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Analysis of Dynamic Behavior of Gas Bubbles and Solid Particles in an Oscillatory Baffled Reactor and Its Application to Design of Hydrogenation Process

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In this paper, the dynamic behavior of gas bubbles and flow in a liquid-gas-solid oscillatory baffled reactor (OBR) was analyzed. A method based on baffle and oscillating flow induced vorticity was employed to analyze the dynamic gas bubble behavior and elucidate key parameters that govern the flow phenomena and reactor performances. Through visualization experiment for gas flow, it was observed that the fraction of gas bubbles inside OBR with oscillation increased up to 2.9 times than that without oscillation at the gas flow rate of 50 mL/min. Then it was observed that increasing the oscillation amplitude promoted the breakage of gas bubbles under the same conditions of oscillatory Reynolds number (Re_o). On the other hand, particle image velocimetry (PIV) analysis revealed that the spatial distribution of streamlines and the magnitude of vorticity was almost same among operating conditions with different amplitudes of oscillation at the same Re_o. In experiments for three-phase hydrogenation of 3-butyn-2-ol, the evaluated OBR showed higher reaction performance than the conventional packed bed reactor (PBR), and at the same Re_o, the OBR with lower amplitude attained higher selectivity. It was considered that control of dynamic behavior of gas bubbles by the frequency and the amplitude of oscillation could enhance the reactor performances in the OBR.

1. Introduction

In industries, batch reactors have been used to produce pharmaceutical products, inks and chemical additives due to their versatility and robustness. However, various drawbacks have been identified, such as a requirement of significant intermediate storage between operations, poor adaptability and economy-of-scale to respond to fluctuating demands, as well as relatively dismal mixing and heat transfer performance (Navarro-Fuentes et al., 2021). These disadvantages have led to the development of a method for continuous flow reactor designs, and which has attracted more attention in a wide range of industrial fields and have been expected to improve energy consumption and process control (Slavnić et al., 2019).

An oscillatory baffled reactor (OBR) for gas-liquid reaction exhibits a good process intensification that can be efficient alternative to conventional reactors (Geng et al., 2021). OBR usually consists of a circular tube with equally spaced baffles. It has already revealed that the interaction between oscillating flow and baffles generates vortices, which promote the dispersion of gas bubbles and breakage of bubble (Bianchi et al., 2020). However, in application of OBR to the gas-liquid-solid (three-phase) reaction process, there is relatively few studies on methodology for design and control of the reactor due to the complex unsteady flow.

Based on the brief literature study above, an aim of this research is to develop a method for optimal design of OBR for gas-liquid-solid reaction. In the present paper, first, an influence of operation variables to dynamic behaviors of liquid and gas in OBR are analyzed by the flow visualization. Next, based on the analytical results of the flow visualization, a method for application of OBR to three-phase hydrogenation process is investigated. The process of interest in this paper is hydrogenation of 3-butyn-2-ol over Pd/Al_2O_3 catalyst to generate 3-buten-2-ol, as shown in Figure 1. It is noted that the selectivity of the reaction is very sensitive towards over-

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hydrogenation, that is, the migration of the double bond can lead to by-products, namely 2-butanol and 2-butanone. A design method for three-phase OBR system will be discussed through an influence analysis of operation variables to conversion of 3-butyn-2-ol and selectivity to 3-buten-2-ol.

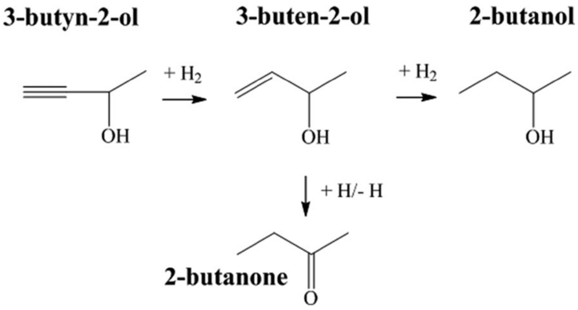


Figure 1: Reaction scheme for the hydrogenation of 3- Butyn-2-ol

2. Experimental

2.1 Flow visualization in OBR

Figure 2(a) shows a schematic diagram of experimental system for flow visualization in OBR. The OBR was made of acryl and consisted of a tube of 26 mm internal diameter. A series of orifice baffles were installed inside the tube. The baffles with a diameter of 20 mm were placed at intervals of 30 mm and have an open cross-sectional area ratio of 25 %. The tube with 250 mm length was surrounded by a rectangular vessel, which was filled with distilled water in order to eliminate distortions due to curvature effect. Nitrogen gas was fed via a porous ceramic sparger placed at the bottom of the tube. The flow rate of gas and liquid were controlled by a mass flow controller (KOFLOC, 3660) and a dual pump (FLOM, KP-22). The oscillating flow was generated by a syringe pump (Hamilton, PSD/6).

First, dynamic behavior of gas bubbles in the tube was observed by video camera (SONY, FDR-AX45). In order to determine the gas flow rate in the following experiments, the gas holdup was measured under the semi-batch mode (only gas flow is continuous) without oscillation. The gas holdup, ε_{G}, was calculated by Eq.(1) and plotted against the gas flow rate. The change in the slope of the increase in gas holdup with respect to the flow rate indicated the transition from the uniform flow to the nonuniform flow.

$$\varepsilon_{\mathrm{G}} = \frac{H^{*} - H}{H} \tag{1}$$

where ε_G is the gas holdup, H is the liquid height in the absence of gas, H^{*} is the liquid height with the presence of gas.

Then the fraction of gas bubbles was estimated from the video images recorded under oscillating operation. The position of the cross section for estimation of the fraction of bubbles was about 120 mm height from bottom of tube. The operating conditions for oscillating flow were determined as follows. The fluid behavior of OBR is governed by the dimensionless parameter, oscillatory Reynolds number, Re_{o}, defined as

$$Re_{\mathrm{o}} = \frac{2\pi f x_{\mathrm{o}} \rho D}{\mu} \tag{2}$$

where f is the oscillation frequency [Hz], x_{o} is the oscillation amplitude [m], ρ is the fluid density [kg/m^3], D is the internal diameter of OBR [m], μ is the fluid viscosity [kg/(m・s)].

The mapping of flow regime in OBR was already well-documented in the literature (Ahmed et al., 2018). For $Re_{\mathrm{o}} < 250$, the flow in the OBR was laminar and low mixing intensity was observed; for $250 < Re_{\mathrm{o}} < 2{,}000$, the flow became progressively turbulent like; for $Re_{\mathrm{o}} > 2{,}000$, the flow became a fully turbulent. It is noted that the local flow characteristics are not same even at the same Re_{o}. In the following experiments, the oscillation conditions were set to $f = 0.64$ Hz, $x_{\mathrm{o}} = 10$ mm and $f = 0.42$ Hz, $x_{\mathrm{o}} = 15$ mm. Both conditions were the same Re_{o} (=1,203), which was well below the oscillatory turbulent regime.

Next, in order to investigate influence of liquid flow to breakage and coalescence of bubbles in more detail, flow pattern of liquid in the OBR was analyzed by particle image velocimetry (PIV). DIAION HP20 (Mitsubishi Chemical Corporation) was used as tracer particles which had the same specific gravity as water. Without supplying the gas, the tracer particles were illuminated on a green laser sheet formed by PIV laser G50 (Kato Koken), and the motion image of the particles was recorded by a high-speed video camera (Kato Koken, k4HD).

Using recorded data, analysis of fluid was carried out by the PIV software (Kato koken, Flow Expert). The operating conditions for oscillating flow were same Re_o as the abovementioned experiment of flow visualization for gas bubbles.

2.2 Three-phase hydrogenation process in OBR

Figure 2(b) shows a schematic diagram of experimental system for three-phase hydrogenation process in OBR. In this setup, the glass apparatus was equipped with a water jacket. The internal diameter and total length of tube were 26 mm and 326 mm. The temperature in the OBR was kept at 323 K. Hydrogen gas was fed via a porous ceramic sparger placed at the bottom of the reactor. Catalyst pellets of 0.5 wt% Pd/Al_2O_3 (Sigma-Aldrich) with equivalent diameter of 3.2 mm, were packed in the reactors in two different ways. For the packed bed reactor (PBR), only one segment was packed with 16.6 g of catalyst. On the other hand, only 4.6 g of catalyst, which was distributed evenly throughout the four segments, was placed on the baffles. In the latter, wire meshes were installed on the baffles to keep the pellets inside the segments.

The working fluid was given as 0.19 M solution of 3-butyn-2-ol (Sigma-Aldrich) and distilled water, which were flowed through the bottom to the top of the OBR at 8.3 mL/min. On the other hand, hydrogen flow rate was fixed at 0.05 L/min (std). The operating conditions for oscillating flow were the same as the conditions for abovementioned flow visualization. When the inlet valve was opened and hydrogen was introduced, the reaction started and time $t = 0$. During the reaction, the liquid emerged from the top of the tube was collected every 3 min until $t = 15$ min. The images of gas-liquid flow with solid were recorded by a video camera (SONY, FDR-AX45).

The concentrations of 3-butyn-2-ol, 3-buten-2-ol, 2-butanol and 2-butanone in the collected liquid samples were analyzed using a gas chromatograph (Shimazu, GC-14B) with a flame ionization detector (FID). Nitrogen gas was used as the carrier gas. The temperature in the injector and FID were 533 and 548 K. And the temperature in the column oven was held at 313 K for 1 min and then increased to 383 K at a rate of 3.3 K/min. The conversion (*X*) of 3-butyn-2-ol and its selectivity (*S*) to 3-buten-2-ol are estimated by Eq.(3) and Eq.(4).

$$X\ [\%] = \frac{c_{R,i} - c_R}{c_{R,i}} \cdot 100 \qquad (3)$$

$$S\ [\%] = \frac{c_P}{c_{R,i} - c_R} \cdot 100 \qquad (4)$$

where $c_{R,i}$ is the concentration of 3-butyn-2-ol at inlet of the tube, c_R and c_P are concentrations of 3-butyn-2-ol and 3-buten-2-ol at outlet of the tube.

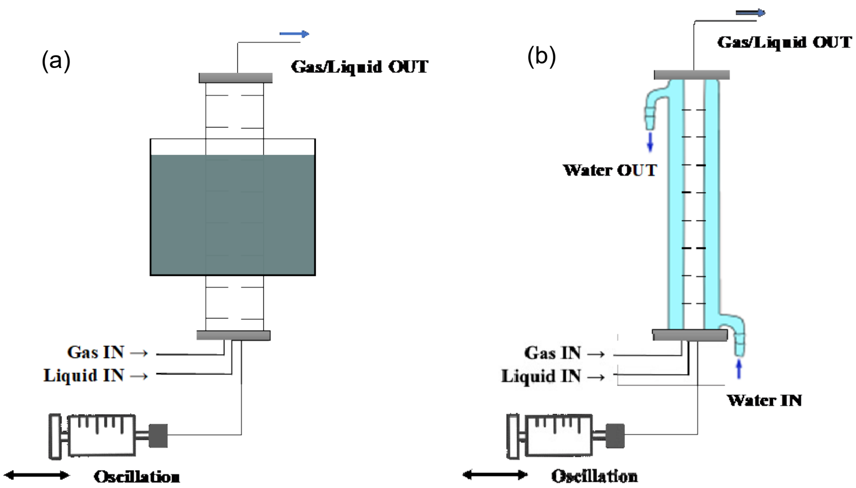


Figure 2: Schematic diagram of the OBR (a: for flow visualization experiment, b: for hydrogenation process)

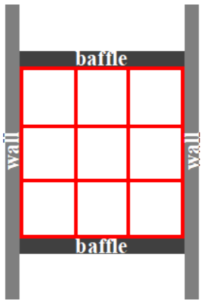
3. Results and discussion

3.1 Analysis of flow pattern in OBR

The gas holdup was measured by changing the gas flow rate *U* in the range of 0.05 – 0.15 L/min. There was seen a change in the slope of the increase in gas holdup with respect to the flow rate at U = 0.075 L/min. By observing behavior of the gas bubbles, it was considered that the dispersion of gas in the liquid flow was relatively uniform in the flow rate range lower than 0.075 L/min. The subsequent experiments were performed under the condition, U = 0.05 L/min.

Next, images for gas bubbles in the tube were analyzed by dividing the cross section between baffles into nine parts as shown in Figure 3(a). Figures 3(b-1) and 3(b-2) show distribution of the percentage of area for bubbles in the section for cases without and with oscillating flow. It was estimated that the coefficient of variation in nine parts decreased from 0.47 to 0.41 due to the oscillation. It was considered that the oscillating flow promoted the dispersion of bubbles. It was also observed the ratio of occupied area of bubbles to the area of the entire section between baffles was increased from 7.0 % to 19.5 % by the oscillation flow. It was confirmed that application of the oscillating flow could make the residence time of gas longer.

Figure 4 shows comparison of behavior of gas bubbles between two oscillation amplitudes (x_0) for same the oscillatory Reynolds number Re_o. It was observed that bubbles became smaller with increasing the oscillation amplitude. Application of the oscillating flow also demonstrated to promote breakage of gas bubbles, which increased the residence time.



(a)

Without oscillation

10.7	13.1	5.7
4.0	6.8	0
4.8	4.0	0.7

(b-1)

With oscillation (%)

13.6	22.6	28.9
11.5	34.1	20.7
7.4	19.4	16.9

(b-2)

Figure 3: Analysis of distribution of the percentage of area for bubbles in the cross section; (a) analytical region, (b-1) without oscillation, (b-2) with oscillation

(a) (b) (c)

Figure 4: Visualization of the gas-liquid flow in OBR; (a) without oscillation (b) x_0 = 10 mm, (c) x_0 = 15 mm

The influence of operating conditions for the oscillating flow to breakage and coalescence of gas bubbles was investigated by using PIV analysis. Figure 5 shows comparison of the spatial distribution of streamlines and the magnitude of vorticity between two oscillation amplitudes for same the oscillatory Reynolds number Re_o. Figure 5(a) and (b) are a 90 ° rotation of the PIV images for OBR. Left side of the image is the top of OBR and its right side is the bottom of OBR. Vortexes were observed near the baffles under both operating conditions. The magnitude of vorticity in the PIV image was indicated by color in range of -5.0×10^{-6} to 1.0×10^{-5}. Comparing the magnitude of vorticity under two different operating conditions at same Re_o, it was seen that values of the magnitude were almost the same. Therefore, it was considered difficult to associate the above-mentioned behavior of breakage of bubbles with the difference in distribution of magnitude of vorticity. In the future work, it is deemed necessary to investigate influences of the oscillation frequency and the oscillation amplitude to behavior of breakage of bubbles, based on other information extracted from PIV analysis results. Further, more representative spatial metrics, such as local shear rate (Mazubert et al.,2016), could be explored in the subsequent works to clarify the influence of regime- and baffle geometry towards bubble breakage behavior.

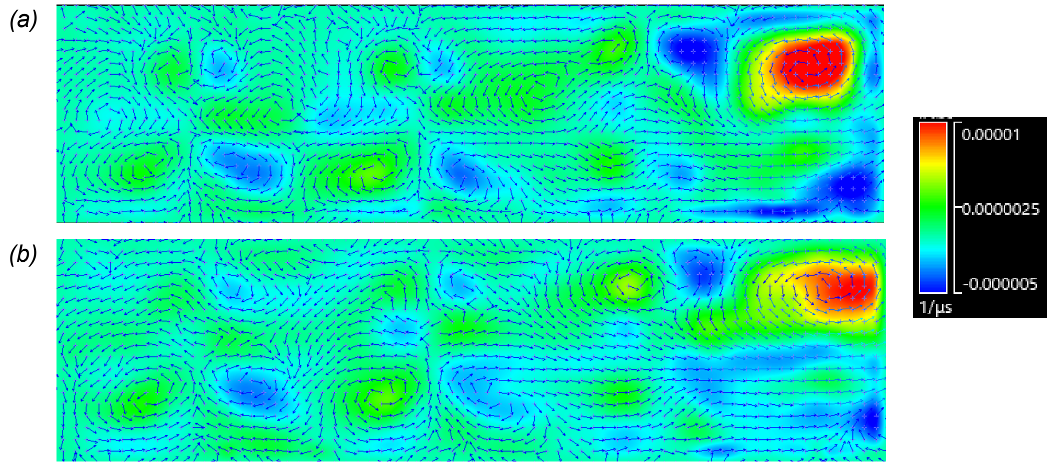


Figure 5: The streamline and the magnitude of vorticity in the OBR; (a) f = 0.64 Hz, x_0 = 10 mm, (b) f = 0.42 Hz, x_0 = 15 mm

3.2 Analysis of behavior of three-phase hydrogenation process

Figure 6 shows the images for the gas-liquid flow with solid catalyst in different conditions. In the PBR (Figure 6(e)), the solid catalyst section prevented the gas from rising and the accumulated gas passed through in forms of large bubbles. In contrast, it was observed that the oscillation flow in OBR promoted the breakage of bubbles and the increase of bubbles quantity. Comparing images (c) and (d) in Figure 6 with images (a) and (b), it was found that breakage of bubbles could be enhanced by increasing the oscillation amplitude, which was similar to the above results without solid catalyst.

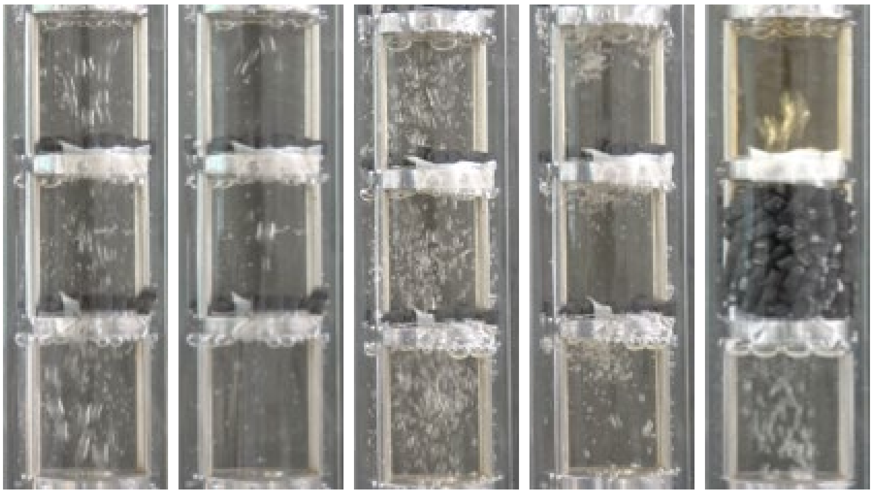

(a) (b) (c) (d) (e)

Figure 6: Visualization of gas flow in hydrogenation process; (a) 10 mm upstroke, (b) 10 mm downstroke, (c) 15 mm upstroke, (d) 15 mm downstroke, (e) PBR

Next, concentrations of 3-butyn-2-ol, 3-buten-2-ol, 2-butanol and 2-butanone in the collected liquid samples were analyzed during reaction process experiments. There was seen a small variation in the concentrations with sampling time. Table 1 shows averaged results of reaction efficiencies for five samples. The attained selectivity of PBR and 10 mm amplitude OBR was almost same. On the other hand, conversion of OBR was noticeably higher than that of PBR. Flow inhomogeneity-associated mass transfer resistance is a well-known phenomenon in conventional PBR (Delgado., 2006), which could render much of the catalyst portion in the bed under-utilized in the reaction. Then, compared to PBR, OBR can be expected to reduce the energy required for the liquid feed pump.

Comparing the results for 10 mm and 15 mm of the oscillation amplitude, the conversion for 15 mm was almost same as that of 10 mm. On the other hand, it was observed that the selectivity of 3-butyn-2-ol to 3-buten-2-ol was lower under condition of 15 mm than that of 10 mm. Since breakage of bubbles and increase in residence time of the bubbles was observed in case of 15 mm by above-mentioned flow visualization, it was considered that these behaviors of gas bubbles could progress full hydrogenation and double bond migration. According to Gonzaĺez-Fernańdez et al. (2020), selectivity of hydrogenation is a strong factor with ratio of gas to liquid in the OBR. Since the OBR intensifies the gas-liquid mixing and the mass transfer between two phases (relative to its energy dissipation), it is considered that the operational assumption for conventional reactors no longer applies in OBR (Ni., 2020). It is necessary to investigate influence of operating variables for the oscillating flow and the gas flow to change in selectivity by combining with results of flow visualization experiments.

Table 1: The average of conversion, selectivity and concentration of 3-buten-2-ol per gram of catalyst

	Conversion (%)	Selectivity (%)	Concentration of 3-buten-2-ol per gram of catalyst (mol/L/g (catalyst))
PBR	71.4 ± 0.83	18.3 ± 1.20	0.0015
OBR (10 mm)	79.2 ± 1.60	18.2 ± 0.90	0.0066
OBR (15 mm)	79.9 ± 4.30	16.6 ± 0.72	0.0061

4. Conclusions

In the present paper, the flow pattern in three-phase OBR and the hydrodynamic behavior were analyzed. It was demonstrated by the image analysis that breakage of gas bubbles was promoted by oscillation with higher amplitude. It was also confirmed that application of the oscillating flow could prolong the residence time of gas. In addition, particle image velocimetry (PIV) analysis revealed that the spatial distribution of streamlines and the magnitude of vorticity was almost same among operating conditions with different amplitudes of oscillation at the same Re_o. Consequently, further investigation on other indices was required to determine key factors that strongly associate to the breakage of bubbles.

In the hydrogenation experiment, it was observed that bubble size in the reactor was smaller in the OBR than in the PBR. In application of the OBR, increasing oscillation amplitude to 15 mm promoted breakage of bubbles. It could be associated with decrease in selectivity towards 3-buten-2-ol by considering increase in reacting H_2 ratio. Subsequent work will focus on control of dynamic behavior of gas bubbles, taking into account the energy consumption in the three-phase OBR and the use of hydrodynamic parameters related to the mass transfer.

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