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***The effects of modes of hydrogen input and reactor configuration
on reaction rate and H₂ efficiency in the catalytic hydrogenation of
alkynol to alkenol***

Francisca Navarro-Fuentes^a, Mark Keane^a and Xiong-Wei Ni^{a}*

^aEPSRC Centre for Continuous Manufacturing and Crystallization (CMAC), Centre for Oscillatory Baffled Applications (COBRA), School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, U.K.

ABSTRACT

Hydrogenation often involves three phases where hydrogen-on-demand is the typical mode of operation in industrial scale reactors. In research labs and publications, however, continuous hydrogen flow was used. This paper investigates the effect of such modes of operation on reaction rate using the selective hydrogenation of 3-butyne-2-ol over Pd/Al₂O₃ to obtain 3-buten-2-ol as the model reaction. The two modes of operation were firstly tested in a commercial PARR stirred tank reactor, then repeated in an oscillatory baffled reactor (OBR) in order to validate the experimental results. Our investigation demonstrates that enhanced reaction performance was obtained when the pressure is kept constant during the reaction by feeding gas as required, i.e. hydrogen-on-demand mode, with up to 10 times better H₂ efficiency. The method of continuous flow of hydrogen in hydrogenation means that excess hydrogen is vented out when operating at ambient or build up at elevated pressures. Our work also enables the comparison of reactor designs on reactor performance, H₂ efficiency was three times higher and the residence time 2.3 times shorter when using the OBR instead of the PARR due to its enhanced and uniform mixing, regardless of the mode of operation.

Keywords

Hydrogen-on-demand, stirrer tank reactor; oscillatory baffled reactor; hydrogenation

* *Corresponding Author:* Tel: 00441314513781, Email: x.ni@hw.ac.uk

INTRODUCTION

Hydrogenation is one of the most encountered synthesis steps in the production of fine chemicals and pharmaceuticals^[1-3] and typically involves three phases where gaseous and liquid reactants are catalyzed by a porous catalyst. Due to phase boundaries, this type of processes is often severely restricted by mass transfer limitations, influencing selectivity, productivity and reaction rate.^[4-6] Consequently, mixing is crucial in promoting and maintaining a narrow gas bubble size distribution with small mean size; prolonging the residence time of these bubbles and enhancing gas hold up within the reactor. Hydrogen efficiency, defined as a ratio of mol of products obtained over mol of hydrogen introduced to the reactor at a fixed time, is a typical indicator for the efficiency of mixing, in turn gas-liquid mass transfer.

Common reactors for multiphase catalytic reactions include stirred tank reactors (STR), packed/trickle bed reactors, bubble columns and recently microreactors where the catalyst is either stationary, e.g. in packed beds and microreactors, or mobile, e.g. in stirred tank reactors (STR). There are generally two modes of operation in terms of hydrogen supply, namely continuous gas flow^[7-16] or gas-on-demand.^[17-21] In the former, hydrogen gas is pumped into the reactor continuously, which is generally termed as the open mode of operation. The word “open” was stemmed from the fact that reactors are open when operated at ambient pressure where the excess of hydrogen is directly vented out. For the gas-on-demand mode, reactors are closed for all cases, gas is supplied whenever the pressure within the reactors is decreased due to the consumption of gas reactant, sometimes it is termed as the on/off operation, or close mode of operation and is mainly used in industrial productions. **Table 1** lists some reactor designs for three-phase catalytic reactions under continuous gas flow operation. It is clear that the hydrogen efficiency is generally very low, suggesting that the majority of the hydrogen did not participate in reactions.

Table 1. Hydrogen utilization in different reactor designs under continuous gas flow operation

Ref.	Reactor Type	Reaction Type	Working conditions				H ₂ efficiency (%)
			Temperature (K)	Pressure (MPa)	vvm (m ³ gas/m ³ liq · min)	Catalyst	
[7]	STR	Catalytic hydrodechlorination of 2,4-dichlorophenol	303	0.1	1.9	Pd/Al ₂ O ₃	0.5
	Coflore aer reactor		303	0.1	0.4		4.3
[8]	Wall-coated capillary microreactor	Selective hydrogenation of 2-methyl-3-butyne-2-ol	333	0.1	1.8	PdZn/TiO ₂	1.4
[9]	STR	Hydrodechlorination of 4-Chlorophenol	313	0.2	0.2	Pd/Al ₂ O ₃	0.2
[10]	STR	Catalytic multiphase reduction of functionalized halogenated aromatics	323	0.1	1	Pd/C	8.7
[11]	Packed bubble column reactor	Hydrogenation of maleic anhydride to 1,4-butanediol	503	9	2.4	CuZn/Al ₂ O ₃	17

So why is the open mode of operation used at all? What are the differences in terms of hydrogen efficiency and reaction time between the two modes of operation in hydrogenation? This work addresses these precise questions. We conduct a systematic research to evaluate and compare the effect of the two modes of operation on reaction rate and H₂ efficiency in a commercially available PARR stirred tank reactor under atmospheric pressure. In order to validate the results from the PARR reactor, the same is carried out in an Oscillatory Baffled Reactor (OBR). The reason of choosing ambient pressure is based on our recent study^[22] where the increase of operating pressures increased the solubility of gas into liquid only and this effect was independent of the reactor design. The added advantages are that ambient pressure operation is the simplest system and the science learnt in ambient operation can faithfully be applied to elevated operations.

The reduction of 3-butyne-2-ol to produce the target intermediate 3-buten-2-ol over Pd/Al₂O₃ catalyst is the chosen model multiphase catalytic hydrogenation used in this work. As shown in **Figure 1**, over-hydrogenation can produce unwanted 2-butanol and migration of the double bond can lead to unwanted 2-butanone.

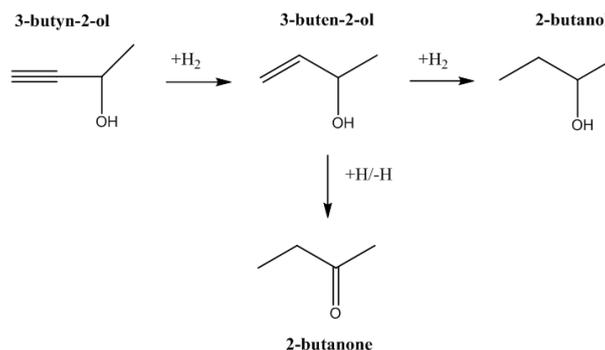


Figure 1. 3-butyn-2-ol hydrogenation network^[22]

EXPERIMENTAL AND ANALYTICAL METHOD

Materials

The reactant used in this research was 3-butyn-2-ol (97%), procured from the Sigma-Aldrich. The reaction was catalyzed by 1 wt. % Pd/Al₂O₃, acquired from the same manufacturer, and sieved into a batch of particle size < 45 μm in diameter. A complete catalyst characterization can be found elsewhere.^[7] Distilled water was chosen as the solvent.

Reactor configuration

PARR stirred tank reactor

The commercial Parr 5500 Series reactor (**Figure 2**) was a 0.1 L vessel of 0.117 m tall and 0.033 m internal diameter constructed in T316 stainless steel and a working volume of 0.06 L. The stirrer drive unit equipped with a four-bladed impeller and a motor delivered the required stirring speeds (320-1600 rpm). A block heater provided the target temperature, which was measured by a thermocouple (J-type) and controlled by the Series 4848 Controller. The vessel was equipped with a gas inlet and outlet valves and a sampling valve connected to an internal dip tube fitted to a 5 microns sintered metal filter that, along with the thermocouple, acted effectively as baffles. The pressure was controlled via a gas regulator installed in the gas line and check by a pressure gauge (0-0.2 MPa), without gas induction system. A gas sparge tube introduced the hydrogen into the reactor, which was measured using a gas flowcontroller (Bronkhorst).

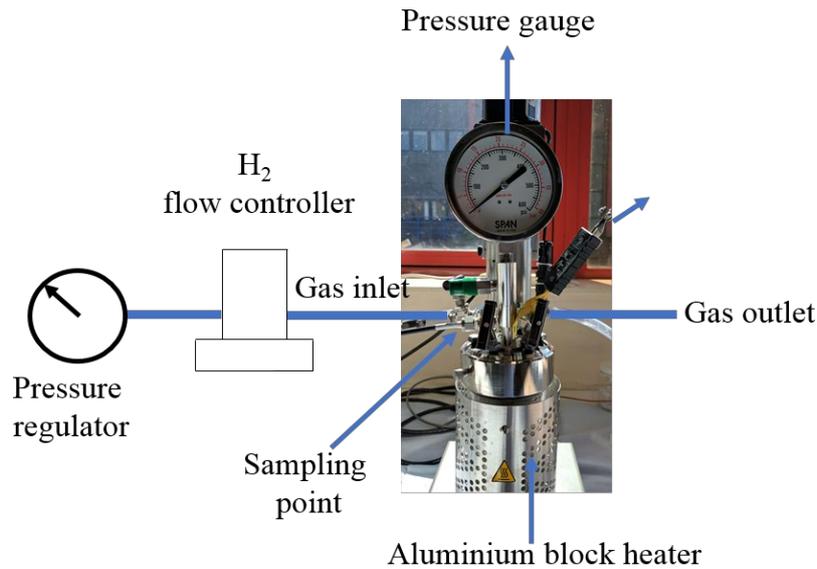


Figure 2. Experimental setup of the PARR

Oscillatory Baffled Reactor

The OBR in **Figure 3** is composed of a stainless steel column of 1.70 m tall and 0.016 m internal diameter. The total working volume was 0.2 L. The baffles (0.002 m in thickness and 25% in baffle open cross-sectional area ratio) are spaced 0.025 m apart. The set of 42 PTFE baffles was connected to a magnetic block situated within the column. A linear motor was connected to an external magnetic ring, facilitating the up and down movements of the baffle set, in turn the oscillation to the system. Oscillation frequency (1-5 Hz) and amplitude (1-25 mm) can be delivered by a programmed control box. Water baths and circulators (Grant) were used to control the temperature of the reactor via three jackets. Hydrogen was supplied at the base of the column via a tubular-shape sparger and measured by a gas flowcontroller (Bronkhorst). The pressure was controlled by a pressure regulator and measured by pressure gauge 0-0.2 MPa.

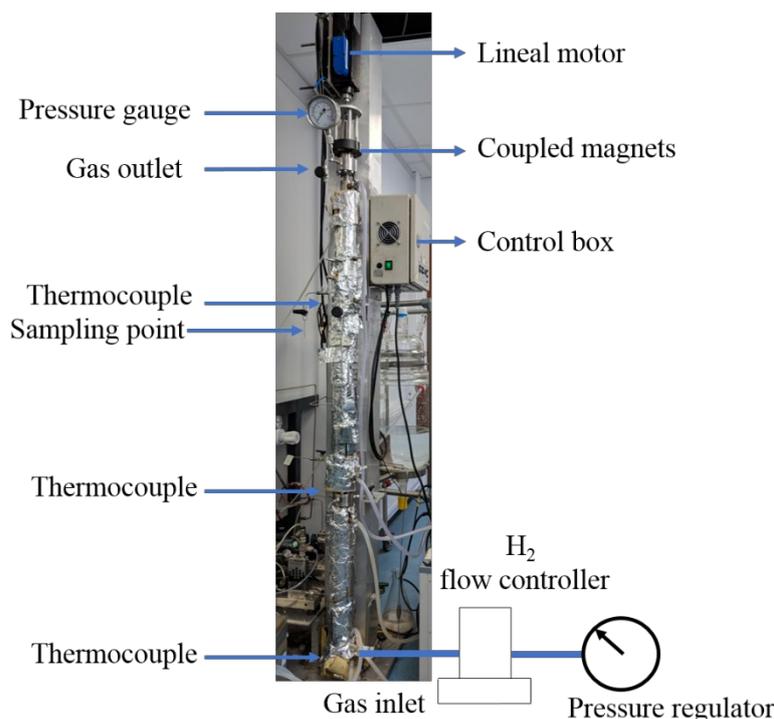


Figure 3. Experimental setup of the OBR

Experimental and analytic procedures

Either reactors were charged with a 0.19 M solution of 3-butyn-2-ol/distilled water and the catalyst at the beginning of each experiment. Catalyst was not reused in this work. Firstly, nitrogen was purged into the reactor containing the slurry under agitation and once the required temperature was achieved, the N₂ was replaced with H₂ by fluxing three times with H₂ at the start (time $t=0$ for the reaction). In the open mode of operation, H₂ was continuously fed into the reactor that is open to ambient, the constant gas flow rate was maintained by means of a mass flow controller. In the close mode of operation, the reactor is closed, and a constant pressure of operation (1.15 barA) was maintained by supplying hydrogen from the reservoir during the course of the reaction (H₂-on-demand system), resulting in an on-off gas flow. The pressure was controlled via a gas pressure regulator and checked by a pressure gauge.

Similar to our previous study,^[22] liquid samples were withdrawn during the course of the reaction and were analyzed in a gas chromatograph (Perkin-Elmer Auto System XL with a Stabilwax® column). A solution of 0.15 M 1-pentanol/distilled water was added to each sample before analysis, the concentrations of 3-butyn-2-ol, 3-buten-2-ol, 2-butanol and 2-butanone were determined by a total carbon mass balance with a reproducibility better than $\pm 5\%$ for repeated reactions. The details of the column and the program used to analyze the samples can

be found elsewhere.^[22] In order to minimize any effect of sample volume on mixing and reaction in a reactor, a maximum ratio samples to the total reaction volume < 10% was maintained.

The reaction conversion (**Equation (1)**) and the selectivity of the products (**Equation (2)**) are determined via the following equations,

$$X(\%) = \frac{c_{A_0} - c_A}{c_{A_0}} \cdot 100 \quad (1)$$

$$S(\%) = \frac{c_i}{c_{A_0} - c_A} \cdot 100 \quad (2)$$

where C_{A0} , C_A and C_i are the initial reactant concentration and the reactant and product i concentration (mol/L) at a given time, respectively. The selectivity of 3-buten-2-ol remained greater than 97% for all the runs, regardless of the reaction conditions or the type of reactor used, indicating there were no internal mass transfer limitations.^[23]

The initial reaction rate is a parameter used for comparison and was calculated as the moles of reactant consumed per unit time and per mass of palladium up to a conversion of 20% in **Equation (3)**,

$$r_o = \frac{\frac{\Delta n_A}{\Delta t}}{m_{Pd}} \quad (3)$$

Power consumption (also known as power dissipation rate or power density) is another parameter employed in this work for comparing reactor performances; **Equation (4)** and **Equation (5)** are the governing equations for OBR and PARR respectively,^[24]

$$\frac{P}{V} = \frac{2 N_b \rho}{3 \pi C_D^2} \frac{1 - \alpha^2}{\alpha^2} x_o^3 \omega^3 \quad (4)$$

$$\frac{P}{V} = \frac{P_o \rho N^3 D_s^5}{\pi D_v^2 L_h / 4} \quad (5)$$

where P/V is the power density (W m^{-3}), N_b the number of baffles per unit length of the baffled tube ($1/\text{m}$), α the ratio of baffle orifice to tube cross-sectional area, ρ the fluid density (kg/m^3), x_o the centre-to-peak oscillatory amplitude (m), ω the angular oscillatory frequency (radians s^{-1}), C_D the coefficient of discharge of the baffles (normally taken as 0.7), P_o the power number that depends on the dimensions and type of stirrer used ($= 3.5$ in this investigation); N the impeller speed (s^{-1}) and L_h the liquid level in the vessel (m), D_s and D_v are the stirrer and tank diameters (m), respectively. Note that **Equation (5)** does not consider the presence of wall baffles in reactors $(P/V)_o$, as there were two baffles (n_B) present in the PARR whose width (B_w) related to D_v is 0.14, therefore, $(P/V)_B/(P/V)_o = 12.5$.^[25]

RESULTS AND DISCUSSION

PARR Reactor

The two modes of operation are evaluated in the PARR for the effects of mixing, hydrogen flow rate, catalyst loading and temperature, each of which are presented below.

Effect of mixing

Mixing greatly influences the breakage of bubbles (i.e. the surface area of bubbles), the uptake of gas by liquid (i.e. mass transfer) and the suspension of catalyst particles.^[26] **Figure 4** plots the initial reaction rate against power consumption (stirring speed) for two modes of operation. We see when power density increases an increase in the initial reaction rate is observed for both modes of operation, which is expected. The trends level off, r_o is unaffected and independently of the mode of operation from the power density of $29\,500\text{ W/m}^3$ onwards, this is the indication of catalytic control for the reaction in both modes.

In terms of operating mode, the reaction rates for the close mode are higher than that for the open mode, except at low mixing, where the contact between gas-liquid phases as well as the suspension of catalyst are poor. This profile indicates that the gas flow in open mode is not optimized.

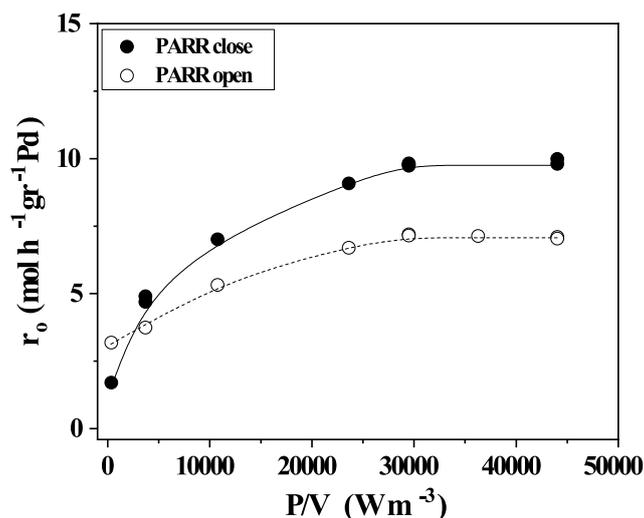


Figure 4. Effect of mixing in term of power consumption (P/V) on the initial reaction rate (r_0). Reaction parameters: initial molar ratio 3-butyn-2-ol/Pd = 1360, $[vvm]_{\text{PARR open}} = 0.85$, temperature = 305 K

Effect of H₂ flow rate

The impact of H₂ flow rate on the initial reaction rate is investigated in terms of vvm in open mode of operation (**Figure 5**), the vvm is defined as a volumetric ratio gas/liquid per minute. A significant increase in r_0 is noticed when the vvm is increased to 2.5, above which, the reaction is insensitive to the H₂ flow rate.

By definition, this evaluation cannot be done in H₂-on-demand mode of operation. However, under the same working conditions, an averaged vvm of 0.05 was obtained in the close operation, resulting in a $r_0 = 10 \text{ mol/h}\cdot\text{gr Pd}$ that is higher than $r_0 = 5 \text{ mol/h}\cdot\text{gr Pd}$ obtained in the open mode at vvm = 0.05, indicating enhanced H₂ utilization for the close mode of operation.

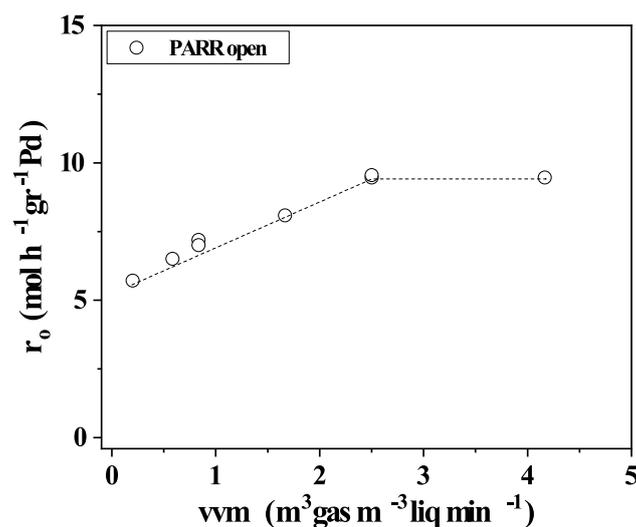


Figure 5. Impact of H₂ flow rate in terms of volumetric ratio gas/liquid per min (vvm) on the initial reaction rate (r_0). Reaction parameters: $P/V = 29\,500\text{ W/m}^3$, initial molar ratio 3-butyn-2-ol/Pd = 1360, temperature = 305 K

Effect of catalyst loading

A direct proportionality between the rate and the catalyst loading is generally accepted for catalytically controlled reactions.^[27] The influence of the catalyst loading is reported by plotting the reciprocal of the initial reaction rate (r_0^{-1}) versus the initial molar ratio of 3-butyn-2-ol/Pd in **Figure 6** in both modes of operation. At high 3-butyn-2-ol/Pd initial molar ratios (i.e. low catalyst amounts), the reciprocal rate linearly decreases with the decrease of this initial molar ratio, suggesting that diffusion resistance is diminishing, and the reaction is catalytically controlled. For low initial molar ratios of 3-butyn-2-ol/Pd < 1360 (i.e. large catalyst loadings), the reciprocal rate no longer depends on the molar ratio, indicating that the reaction is controlled by mass transfer. The trends are similar, indicating that the hydrogenation is under catalytic control for both modes of operation.

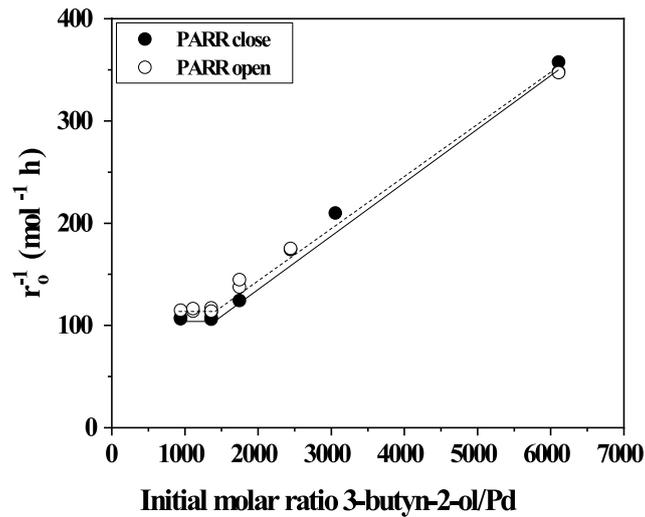


Figure 6. Relationship between catalyst loading in terms of initial molar ratio 3-buten-2-ol/Pd and the reciprocal of the initial reaction rate (r_0^{-1}). Reaction parameters: $P/V = 29\,500\text{ W/m}^3$, $[vvm]_{\text{PARR open}} = 2.5$, temperature = 305 K

Effect of temperature

It is well known that temperature affects reaction rates under catalytic control, whereas temperature has much lesser influence on mass transfer coefficient.^[27] The effect of temperature on the initial reaction rate is plotted **Figure 7** for both modes of operation. Catalytic control is observed in the region where r_0 increases with temperature; above 323 K, however, r_0 becomes independent of temperature for both modes of operation.

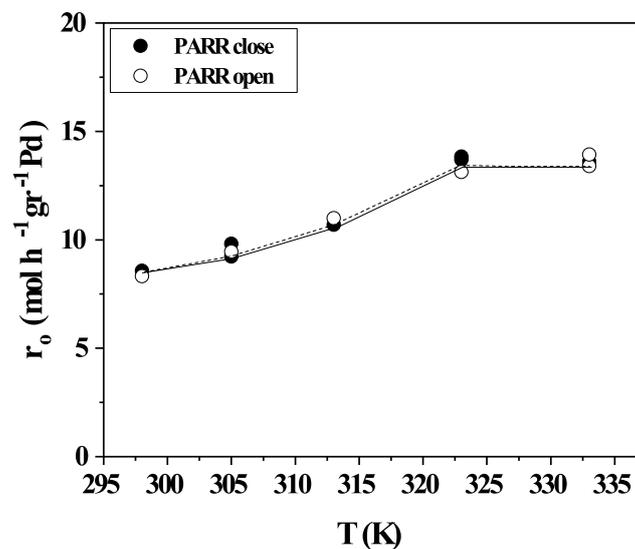


Figure 7. Influence of temperature on the initial reaction rate (r_0). Reaction parameters: $P/V = 29\,500$ W/m^3 and initial molar ratio 3-butyn-2-ol/Pd = 1360, $[vvm]_{PARR\ open} = 2.5$

In summary, conditions for catalytic control in the PARR are identified. Although the mode of hydrogen operation does not affect the trends of the initial reaction rates, the H_2 utilization differs, which will be discussed in the comparison section of this paper.

OBR Reactor

In order to validate the results from the PARR reactor, the same reaction is carried out in an OBR. As one of the purposes of this investigation is to compare the performances of each reactor, the basis for such a comparison consists of the same working conditions that have led to catalytic control in the PARR as

- Power consumption of $P/V = 29\,500$ W/m^3
- $[vvm]_{PARR\ open} = 2.5$
- Initial molar ratio of 3-butyn-2-ol/Pd = 1360
- Temperature of reaction = 323 K

These conditions are unchanged regardless of the mode of operation.

Effect of oscillatory mixing

The influence of oscillatory mixing evaluated in terms of oscillatory velocity on the initial reaction rate (r_0) is plotted in **Figure 8** for two modes of operation.

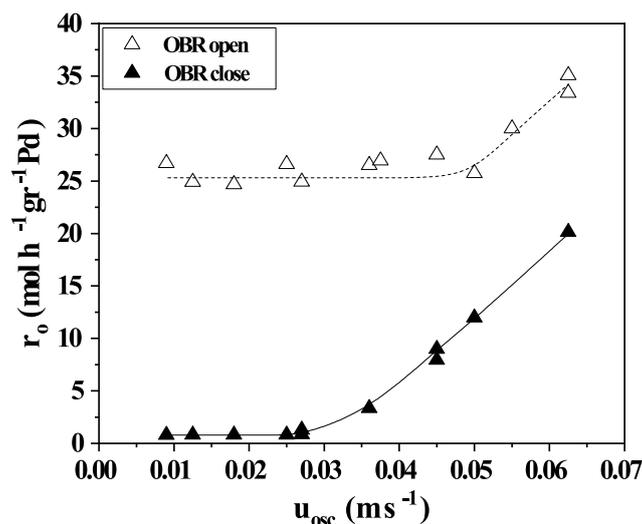


Figure 8. Oscillatory velocity (u_{osc}) against the initial reaction rate (r_0) at two different modes of operation: \blacktriangle OBR close, Δ OBR open: vvm = 2.5. Reaction parameters: initial molar ratio 3-butyne-2-ol/Pd = 1360, temperature = 323 K

The imposed oscillatory movement of the baffles produces a periodical generation and cessation of eddies,^[28] leading to chaotic mixing. The length of vortices and the periodicity of eddy motions can be adjusted by changing oscillation amplitude and frequency, respectively.^[29] For both modes of operation, the reaction rates are constant for low oscillatory velocities (low mixing), then linearly increase with the increase of oscillatory velocities (high mixing). At low mixing region, oscillatory motions are not sufficiently strong to break up bubbles, hence no improvement in the initial rate is noticed in this region. At high oscillation regime, the intensive and uniform mixing breaks up bubbles, leading to a decrease in bubble size; these bubbles are trapped in the vortices for longer periods of time, enhancing the bubble residence time as well as the gas holdup within the system, resulting to a linear increase in r_0 with the increase of oscillatory velocity.

There are three features that need to be noted. Firstly the initial reaction rates for the open mode of operation are higher than that for the close mode for all oscillation conditions. This is a new finding, mainly due to the higher amount of hydrogen fed into the reactor, 2.5 vvm in the former with respect to 0.1 vvm on averaged in the latter. Unlike in traditional stirred tank where excess gas is either vented out at the open mode of operation or building within the reactor at the close mode of operation, the higher input of hydrogen in the OBR leads to more interactions between hydrogen and the moving baffles. **This demonstrates the enhanced capability of breaking and maintaining bubbles in OBR at increased aeration rates.** In this work,

we have not yet identified the maximum vvm at which the reaction rate is independent of H₂ flow rate.

Secondly the reaction rate stays unchanged at low mixing region where the mixing intensity is not sufficiently strong to break and maintain bubbles. Thirdly when mixing intensity increases, the reaction rates increase linearly with the increasing oscillation velocity, but we see an earlier rise in the initial reaction rate for the close mode operation than for the open mode due to lesser hydrogen presence.

We also note that the conditions in the PARR reactor that led to catalytic control in the reaction do not exhibit the same effect in the OBR, an increasing trend of the initial reaction rate with the oscillatory velocity is still seen, indicating that the capacity of mixing in OBR is much wider and offers more improvements in r_0 than in the PARR reactor.

H₂ efficiency and residence time

The effects of both modes of operation on H₂ efficiency and residence time (RT) are evaluated and represented in **Table 2**.

Table 2. H₂ efficiencies and residence times (RT at X = 95%) for the OBR at two modes of operation. Reaction parameters: P/V = 14 650 W/m³, temperature = 323 K, initial molar ratio 3-butyn-2-ol/Pd =

1360

Run no.	vvm (m ³ gas m ⁻³ liq min ⁻¹)	RT (min)	H ₂ efficiency (%)
Open mode			
<i>1</i>	2.5	19	9
Close mode			
<i>2</i>	n/a	27	62

The process advantages by the close mode can clearly be seen in **Table 2** with 3 times increase in hydrogen efficiency (see runs 1 and 2), at the expenses of residence time that on the other hand increases by 30%. This is caused by the higher amount of hydrogen input into the reactor, more oscillation intensity is consumed by breaking and maintaining the bubbles, leading to less oscillation energy for mass transfer of hydrogen into the liquid media . The

results in the OBR verify the data from the PARR reactor, concluding that open mode of gas supply is not only inefficient, but also unsafe (H_2 is directly vented out in ambient pressure). This mode of operation is not recommended in either lab or industrial environment.

Comparison of PARR and OBR

The second purpose of this paper is to compare reactor performances for the two operating modes.

Reactor efficiency

The reactor efficiency is investigated by plotting the initial reaction rate against power consumption (W/m^3) for both reactor designs, as shown in **Figure 9** under the same reaction conditions for the two modes of operation.

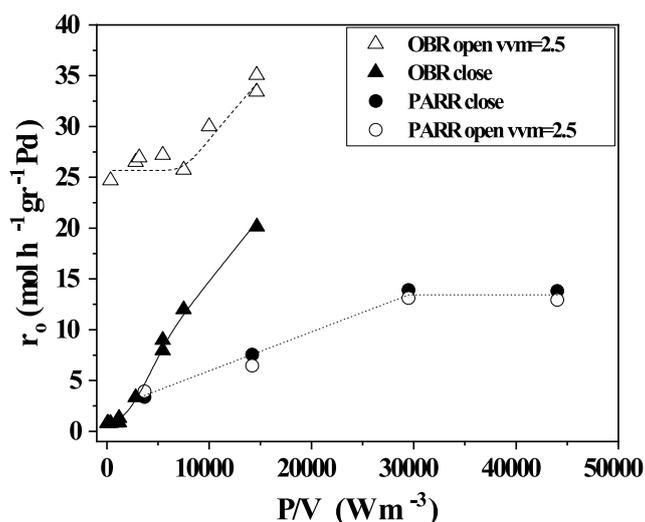


Figure 9. Reactor efficiency in terms of power density (P/V) for the PARR and the OBR under two different modes of operation: open (dashed line) and close (dotted line). Reaction parameters: initial molar ratio 3-butyn-2-ol/Pd = 1360, $[v_{vm}]_{OPEN} = 2.5$, temperature = 323 K

In the PARR, the catalytic control is reached for P/V equaling or greater than 29 500 W/m^3 for both modes, whereas we see that the initial reaction rate increases with the increase of power dissipation in the OBR, this implies that mass transfer is controlling under these oscillation conditions or in other words, the capacity of mixing in the OBR is far greater than that in the PARR reactor. Note that it was not possible to achieve catalytic control for the design and setup of the OBR. Even though the reaction is controlled by mass transfer, about 3 times

less power consumption is required in the OBR to achieve the same reaction rate obtained in the PARR under catalytic control. For the open mode, the reaction rate in the OBR is 2.6 times higher than that obtained in the PARR under the same vvm (= 2.5) with half the power density required. The rate achievable in the OBR in the open mode is also higher than that in the PARR reactor, reflecting the enhanced mixing in the former.

H₂ efficiency and residence time

Hydrogen efficiency and reaction time to achieve 95% conversion are summarized in **Table 3** for both reactors under the two modes of operation. Note that the basis of comparison consists of the initial molar ratio of 3-butyn-2-ol = 1360, reaction temperature = 323 K and vvm = 2.5 in open mode of operation but the power dissipation in the OBR is about half of the benchmark conditions in the PARR.

Table 3. H₂ efficiencies and reaction times (RT) for PARR and OBR at different modes of operation.

Reaction parameters: $(P/V)_{\text{PARR}} = 29\,500\text{ W/m}^3$, $(P/V)_{\text{OBR}[\text{max}]} = 14\,650\text{ W/m}^3$, $[\text{vvm}]_{\text{OPEN}} = 2.5$,
temperature = 323 K, RT at X = 95%

Run no.	Reactor	Initial molar ratio 3-butyn-2-ol/Pd	RT (min)	H ₂ efficiency (%)
Open mode				
<i>1</i>	PARR	1360	44	3
<i>2</i>	OBR	1360	19	9
<i>3</i>	OBR	4525	25.5	6.5
Close mode				
<i>4</i>	PARR	1360	44	27
<i>5</i>	OBR	1360	27	62
<i>6</i>	OBR	4525	38.4	45

In the PARR reactor, the H₂ efficiency is improved from 3% in the open to 27% in the close mode, translating as about 10 times higher H₂ efficiency (see runs 1 and 4). Likewise, in the OBR, the H₂ efficiency is improved from 9% in the open to 62% in the close mode, giving 7 times improvement in H₂ utilization, with an increment in the reaction time of 30% due to mass transfer controlling the reaction (see runs 2 and 5). We see that the H₂ efficiency is enhanced when the reactor operates in close mode, regardless the type of reactor.

When the systems operate in open mode (see runs 1 and 2), the PARR has a 3% H₂ efficiency compared to 9% in the OBR, giving 3 times more improvement, accompanied by 2.3-fold reduction in the reaction time. When the systems operate in hydrogen-on-demand mode (see runs 4 and 5), it is 27% in the PARR versus 62% in the OBR (2.3-fold higher H₂ efficiency) combined with a 40% reduction in the reaction time. These are due to the uniform and efficient mixing in the OBR.

When catalyst loading is reduced by 70% in the OBR to match that used in the PARR (i.e. higher initial molar ratio 3-butyne-2-ol/Pd, see runs 3 & 6), the hydrogen efficiency and the reduction in residence time in the OBR are still better than that in the PARR.

CONCLUSION

The two main conclusions from this work are a) enhanced process performance was found under the close mode of operation in the PARR and in the OBR (10 and 7 times higher H₂ efficiency in close mode compared with open mode, respectively) due to the effective utilization of hydrogen; the use of continuous hydrogen flow in three phase catalytic hydrogenation reactions should be replaced by hydrogen-on-demand mode; b) significantly better process performance can be seen in the OBR compared to that in the PARR (up to 3 times better H₂ utilization) due to uniform and effective mixing achieved in the former.

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