Comparison of a monolith and a confined Taylor flow (CTF) reactor for propene epoxidation

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Abstract

Heterogeneous catalytic epoxidation of propene to propene oxide with hydrogen peroxide was investigated in a monolith and a confined Taylor flow (CTF) reactor in which titanium silicalite (TS-1) catalyst was coated on the walls. The influence of gas and liquid superficial velocity on the hydrodynamic characteristics of the monolith and CTF reactor was also investigated under Taylor flow regime at atmospheric and high pressure. The reactors showed distinctly different hydrodynamic properties which in turn led to different performance for propene epoxidation. The production rate of propene oxide was higher in the monolith reactor due to its larger catalyst coating area, larger mass-transfer surface area and more frequent recycling of liquid flow. A variation of reactor column structures confirmed that the propene oxide production was highly dependent on the catalyst coating area and cross-sectional area of the reactor column. High operating pressure made a significant impact on the length of Taylor bubbles and the propene oxide production rate was found to increase in proportion to the operating pressure.

Keywords: Propene oxide; Hydrogen peroxide; Titanium silicalite (TS-1); epoxidation; Confined Taylor flow (CTF) reactor; Monolith reactor
Nomenclature

\( C_0, \ C_1 = \text{Constants} \ [\text{-}] \)

\( Ca = \text{Capillary number} \ (\mu_L U_{TB} / \sigma_L) \ [\text{-}] \)

\( D_t = \text{Tube diameter} \ [\text{m}] \)

\( Eö = \text{Eötvös number} \ \left( (\rho_L - \rho_G) g D_t^2 / \sigma_L \right) \ [\text{-}] \)

\( g = \text{Gravitational acceleration} \ [\text{m/s}^2] \)

\( L_{LS} = \text{Liquid slug length} \ [\text{m}] \)

\( L_{TB} = \text{Taylor bubble length} \ [\text{m}] \)

\( Q_G = \text{Gas flow rate} \ [\text{mL/min}] \)

\( Q_L = \text{Liquid flow rate} \ [\text{mL/min}] \)

\( U_{LS} = \text{Liquid slug rise velocity} \ [\text{m/s}] \)

\( V_{GL} = \text{Two-phase superficial velocity} \ (V_G + V_L) \ [\text{m/s}] \)

\( U_{TB} = \text{Taylor bubble rise velocity} \ [\text{m/s}] \)

\( V_G = \text{Gas superficial velocity} \ [\text{m/s}] \)

\( V_L = \text{Liquid superficial velocity} \ [\text{m/s}] \)

Greek letters

\( \varepsilon = \text{Gas injection ratio} \ (V_G / (V_G + V_L)) \ [\text{-}] \)

\( \rho_G = \text{Gas density} \ [\text{kg/m}^3] \)

\( \rho_L = \text{Liquid density} \ [\text{kg/m}^3] \)

\( \mu_L = \text{Liquid viscosity} \ [\text{Pa s}] \)

\( \sigma_L = \text{Liquid surface tension} \ [\text{N/m}] \)
1. Introduction

Propene is an important petrochemical feedstock with the second largest volume after ethene in the chemical industry and its demand has increased rapidly at an annual growth rate of 4–5%. Its global production capacity reached 109 million tonnes in 2014 and is anticipated to expand to 165 million tonnes a year by 2030 [1, 2]. Propene is used to manufacture a variety of chemical products such as polypropene, acrylonitrile, propene oxide, cumene, acrylic acid, oxo-alcohols and isopropyl alcohols, among which propene oxide accounts for approximately 10% of propene consumption as the third largest derivative. Subsequently, propene oxide is employed for the production of polyether polyols (65%), propene glycols (30%) and propylene glycol ethers (4%) and the propene oxide market has also grown fast in conjunction with propene market expansion [3].

The chlorohydrin process that has the longest history in the propene oxide industry occupied the majority of propene oxide production in 1970. Since then, due to its environmental liabilities, the hydroperoxidation process snatched attention and achieved a similar production capacity share in 2000. However, the hydroperoxidation process suffers from the marketability of co-products that are produced simultaneously in quantity. As a result, considerable attention has been paid to the direct epoxidation of propene using hydrogen peroxide oxidant (HPPO: hydrogen peroxide propene oxide) as an eco-friendly and profitable route in which the reaction is carried out under mild conditions and water is only one byproduct [4, 5, 6, 7].

Titanium silicalite (TS-1) catalyst has been extensively investigated for the direct epoxidation because of high selectivity to propene oxide and high hydrogen peroxide conversion since Clerici and co-workers first demonstrated that TS-1 can be used efficiently as a catalyst for the epoxidation of various olefins [8, 9, 10]. Finally, the first commercial-scale propene oxide plant based upon the HPPO technology was built by Evonik and SKC in South Korea in 2008 [5]. In the Evonik‒Uhde process, the highly exothermic epoxidation reaction is carried out in a specific fixed-bed reactor featured with high heat removal efficiency [11]. However, it is still highly necessary to develop a more efficient reactor concept employing catalyst immobilization that allows to eliminate the separation of nano-scaled TS-1 particles from it reaction liquid, enhance the stability of reactor operation and improve the economic feasibility of the process.

Several conventional types of reactor such as slurry, packed-bed and fluidized-bed reactor have been employed dominantly for catalytic gas-liquid-solid reactions in the chemical and petrochemical industry. Nevertheless, monolith reactors have drawn an increasing particular interest as a promising alternative since the use of structured packing, called “monolith”, is expected to overcome the limitations and drawbacks of conventional reactors [12, 13, 14, 15, 16]. A monolith consists of a bundle of narrow parallel channels in which
catalyst materials are impregnated on or inside the walls. Its regular structure provides lower pressure drop, enhanced mass and heat transfer efficiency and ease of scale-up. Also, the separation of catalyst from product chemicals is unnecessary. However, in the gas-liquid monolith reactor, particularly at large scale, the maldistribution of gas and liquid over the multiple channels is a challenging issue due to its detrimental impact on the reactor performance [17]. Therefore, many researchers have investigated the flow distribution characteristics and examined various distributors to achieve a homogeneous distribution of gas and liquid [18, 19, 20, 21].

In a multiphase monolith reactor, it is important to properly adopt a flow configuration and a hydrodynamic regime according to the relative flow rates of gas and liquid phase as these aspects significantly affect the reactor performance [22, 23]. Among various patterns, due to the high mass-transfer rate between phases, special attention has been paid to slug flow or Taylor flow regime, in which gas bubbles and liquid slugs move consecutively through the monolith channel [24, 25, 15]. Vaitsis and colleagues suggested a novel design of monolith reactor, the confined slug flow (CSF) reactor, in which a rod was attached to the inner wall of monolith channel. They attained a slug flow regime with the catalyst insert inside a capillary and claimed that it opened the possibility of employing catalyst rods in monolith blocks [26].

As to the catalytic epoxidation of propene with hydrogen peroxide and TS-1 using methanol/water mixture, a number of papers have been published but most prior studies have been conducted in autoclave reactors. Only a limited number of researchers studied the propene epoxidation in gas-lift loop reactors or continuous flow fixed-bed reactors [27, 28, 29, 30, 31, 32, 33]. Thus, we scrutinized a confined Taylor flow (CTF) reactor as a unique reactor concept in one of our previous papers [34]. The aim of this paper is to advance the understanding of such structured reactors as conventional monolith and CTF reactor by comparing their hydrodynamic aspects and catalytic performances at atmospheric and high pressure. The hydrodynamic properties such as Taylor bubble length, bubble rise velocity, liquid slug length and slug rise velocity with respect to gas and liquid flow rate were investigated under Taylor flow regime.

The monolith and CTF reactor had different reactor column structures and showed very different hydrodynamic properties which in turn led to distinct performances for propene epoxidation. High operating pressure was observed to have a considerable influence on the hydrodynamics, in particular Taylor bubble length, and the propene oxide production rate increased in proportion to the operating pressure.
2. Material and Methods

2.1. Catalyst preparation

TS-1 catalyst was synthesized on the basis of the method described in the original patent by Taramasso and co-workers [35]. A solution of 1.5 g of tetraethyl orthotitanate (Sigma-Aldrich) was gradually added to 45 g of tetraethyl orthosilicate (Merck) with magnetic stirring for 30 min. 100 g of 20 wt% tetrapropylammonium hydroxide solution (Merck) was then gradually added to the mixed solution under stirring for an additional 30 min. After keeping the mixture at 60 °C for 3 h, 56 g of deionized water was added to the solution. The composition of the final solution was the same as the molar reagent ratios employed by Clerici et al. [9] The resulting solution was transferred to an autoclave in an oven and crystallized at 175 °C for 48 h without stirring. After cooling the solution to room temperature, the crystalline product was separated by centrifugation, followed by washing with deionized water. The step of washing and separation was repeated five times. The solid product was dried at 100 °C for 2 h and then finally calcined at 550 °C for 5 h in an air-atmosphere furnace. The resulting catalyst lump was ground into a powder using a pestle and mortar.

For its application to monolith and CTF reactor, the TS-1 catalyst prepared was immobilized on the inner wall of 500 mm long alumina tubes with 8 mm inner diameter (Multi-lab) and on the surface of 500 mm long alumina rods with 4 mm diameter (Multi-lab). Silica nanoparticles in the range of 10–50 nm (LUDOX® AS-40 colloidal silica, Sigma-Aldrich) were used together in order to enhance the mechanical strength of the catalyst coating because it was impossible to make a stable coating using TS-1 particles only. The silica nanoparticles with smaller size helped TS-1 particles with larger size get stuck not only on the alumina surface but also on other TS-1 particles.

For CTF reactor, a rod was dipped in a slurry of 20 wt% TS-1 and 15 wt% silica in deionized water. When the weight percent of silica in the slurry was less than 15 wt%, the durability of coating was reduced, on the other hand, when it was greater than 15 wt%, the activity of catalyst coating was likely to decrease because the active surface of TS-1 was covered excessively by inert silica nanoparticles. To get a predetermined weight of coating (1 ±0.01 g), drying and dipping were repeated about 10 times. During the last repetitions, when a tiny amount of coating needed to be added to minimize the deviation from the predetermined weight, further diluted slurries, but still with the same ratio of TS-1 to silica, were used. In this case, the catalyst loading will be indicated as 2.0 g/m as the length of the rod is 0.5 m.

Similar procedures were employed to immobilize TS-1 catalyst on the inner surface of alumina tube for monolith reactor. Approximately 4 mL of a solution of 20 wt% TS-1 and 15 wt% silica in deionized water was
injected into an alumina tube and the both sides of the tube were closed. Then, the tube was shaken many times to make the whole inner surface wet. The remaining catalyst solution was drained from the tube and the tube was dried. Drying and coating were repeated about 10 times to get a predetermined weight of coating (1 ±0.01 g).

2.2. Epoxidation of propene

A 500 mm long alumina tube with TS-1 coating on the inner wall was used as a monolith reactor. The CTF reactor consisted of a 500 mm transparent polycarbonate tube (Cole-Parmer) and an alumina rod coated with TS-1 catalyst that was positioned axis-symmetrically in the reactor tube. For clarity, in this paper, the term “CTF reactor” is used when a rod is contained in the middle of reactor column, while the term “monolith reactor” is used when there is no rod. As seen in Fig. 1, the inner diameter of the reactor columns was 8 mm and the diameter of the rod was 4 mm, therefore a flow space of only 2 mm between the rod and the tube wall was assigned in the CTF reactor.

![Fig. 1 – Schematic representation of (a) a monolith and (b) a confined Taylor flow (CTF) reactor.](image)

In the vertical reactor columns in which gas and liquid flow simultaneously, four different flow configurations possible: co-current downward gas and liquid flow, co-current upward gas and liquid flow, counter-current upward gas flow and downward liquid flow, and counter-current downward gas flow and upward liquid flow. Besides, for co-current upward gas and liquid flow, various flow patterns, one of which is
Taylor flow, can be formed according to the relative flow rates of gas and liquid phase. In this study, co-current upward gas and liquid flow was investigated because it was the only flow configuration giving stable Taylor flow over a wide range of gas and liquid flow rates [36]. Both gas (10% C₃H₆ in N₂) and liquid flow (H₂O₂ 0.35 wt%, CH₃OH 50 wt%, H₂O 49.65 wt%) enter via bottom of the columns and their gas and liquid superficial velocities are listed in Table 1.

The hydrodynamic characteristics of Taylor flow are strongly affected by the design of gas and liquid inlet. The novel design of the gas and liquid inlet and the rod support anchored inside the gas tube, shown in Fig. 1, is expected to improve the stability of Taylor flow with the help of the centrally mounted rod by minimizing the disruption to the gas and liquid flow that are introduced simultaneously at the bottom of the column.

<table>
<thead>
<tr>
<th>Case</th>
<th>V₇ [m/s]</th>
<th>V₈ [m/s]</th>
<th>ε</th>
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<tbody>
<tr>
<td>1</td>
<td>0.036</td>
<td>0.022</td>
<td>0.62</td>
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<tr>
<td>2</td>
<td>0.071</td>
<td>0.022</td>
<td>0.76</td>
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<tr>
<td>3</td>
<td>0.142</td>
<td>0.022</td>
<td>0.87</td>
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<tr>
<td>4</td>
<td>0.036</td>
<td>0.044</td>
<td>0.45</td>
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<tr>
<td>5</td>
<td>0.071</td>
<td>0.044</td>
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<tr>
<td>6</td>
<td>0.142</td>
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<tr>
<td>7</td>
<td>0.036</td>
<td>0.088</td>
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<tr>
<td>8</td>
<td>0.071</td>
<td>0.088</td>
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<tr>
<td>9</td>
<td>0.142</td>
<td>0.088</td>
<td>0.62</td>
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The reactors were operated in a semi-batch mode where the gas flow passed once through the reactor column and was discharged from the system, but the liquid flow was repeatedly recycled throughout an experiment. An in-house infra-red detection unit connected with a data logger (TracerDaq) and computer system, built by Electronics Workshop of Chemical Engineering Department at Imperial College London, was attached on the top part of reactor column to collect hydrodynamic data. The detectors were 2 cm apart. The time delays between the signals from the first and second detector were recorded over a time period of 25 s and then used to calculate mean values of hydrodynamic properties of Taylor bubbles and liquid slugs. The details of data collection and calculation method can be found in our previous paper [34]. The reaction products were sampled at regular time intervals via a liquid sample point located at the outlet of the reactor column.

The gas and liquid flow rates were controlled by mass flow controllers (Brooks and Bronkhorst) and a double-headed peristaltic pump (Masterflex), respectively. The peristaltic pump gave stable liquid flow over a
wide range of flow rates at atmospheric pressure. A dosing pump with incorporated hydraulic diaphragm (Milton Roy) was employed to provide liquid flow at elevated pressures. Photographs of Taylor gas bubbles and liquid slugs formed in the monolith and CTF reactor were taken using an Olympus high speed camera (i-SPEED 3).

The concentrations of hydrogen peroxide were determined by iodometric titration. Liquid samples were analyzed on a gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector and a capillary column (30 m × 0.32 mm) with nitroterephthalic acid-modified polyethylene glycol (0.25 μm) as the stationary phase. Propene oxide was the main product; propene glycol and propene glycol monomethyl ether were the byproducts. The selectivity of all byproducts always remained lower than 10%.

The reproducibility of experiments in the monolith and CTF reactor was tested at normal operating conditions (case 5 in Table 1) and the experimental error was found to be within ±3%.

3. Results and discussion

3.1. Catalyst characterization

The TS-1 catalyst prepared was characterized using various analytical techniques and found to be in good agreement with the data provided in the original patent [35]. The analysis results of XRD, FT-IR, UV–vis, SEM, TEM, TGA and BET were presented in our previous papers [37, 38]. An even distribution of TS-1 particles on the alumina rod and tube wall was achieved through the coating method and confirmed by a SEM image that was also shown in our previous paper [34]. The coating layer was found to be sufficiently stable to endure the operating conditions under Taylor flow regime. Less than 1 wt% of original weight of TS-1 catalyst coating was lost at normal operating conditions, indicated as case 5 in Table 1, for 5 h.

3.2. Hydrodynamics in monolith and CTF reactor at atmospheric pressure

The hydrodynamic characteristics of the multiphase reactors under consideration depend on various factors such as tube size, flow rate of gas and liquid, gravity, viscosity, density and surface tension and so on. Indeed, the distribution of phases and the flow pattern are varied in terms of tube diameter. Researchers suggested different values of Eötvös number ($E_o$) for the criterion to judge if a tube diameter can be considered “small”. Bretherton claimed that surface tension dominated flows are achieved when Eötvös number was below 3.37 [39] and White and Beardmore also suggested a similar criterion of Eötvös number < 4 [40]. According to the papers by Suo and Griffith and Brauner and Maron, the Eötvös number for the criterion can range from 0.88 to 39.4 [41,
The 8 mm diameter tube for monolith reactor and the 4 mm hydraulic diameter tube for CTF reactor employed in this study give Eötvös numbers of 8.7 and 2.2, respectively. Therefore, it can be reasonably assumed that surface tension force almost dominates gravitational force but both forces can still exist to simultaneously influence the hydrodynamic properties in the monolith and CTF reactor.

For two-phase co-current upward flow in vertical tubes (d > 1 cm), four types of flow regime are formed as the gas flow rate increases: bubble flow, slug flow, churn flow and annular flow [43]. In slug flow, dispersed small gas bubbles coalesce to form large bubbles with diameters approaching that of the tube. The phases separate into bullet shaped gas bubbles and liquid slugs containing entrained gas bubbles. However, smaller bubbles dispersed in the liquid slugs disappear in capillaries with smaller diameter, which is designated as Taylor flow.

To achieve the Taylor flow regime in capillary tubes, the gas injection ratio ($\varepsilon$) that is linked with the transition of flow patterns is known to be in the range of 0.2–0.9 [44]. Similarly, in this study, a stable Taylor flow was obtained over a gas injection ratio range of 0.29–0.87 as shown in Table 1. The capillary number ($Ca$), defined the ratio between viscous forces and surface tension, ranges from $1.5 \times 10^{-3}$ to $4.7 \times 10^{-3}$ for the monolith reactor and $2.2 \times 10^{-3}$ to $5.4 \times 10^{-3}$ for the CTF reactor when nitrogen and water are used at the flow conditions mentioned in Table 1. When the liquid mixture containing 50wt% methanol instead of pure water is used for propene epoxidation experiments, the capillary numbers are expected to increase by approximately 12.5% due to the change of viscosity and surface tension of the liquid flow. The increase of capillary number is known to lead to shorter Taylor bubble length and higher Taylor bubble rise velocity, and also influence other hydrodynamic properties of Taylor flow [45, 46]. However, in this study, the impact of increased capillary numbers on the hydrodynamic properties is expected to be insignificant because the reactor columns used in the experiments are not microchannel and the capillary numbers only slightly increase. In Fig. 2, the gas and liquid superficial velocities used in this study are presented with the flow pattern maps in the literature [47, 48, 49]. It can be seen that all the points representing nine operating conditions exist in the region of Taylor flow regime.
Fig. 2 – Operating conditions in flow pattern maps for vertical upward flow in circular tubes.

Fig. 3 shows Taylor gas bubbles with different lengths formed at various gas and liquid flow rates of nitrogen and water in the reactor columns. Even when the length of Taylor bubbles was short, Taylor bubbles separated by liquid slugs were clearly observed without small dispersed gas bubbles in both reactors. However, in the CTF reactor, more stable Taylor bubbles were produced at more regular intervals and the bubbles formed at the bottom of column moved upward without rotation around the rod on their way to the top.

Fig. 3 – Photographs of Taylor gas bubbles at various gas ($V_G$) and liquid superficial velocities ($V_L$) of nitrogen and water in monolith and CTF reactor.
The hydrodynamic data obtained under the operating conditions defined in Table 1 are summarized in Table 2. In both reactor columns, the shortest length of Taylor bubbles was gained at the lowest gas flow rate and the highest liquid flow rate (case 7) while the longest length of Taylor bubbles was gained at the highest gas flow rate and the lowest liquid flow rate (case 3).

Table 2 – Mean hydrodynamic data of monolith and CTF reactor (standard deviation in parentheses).

| Case | Monolith reactor | | | CTF reactor | | |
|------|------------------|------------------|------------------|------------------|------------------|
|      | L_{TB} [cm] | U_{TB} [cm/s] | L_{LS} [cm] | U_{LS} [cm/s] | L_{TB} [cm] | U_{TB} [cm/s] | L_{LS} [cm] | U_{LS} [cm/s] |
| 1    | 1.10             | 10.94            | 2.09           | 9.90            | 3.72             | 16.02           | 10.20           | 18.07           |
|      | (0.86)           | (0.89)           | (2.24)         | (0.97)          | (0.94)           | (0.85)          | (5.26)          | (3.96)          |
| 2    | 2.18             | 15.29            | 1.73           | 14.42           | 6.22             | 21.87           | 12.29           | 30.77           |
|      | (1.58)           | (2.32)           | (2.13)         | (3.07)          | (1.89)           | (7.61)          | (5.34)          | (6.61)          |
|      | (2.61)           | (5.52)           | (3.84)         | (6.80)          | (3.80)           | (2.33)          | (1.57)          | (10.12)         |
| 4    | 0.87             | 13.59            | 2.88           | 12.59           | 2.41             | 18.26           | 7.92            | 21.10           |
|      | (0.61)           | (1.18)           | (2.34)         | (2.27)          | (0.62)           | (2.27)          | (3.40)          | (3.24)          |
| 5    | 1.67             | 20.04            | 1.85           | 17.64           | 4.81             | 22.41           | 9.17            | 28.23           |
|      | (1.20)           | (7.11)           | (2.04)         | (5.75)          | (1.13)           | (1.38)          | (4.83)          | (7.00)          |
| 6    | 3.93             | 27.23            | 2.51           | 27.41           | 9.38             | 32.33           | 10.04           | 43.21           |
|      | (2.41)           | (5.68)           | (2.47)         | (6.20)          | (2.98)           | (6.69)          | (4.01)          | (13.31)         |
| 7    | 0.56             | 19.88            | 3.46           | 17.66           | 1.34             | 25.27           | 5.68            | 26.66           |
|      | (0.36)           | (3.28)           | (2.22)         | (2.03)          | (0.68)           | (3.27)          | (2.92)          | (4.10)          |
| 8    | 1.28             | 24.52            | 2.78           | 21.88           | 3.49             | 27.84           | 8.37            | 32.58           |
|      | (0.90)           | (3.94)           | (2.25)         | (2.88)          | (1.29)           | (3.49)          | (4.53)          | (8.68)          |
| 9    | 2.82             | 33.91            | 2.24           | 30.90           | 7.08             | 38.93           | 10.66           | 52.06           |
|      | (1.52)           | (3.60)           | (0.80)         | (3.86)          | (2.31)           | (4.51)          | (6.83)          | (17.04)         |

As shown in Fig. 1, different shapes of Taylor bubble are produced in the monolith and CTF reactor column. The Taylor gas bubbles formed in the CTF reactor are radially asymmetric and hence do not occupy the whole cross-sectional area of the annulus, while the Taylor gas bubbles formed in the monolith reactor are symmetric to occupy almost the whole cross-section of the tube except a thin liquid film between gas bubbles and the tube wall. As a result, the Taylor bubbles rose faster in the CTF reactor when the same liquid and gas superficial velocities were employed [50]. The difference of Taylor bubble rise velocity is presented in Fig. 4.
Fig. 4 – Taylor bubble rise velocity ($U_{TB}$) vs. two-phase superficial velocity ($V_{GL}$).

Fig. 4 also shows the linear relationship between two-phase superficial velocity and Taylor bubble rise velocity through a flowing liquid in the vertical tubes. The relationship was first presented by Nicklin et al. [51] and has been widely investigated by other researchers [52, 53, 54, 50, 44, 26]. The relationship can be expressed by the following equation.

$$U_{TB} = C_0 V_{GL} + C_1 \sqrt{gD_t} \quad (1)$$

where $C_0$ and $C_1$ are constants. This equation, however, does not necessarily mean that Taylor bubble rise velocity is a linear function of two-phase superficial velocity because $C_0$ is known to be correlated to two-phase superficial velocity through several dimensionless numbers such as Reynolds, Weber, Eötvös, and Froude number [55]. Nevertheless, the linear relation (1) has been extensively employed to analyze Taylor bubble rise velocity for practical purposes. The second term on the right hand side, called drift velocity, represented the rise velocity of gas bubble in a stagnant liquid.

Interestingly, from the data in Fig. 4, almost the same value of $C_0$ (1.29) was obtained from both reactor columns in spite of their different hydraulic diameters. A possible explanation for this negligible difference of $C_0$ values observed in this study is that the difference of hydraulic diameters is very small and therefore has an insignificant influence on $C_0$. Researchers, for example, suggested the following equation of $C_0$ in terms of Eötvös number for laminar flow that is the flow regime created by the operating conditions of the monolith and CTF reactor columns [55, 56]. According to the Eq. (2), the difference of the Eötvös numbers of the reactor columns (8.7 and 2.2) leads to only 1.3% difference of $C_0$ values that can be masked by the experimental error.
\[ C_0 = 2.29 \left[ 1 - \frac{20}{\delta_0} \left( 1 - e^{-0.0125\delta_0} \right) \right] \]  

(2)

With regard to \( C_s \), it was 0.13 for the monolith and 0.42 for the CTF reactor column, respectively. This means that the different hydraulic diameter of the monolith and CTF reactor column in this study made a meaningful effect only on the drift velocity.

Similar to the Taylor bubble rise velocity, in both reactor columns, the Taylor bubble length increased linearly with the gas superficial velocity at a fixed liquid superficial velocity (Fig. 5a). On the other hand, it decreased with an increase in the liquid superficial velocity at a fixed gas superficial velocity (Fig. 5b). The Taylor bubble length is expected to be directly proportional to the gas injection ratio when Taylor bubble frequency and shape remain similar without a dramatic change and affected by any insert in the reactor column. It is apparent in Fig. 5a that the presence of the rod led to longer Taylor bubbles and the slopes of the lines increased with a decrease of liquid superficial velocity [44].
The liquid slug length showed somewhat different aspects with respect to gas and liquid superficial velocities as can be seen in Fig. 6. At a low gas superficial velocity \(V_G = 0.036\) m/s, the liquid slug length increased with increasing liquid superficial velocity in the monolith reactor column, while it decreased with increasing liquid superficial velocity in the CTF reactor column. On the other hand, at a high gas superficial velocity \(V_G = 0.142\) m/s, the liquid slug length decreased with increasing liquid superficial velocity in the monolith reactor column, while it increased with increasing liquid superficial velocity in the CTF reactor column.

In both reactors, a higher spread of hydrodynamic data was observed when the level of flow turbulence determined by operating conditions was higher. Fig. 7 reveals that there was a slight increase of Taylor bubble frequency with two-phase superficial velocity and an apparent decrease with gas injection ratio. The frequency of Taylor bubbles with respect to two-phase superficial velocity or gas injection ratio was lower in the CTF reactor column mainly due to the increased length of Taylor bubbles in the CTF reactor column.
Fig. 7 – Frequency of Taylor bubbles vs. (a) two-phase superficial velocity ($V_{GL}$) and (b) gas injection ratio ($\varepsilon$).

3.3. Propene epoxidation in monolith and CTF reactor at atmospheric pressure

Hydrogen peroxide is indeed a powerful oxidizing agent but its spontaneous decomposition to water and oxygen gas even at room temperature is one drawback that limits its utilization efficiency in continuous reactors. In this study, 9.5% hydrogen oxide decomposition was observed after 5 h at normal operating conditions depicted as case 5 in Table 1. It is more vigorous compared to the level found in an autoclave reactor [37].

Fig. 8 shows the influence of TS-1 catalyst loading on the production rate of propene oxide. It can be seen that the difference of propene oxide production was negligible in the CTF reactor, which confirms that only TS-1 exposed to the coating surface was highly active for the propene epoxidation and therefore the CTF reactor was operated under internal mass-transfer limiting conditions. In the monolith reactor, on the other hand, there
was a slight increase of propene oxide concentration with an increase of TS-1 catalyst loading, particularly from 1.0 g/m to 2.0 g/m, which means that the monolith reactor was under transition regime conditions switching from kinetic to mass-transfer control. These results demonstrate that 1.0 g/m of TS-1 was sufficient to remove the kinetic resistances for the surface of the rod with 4 mm OD in the CTF reactor but insufficient for the inner surface of the monolith reactor with 8 mm ID because the surface area for catalyst immobilization became fourfold in the monolith reactor. For a fair comparison of different reactors, 2.0 g/m of TS-1 coating was selected for further experiments to provide a proper thickness and an even distribution of catalyst materials.

![Graph showing influence of catalyst loading on propene oxide production](image)

**Fig. 8** – Influence of catalyst loading on propene oxide production. Reaction conditions: 40 °C, 1 atm, 5 h, 1.0–3.0 g/m TS-1 coating, V\(_G\) 0.071 m/s (10% C\(_3\)H\(_6\)/N\(_2\)), V\(_L\) 0.044 m/s (H\(_2\)O 0.35 wt%, CH\(_3\)OH 50 wt%, H\(_2\)O 49.65 wt%).

The propene oxide production rates in both reactors are compared with respect to two-phase superficial velocity and Taylor bubble length in Fig. 9. The production rate of propene oxide was higher in the monolith reactor than in the CTF reactor (Fig. 9a). This can be explained by three factors. Firstly, the catalyst coating area of the monolith reactor was four times larger than that of the CTF reactor. Secondly, the length of Taylor bubbles was shorter and their frequency was higher in the monolith reactor, which led to the increase of mass-transfer surface area of gas bubbles. The interphase mass transfer occurs via three steps (gas-liquid, liquid-solid and gas-solid mass transfer) and is very complex in the Taylor flow [24]. However, it is assumed that the difference of mass-transfer area between the reactors, rather than that of mass-transfer coefficient, has a bigger impact on the actual rate of mass transfer as the reactor configurations and operating conditions used in the
reactors do not lead to significant differences of capillary number, Reynolds number and other dimensionless numbers that are used to calculate the mass-transfer coefficients. Thirdly, the liquid flow in the monolith reactor was recycled to the feed tank in a shorter time due to the higher liquid flow rates used in the monolith reactor.

In Fig. 9b, the concentration of propene oxide produced basically decreased with an increase in Taylor bubble length. When the liquid superficial velocity was constant, the propene oxide concentration decreased with increasing gas superficial velocity in both reactors because the Taylor bubble length and bubble rise velocity increased at the same time. On the other hand, when the gas superficial velocity was constant, the propene oxide concentration increased linearly with increasing liquid superficial velocity or decreasing Taylor bubble length in the monolith reactor while it did not show a linear relationship with the liquid superficial velocity or Taylor bubble length in the CTF reactor. Therefore, it can be said that mass-transfer surface area dominated the performance of the monolith reactor but mass-transfer surface area and residence time competed to dominate the performance of the CTF reactor in the range of gas and liquid flow rates adopted in this study.

The productivities of propene oxide were in the range of 0.008–0.022 g\textsubscript{PO}/(g\textsubscript{cat} h) in the monolith reactor and 0.005–0.012 g\textsubscript{PO}/(g\textsubscript{cat} h) in the CTF reactor, respectively. The production rates are much lower than 0.5–2.5 g\textsubscript{PO}/(g\textsubscript{cat} h) found in the capillary and fixed-bed microreactors by Truter et al. [57] and 0.5–3.0 g\textsubscript{PO}/(g\textsubscript{cat} h) found in the microstructured reactors using direct gas-phase epoxidation by Klemm et al. [58] The low productivities per amount of catalyst and time obtained in this study are mainly due to the rather thick catalyst coating layer and the very mild operating conditions such as low reactant concentrations, short residence time of gas and liquid flow and atmospheric operating pressure. In future investigations, therefore, the catalyst coating thickness and operating conditions can be optimized to achieve 1 g\textsubscript{PO}/(g\textsubscript{cat} h) that is regarded as an industrially relevant target [57, 58].
Fig. 9 – Influence of (a) two-phase superficial velocity ($V_{GL}$) and (b) Taylor bubble length ($L_{TB}$) on propene oxide production. Reaction conditions: 40 °C, 1 atm, 5 h, 2.0 g/m TS-1 coating, $V_G$ 0.036–0.142 m/s (10% C$_3$H$_6$/N$_2$), $V_L$ 0.022–0.088 m/s (H$_2$O$_2$ 0.35 wt%, CH$_3$OH 50 wt%, H$_2$O 49.65 wt%).

3.4. Propene epoxidation in various reactor columns at atmospheric pressure

A further study was done to compare the performance of propene epoxidation in various reactor columns. A 4mm OD rod (A), a 8 mm ID tube (B), a 8 mm ID tube containing a 4 mm OD rod (C) and a 4 mm ID tube (D) were employed for the column structure variations (Fig. 10).
The experimental cases are summarized in Table 3. The gas and liquid flow rates were adjusted according to the cross-sectional area of each reactor column to apply the same gas and liquid superficial velocities as case 5 in Table 1 to all reactor columns. The case I, case II and case III basically had the same structure as the CTF reactor, but the position of immobilized TS-1 catalyst was different. Only the outer surface of the rod was coated with TS-1 in case I. On the other hand, only the inner surface of the 8 mm tube was coated with TS-1 in case II. In case III, both the rod outer surface and the tube inner surface were coated with TS-1. A rod was not contained in case IV and case V in which only the inner surface of tubes was coated with TS-1. An 8 mm ID tube and a 4 mm ID tube were employed for case IV and case V, respectively.

**Table 3 – Experimental cases for various structures of reactor column.**

<table>
<thead>
<tr>
<th>Case</th>
<th>Structure</th>
<th>TS-1 catalyst coating</th>
<th>Catalyst coating area [mm²]</th>
<th>Cross-sectional area [mm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>C</td>
<td>rod outer surface (1 g)</td>
<td>12.6</td>
<td>37.7</td>
</tr>
<tr>
<td>II</td>
<td>C</td>
<td>tube inner surface (1 g)</td>
<td>50.3</td>
<td>37.7</td>
</tr>
<tr>
<td>III</td>
<td>C</td>
<td>rod outer surface (1 g) + tube inner surface (1 g)</td>
<td>62.8</td>
<td>37.7</td>
</tr>
<tr>
<td>IV</td>
<td>B</td>
<td>tube inner surface (1 g)</td>
<td>50.3</td>
<td>50.3</td>
</tr>
<tr>
<td>V</td>
<td>D</td>
<td>tube inner surface (1 g)</td>
<td>12.6</td>
<td>12.6</td>
</tr>
</tbody>
</table>

The propene oxide production through the reactor columns is compared in Fig. 11. Based on the amount of propene oxide produced for 5 h, case III showed much higher production than all other cases as a double amount of TS-1 catalyst was immobilized and its coating area was the largest in case III (Table 3). However, if the performance is compared based on per unit area of catalyst coating, case III cannot be said to be efficient because its production rate is just half of case I.
When 1 g of TS-1 catalyst was immobilized on the inner surface of 8 mm ID tube, after 5 h the propene oxide concentration of case IV was slightly higher than that of case II. This is due to the longer Taylor bubble length in case II, leading to the reduction of contact area between Taylor bubbles and tube inner surface, which was created by the presence of rod inside the reactor column. The performance difference is maintained when compared per unit area of catalyst coating as these cases have the same coating area. Moreover, due to the higher liquid flow rate used in case IV, the liquid flow of case IV was recycled to the feed tank in a shorter time and therefore a slight additional increase of propene oxide concentration attributed to the liquid flow frequently passing through the reactor column might be included in the observed concentration of propene oxide in case IV.

When the position of TS-1 coating was changed from tube inner surface (case II) to rod outer surface (case I) with the same CTF reactor structure, the propene oxide concentration after 5 h decreased due to the reduced catalyst coating area and nevertheless the performance of case I was significantly better on the basis of production rate per unit area of catalyst coating. An implication of this finding might be that the mass transfer occurring in the CTF reactor structure is more intense between the fluid and the rod than between the fluid and the tube inner wall, because the performances of case I and case II were measured under the identical operating conditions leading to the same hydrodynamic properties. In comparison of case I to case V, the concentration of propene oxide after 5 h and the production rate per unit area of catalyst coating were higher in case I even though the same amount of TS-1 catalyst was coated on the same coating area. This might be because the different tube structure and smaller cross-sectional area exerted an detrimental effect on the performance of hydrodynamic behaviors in case V. In addition, the lower liquid flow rate employed in case V made the time required to recycle the liquid flow longer. It was notable that the selectivity to propene oxide was maintained similar over 90% in all five cases.
Fig. 11 – Propene oxide production in various reactor columns. Reaction conditions: 40 °C, 1 atm, 5 h, 2.0–4.0 g/m TS-1 coating, \( V_G \) 0.071 m/s (10% \(?CH\_2\_N\_2\)), \( V_L \) 0.044 m/s (\( \text{H}_2\text{O}_{20.35} \) wt%, \( \text{CH}_3\text{OH} \) 50 wt%, \( \text{H}_2\text{O} \) 49.65 wt%).

3.5. Propene epoxidation in monolith and CTF reactor at high pressure

In multiphase reactors, an increase of operating pressure leads to an increase of the amount of gaseous compound dissolved in the liquid phase. The hydrodynamic characteristics are also expected to vary in terms of operating pressure and in turn affect the reactor performance. To investigate such aspects, additional experiments using the monolith and CTF reactor column were carried out in a pressurized reactor system. The same gas and liquid flow rates that were employed for case 5 in Table 1 were used.

Predictably, the length of Taylor bubbles was found to become much shorter even when the operating pressure was slightly increased to 2.5 atm, which is because the gas volume easily shrinks in terms of elevated pressure. However, the Taylor bubble length showed a slight reduction when the operating pressure was increased further up to 10 atm and the impact of operating pressure on Taylor bubble rise velocity, liquid slug length and liquid slug rise velocity was insignificant in the entire range of operating pressures.

As can be seen in Fig. 12, the concentration of propene oxide produced increased in proportion to the operating pressure, which could be attributed to the increase in dissolved concentration of propene in the solvent mixture as only minor difference was observed from the hydrodynamic data at high pressures. The dependence of propene oxide concentration on the operating pressure was nearly linear. In the literature, the same trend was observed in some multiphase hydrogenation reactions in monolith reactors [59, 60, 61, 62, 63]. Such linear dependences were explained by the fact that the solubility of gas is directly proportional to pressure according to Henry’s law. Therefore, the productivities of propene oxide have greatly increased, compared to the
productivities obtained at atmospheric pressure, to 0.29 and 0.25 g<sub>PO</sub>/(g<sub>cat</sub> h) at 10 bar in the monolith and CTF reactor, respectively. It is notable that the selectivity to propene oxide was maintained greater than 90%, regardless of operating pressure, in the monolith and CTF reactor.

Fig. 12 also shows that the performance of the monolith reactor was always better than that of the CTF reactor and the slope of dependency between propene oxide concentration and operating pressure was slightly steeper in the monolith reactor. Therefore, the difference of propene oxide concentration after 5 h became larger at high operating pressure.

The solid and dashed lines shown in Fig. 12 were drawn with the propene oxide concentrations calculated by multiplying the propene oxide concentration obtained at atmospheric pressure and the ratio of relative operating pressures. The increasing slopes were similar to the experimental results but the experimental values were slightly higher than expected. This difference might be due to the fact that this calculation was based on the propene oxide concentration gained under atmospheric pressure at which longer Taylor bubbles, resulting in smaller mass-transfer surface, were formed.

![Graph](image)

**Fig. 12 – Influence of operating pressure on propene oxide production.** Reaction conditions: 40 °C, 0–10 atm gauge pressure, 2.0 g/m TS-1 coating, Q<sub>G</sub> 214 mL/min (10% C<sub>3</sub>H<sub>6</sub>/N<sub>2</sub>) and Q<sub>L</sub> 133 mL/min (H<sub>2</sub>O 0.35 wt%, CH<sub>3</sub>OH 50 wt%, H<sub>2</sub>O 49.65 wt%) for monolith reactor, Q<sub>G</sub> 161 mL/min (10% C<sub>3</sub>H<sub>6</sub>/N<sub>2</sub>) and Q<sub>L</sub> 100 mL/min (H<sub>2</sub>O 0.35 wt%, CH<sub>3</sub>OH 50 wt%, H<sub>2</sub>O 49.65 wt%) for CTF reactor.

4. Conclusions

The hydrodynamic characteristics of co-current upward gas and liquid flow were explored in a monolith and a confined Taylor flow reactor with a variation of gas and liquid superficial velocity and compared in relation to
propene epoxidation. These two reactors showed some similar hydrodynamic behaviors such as the linear relationship between Taylor bubble rise velocity and two-phase superficial velocity and that between Taylor bubble length and gas superficial velocity at a constant liquid superficial velocity. However, in principle, distinctly different values and trends of hydrodynamic properties such as Taylor bubble length, bubble rise velocity, liquid slug length and slug rise velocity were observed in the reactors, due to the different shape of Taylor bubble and cross-section of the reactor column. It is worth noting that shorter lengths of Taylor bubble and liquid slug were obtained with higher frequencies of Taylor bubbles in the monolith reactor column.

The propene oxide production decreased with an increase in the gas superficial velocity in both reactors when the liquid superficial velocity was constant, because the Taylor bubble length and bubble rise velocity increased at the same time. On the other hand, when the gas superficial velocity was constant, the propene oxide production increased linearly with an increase in the liquid superficial velocity or with a decrease in the Taylor bubble length in the monolith reactor while it did not show a linear relationship with the liquid superficial velocity or Taylor bubble length in the CTF reactor. The production rate of propene oxide was higher in the monolith reactor due to its larger catalyst coating area, shorter Taylor bubble length and shorter time for recycling of liquid flow.

A further investigation into the effect of various reactor column structures revealed that the production rate of propene oxide was determined mainly by catalyst coating area and cross-section area of the reactor column that affects the hydrodynamic properties.

High operating pressure made the length of Taylor bubbles significantly shorter and the propene oxide production rate increased in proportion to the operating pressure. This was explained by the increase in dissolved concentration of propene in the liquid solvent because only minor difference was observed from the hydrodynamic data at high pressures. The performance of the monolith reactor was better than that of the CTF reactor in the entire range of operating pressures and the slope of dependency between propene oxide concentration and operating pressure was slightly steeper in the monolith reactor.

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References


