2P4-2

Effect of Gas Saturation on Sonochemical Generation of H_2O_2 and NO_2^-/NO_3^- in a 300 kHz Sonoreactor

Taehui Park [1,2†], Seokho Yoon [1,2], Younggyu Son [1,2*]
([1]Dept. Environ. Eng., Kumoh Nat'l Inst. Technol.; [2]Dept. Energy Eng. Converg., Kumoh Nat'l Inst. Technol.)

1.Introduction

Recently, there has been increasing interest in the on-site generation of H_2O_2 using various methods has been increasing to reduce the risk and cost of H_2O_2 storage, transportation, and use. Sonochemical methods have been proven to be effective for H_2O_2 generation for decades.[1)]

In the high-frequency range of 300–500 kHz, elevated rates of generation are achievable due to enhanced radical production and oxidation reactions facilitated by precise bubble contraction/expansion. The introduction of dissolved gases augments these oxidation processes, profoundly impacting cavitation-induced ultrasonic chemical oxidation.

Notably, the presence of nitrogen gas (N_2) in the liquid phase leads to sonochemical production of NO_2^-/NO_3^- , contributing to the modulation of overall sonochemical oxidation activity.[1),2)] Hence, for enhanced sonochemical oxidation and increased H_2O_2 production, a comprehensive grasp of NO_2^- and NO_3^- production characteristics becomes imperative.[3)]

This study explores the impact of gas saturation on H_2O_2 and NO_2^-/NO_3^- production using a 300 kHz ultrasonic reactor system.

To visually illustrate the enhancement resulting from gas saturation, the study employed the SCL method to confirm the effects of Ar, O_2, N_2, and binary gas mixtures.[4)]

2. Materials and Methods

Hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH) are from Samchun Pure Chemical Co. ltd. (KOR). Potassium biphthalate ($C_8H_5KO_4$) was acquired from Daejung Chemical & Metals Co. ltd. (KOR). Potassium iodide (KI) and ammonium molybdate [$(NH_4)_2MoO_4$] were purchased from Junsei Chemical Co. ltd. (JPN). Luminol (3-aminophthalhydrazide, ($C_8H_7N_3O_2$) was acquired from Sigma–Aldrich Co. (USA). All chemicals were used as received.

An acrylic cylindrical sonoreactor was used in this study, equipped with a 300 kHz transducer

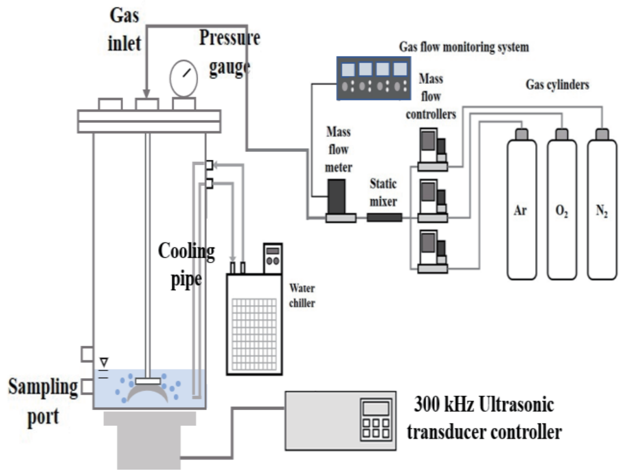

Fig. 1 Schematic of the sonoreactor with the gas supply system

module (Mirae Ultrasound Tech, Bucheon, Korea) was placed at the bottom as shown in **Fig. 1**. The inner diameter and height of the sonoreactor are 150 mm and 350 mm, respectively. The liquid height was 5 λ (25 mm), and the temperature in the liquid body was maintained at 20° C. using a cooling system consisting of a cooling pipe attached to the side wall of the reactor and a water chiller.

The working electrical power was 80 W, measured using a power meter (HPM-300A; ADpower, KOR). The mode was: saturation/closed mode, where the liquid was saturated with a gas or gas mixture and the top of the reactor was covered with a sealing lid (the gas content in the headspace was considered to be the same as the gas content in the liquid body.

Gas was delivered into the liquid body using a microporous glass sparger (pore size: 20–30 μm) equipped with an acrylic pipe. The sparger was placed 1 cm above the reactor bottom. The gas flow rate for saturation was 3 L/min.

E-mail: †pth7643@kumoh.ac.kr, *yson@kumoh.ac.kr

The concentrations of sonochemically generated H_2O_2 was spectrophotometrically analyzed using solution A (0.1 M potassium biphthalate), solution B (0.4 M KI, 0.06 M sodium hydroxide, and 10^{-4} M ammonium molybdate), and a UV–vis spectrophotometer (SPECORD 40; Analytic Jena AG, Jena, DEU)

The sonochemically active zone was visualized using luminol solution (0.1 g/L luminol and 1 g/L NaOH) in a completely dark room. Sonochemiluminescence(SCL) images were acquired using an exposure-controlled digital camera (α58; Sony Corp., JPN) with an exposure time of 30 s.

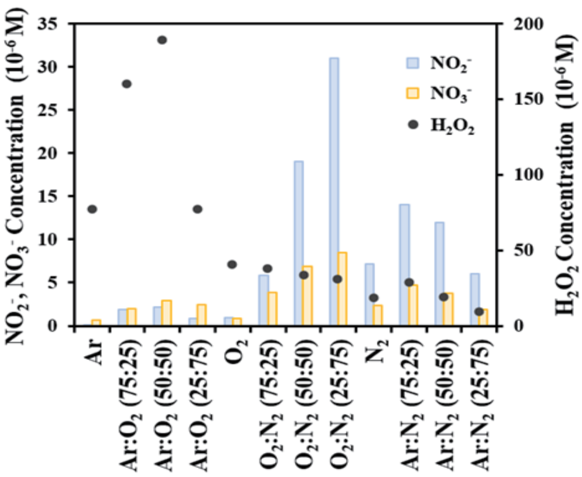

Fig. 2 Sonochemically generated concentrations of NO_2^- , NO_3^- .and H_2O_2 under the saturation/closed mode using Ar, O_2, and N_2 for 300 kHz. The irradiation duration was 60 min.

3. Results and discussion

Fig. 2 shows the concentations of NO_x ions and H_2O_2 produced with ultrasonic irradiations under various different ratios of gases dissolved conditions. In a saturated/closed gas mode, we investigated 12 gas conditions, including Ar 100%, O_2 100%, N_2 100%, and binary gas mixtures (75:25, 50:50, 25:75). Ar:O_2(50:50) exhibited the highest H_2O_2 yield(189 $\times 10^{-6}$ M), while O_2:N_2(25:75) showed the most significant NO_2^- and NO_3^-production(NO_2^- 31×10^{-6} M), (NO_3^- 8.5×10^{-6} M).

To compare the enhancement of the sonochemical activity visually, the SCL images were obtained as shown **Fig. 3**. Ultrasonic reaction region (Blue light) was observed under the condition of being saturated with oxygen and argon, however a weaker ultrasonic active region was observed under the condition of being saturated with nitrogen.

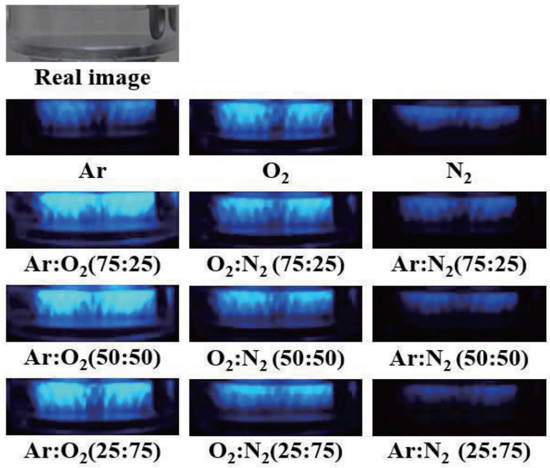

Fig. 3 Sonochemically generated concentrations of NO_2^- , NO_3^- .and H_2O_2 under the saturation/closed mode using Ar, O_2, and N_2 for 300 kHz. The irradiation duration was 60 min.

Among the 12 conditions, the Ar/O_2 mixture gas observed a noticeably brighter and larger SCL region indicating an enhanced sonochemical active region, which tends to be consistent with hydrogen peroxide production.

Acknowledgement

This work was supported by the National Research Foundation of Korea [NRF-2021R1A2C1005470] and by the Korea Ministry of Environment (MOE) as “Subsurface Environment Management (SEM)” Program [project No. 2021002470001].

References

1) Y. Son, and J. Seo, Ultrason. Sonochem. **90**, 106214 (2022).
2) Y. Son, and J. Choi, Ultrason. Sonochem. **92**, 106250 (2023).
3) Supeno, and P. Kruus, Ultrason. Sonochem. **7**, 109 (2000).
4) J. Choi, and Y. Son, Ultrason. Sonochem. **97** 106452 (2023).
5) Y. No, and Y. Son, Jpn. J. Appl. Phys. **58** SGGD02 (2019).