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Sonochemical Production of H_2 using Water/Organic Acid Mixtures in a 300 kHz System

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1. Introduction

Ultrasonic cavitation technology holds significant potential in environmental engineering due to its ability to apply chemical oxidation /reduction reactions for the degradation of various organic substances.[1)] These reactions are driven by the sonochemical and sonophysical effects resulting from ultrasonic cavitation phenomena.[2,3)] The sonochemical effects include thermal decomposition and radical reactions, while the sonophysical effects involve shock waves and liquid-phase mixing.[4)]

In recent years, the production of organic industrial wastewater, particularly that containing organic acids and alcohols, has been steadily increased.[5)] This wastewater has prompted the need for innovative approaches to its effective reuse, such as through hydrogen energy production. In a previous study, we found the possibility to generate hydrogen from alcohol solutions.[6,7)] However, in this study focuses on optimizing hydrogen generation through sonochemical reduction reactions using water/organic acids solutions in a 300 kHz ultrasonic system. Specifically, the research investigates the impact of various organic acids (Formic acid(FA), Acetic acid(AA), Propionic acid(PA), Butyric acid(BA)) on hydrogen production, aiming to enhance the efficiency of reusing industrial wastewater containing organic matters.

2. Materials and Methods

Chemicals used in this study were sourced as follows: formic acid (85.0%, Extra Pure), acetic acid glacial (99.7%, Special Grade), propionic acid (99.0%, Extra Pure) hydrochloric acid solution (1.0 mol/L), and sodium hydroxide solution (5.0 mol/L) were all provided by Samchun Pure Chemical Co., Ltd. (KOR). n-butyric acid (500 mL, Cica-Reagent) was obtained from Kanto Chemical Co., Inc. (JPN). All chemicals were used as received without further purification.

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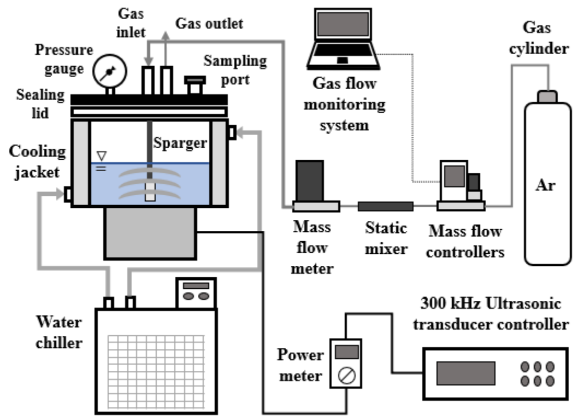

Fig. 1 Schematic of the 300-kHz Double-walled Pyrex Sonoreactor with the Gas Supply System and Cooling System.

The ultrasonic system is schematically illustrated in **Fig. 1**. It comprised a double-walled pyrex reactor (D × H: 105 mm × 125 mm) equipped with a 300 kHz ultrasonic transducer module (Mirae Ultrasonic Tech., KOR). A cooling water system was implemented to maintain the solution temperature at 20 ± 2.5 °C by circulating water around the reactor. The volume of solution is 220 mL (5 λ, $h_{solution}$ = 2.5 cm), and the ultrasonic transducer operated at a electric power of 80 ± 2 W.[6,7)] The argon gas 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 in 20 min before sonication. Hydrogen analysis was conducted via gas chromatography with a thermal conductivity detector (GC-TCD, Agilent 8890, USA). The kinetic constants were calculated by following the zeroth-order reaction.

The pH of the solution was adjusted to 3, 6, and 9 by titration with hydrochloric acid (HCl) and sodium hydroxide (NaOH), using a pH meter (OHAUS Starter 300).

3. Results and Discussions

The generation rate of hydrogen under ultrasonication system at various organic acids concentrations for four carboxylic acids in **Fig. 2**.

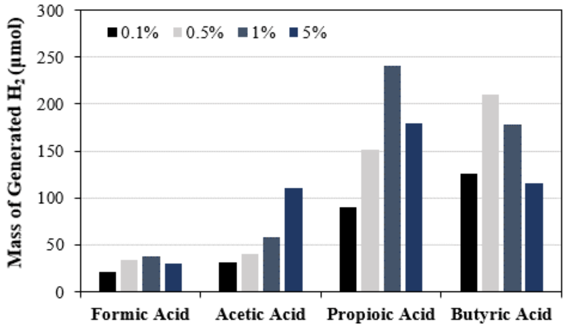

Fig. 2 Mass of Generated Hydrogen of Various Organic Acids under Different Acid Concentrations (300kHz, 60min, pH 6).

The hydrogen production rates vary depending on the concentration of the acids. The kinetic constants of hydrogen production for the concentration of acids (0.1, 0.5, 1, and 5%) are calculated as: FA 21.8, 34.0, 37.7, and 30.3 μmol/hr; AA 31.0, 39.8, 57.7, and 110.6 μmol/hr; PA 89.8, 151.9, 240.5, and 178.9 μmol/hr; BA 126.5, 210.0, 178.3, and 115.6 μmol/hr, respectively. Previous studies have shown that organic compounds with higher molecular weights have optimal hydrogen production rates at lower concentrations, and this study appears to produce similar results ($PA_{Opt.}$ = 1 %, $BA_{Opt.}$ = 0.5 %). In the concentration below 5%, the hydrogen production rate appears to increase with higher molecular weight acids. However, further research is needed to optimize hydrogen generation conditions, particularly for concentrations higher than 5% in the case of lower molecular weight acids.

Fig. 3 shows that the effects of initial pH at kinds of propionic acid concentrations. The three pH values (pH 3, 6 and 9) were selected to evaluate the effect of ionic form of acid (HA or HA^-) that relative to the pKa value (propionic acid (pKa ≈ 4.87)) in the water/acid solution. The kinetic constants of hydrogen production for the concentrations of the acid (0.1, 0.5, 1, and 5%) are calculated as: pH 3 63.1, 127.7, 144.0, and 193.9 μmol/hr; pH 6 89.8, 151.9, 240.5, and 178.9 μmol/ hr; pH 9 45.2, 43.7, 44.2, and 91.4 μmol/hr, respectively. When the acid is present in the form HA- rather than HA, a greater amount of hydrogen is produced. It is also noted that hydrogen production is hindered under conditions with a high concentration of OH^- ions, as in the pH 9 solution. However, since these results are based on conditions tested with a specific organic acid (PA), further research is essential. This includes data on different types of acids and supporting information, such as by-products or ions produced during sonication.

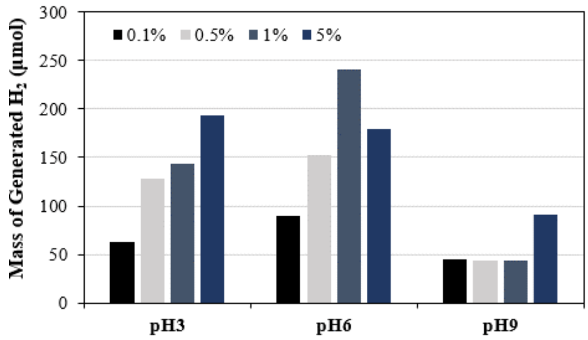

Fig. 3 Mass of Generated Hydrogen of Propionic Acid Solution under Different pH Conditions in Various Acid Concentrations (300kHz, 60min).

Acknowledgment

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