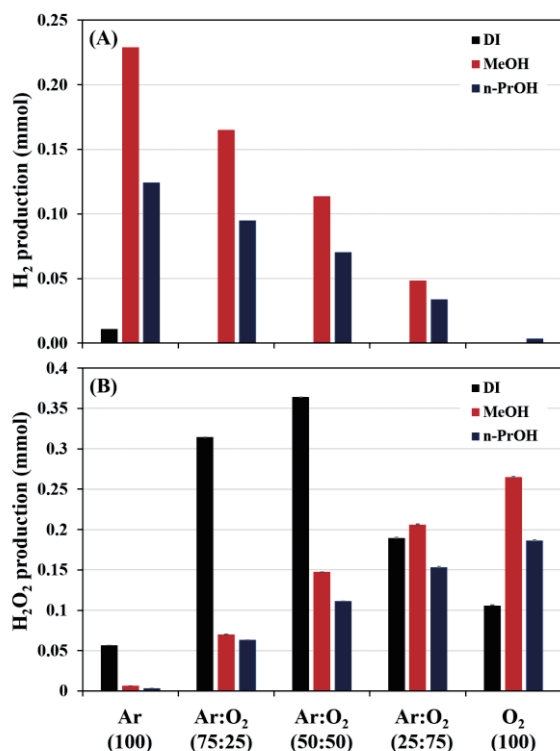
Concentration of H<sub>2</sub>O<sub>2</sub> generated through sonochemical processes was measured using a spectrophotometer (SPECORD 40; Analytic Jena AG, Jena, DEU) at 353 nm and using solution A (0.1 M potassium biphthalate) and solution B (0.4 M potassium iodide,  $6.0 \times 10^{-2}$  M sodium hydroxide, and  $10^{-4}$  M ammonium molybdate) is used to analyze H<sub>2</sub>O<sub>2</sub> concentration.

### 3. Results and Discussions



**Fig. 2** Hydrogen production in various organic solvents at different alcohol concentrations (300 kHz, 30 min, Ar saturated)

The amount of hydrogen generated under ultrasonic irradiation at various alcohol concentrations for three aliphatic alcohols is shown in **Fig. 2**. The hydrogen production is different depending on the concentrations of alcohols. The kinetic constants of hydrogen production for the concentrations of alcohols (0.1%, 0.5%, 1%, 5%,



**Fig. 3** Hydrogen(A) / hydrogen peroxide(B) production of deionized water(DI) / methanol (MeOH, 5%)/n-Propanol(n-PrOH, 0.5%) under different dissolved gas conditions (300kHz, 30min)

10%, and 20%) are calculated as: Methanol 0.90, 1.91, 2.78, 6.44, 4.58, and 2.10  $\mu\text{mol}/\text{min}$ ; Ethanol 2.21, 4.14, 4.15, 2.34, 1.30, and 0.72  $\mu\text{mol}/\text{min}$ ; n-propanol 3.66, 5.19, 4.74, 3.04, 1.10, and 0.42  $\mu\text{mol}/\text{min}$ , respectively.

**Fig. 3** shows that the comparison between hydrogen and hydrogen peroxide production under different kinds of Ar:O<sub>2</sub> mixed gas conditions. In deionized water, hydrogen was generated only under the condition of 100% Ar saturation, and the amount was very small compared to other alcohols. The kinetic constants of hydrogen production for different dissolved gas conditions (Ar, Ar:O<sub>2</sub>(75:25), Ar:O<sub>2</sub>(50: 50), Ar:O<sub>2</sub>(25:75), O<sub>2</sub>) are calculated as: Methanol 7.63, 5.50, 3.79, 1.61, and 0  $\mu\text{mol}/\text{min}$ ; n-propanol 4.15, 3.16, 2.34, 1.13, and 0.12  $\mu\text{mol}/\text{min}$ , respectively.

Hydrogen peroxide production in deionized water demonstrated significant oxidation under mixed gas conditions, consistent with prior studies.<sup>7,8)</sup> However, solutions containing methanol and n-propanol exhibited an increase in hydrogen peroxide production as the oxygen content in the dissolved gas rose.

### Acknowledgment

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