A Hydrodynamic Study of Benzyl Alcohol Oxidation in a Micro-Packed Bed Reactor

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Abstract: The various flow regimes prevalent during gold-palladium catalyzed benzyl alcohol oxidation in a micro-packed bed reactor and their influence on reaction performance are identified. The reaction is studied in a 300μm deep x 600μm wide silicon-glass micro-structured reactor packed with 65μm catalyst particles at a temperature of 120°C, pressure of 1 bar (g), using pure oxygen and neat benzyl alcohol as the feed. Significant improvement in the conversion and selectivity to the main product, benzaldehyde, is observed with increasing gas flowrate and decreasing liquid flowrate, which coincides with a change in the flow pattern from "liquid-dominated slug" (segregated regions of liquid and gas slugs) to "gas-continuous trickle" (thin film coated catalyst particles with gas flowing through the voids). The latter flow regime results in enhanced external mass transfer due to an increase in the available interfacial area and shorter diffusional distances. Results show selectivity up to 81% at a catalyst space time of 76 $g_{cat}g_{alc}^{-1}$.s, outperforming a conventional batch laboratory reactor.

Keywords: Multiphase hydrodynamics, Catalytic alcohol aerobic oxidation

1. Introduction

The selective aerobic oxidation of alcohols is of great importance industrially due to the value of their products as intermediates for the fine chemical, pharmaceutical, agrochemical and perfume industries. The use of molecular oxygen to replace traditional heavy metal oxides has brought about a new 'green', low cost process for these reactions. However, the presence of both gaseous and liquid reactants results in added transport resistances. Characteristic times of physical processes in conventional reactors range between 10 to 10^{-3} s (Hessel et al., 2009), hence interference of these processes with reaction kinetics can limit the reaction performance significantly. Microreactors provide well-defined conditions, intensified heat and mass transfer, and minimal consumption of reagents and catalyst (Al-Rifai et al., 2013). They are excellent laboratory tools for conducting kinetic studies, where the hydrodynamics is of importance because it affects mass transfer and residence time distributions. Despite the advantages cited above, the hydrodynamics of micro-packed bed reactors are still not fully understood. Deviations exist from what is commonly observed in the macroscale due to a strong increase in the effect of capillary forces when scaling down reactor and particle size (Faridkhou et al., 2013). Current work on hydrodynamics in packed bed microreactors is limited to contributions towards flow mapping in packed bed microreactors (Faridkhou et al., 2013; Losey et al., 2001; Faridkhou and Larachi, 2014; van Herk et al., 2009) and gas-liquid flow through microfabricated structures (McGovern et al., 2009; Krishnamurthy and Peles, 2007). Under certain operating conditions, there may be similarities to the phenomena observed in the macroscale. A trickle bed reactor consists of a bed of catalyst particles with the interstitial spaces forming a complex pattern of interconnecting and randomly distributed pores. When gas and
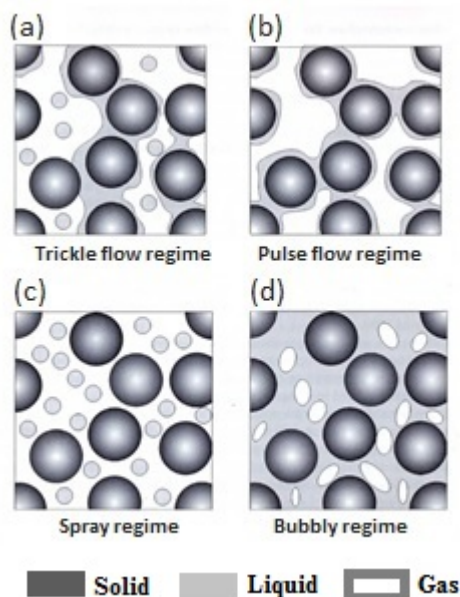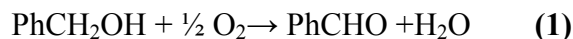
Fig. 1. Types of flow regimes in trickle bed reactors (Ranade et al., 2011).

liquid reactants flow over these catalyst particles, complex interactions between the flowing fluid phases and the stationary solid particles lead to differing flow patterns. These flow patterns depend on a number of factors: packing density, gas and liquid velocities, particle size, and physical properties of the fluid phases (Ranade et al., 2011). The various types of flow regimes prevalent in a macroscale trickle bed reactor are shown in figure 1. Trickle-flow (figure 1a) in packed bed reactors results when both gas and liquid flow rates are relatively low, the gas phase is continuous and the liquid phase is dispersed. Increasing the gas flow rate leads to pulse flow (figure 1b), where both the gas and liquid form the continuous phase. At high liquid throughputs, the liquid phase becomes continuous and the gas phase is dispersed – corresponding to the bubbly flow regime (figure 1d) (Ranade et al., 2011; Lee, 1985).

In this study, we examine the influence of gas and liquid flow rates on the flow regimes observed in a microstructured packed bed reactor and its subsequent effect on benzyl alcohol oxidation. On gold-palladium nanoalloys supported on titanium dioxide, the

reaction proceeds via two pathways: the direct catalytic oxidation of benzyl alcohol to benzaldehyde which takes place in the presence of O_2 (**1**), and a disproportionation reaction which gives equal amounts of benzaldehyde and a side product, toluene (**2**) (Enache et al., 2006).

$$PhCH_2OH + \frac{1}{2}\,O_2 \rightarrow PhCHO + H_2O \qquad \textbf{(1)}$$

$$2PhCH_2OH \rightarrow PhCHO + PhCH_3 + H_2O \;\textbf{(2)}$$

The focus of the work is two-fold: the first is flow regime mapping – identification of the flow regimes present in a micropacked bed reactor and their dependence on inlet flow conditions; the second is to assess the practical implications of these flow regimes, by studying the hydrodynamic impact on the performance of Au-Pd/TiO_2 catalyzed benzyl alcohol oxidation.

2. Methods

2.1 Catalytic microstructured reactor

The silicon-glass microreactors used in this work were fabricated using photolithography and deep reactive ion etching and sealed via anodic bonding to glass (Cao et al., 2011). The serpentine microchannel dimensions are 600μm (W) × 300μm (H) × 190mm (L) (figure 2). The gas is introduced into a liquid flow path via a T-junction, and the gas-liquid mixture then travels down the serpentine channels in slug (or annular) flow depending on the gas-to-liquid ratio, before reaching the catalytic bed. At the end of the microchannel, retention posts are used to retain the catalyst.

The catalyst used for both flow mapping and reaction was 0.05 wt% Au-0.95 wt% Pd/TiO_2 prepared via a modified impregnation method (Sankar et al., 2012). The prepared catalyst powder was pelletized and the desired sieve fraction (63-75μm) was obtained by crushing and sieving. The actual particle size was measured to be 65μm ± 14μm. The catalyst was loaded into the microreactor by applying a vacuum to the outlet port, and

sandwiched in between 3mm and 1mm of glass beads on the inlet and outlet of the channel respectively (figure 2). Liquid alcohol (benzyl alcohol, 99.98%, Sigma–Aldrich) was delivered into the reactor by a syringe pump (PhD Ultra, Harvard Apparatus). Oxygen flow was regulated by a mass flow controller (Brooks 5850TR) and directed to the gas inlet of the reactor. The effluent from the reactor was passed into a small glass vial (2 mL) which was located in a cold trap (ice-water bath), where gas and liquid were separated and the liquid product collected. The temperature was controlled to 120°C using a heating and temperature control unit (Watlow CAL 9900). The pressure was regulated to 1 bar (g) in all experiments using a backpressure regulator (Swagelok SS BP Regulator). Gas flow rates reported are in mL/min at reaction conditions (120°C and 1 bar (g)). Two liquid flowrates were used for the reaction: 0.75μl/min and 3μl/min keeping the space time constant at 76 $g_{cat}g_{alc}^{-1}$.s by altering the mass of catalyst (1mg and 4mg respectively). Start-up procedures consisted of oxygen flow at reaction conditions for one hour, followed by introduction of the liquid. Sampling was carried out every 30 minutes, until steady state was reached. When studying the effect of flow regimes, the gas flowrate was increased sequentially from low to high.
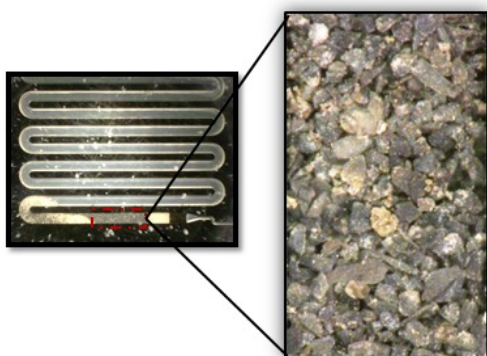

Fig. 2. Microchannel with packed bed and a higher magnification image of the catalytic bed.

2.2 Flow regime mapping

The range of superficial liquid velocities studied were 0.001 cm/s to 0.004 cm/s (0.75 - 3µl/min) while the superficial gas velocities ranged from 5 cm/s to 130 cm/s (0.6 – 10 Nml/min), utilising benzyl alcohol as the liquid feed, and under typical reaction temperature (120°C) and pressure (1 bar(g)). Flow maps generated were with particles of 65µm ± 14µm and the typical catalyst bed length was 3.2 mm. Flow observation was carried out via visualisation of the contacting patterns using a microscope (Keyence VHX 600). To aid visualization of the liquid, benzyl alcohol soluble red dye (Sepisol Fast Red) was dissolved in the flow medium; the dye tends to colour yellow when the thickness of the liquid bulk is large and pink when low. Pressure drop during flow mapping was <1 psi and gas flowrates were corrected for differences in pressure with changing flowrates. Gas flow rates reported are in mL/min at reaction conditions (120°C and 1 bar (g)).

2.3 Reaction analysis

Quantitative analysis was carried out using an Agilent 6890 GC with FID, a HP-INNOWax (19091- 133) capillary column and an auto-liquid-sampler. For GC analysis, 10μL of the collected sample was diluted using 0.5 mL of 3% (v/v) butanol in o-xylene as an external standard. Blank experiments were carried out where a typical reaction mixture was fed into an empty reactor at reaction conditions (120°C and 1 bar (g)) and the sample analysed at the exit in order to ensure the absence of homogeneous reactions and that no loss of components into the gas phase was taking place at the high g:l ratios. Results showed the inlet mixture composition was unchanged.

3. Results

3.1 Hydrodynamics

Three main types of flow regimes were identified (figure 3): "liquid-dominated slug",
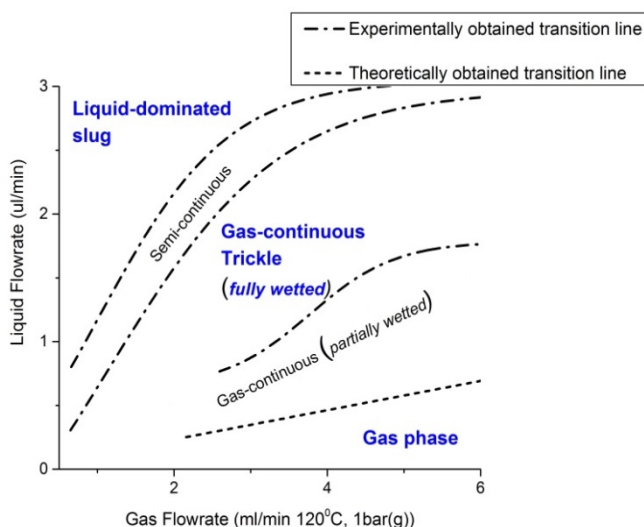
Fig. 3. Flow regimes observed in micro-packed bed reactor under benzyl alcohol oxidation reaction conditions (65μm).

"gas-continuous trickle (fully wetted)", and "gas phase". At the transition boundaries, two intermediate patterns were identified: "Semi-continuous" and "gas-continuous trickle (partially wetted)". Flow regimes were dependent on the gas and liquid flowrates. High gas and low liquid flowrates favoured gas-continuous trickle flow, while low gas and high liquid flowrates favoured liquid-dominated slug flow. Liquid dominated slug flow exhibited segregated regions of gas and liquid. The liquid occupied the majority of the bed and covered the particle interstitial voids, leaving the gas-liquid surface to reside at the interface of a few gas channels (figure 4a). The transition to gas-continuous trickle flow took place with an increase in gas-to-liquid ratio. This flow regime consisted of a continuous gas phase whilst the liquid is sheared to a more uniformly distributed thin film surrounding the catalyst particle (figure 4c) – a flow pattern which has been associated with conventional trickle bed reactors (figure 1a**)**. Along the boundary separating the two regimes exists a transitionary flow regime - semi-continuous in nature - where gas and liquid have an equal and constant share of the bed without significantly perturbing each other

(figure 4b), similar to the distribution in figure 1b, however no pulsing was observed. A third flow regime appears with a further increase in gas-to-liquid ratio, defined as "gas-continuous trickle (partially wetted)" (figure 4d). This is a region where the catalyst pellets are incompletely wetted and the majoritiy of the bed is in the gas phase, the liquid trickles down in the form of "rivulets" rather than in the form of a film. Finally, at very high gas:liquid ratios the bed transitions into a gas phase regime (figure 4e). In order to capture the onset of this transition accurately, it was calculated based on vapour-liquid equilibria.

The dynamics inside the catalytic bed were highly dependent on the flow pattern establishment preceding the bed. Slug flow in the empty channel just upstream manifested into slug behavior in the bed, with periodic wetting and drying of the particles, whilst annular flow resulted in stable flow conditions with the gas and liquid not significantly perturbing each other. This is also largely affected by the microchannel gas/liquid introduction methods. The microreactor used in this work introduced gas into a liquid flow path via a T-junction. This produced stable liquid slugs and at the high gas-to-liquid ratios studied, the flow pattern in the empty channel was predominantly slug-annular.

In contrast to macro-scale reactors, although the gas-continuous trickle is observed here, pulse flow is not. This is not surprising, as with a Reynolds number of the order of 1, inertia-induced pulsing is unlikely. The lack of pulsing behaviour has been reported in previous hydrodynamic studies in micro-packed bed reactors (van Herk et al., 2005). Further, the "liquid dominated slug" flow is close to the bubbly regime (figure 1d) in conventional packed bed reactors but with much larger gas bubbles. The spray regime (figure 1c) is not observed in the micro-packed bed and this is attributed to the dense packing and low bed porosity. Instead, a predominantly gas phase regime exists in the micro-packed bed.
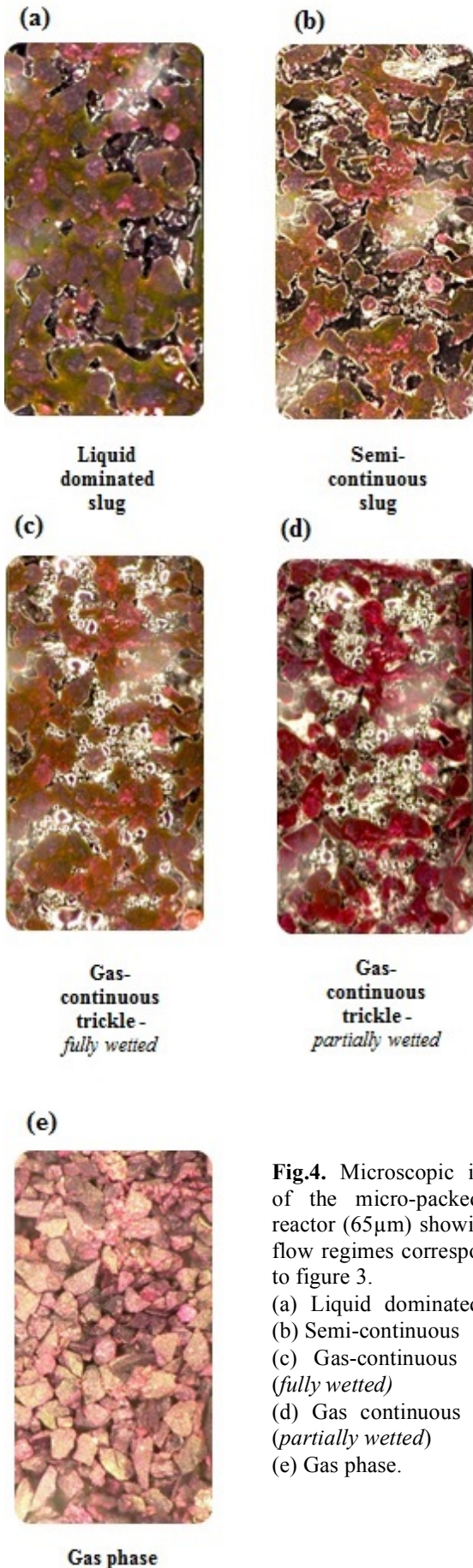
Fig.4. Microscopic images of the micro-packed bed reactor (65μm) showing the flow regimes corresponding to figure 3.
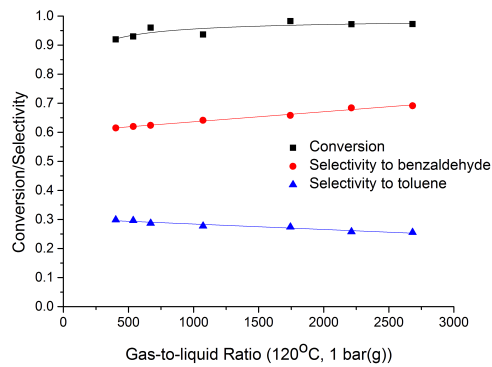(a) Liquid dominated slug
(b) Semi-continuous
(c) Gas-continuous trickle (*fully wetted*)
(d) Gas continuous trickle (*partially wetted*)
(e) Gas phase.

3.2 Impact of hydrodynamics on reaction performance

The influence of gas flowrate on the gas-liquid mass transfer coefficient has been long established in trickle bed reactors (Ranade et al., 2011). Increase in gas flowrate enhances the interaction between the gas and liquid phases as well as the spreading of liquid, leading to an increase in gas-liquid interfacial area. The reaction performance in the different flow regimes is shown in figure 5. Figure 5a shows reaction performance in the liquid dominated slug as it transitions into the semi-continuous flow regime. The reaction performs better at high gas flowrates in terms of both conversion and selectivity to benzaldehyde as the liquid slugs are sheared smaller (see figure 4a and b), increasing the gas-liquid interfacial area. Figure 5b shows the reaction performance in the gas-continuous trickle (fully wetted) flow regime, where no significant change in selectivity and a small improvement in conversion is observed. This indicates that the increase in gas flowrate - whilst operating in the gas-continuous trickle flow regime - does not affect mass transfer significantly, as the liquid film is sufficiently sheared and any further increase in gas flowrate has only a small additional benefit. Figure 5c shows results obtained at very high gas-to-liquid ratios (>4000) where the transition between gas-continuous trickle to gas phase takes place. At g:l=8000, 93% of the benzyl alcohol evaporates to the gas phase. At this point, there is direct contact between the catalyst surface and the oxygen (gas-solid mass transfer) on the dry surface of the catalyst particle, resulting in an increase in the selectivity to benzaldehyde to 90%. However, this is at the expense of a reduction in conversion to 20%. The drop in conversion may be due to the lower concentration of benzyl alcohol in the reactor at these conditions.
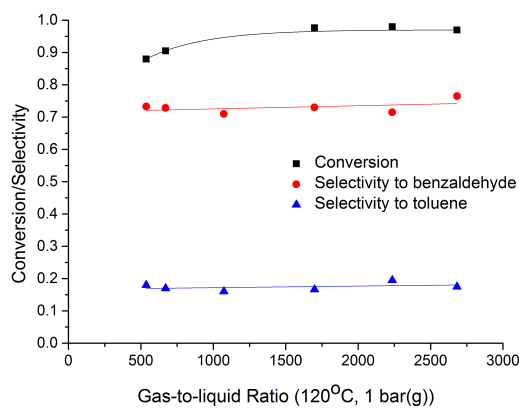
A

Liquid-dominated slug --> Semi-continuous

B

Gas-continuous trickle (fully wetted)

C

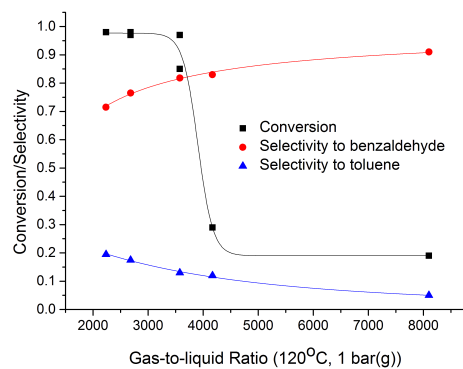**Gas-continuous trickle (partially wetted) --> Gas phase**

Fig. 5. Conversion and selectivity with increasing gas-to-liquid ratio at the three different flow regimes. **(A)** Liquid dominated slug and semi-continuous flow regimes using one selected liquid flowrate (3μl/min). **(B)** Gas-continuous (fully wetted) flow regime using one selected liquid flowrate (0.75μl/min). **(C)** Gas-continuous trickle (partially wetted) and gas phase using one selected liquid flowrate (0.75μl/min).

When reaction results are superimposed on the flow map (figure 6), the relationship between selectivity and flow pattern can be seen. Improved distribution of liquid and a larger gas-liquid interfacial area exists at the gas-continuous trickle flow regime. This enhances gas-liquid mass transfer and transfer of oxygen to the catalyst active site, hence promoting the oxidation reaction (**1**) that produces benzaldehyde exclusively.

Selectivity in the gas-continuous trickle flow regime is 81%, which is higher than what is achievable using a 50ml batch glass stirred reactor at the same conditions (120°C, 1bar O_2), where the selectivity is 74%. Due to the duality of the reaction mechanism, where the oxidation reaction requires the presence of oxygen, the availability of oxygen at the active sites determines which pathway dominates. Whilst in the batch stirred glass reactor there is perfect mixing, the packed bed reactor suffers from mass transfer limitations; those are overcome by operating at high gas flowrates. The packed bed reactor only begins to outperform the batch reactor when the catalyst is partially wetted (gas-continuous trickle, partially wetted regime) – and when there is
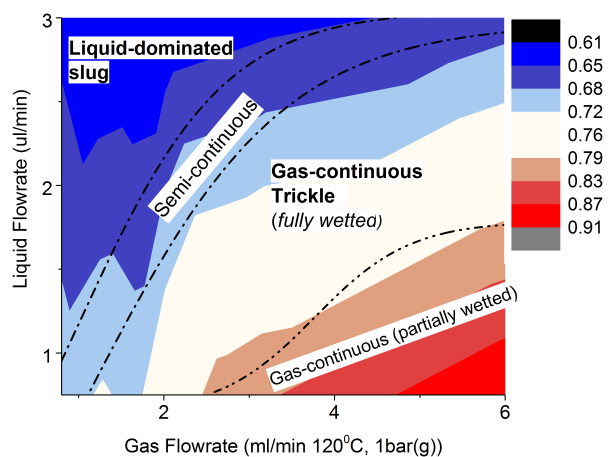

Fig. 6. Superimposed benzaldehyde selectivity contour map (data from figure 5) and flow regime map (from figure 3).

the added benefit of gas-solid mass transfer. In the gas-continuous (partially wetted) regime, a selectivity of 90% is observed, but that comes at the cost of a reduction in conversion.

4. Conclusions

The gas-liquid hydrodynamics in a packed bed microreactor has been investigated for benzyl alcohol oxidation on Au-Pd/TiO$_2$ catalyst. Results show a transition in the flow pattern from "liquid-dominated slug" to "gas-continuous trickle" with an increase in gas flow and a decrease in liquid flow. The gas-continuous trickle flow regime benefits from sufficiently wetted catalysts with a continuous gas flow path, maximising the gas-liquid interfacial area. This enhanced mass transfer promotes the oxidation reaction pathway, improving benzaldehyde selectivity. Selectivity up to 10% higher than a conventional stirred glass reactor is observed when operating in the gas-continuous trickle regime. At very high gas-to-liquid ratios (>4000 for 0.75µl/min liquid flowrate), the hydrodynamics transition into predominantly "gas phase" flow where the selectivity is highest, but the conversion plummets. There are some similarities to the hydrodynamics in conventional packed bed reactors. For instance, the gas continuous trickle flow regime observed in the microreactor is common among trickle bed reactors. However, there are also differences, such as the absence of pulsing in the microscale due to the lack of inertial forces. Due to the low liquid flowrates, the high gas-to-liquid ratios operated at in these micro-packed beds are far higher than typically employed in a conventional packed bed reactor.

5. References

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