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3D simulations of a microchannel reactor with diffusion inside the catalyst layer for 1-butanol dehydration reaction in gas phase

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Abstract

3D and a 2D-axisymmetry models in COMSOL Multiphysics[®] environment were developed to address modeling strategies to optimize the performance of wall-coated microstructured reactors operated to study gas-phase reactions under isothermal conditions. The kinetics for 1-butanol dehydration reaction was derived in our previously published research. Typically ideal models are used for modelling bulk flow in the free channel with diffusion-reaction at the surface of the layer. However in order to solve the system non-idealities, we used non-ideal models to simulate the flow field inside the free channel and diffusion-reaction in the catalyst coating. The obtained results from the 3D and 2D-axisymmetry models developed in COMSOL Multiphysics[®] were compared mainly with 2D-PFR-type model developed in MATLAB[®]. The one-way coupling between the fluid flow and transport of the components revealed that flow field non-idealities effect the performance predictions for the system. The performance and efficiency of the washcoat catalyst in microstructured reactors can be improved by controlling the thickness of the catalyst layer. As a conclusion, to optimize the performance of microstructured reactors the effect of reactor flow field must also be considered besides, the other key operational parameters such as global residence time, reaction conditions and catalyst layer thickness.

Keywords:

Microreactor, 3D modeling, CFD, Laminar flow, Diffusion–reaction, 1-Butanol, Dehydration

1. Introduction

Microstructured reactors are miniaturized reactor systems which have at least one dimension below the millimeter scale. A microstructured reactor can have single or multiple parallel channels. One of the major benefits of utilizing microreactor technology is that the conventional scale-up is replaced by number-up. Microstructured reactors are nowadays widely applied to study both gas phase and liquid phase reactions due to their advantages related to mass and heat transfer. Especially the type of microstructured reactors where the catalyst is coated on the walls of the channels. If the catalyst layer is thin enough ($< 50 \mu\text{m}$), both external and internal mass transfer resistance can be avoided (Khan et al., 2015; Schmidt et al., 2013). With such small dimensions heat transfer is also fast enough to operate

in isothermal conditions for highly exothermic and endothermic reactions (Walter et al., 2005). The empirical correlations for external and internal mass transport have been reported and discussed by e.g. Kolb and Hessel (2004), Görke et al. (2009), Reschetilowski (2013) and Lopes et al. (2011). Examples include modified form of Mears criterion (Mears, 1971) external mass transfer and Weisz-Prater criterion (Weisz and Prater, 1954) internal mass transfer. Based on the reported results in our previous work Khan et al. (2015) both the external and internal mass transfer resistances can be neglected when the catalyst layer is thin enough.

Dehydration of 1-butanol to butenes and dibutyl ether is an important industrial reaction towards the production of fine chemicals. Bio-based butanol (1-butanol) is produced from renewable sources using biotechnical routes e.g. by ABE fermentation (Chen et al., 2014). The kinetics for 1-butanol dehydration reaction over $\gamma\text{-Al}_2\text{O}_3$ catalyst coated on the walls of a microchannel reactor was presented in our previous work (Khan et al., 2015). It was demonstrated that the experiments were

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performed in kinetic regime in a microchannel reactor by utilizing the advantages related to heat and mass transfer. Both external and internal mass transfer resistance could be neglected. A 2D-PFR-type dynamic model was developed and solved in MATLAB[®] environment to describe the flow field in free channel and diffusion-reaction in the catalyst layer. The model equations were set up by assuming plug flow conditions in the free channel coupled with diffusion-reaction in the catalyst layer. Typically ideal models are used for modelling bulk flow in the free channel with diffusion-reaction at the surface of the layer. In order to solve the system non-idealities, it is desirable to use non-ideal models to simulate the flow inside the free channel and diffusion-reaction in the catalyst coating. The microchannel reactors are usually operated under laminar flow conditions (Kolb and Hessel, 2004). In order to solve the flow field with laminar flow conditions and to properly visualize the presence of concentration gradients in the radial direction due to convection dominance in the free channel domain, the 2D microchannel reactor model was extended in this study to a 3D model in COMSOL Multiphysics[®] environment. In other literature different authors such as Cao et al. (2005), Peela and Kunzru (2011), Karim et al. (2005), etc. have presented 2D models using Computational Fluid Dynamics (CFD) and diffusion-reaction inside the catalyst layer to describe the microchannel reactors and to discuss the effect of the flow field on the performance of such microstructured reactors. Due to the very small dimensions of the channels used for our reactor system, solving the system with a 3D model in CFD software, such as COMSOL Multiphysics[®], should be useful to provide further insights into the flow field and for comparison with the 2D CFD models, as well as 2D-PFR-type models.

The scope of this work is to apply a 3D model for a single cylindrical channel coated with catalyst to simulate the flow field inside the free channel and to study the effect of the laminar flow field on the transport of components inside the channel. Furthermore, through visualization of the results, further elaborating the development of concentration gradients in the free channel in the radial volume element as well as in the axial direction. The effect of the catalyst layer thickness on the performance of the microstructured reactor will also be studied. Kinetics for 1-butanol dehydration reaction from Khan et al. (2015) is used for simulations and comparison with the experimental data.

2. Model set up

The reaction simulated in this work is the dehydration of 1-butanol to butenes and dibutyl ether (Khan et al., 2015), which was carried out in a sandwich-type structured microchannel reactor composed of two plates coated with pure γ -alumina catalyst (Zapf et al., 2003). The plates (14 channels, width 500 μm and depth 250 μm , see Figure 1a) were obtained from IMM (Institute für Mikrotechnik Mainz GmbH, Germany). The microchannel reactor is assumed to operate isothermally in atmospheric pressure under uniform conditions and thus a single channel (Figure 1b) can be modeled to represent all the channels in the reactor domain. Inside empty space of the channel laminar flow is assumed to prevail based on the calculated Reynolds number, $\text{Re}=10\text{--}39$. Inside the free channel isotropic molecular diffusion is assumed. Diffusion and reaction in the porous coating of the channel walls take place via heterogeneously catalyzed gas-phase reactions and diffusion inside the catalyst layer as well is assumed to be isotropic. The flow distribution was assumed even among all the channels thus a single channel was modeled and similar results in all channels were assumed.

2.1. Model equations

The model equations solved in COMSOL Multiphysics[®] 5.1 are provided in dimensional form since there are small number of dependent variables. The flow field in the free channel was solved with laminar flow equation in steady state, whereas the components' transport in the free channel domain and in the catalyst layer domain was solved separately with dynamic convection-diffusion equations coupled at the interface of the two aforementioned domains.

2.1.1. Fluid flow in the free channel

The flow inside the channel is laminar and is given by Navier-Stokes equations,

$$\rho \frac{\partial u}{\partial t} + \rho(u \cdot \nabla)u = \nabla \cdot (-PI + \tau) + F \quad (1)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0. \quad (2)$$

Equation 1 is conservation of momentum for the compressible Newtonian fluids and Equation 2 is the continuity equation. Here ρ is the density (kg/m^3) of the fluid, u is the velocity (m/s) of the fluid, τ is the viscous stress tensor (Pa), F is the volume force vector (N/m^3) and P is the pressure (Pa).

(a) Microchannel reactor plate with channel dimensions, diameter $500\mu\text{m}$, depth $250\mu\text{m}$ and length 25 mm.

(b) Cross section of the half cylindrical channel. R_1 is the radius of inner cylinder, R_2 is the radius of outer cylinder, δ_s is the difference between the two radii and corresponds to the deposited catalyst (S) layer thickness. G represents gas-phase in the free channel domain.

Figure 1 Representation for the single channel model and different domains in the channel.

The flow equation was solved in the steady state. The calculated velocity flow field serves as input for the flow velocities of chemical components in the channel. There is one-way coupling between the fluid flow equation and components' transport equation. The fluid inside the free channel was assumed to behave as an ideal gas.

2.1.2. Convection and diffusion in the free channel

The transport of the components (bulk-phase) in the channel is described by convection-diffusion equation. The time dependent mass balance equation solved is

given as,

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) + u \cdot \nabla c_i = 0 \quad (3)$$

where D_i is the molecular diffusion coefficient (m^2/s) of a chemical component, c_i is the component concentration (mol/m^3) and u is the velocity (m/s) of the fluid. The molecular diffusivity was calculated from Wilke's approximation.

$$D_i = \frac{1 - x_i}{\sum_{k=1}^N \frac{x_k}{D_{ik}}} \quad (4)$$

Where x is the molar fraction of the components. Binary molecular diffusion coefficients D_{ik} used in Wilke equation were estimated using Fuller-Schettler-Giddings (Fuller et al., 1966) equation.

$$D_{ik} = \frac{T^{1.75} \cdot \sqrt{\frac{1}{M_i} + \frac{1}{M_k}}}{P \cdot (v_i^{1/3} + v_k^{1/3})} \cdot 10^{-7} \text{m}^2/\text{s} \quad (5)$$

Where D_{ik} is the binary molecular diffusion coefficient (m^2/s) of the components', T is the temperature (K), M is the molecular mass of the components (g/mol), P is the pressure (atm) and v is the volume contribution of the molecules. The volume contributions of the molecules were obtained from literature (Poling et al., 2000).

2.1.3. Diffusion and reaction in the catalyst layer

The transport of species in the catalyst layer was described by diffusion and reaction equation. Since at the reactor walls, i.e. catalyst layer surface the velocity was zero, the terms left in the time dependent mass balance equation solved is given as,

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_{ei} \nabla c_i) + R_i = 0 \quad (6)$$

where D_{ei} is the effective diffusivity coefficient (m^2/s) of the components, c_i is the concentration (mol/m^3) of the components and R_i is the generation rate ($\text{mol}/(\text{m}^3 \cdot \text{s})$) of the component i .

The effective diffusion coefficient D_{ei} of components were estimated by using the porosity (ϵ) and the tortuosity (τ) of the catalyst

$$D_{ei} = \left(\frac{\epsilon}{\tau}\right) D_i. \quad (7)$$

In case of 3D-model the velocity field was set as zero in the catalyst layer. Diffusion for both 3D and 2D-Axisymmetry models were assumed to be isotropic.

2.1.4. Kinetic model for 1-butanol dehydration

Reaction was assumed to take place only in the catalyst layer. The dehydration reaction (Figure 2) kinetics was described with power law approach (Khan et al., 2015).

The rate equations for the main reactions in the system are presented here,

$$r_1 = k_1 \cdot c_A \quad (8)$$

$$r_2 = k_1 \cdot (c_A^2 - \frac{1}{K_{eq}} \cdot c_C \cdot c_D) \quad (9)$$

$$r_3 = k_3 \cdot c_D \quad (10)$$

where, A is 1-butanol, B is 1-butene, C is water and D is dibutyl ether. Power law considers ether formation and decomposition as second order reactions and the rest of reactions as first order reactions. There are three rate constants in temperature-dependent form and the rate constant for the backward reaction k_{-2} is expressed with K_{eq} obtained from thermodynamic equilibrium constant calculations. All of this data is taken from Khan et al. (2015).

The generation rates used as reaction terms in Equation 6 for all components in the system taking into account the stoichiometry are given as,

$$R_A = (-2r_1 - 2r_2) \cdot \rho_b \quad (11)$$

$$R_B = (2r_1 + 2r_3) \cdot \rho_b \quad (12)$$

$$R_C = (2r_1 + r_2 + r_3) \cdot \rho_b \quad (13)$$

$$R_D = (r_2 - r_3) \cdot \rho_b. \quad (14)$$

2.1.5. Flow modeling boundary conditions

In this section boundary conditions for closing the respective equations discussed in Section 2.1.1, are presented.

Boundary condition for the laminar inflow described by Equation 2 is given as,

$$u = -u_0 \cdot n \quad (15)$$

Inlet boundary condition is provided as laminar inflow where entrance length was set to be 5% of the channel length. At the walls, no slip boundary condition was used, i.e. assuming $u=0$ and at the outlet pressure boundary condition was used. Furthermore, following initial condition at $t=0$ is used.

$$u_0 = u_{ave}(inlet) \quad (16)$$

2.1.6. Reaction modeling boundary conditions

In this section boundary conditions for closing the respective equations discussed in Sections 2.1.2–2.1.3, are presented.

Following boundary condition is valid for the transport of the components inside the channel (Eq. 3) at the inlet of the channel,

$$c_i(l = 0) = c_{i,gas}(in). \quad (17)$$

At the outlet it is assumed that there is no flux,

$$n \cdot (-D \nabla c_i) = 0. \quad (18)$$

Moreover, the initial condition at $t=0$, was provided as a step increase so that the concentration is ramped up from zero to avoid non-physical results at the beginning of the simulation.

Boundary condition for the component transport across the interface of free channel domain and catalyst layer domain are embedded in the COMSOL Multiphysics® 5.1 modules. These boundary conditions at the interface were described as,

$$n \cdot N_i = -D_{ei} \nabla c_i^s, \text{ where, } c_i^s = c_i^b. \quad (19)$$

Regarding outside surface of the catalyst layer (i.e. catalyst layer - metal wall interface) it was assumed that molar fluxes of all the components are zero,

$$n \cdot N_i = 0. \quad (20)$$

2.2. Geometry and meshing

A simple cylindrical channel was drawn using COMSOL Multiphysics® geometry module. The catalyst layer was added to the walls of the channel. A full channel as well as a half channel were used for modelling in 3D. Moreover, a circular channel geometry was generated for a 2d-axisymmetry case.

The meshing for a full and half cylindrical channel are provided in Figure 4. As most of the activity takes place at the interface between the free channel and the catalyst layer, thus the mesh at the interface was refined.

The mesh at the interface was made denser by adding boundary layer closer to the interface both on the free channel side and the catalyst layer side. In axial direction the number of grid points was controlled to avoid formation of coarser cells.

For 2D-axisymmetrical channel geometry, mesh strategy similar to the 3D geometry was used. A circular channel geometry was drawn for the 2D-axisymmetry case. The generated mesh for 2D-axisymmetrical channel is presented below in Figure 5.

Figure 2 Reaction scheme used for 1-butanol dehydration over γ -alumina modified from (Berteau et al., 1985).

Figure 3 A single channel geometry, full channel (a) and half channel (b) with dimensions, $L=25$ mm, $d=500\mu\text{m}$ and with catalyst layer of $25\mu\text{m}$.

2.3. Sensitivity analysis

The tests for mesh independence were performed both in axial and radial direction. In axial direction the mesh was made denser by increasing number of grid points from 30, 60 and 80. After 60 mesh points no difference was observed for the axial concentration profiles of 1-butanol in reaction case. Finally 80 grid points were used for final simulation case. These tests were made with 40 grid points in radial direction. Respectively, in radial direction the catalyst layer domain was made denser with increasing the number of grid points from 20, 30 and 40. The concentration profile of 1-butanol in the catalyst layer was found to be constant after 30 grid points. The refinement of the mesh

Figure 4 Generated mesh for a single channel geometry, full channel (a) and half channel (b) with dimensions, $L=25$ mm, $d=500\mu\text{m}$ and with catalyst layer of $25\mu\text{m}$.

on the free channel domain side was evaluated by observing the magnitude of transported flux across the interface boundary. The number of boundary layers on the free channel side were increased from 3 to 5 and 10 layers. The transported flux values were found to be constant after 5 boundary layers on free channel domain side. Thus flux transported to the boundary interface was grid-independent when 5 boundary layers or more were used. The finally used mesh consisted of 30 grid points in the catalyst layer with 20 boundary layers, and 10 boundary layer points on the free channel side. In axial direction the free channel was divided with 80 grid points. The number of cells in the 3D full channel

Figure 5 2d-axisymmetry case, single channel geometry (a) and generated mesh (b).

case was 35680, for 3D half channel case 5480 and for the 2D-axisymmetry case the number of elements was 4420. Near the wall cells percentage in the whole mesh for the finally chosen case was around 25–30%.

3. Results and discussions

The differences between 2D-axisymmetry and 3D model are minimal as the geometry is not changing in tangential direction in pipe flow which is observed from simulation results for both the 3D model and 2D-axisymmetry models. However, to demonstrate the effect of all the key parameters implementing a 3D model based on single channel in micro-scale dimensions can be very convenient for the readers as well. Therefore, 2D-axisymmetry and 3D model results are presented side-by-side. The results for 2D-axisymmetry model are visualized in simple 2D domain and using the 2D-revolution feature of COMSOL Multiphysics® 5.1 to generate 3D visualization. Concentration profiles for the free channel domain and the catalyst layer domain

are visualized separately for both the domains for 2D-axisymmetry case, whereas for 3D-model they are presented as combined.

3.1. Velocity field in the free channel

3D slice plots for the velocity field of the bulk flow in the free channel (full and half channel) are presented in Figure 6. The average inlet velocity is 0.87 m/s but due to the development of laminar flow regime the maximum velocity reached is $1.73 \text{ m}\cdot\text{s}^{-1}$ in the center of the channel. The flow in the center of the channel is dominated by convection and close to the walls ($r=R$) the velocity reaches zero due to parabolic velocity profile development.

Figure 6 Velocity profile visualization for bulk phase in 3D (a) full channel and (b) half channel.

The velocity profile in the free channel domain for the 2D-axisymmetry case is presented in Figure 7. The trend for the velocity contours is similar to the 3D case.

3.2. Concentration profiles

3D surface plots (catalyst layer outer surface) for reactant 1-butanol and product 1-butene are presented in Figure 8 (full channel) in steady state with residence time of 0.03 s. Presence of axial and radial gradients can be observed easily in the figure. The axial gradients are present due to the transport and reaction of 1-butanol

Figure 7 Velocity profile visualization for bulk phase in 2D-axisymmetry case for the free channel, (a) 2D contours and (b) 2D-revolution contours.

along the length of the reactor whereas, the radial gradients are generated from the residence time differences in the radial volume and diffusion-reaction of the components in the catalyst layer. These gradients are more prominent in Figure 9 (half channel). A more detailed visualization and description is presented applying 2D-axisymmetry case.

For the 2D-axisymmetry case the concentration contours in the free channel (bulk domain) are presented in Figure 10 for reactant (a) and product (1-butene) (b) at contact time of 0.03 s. The transport and development of the concentration profile for the reactant and product components in the bulk domain can be observed clearly from Figure 10. As the solution reaches steady state for the contact time of 0.03 s, the reactant component is consumed by the reaction and at the outlet the conversion reaches up to 80%. Similarly as the reactant is consumed by the reaction and product species (1-butene) are formed by the reaction, maximum concentration of the product species (1-butene) is observed at the outlet. The presence of radial concentration gradients in the free channel domain are corresponding to the residence time difference in the radial volume elements. Since convection is dominating and due to low back mixing related to a low value of Peclet number ($Pe=29.3$), the radial concentration gradients are evident.

Figure 8 Surface plots for (a) reactant (1-butanol) and (b) product (1-butene) in full channel geometry at residence time 0.03s.

Figure 9 Surface plots for (a), reactant (1-butanol) and (b) product (1-butene) in half channel geometry at residence time 0.03s.

Figure 10 Free channel (bulk domain) steady state concentration contours (a) reactant (1-butanol) and (b) product (1-butene) at contact time of 0.03 s generated from 2d-axisymmetry case.

Interestingly concentration gradients can be observed in the radial direction at any point across the length of the free channel domain from channel axis $r=0$ to the reactor wall $r=R$. Considering the reactant (1-butanol), this happens mainly due to two reasons. Firstly, the molecules closer the catalyst layer surface ($r=R$) are diffused to the catalyst layer and react to form the products. The concentration of the reactant is therefore lower closer to the catalyst layer surface, $r=R$ and higher close to the channel center, $r=0$. Secondly, as the flow velocity in the center of the channel is maximum the molecules present in the center of the channel ($r=0$) are transported faster than compared to the ones present close to the channel walls ($r>0$) and do not have enough time to diffuse to the catalyst layer. Due to this parabolic velocity profile the residence time of molecules varies in the free channel based on the radial position. Thus the radial concentration profiles emerge in the radial volume elements due to the residence time differences. These radial concentration profiles are counter effected by the molecular diffusion in the radial direction. In case where convection is dominating a gradient is observed in the concentration of the reactant and products in the radial direction in the free channel domain. (Salmi et al., 2011)

The concentration contours in the catalyst layer are presented in Figure 11 for reactant (a) and product (1-butene) (b) at contact time of 0.03 s. In the catalyst layer the diffusional flux is assumed in both r (radial) and z (axial) directions. Due to Dirichlet boundary conditions, the concentration of the components at the catalyst layer surface corresponds to the concentration at the closest point in the bulk phase. Thus the observed concentration gradients at the catalyst layers external surface (in axial direction) are formed due to development of concentration gradients in the gas phase in radial volume elements owing to the diffusion-reaction in the catalyst layer. Inside the catalyst layer, the concentration of the reactant (1-butanol) decreases in radial direction due to the reaction. The concentration profile of the reactant is influenced by the thickness of the catalyst layer. More detailed analysis of the reactant concentration profile inside the catalyst layer for different layer thicknesses is presented and discussed in Figure 12. Correspondingly to the 1-butanol concentration profiles, it can be observed that product concentrations are highest closer to the outlet since most of the reactant has already been converted into the products.

Figure 11 Catalyst layer (catalyst domain) steady state concentration contours for (a) the reactant (1-butanol) and (b) product (1-butene) at contact time of 0.03 s, generated from 2d-axisymmetry case.

The radial concentration profile of the reactant 1-butanol at the entrance of the channel in the catalyst

layer in steady state is presented in Figure 12. This plot was generated at first grid point from the inlet by creating a 3D-cut line along the radial direction from surface of the catalyst layer to the channel wall. The change in the concentration of the reactant in the radial direction within the catalyst layer is not that significant for the average catalyst layer thickness of $25\ \mu\text{m}$ used in the experimental conditions. For the catalyst layer thicknesses beyond $40\ \mu\text{m}$ there is a significant decrease in the concentration of the reactant component due to effect of mass transport resistance. Thus for layer thicknesses higher than $40\ \mu\text{m}$ the reaction is seriously limited by internal mass transport resistance.

Figure 12 Simulated 1-butanol concentration profiles inside the catalyst layer for 15–200 μm layer thicknesses close to the entrance for residence time of 0.03 s.

3.3. Comparison of 2D (Matlab) and 3D (COMSOL) models

A comparison of the 2D–PFR–type model Matlab[®] and 3D & 2D–axisymmetry COMSOL Multiphysics[®] models, is presented in Figure 13. Since for COMSOL models the results for 3D model case and 2D–axisymmetry case were similar, COMSOL results will be referred to as 3D model results in this section, whereas Matlab model results will be referred to as 2D model results for ease of understanding.

Comparison for the reactant (1-butanol) concentration profile inside the catalyst layer simulated for different layer thicknesses, with 2D–PFR–type model (Matlab[®]) and 3D–model (COMSOL Multiphysics[®]) is presented in Figure 13. For the catalyst layer thickness of $15\ \mu\text{m}$ the results for the concentration profile obtained from 2D and 3D models were very close to each other. As the layer thickness was increased from $15\ \mu\text{m}$, a drop in the concentration profile was observed for 3D model as compared to 2D model. However, the

overall drop in concentration was still not that significant for the average layer thickness of $25\ \mu\text{m}$ applied in the experiments. The deviation encountered in the results was between 2–25 % as the layer thickness was increased from $15\ \mu\text{m}$ to $200\ \mu\text{m}$.

Figure 13 Simulated 1-butanol concentration profiles inside the catalyst layer for 15–200 μm layer thicknesses close to the entrance for residence time of 0.03 s. Results for 3D–model (COMSOL Multiphysics[®]) are presented with 'solid' lines and for 2D–PFR–type model (Matlab[®]) are presented with 'dashed' lines.

Figure 14 1-butanol concentration profile in axial direction (free channel) across the reactor length, Matlab 2D–PFR–type-model (dashed lines) and COMSOL 3D model (solid lines).

In Figure 14, a comparison for the predicted concentration profiles of 1-butanol in free channel (axial direction) obtained from 2D–PFR–type model and 3D model are presented across the reactor length. For the comparison purposes only two catalyst layer thicknesses were selected, $25\ \mu\text{m}$ which was the average catalyst layer thickness for the MCR and $200\ \mu\text{m}$. Since in 3D model

the concentration gradients were present in radial direction due to laminar profile the axial concentration profile in the free channel was taken as an average of the radial concentration profile at each axial point across the length of the reactor. For the 2D-PFR-type model the free channel concentration was taken close to the catalyst surface.

From Figure 14 it is observed that for the $25\ \mu\text{m}$ layer thickness the 2D-PFR-type model predicts more consumption of reactant compared to the 3D model. Whereas for the $200\ \mu\text{m}$ layer thickness the predicted concentration profiles for both the models are relatively close to each other. The lower conversion predicted by the 3D model compared to the 2D-PFR-type model is due to the fact that the 3D model includes effects of axial as well as radial gradients in the concentration. Radial gradients lead to lower reactant concentrations close to catalyst layer in free channel resulting in lower reaction rate in the layer. Axial gradients increase backmixing also resulting in lower reactant concentrations. The effect is more prominent with thinner catalyst layer since in case of a thicker layer the slow reaction in the catalyst layer due to mass transfer resistances levels out the differences in the free channel.

To further explain the effect of developed radial concentration profiles in the free channel (bulk flow), the radial concentration profiles simulated by 3D model for layer thicknesses of $25\ \mu\text{m}$ and $200\ \mu\text{m}$ are presented in Figure 15. The concentration profiles were taken close to the outlet of the free channel for the cross-section.

Figure 15 1-butanol radial concentration profile (free channel) at the outlet for the cross-section (dimensionless) of the channel, solved with 3D model.

From the Figure 15 it is clearly observed that at the center of the channel ($r=0$) the concentration at the outlet is higher compared to the channel walls ($r=R$). This is a typical behavior associated with parabolic veloc-

ity profiles where the residence times for the reacting molecules are different across the radial direction. As discussed in Section 3.2.

4. Conclusions

A heterogeneous model with transport characteristics in the structured microchannel reactor was successfully applied in this work. The 3D and 2D-axisymmetry models developed and solved in COMSOL Multiphysics® environment were able to capture the effect of simultaneous convective flow and molecular diffusion flux as well as laminar flow profile on the concentration of reacting components in the free channel. The one-way coupling between the fluid flow (in the free channel) and component transport demonstrated the effect of the flow field on the transport of the components to and from the catalyst layer. Comparison of a 3D model (COMSOL Multiphysics®) with the PFR-type 2D-model (Matlab®) further cemented the fact that laminar flow profile and presence of the radial gradients in the free channel domain are necessary to account for chemical processes in coated microchannels. The thickness of catalyst layer is an important parameter in terms of performance of the wall coated microstructured reactors. Simulation results in this study have shown that with a catalyst layer thickness of $< 25\ \mu\text{m}$ internal mass transport resistances are not significant. Thus the performance and efficiency of washcoat catalyst in microstructured reactors can be improved by controlling the thickness of the catalyst layer. In terms of design strategies to improve the overall performance for the wall coated microstructured reactors applied for gas phase operations, certain strategies are necessary. Creating turbulence in the flow field to increase mixing would increase the residence time for the molecules and thus overall efficiency can be increased.

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Nomenclature

c	concentration of components in the catalyst layer ($\text{mol}\cdot\text{m}^{-3}$)
$c_{(i,gas)}$	concentration in the gas phase in the free channel ($\text{mol}\cdot\text{m}^{-3}$)
c_i^b	concentration of gas species in bulk (free channel) ($\text{mol}\cdot\text{m}^{-3}$)
c_i^s	concentration of gas species at catalyst surface ($\text{mol}\cdot\text{m}^{-3}$)
D_i	molecular diffusivity ($\text{m}\cdot\text{s}^{-2}$)
D_{ei}	effective diffusion coefficient ($\text{m}\cdot\text{s}^{-2}$)
D_{ik}	binary diffusion coefficient ($\text{m}\cdot\text{s}^{-2}$)
δ_{cat}	catalyst layer thickness (μm)
E	activation energy (kJ/mol)
ϵ	catalyst layer porosity
ϵ_b	void fraction in channel
ϵ_p	catalyst particle porosity
η	effectiveness factor
i	subscript for components
k	reaction rate constant ($\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)
k_{eq}	thermodynamic equilibrium constant
M_i	molecular mass ($\text{g}\cdot\text{mol}^{-1}$)
n	normal direction vector
N	Molar flux ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
P	pressure (bar)
r	rate of reaction ($\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$)
R	general gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
R_A	Reaction rate based on stoichiometry for 1-butanol
R_B	Reaction rate based on stoichiometry for 1-butene
R_C	Reaction rate based on stoichiometry for water
R_D	Reaction rate based on stoichiometry for di-butyl ether
ρ_B	bulk density ($\text{kg}\cdot\text{m}^{-3}$)
T	reaction temperature
τ	catalyst layer tortuosity
u	velocity ($\text{m}\cdot\text{s}^{-1}$)
u_0	inlet velocity at time $t=0$ ($\text{m}\cdot\text{s}^{-1}$)
u_{ave}	average velocity of parabolic velocity profile ($\text{m}\cdot\text{s}^{-1}$)
v_i	volume contributions of molecules
A	subscript for 1-butanol
B	subscript for 1-butene
C	subscript for water
D	subscript for dibutyl ether
∇	differential operator

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