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A comparative study of residence time distribution and selectivity in a monolith CDC reactor and a trickle bed reactor

R. Kulkarni [a,*], R. Natividad [a], J. Wood [a], E.H. Stitt [b], J.M. Winterbottom [a]

[a] Centre for Formulation Engineering, Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
[b] Johnson Matthey Catalysts, P.O. Box 1, Belasis Avenue, Billingham, Cleveland TS23 1LB, UK

Abstract

A comparative study of the performance of a trickle bed reactor (TBR) and a monolith cocurrent downflow contactor (CDC) reactor in terms of selectivity and residence time distribution was conducted for the hydrogenation of 2-butyne-1,4-diol (B). Selectivity (*S*) towards 2-butene-1,4-diol was investigated with the solvent 2-propanol and a 30% (v/v) 2-propanol/water mixture (M) in batch recycle mode. Liquid residence time distribution (RTD) curves were obtained for both reactors. Although both reactors presented almost identical hydrodynamic behaviour, i.e. RTD, significant differences regarding selectivity towards the alkene were observed in both solvents. The use of 2-propanol gave lower selectivities in both reactors, but even then the monolith reactor was superior. In the monolith CDC, the liquid RTD curve was also obtained at different radial positions. RTD profiles across the monolith showed that from the centre to the column wall there is possibly an increased retention of material and despite this, overall selectivity does not appear to be considerably depressed by the backmixing that the above result implies in 2-propanol/water where the selectivity was found to be 100% towards the intermediate (C).

Modelling of the monolith CDC reactor was also conducted to predict RTD. The models tested were tanks-in-series, piston exchange and piston dispersion exchange; from which, piston exchange model was found to best predict and fit the experimental data.

Keywords: Hydrogenation; Residence time distribution; Butynediol; Multiphase reactors; Structured reactors

1. Introduction

In the last decade, intensive work has been done to extend the application of monoliths to liquid–gas systems [1–3]. Monoliths offer several advantages over traditional random fixed beds or slurry reactors, such as better mass transfer characteristics, higher volumetric productivity for a smaller amount of catalyst, elimination of filtration step and lower pressure drop. In spite of so many advantages the successful engineering of a monolith reactor is still a challenge, in terms of cost, achieving uniform gas–liquid distribution at the inlet and understanding reaction behaviour. Trickle bed reactors on the other hand are well established in industry. For industrial design trickle beds are assumed to have plug flow, but when tested in laboratory they exhibit significant axial dispersion. This dispersion can be reduced by dilution of the bed with inert particles, hereafter called fines. Dilution of the bed improves flow behaviour considerably [4–7]. It will be demonstrated that RTD curves obtained under such conditions, and when compared for trickle beds diluted with fines and monolith reactors, show striking similarity. This suggests that hydrodynamic behaviour in the two reactors is identical, and hence provides a basis for comparison.

As shown by several researchers [5,8,9], dilution of trickle bed leads to decoupling of kinetics and hydrodynamics. The kinetics obtained under such conditions represents true kinetics. Previous studies have compared TBR with monoliths for their hydrodynamic and mass transfer characteristics [10–13]. Monolith reactors have low mass transfer resistances and hence kinetics is closer to true

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* Corresponding author. Tel.: +44 121 414 5339.
E-mail address: rxk242@bham.ac.uk (R. Kulkarni).

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Nomenclature

A_2	liquid solid mass transfer area (m^2)
B	2-butyne-1,4-diol
C	2-butene-1,4-diol
C_d	concentration of tracer in dynamic liquid ($kmol/m^3$)
C_s	concentration of tracer in dynamic liquid ($kmol/m^3$)
D_{ax}	axial dispersion coefficient (m^2/s)
kg_{Pd}	mass of palladium (kg)
k_2	liquid–solid mass transfer coefficient ((m/s)(m^2 total area)(g^{-1} catalyst))
L	length of reactor (m)
N	number of tanks
Pe	Peclet number (dimensionless)
S	selectivity to 2-butene-1,4-diol
t_m	mean residence time per tank (s)
v_d	dynamic liquid velocity (m/s)

Subscripts

i	number of tank
m	mean
PE	piston exchange
PDE	piston dispersion exchange

Greek letters

δ_f	film thickness (m)
θ	dimensionless time
μ_L	liquid viscosity (kg/(m s))
σ	variance
ϕ	dynamic liquid fraction (m^3/m^3)

kinetics. The novel aspect of this paper is comparison of the two reactors under similar hydrodynamic conditions. Although other researchers have previously compared TBR and monolith reactors, they used an undiluted TBR and monolith with showerhead distributor. This is the first time a CDC monolith has been compared with a TBR being (a) TBR diluted with fines, (b) RTD measured under reaction conditions and (c) measured radially in the case of monolith. The objective of this work was to investigate reactor performance under similar operating and hydrodynamic conditions for the two reactors. This was done in two steps, firstly by achieving similar residence time distribution in both the reactors and then comparing selectivity for 2-butyne-1,4-diol (B) hydrogenation reaction. A monolith reactor operates in a Taylor flow regime, and trickle flow reactor is operated in trickle regime. To achieve these conditions different gas and liquid flows are required. Hence, the comparison of reactors was based on achieving similar residence time, which also means similar reactive volume in the reactors. Space velocities are kept similar.

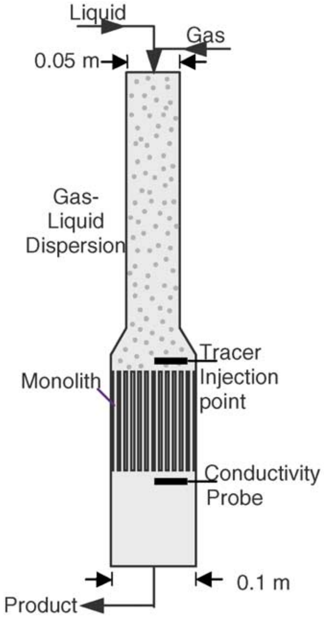


Fig. 1. Monolith CDC reactor.

2. Experimental methods

2.1. Equipment

Fig. 1 depicts the experimental set-up of the monolith CDC reactor. The column is made of glass and stainless steel was used for the piping. Briefly, the operation of the monolith CDC consists of flooding the column with reaction solution and introducing hydrogen to top of the CDC, in such a way that a bubble dispersion is obtained along the column. The flow of liquid is downwards and by adjusting the gas/liquid velocity ratio the bubbles can be introduced into the monolith producing Taylor flow or, more strictly speaking, slug flow. This phenomenon has been already experimentally observed and reported [14]. The bubbles exiting the monolith flow towards the wall of the CDC where they ascend to be redispersed once again by the inlet energy produced on the top of the CDC by a nozzle type effect. A more detailed operation of the monolith CDC has been reported elsewhere [15,16]. The total volume loaded of reaction solution was 0.01 m^3.

The TBR is illustrated in Fig. 2 and consists of a glass column that measures 35 cm in length and 5 cm in diameter. The catalyst bed was comprised of spherical catalyst particles with a diameter of 6 mm which were tapped gently when they were added to bed. In order to ensure dense and uniform loading, the bed was packed in stages with equal aliquots of catalyst and fines added, followed by tapping. The amount of fines added was just enough to fill the voids. Calculations of the amount of fines required and the packing procedure was followed as recommended elsewhere [17]. The experimental set-up allowed the variation of superficial liquid velocity in the range of 1.2–6 mm/s and the superficial gas velocity between 1.7 and 5.1 mm/s. Silica carbide fine particles of

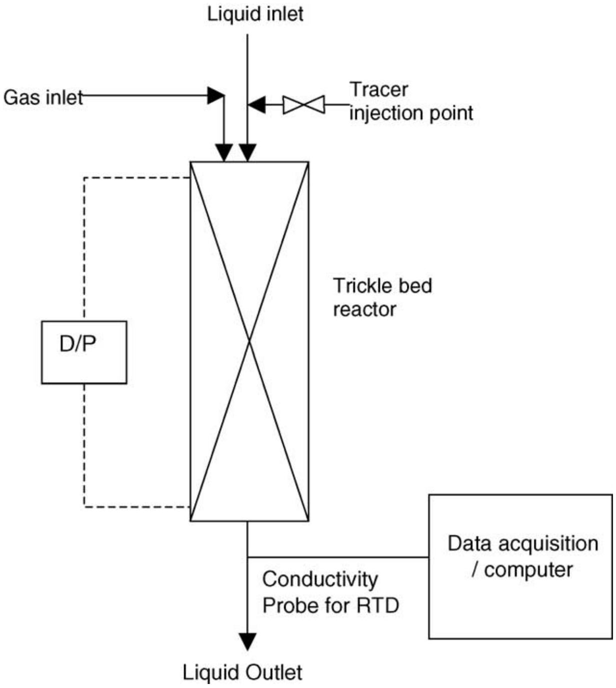


Fig. 2. Trickle bed reactor.

0.2 mm diameter were added to dilute the bed. Dynamic liquid holdup was measured by the "stop flow" technique; simultaneously closing both gas and liquid inlet and outlet valves and the reactor was drained. The remaining holdup is measured by weighing the reactor after draining and subtracting weight of dry reactor. This static holdup comprises liquid held within the catalyst pores and in a film around the surface of the catalyst pellet.

2.2. Catalysts

For the experiments in the monolith CDC, an α-Al_2O_3 wash-coated cordierite monolith was impregnated with Pd at 1% loading from a proprietary source by Johnson Matthey according to standard industrial specification. The precursor-monolith catalyst was able to be activated simply by reduction with hydrogen in water at room temperature for 1 h. This process was carried out in the CDC. Pd/Al_2O_3 catalyst was used in both the reactors. In the TBR the catalyst was in form of a 6 mm spherical alumina support, impregnated with Pd which was activated in a similar manner to the monolith. The catalyst was in the form of egg shell.The monolith washcoat thickness and trickle bed thickness were different, because standard industrial catalysts were used in the study. The main characteristics of the catalysts used in both, the monolith CDC and TB reactors, are summarized in Table 1.

2.3. Product analysis

Product analysis was conducted by gas chromatography using either a Cambridge-Ai-Model 94 or Perkin-Elmer instrument, fitted with a FID detector and a 30 m × 0.32 mm internal diameter DB-wax column.

Table 1
Characteristics of the Pd catalyst for both, monolith CDC and TB reactors

Reactor	Monolith	TBR
Washcoat thickness (m)	30×10^{-6}	–
kg_{Pd}/bed	1.73×10^{-3}	2.4×10^{-3}
Pore diameter (m)	3.2×10^{-6}	–
External area (m^2/m^3)	3846	–
Cells/m^2	62×10^4	
Particle size (diameter) (mm)	–	6
Egg shell thickness (μm)	–	100
Reactor diameter (m)	10.03×10^{-2}	5×10^{-2}
Length of bed (m)	15.24×10^{-2}	35×10^{-2}

2.4. Selectivity studies

In both reactors, the effect of solvent on selectivity towards 2-butene-1,4-diol was studied by conducting the hydrogenation reaction under two different solvents, i.e. 2-propanol and a binary solvent comprising 30% (v/v) 2-propanol in water (M); the reason for using M has been explained elsewhere [3]. The reaction conditions were 328 K, 200 kPa (absolute pressure) and 0.1162 kmol/m^3 as initial concentration of 2-butyne-1,4-diol. The liquid flowrate in the monolith was 1.15×10^{-4} m^3/s and the gas flowrate was 1.33×10^{-5} m^3/s. When the solvent was 2-propanol, the monolith had to be placed in the upper section of the glass column due to operational reasons explained in detail elsewhere [3]. In this case, liquid and gas flowrates were 1.15×10^{-4} and 1.16×10^{-5} m^3/s. The initial concentration of 2-butyne-1,4-diol was reduced to 0.055 kmol/m^3 in order to keep the ratio 2-butyne-1,4-diol mass to catalyst mass constant. In the TBR, the liquid flowrate was 8.3×10^{-6} m^3/s and gas flowrate was 6.6×10^{-6} m^3/s, respectively.

2.5. Residence time distribution (RTD) studies

The liquid RTD was determined under reaction conditions by means of a well-known tracer response technique. A pulse of tracer solution (KCl) was injected into the reactors at a certain time ($t = 0$) and the outlet signal was detected by conductivity probe and recorded by Lab View software (National Instruments, USA). Injection and detection points are illustrated in Figs. 1 and 2 for the monolith CDC and TBR, respectively. The probe to measure conductivity was previously calibrated so the tracer concentration could be determined from the recorded conductivity profile. The injection system was similar to that described in earlier works [16]. In the monolith CDC, the detection probe was moved across the radial section to obtain information on the flow in different sections of the monolith. Conductivity profiles were determined at $x/R = 0$, 0.3, 0.6 and 1.0; where x indicates the distance from the centre of the monolith and R the radius of the monolith.

3. Results

3.1. Liquid RTD studies

The injection of tracer was performed as quickly as possible and was assumed that a negligible amount of dispersion between the point of injection and the entrance of the monolith and the catalytic bed in the TBR occurred so as to obtain as closely as practical a δ-pulse of tracer at the inlet. The first and second moments of the *E*-curve are typically used to compare RTD curves rather then using the entire distributions [18]. The mean residence time and variance are formed from the first and second moments of the *E*-curve. These two moments have also been used in the calculation of model parameters, such as Peclet number.

Fig. 3 is a dimensionless *E*-curve and it indicates that both the trickle bed and monolith reactor have almost identical residence time distributions. Monolith reactors are characterised by slug flow or Taylor flow. In this type of flow, gas bubbles and liquid slugs move with constant velocity through the monolith channels, the gas is separated from the catalyst only by a very thin liquid film. For this flow regime, a higher mass transfer of gas to the catalyst is expected as compared to that of a trickle bed. The better plug-flow behaviour in the reactor for this flow regime results in higher selectivity towards the desired product in selective reactions with unwanted consecutive reactions. Trickle beds have voids or dead zones in the bed, which give rise to local mixing zones. Addition of fines reduces these to a large extent and results in a shift towards better plug flow behaviour. Residence time distributions obtained in both the reactors were at the outlet of reactor and hence they represent average phenomena at the outlet. *E*-curves characterise the length of time various species spend in the reactor at reaction conditions, but they do not give any idea about how they spend their time in reactor. Even though they appear identical in Fig. 3, it is only an indication that space times are equal; nevertheless the addition of fines to the TBR gave significant improvement in selectivity, which is discussed in next section.

Monoliths are also known as multicapillary reactors. Hence, fluid flow in one capillary is taken as same in all other capillaries in monolith, which is debatable. Fig. 4 indicates that there is actually a difference in dispersion within the channels across the radial position in the monolith. This could be due to differing velocities across the column cross-section. As the fluid flows from the 2-in. section of the column to the 4-in. section, it is possible that velocity near the column centre is higher than at the walls. Hence, in the monolith the channels near the centre display a lower mean residence time than those at the edge. Although impossible to detect in opaque monoliths by observation, magnetic resonance imaging (MRI) studies have shown that reverse flow also occurs in monoliths, which could lead to a significant back mixing effect [14]. However, it should be noted that MRI measurements were made, out of necessity, in a closed O_2/H_2O system, which eventually becomes unstable because of O_2 saturation of the liquid. In this case of a reaction a steady state regime occurs because the hydrogen gas is being consumed by reaction and cannot accumulate and saturate. Hence, the flow field is more stable but this has not yet been verified with MRI because it has not been possible to have metal present (i.e. catalyst) in the MRI equipment.

3.2. Selectivity studies

The selective hydrogenation of B reaction produces C, whose further hydrogenation leads to the saturated diol as follows, 2-butene-1,4-diol being a raw material for the manufacture of endosulfan (insecticide) and Vitamin A, makes its production industrially important. A difficulty inherent to this process is the appearance of side products, i.e. crotyl alcohol and γ-hydroxybutyraldeyde, as a consequence of double bond isomerization and hydrogenolysis reactions [15].

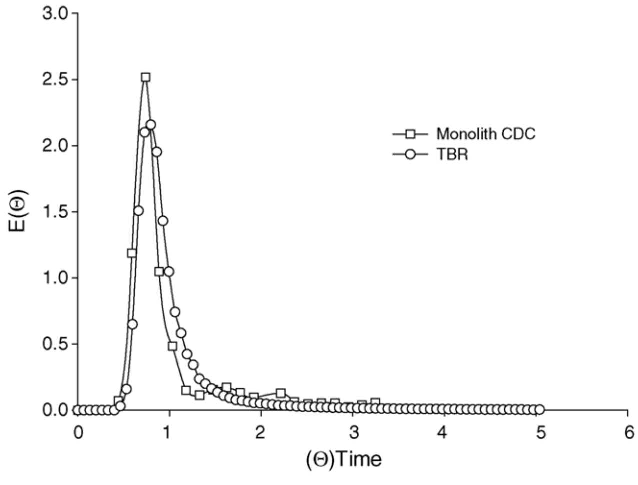


Fig. 3. *E*-curves in trickle bed reactor and monolith CDC reactor.

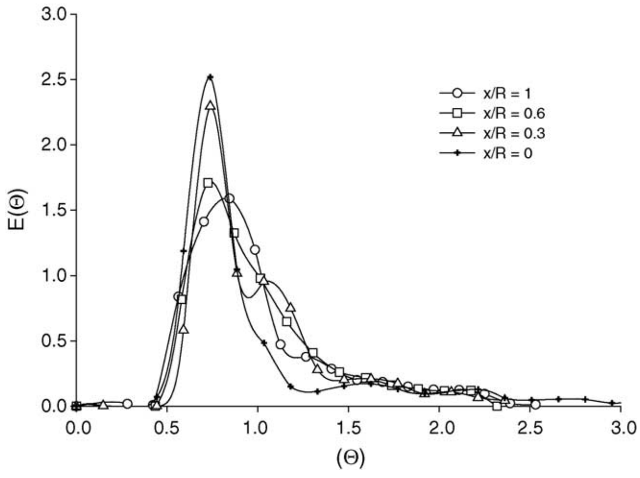


Fig. 4. *E*-curves in the monolith monolith CDC reactor at different positions.

It is a common belief that monolith reactors outperform trickle bed reactors regarding selectivity due to differences in hydrodynamic behaviour. While Taylor flow in the monolith is close to plug flow, a higher degree of dispersion is expected in the TBR that, is thought, leads to a poorer selectivity. In this study, however, differences in selectivity have been found despite flow in both reactors approaching plug flow (Fig. 3). In this study, selectivity has been calculated as follows, S = moles of C/moles of products.

The differences in performance with respect to selectivity are shown in Figs. 5–8 for both reactors and both solvents. Results from these four sets of experiments were selected from a large series of on going studies, in order to compare the performance of the two reactors and illustrate the differences in selectivity. These differences could be ascribed to a kinetic effect since both reactors present a reasonably good approach to plug flow (Fig. 3). It can be clearly observed that the selectivity towards 2-butene-1,4-diol was superior in the monolith CDC with both solvents. However, the effect is more significant with the binary solvent. Besides, it is also remarkable that with 2-propanol the loss in selectivity in the TBR is mainly due to the appearance of side products, while in the monolith CDC the selectivity drops firstly due to the formation of butane-1,4-diol and only later on to the appearance of side products. By comparing product distributions obtained with both solvents, it is observed that the use of water suppresses hydrogenolysis reaction and therefore the products of this side reaction. This phenomenon has been previously observed for the same reaction and has been ascribed to a deeper solvolysis of the carbon bonded OH group in case of water [19]. Nevertheless, some differences in selectivity are still observed between the two reactors when using the mixture solvent predominant in water (Figs. 5 and 6).

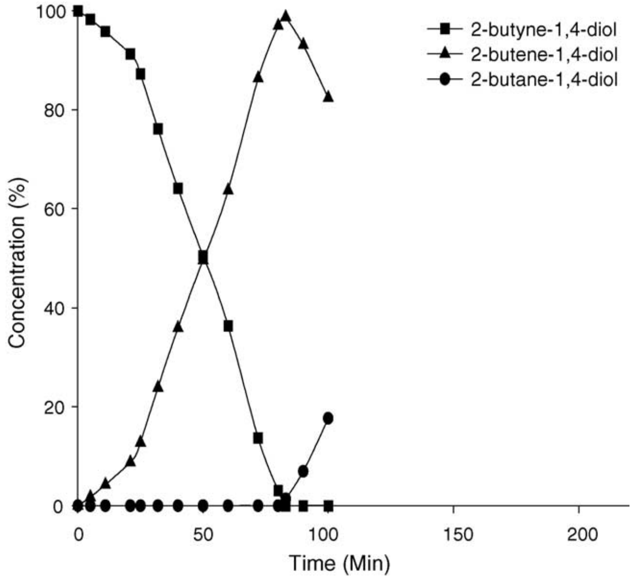


Fig. 5. Product distribution in monolith CDC with 30% (v/v) 2-propanol/water as solvent.

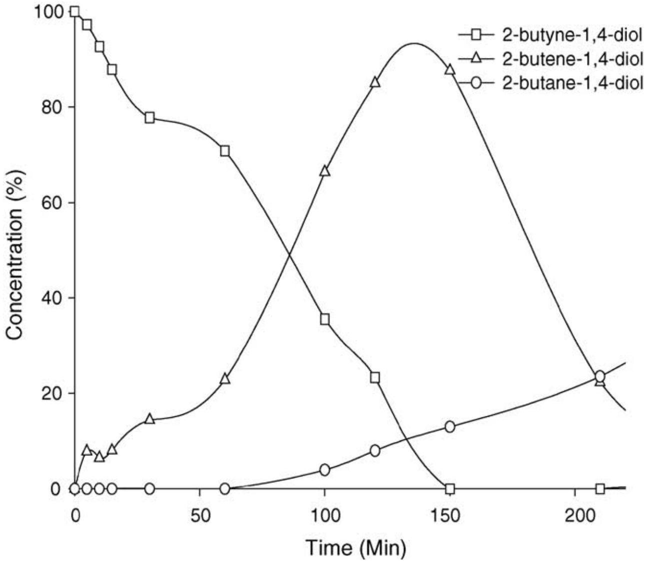


Fig. 6. Product distribution in TBR with 30% (v/v) 2-propanol/water as solvent.

The selectivity towards the olefin with solvent M in the monolith CDC is 100% while in the TBR is 85% as conversion approaches 100%. The catalyst are both egg-shell in property and it is suggested therefore that selectivity differences may be due to difference in the boundary layer thickness between the two reactors, leading to a difference in hydrogen population at the surface of catalyst. The boundary layer thickness in the monolith is a function of the gas bubble-wall distance and is possible at least an order of magnitude lower than that in the TBR. This could then lead to lower selectivity in the TBR. Since both the catalysts are eggshell layered, boundary layer is the important factor not the thickness of catalyst layer (Fig. 9).

It is acknowledged that slightly different pre-treatments of the catalyst prior to reaction were used. In the monolith CDC, the catalyst was pre-reduced in water and hydrogen for 1 h, after which the water was replaced with reaction

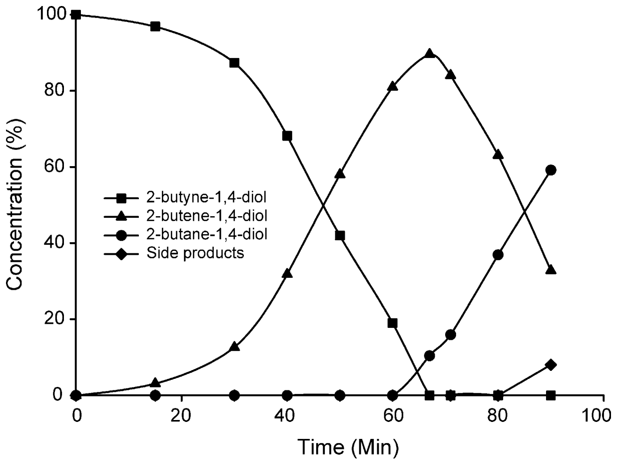


Fig. 7. Product distribution in monolith CDC with 2-propanol/water as solvent.

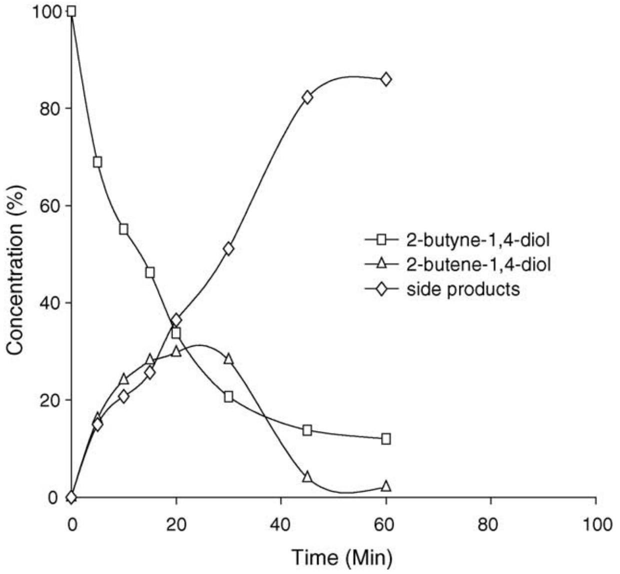


Fig. 8. Product distribution in TBR with 2-propanol/water as solvent.

solvent, first to purge the water from the system and then the reaction solution was added so that the reaction solution contained the desired initial concentration of 2-butyne-1,4-diol and was allowed to stand for 0.5 h before being circulated and hydrogen being added. In the TBR, catalyst is similarly pre-reduced by water and hydrogen for 2 h and then the reactor is started in pulsing /high interaction regime and then flowrates are reduced to operational or experimental ones. The detrimental effects on the catalytic activity of Pd catalyst with 2-butyne-1,4-diol pre-treatment have been reported [20]. The effect of an inefficient wetting on the selectivity of consecutive reactions is also documented [21].

In the case of 2-propanol, besides the factors aforementioned, it is also possible that 2-propanol could act as a hydrogen donor solvent, thus giving a different route for hydrogen presentation at the surface, which may be less selective. It should be noted that 2-propanol/water solution containing 2-butyne-1,4-diol all have pH values in the range 3.5–5.5, indicating proton activity [22]. In addition, hydrogenolysis reaction may be favoured if the hydrogen population is lower, thus allowing dehydration reactions to occur (see Scheme 1), which results in other saturated and semi-saturated products (e.g. *n*-butanol, *n*-butyraldehyde) especially when 2-butyne-1,4-diol has been hydrogenated [23]. Addition of KOH has been reported to suppress side reactions involving dehydration/hydrogenolysis, leading to enhanced selectivity to 2-butene-1,4-diol and this is shown in Table 2.

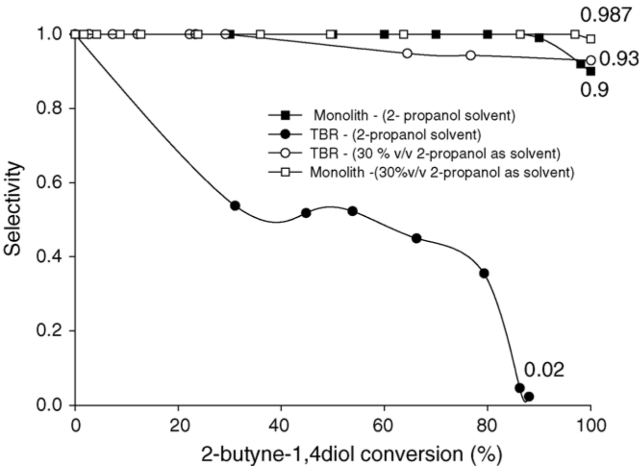


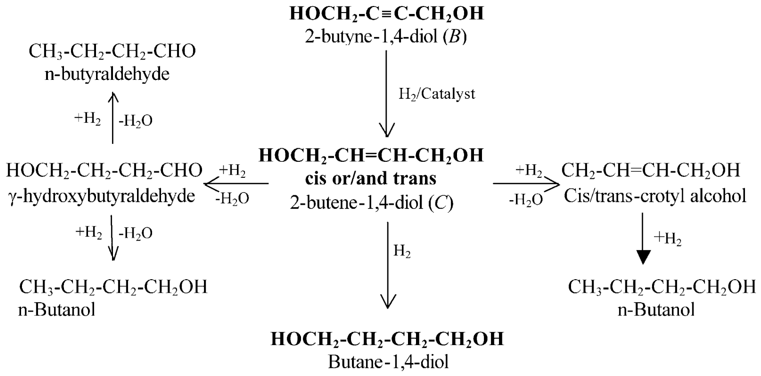
Fig. 9. Selectivity vs. conversion of 2-butyne-1,4-diol in TBR and monolith CDC.

3.3. Modelling of flow behaviour in the monolith CDC

Kulkarni et al. [7] already reported the modelling of RTD for TBR with fines based on the Iliuta [24] model of axial dispersion in a bed of porous particles. The model shows a close fit to experimental RTD data. Hence, in this paper only modelling of RTD in monolith will be discussed in detail. In order to mathematically reproduce the existing liquid RTD in a monolith reactor, some successful attempts have been made [25–27]. The system studied by such authors is, however, different to the monolith CDC. In one of the reports [25], flow was upwards and the RTD obtained showed a long tail that was attributed to a high degree of mixing for the liquid phase within the monolith. The tailing effect was modelled by using tanks-in-series model and for the rest of the curve an axial dispersion model with open-open vessel boundary conditions was used. The dispersion coefficient was found to be substantially higher than would be expected for either laminar flow in pipes or flow in a packed bed. Based upon this fact, it was concluded that the liquid phase in a monolith froth reactor exhibits mixing of a similar magnitude as would be obtained in a continuously stirred tank reactor.

In another study [28], the residence time distribution of Taylor flow in a round single capillary was reported and compared to the RTD obtained previously in the monolith froth reactor [26]. It was shown that in upward flow, the degree of back mixing in the monolith did not agree with that of a single capillary. This disagreement was ascribed to a certain degree of recirculation in the monolith block combined with the spread in velocities.

A mathematical analysis of Taylor flow has been reported [29] and liquid slugs have been modelled as a CSTR. Assuming complete mixing, however, has been found to over predict the experimental results [30]. This fact led to the conclusion that the mixing of the liquid film into the succeeding liquid slug is incomplete. By considering that only a fraction of the liquid film mixes with the liquid slug while the remaining fraction bypasses the liquid slug and by applying the CSTR by-pass model [31], a good prediction of upward Taylor flow was obtained [29]. The fraction of liquid film bypassing the liquid slug was found to be almost independent of the unit



Scheme 1. Reaction network for 2-butyne-1,4-diol hydrogenation.

cell length and depended rather on velocity. It increases when cell velocity is increased.

In a cocurrent downflow monolith column, where liquid and gas were presented on top of monolith, liquid RTD curves were found asymmetric and the tailing effect was ascribed to the film liquid acting as stagnant layer [27]. The *E*-curve was predicted successfully by applying the piston dispersion exchange (PDE) model, which is widely used for packed bed columns [24,32]. In the same study, a reasonable, good prediction of liquid RTD in a single capillary was obtained by using piston exchange (PE) model.

The tanks-in-series model and piston dispersion exchange model have been successfully applied previously to monolith systems [25,27]. Therefore, such models were considered as starting point for the prediction and description of liquid RTD in the monolith CDC.

The tanks-in-series model is well documented [18] and *E*-curve is given by,

$$t_m E = \left(\frac{t}{t_m}\right)^{N-1} \frac{N^N}{(N-1)!} e^{-tN/t_m} \ldots t_{m,i} = \frac{t_m}{N} \ldots \sigma^2 = \frac{t_m^2}{N} \tag{1}$$

Eq. (1) was applied to model the monolith RTD; the results obtained are graphically shown in Fig. 10.

In the PDE model, the flow is split into two zones, one that is considered stagnant (liquid film) and the other dynamic. A dispersion term is also added to the dynamic zone equation as an attempt to predict the velocity distribution over the channels [27]. The convection present in the dynamic zone is represented by the second term on the right hand side of Eq. (2), where ϕ is the dynamic liquid fraction.

$$\frac{\partial C_d}{\partial t} = \frac{1}{\phi Pe}\frac{\partial^2 C_d}{\partial x^2} - \frac{1}{\phi}\frac{\partial C_d}{\partial x} - \frac{n}{\phi}(C_d - C_s) \tag{2}$$

$$\frac{\partial C_s}{\partial t} = \frac{n}{1-\phi}(C_d - C_s) \tag{3}$$

where,

$$\theta = \frac{t v_d \phi}{L}; \quad Pe = \frac{v_d L}{D_{ax}}; \quad x = \frac{z}{L}; \quad n = \frac{k_2 A_2 L}{v_d \phi}$$

For the solution of the differential equations a routine in modelling package gPROMS (PSE, UK) was developed and the boundary conditions set were:

$$C_d|_{t=0} = 0; \qquad C_s|_{t=0} = 0; \qquad C_d|_{x=0} = \delta(0); \qquad \left.\frac{\partial C_d}{\partial x}\right|_{x=1} = 0.$$

The computational routine included the optimisation of ϕ, which was initially guessed and optimised by a minimization method. For each ϕ, a Peclet number was

Table 2
Comparison of effect of base on selectivity (Source: Ref. [23])

Base	Solvent	Selectivity
No	Water	0.904
No	2-Propanol	0.704
0.1 g/L KOH	Water	0.969
0.1 g/L KOH	2-Propanol	0.97
0.1 g/L NaOH	2-Propanol	0.978

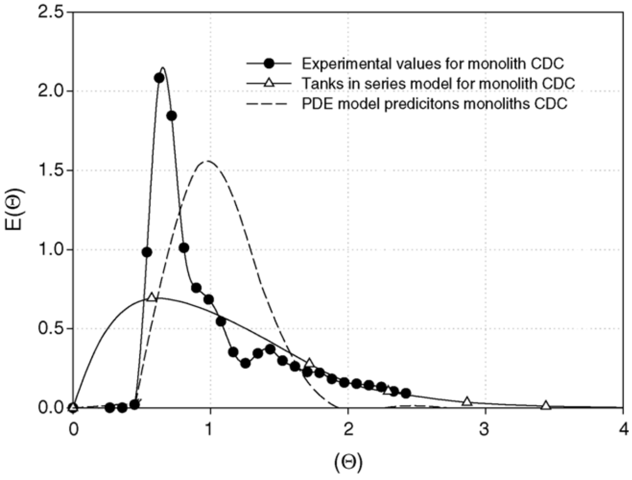


Fig. 10. *E*-curves obtained in the monolith experimentally and predicted by tanks-in-series model & PDE model.

calculated from its relationship with the variance of *E*-curve [27]:

$$\sigma_{\mathrm{PDE}} = \sqrt{\frac{2}{Pe} + \frac{3}{Pe^2} + \frac{2(1-\phi)^2}{n}\left(\frac{1}{Pe}+1\right)} \tag{4}$$

and then substituted in the system of differential equations. Variance was first calculated as described in Ref. [18]. The estimated value of ϕ was 0.75 and a Peclet number of 13 was calculated.

Tanks-in-series model and PDE model were found to overpredict the backmixing and/or maldistribution of velocities in the monolith (Fig. 10). Therefore, it was decided to try the piston exchange (PE) model that is similar to the PDE model but without the axial dispersion term. The PE model has been shown [27] to describe with reasonable accuracy the flow in a single capillary channel. Such a model is given by the following set of differential equations,

$$\frac{\partial C_{\mathrm{d}}}{\partial t} = -v_{\mathrm{d}}\frac{\partial C_{\mathrm{d}}}{\partial t} - \frac{k_2 A_2}{\phi}(C_{\mathrm{d}} - C_{\mathrm{s}}) \tag{5}$$

$$\frac{\partial C_{\mathrm{s}}}{\partial t} = \frac{k_2 A_2}{1-\phi}(C_{\mathrm{d}} - C_{\mathrm{s}}) \tag{6}$$

where the mass transport parameters were calculated as described by Winterbottom et al. [15]. The diffusion coefficient of KCl in the solvent M was determined with the equation proposed [33] and the value obtained for k_2A_2 was 0.021 s^{-1}, $\phi = 0.8$ (confidence interval = 0.01).

For this model, variance is given by

$$\sigma_{\mathrm{PE}} = \sqrt{\frac{2(1-\phi)^2}{n}} \tag{7}$$

However, ϕ was found in a similar fashion as described for the PDE model. Fig. 11 shows both liquid RTD curves, the one obtained experimentally and the one predicted by PE model. It is observed that PE model provides of a good description of the flow in the monolith under the conditions investigated.

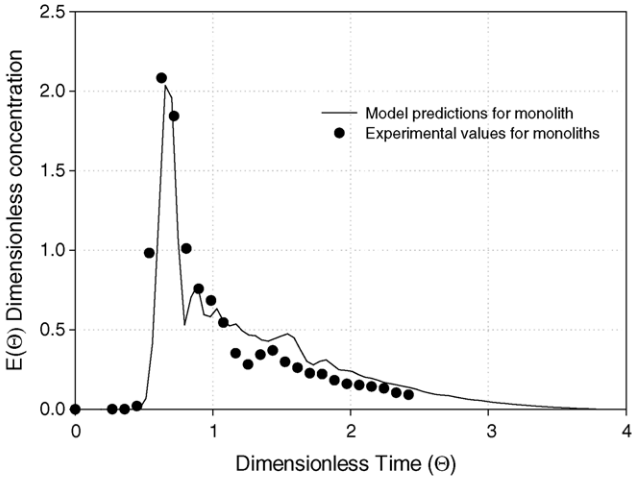


Fig. 11. *E*-curves obtained in the monolith experimentally and predicted by PE model.

4. Conclusions

A systematic comparison of residence time distribution and selectivity in the monolith and trickle bed reactor has been carried out. Under the gas and liquid velocities studied, the liquid RTD was almost identical in the monolith and TBR. The tail observed in the two RTDs is thought to result from stagnant liquid in the catalyst pore of the TBR and from the film on the channel walls in the monolith. Selectivity to butene-diol was higher in the monolith during hydrogenation of butyne-diol, compared with the TBR. Assuming both Pd/Al_2O_3 catalysts to have similar properties and knowing the RTD to be very similar for both reactors, it is tentatively suggested that difference between the reactors is due to H_2 population on catalyst surface. In the monolith reactor the thin film experienced during Taylor flow leads to a high H_2 population at the catalyst surface, explaining the relatively fast conversion of butyne to butene-diol. In the TBR the film surrounding the catalyst particles is thought to be thicker, leading to lower H_2 population on catalyst surface. This explains the slower rate of conversion, and could also influence the selectivity. Unlike the water based solvent, 2-propanol promotes side reactions and therefore affects negatively selectivity towards C, which could be related to molecular interaction between the solvent and catalyst. It is thought that water suppresses the side reactions that occur. Finally, it was shown that the monolith CDC reactor RTD could be modelled using a piston exchange model. The monolith reactor offers the advantage of a reasonably well-characterised flow pattern, low-pressure drop and excellent selectivity, making it suitable for application in the fine chemicals industry and ‘‘green’’ chemical processing.

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