Computational Fluid Dynamics for Microreactors Used in Catalytic Oxidation of Propane

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Abstract: The optimal design of a microreactor for a specific application can be explored based on simulation results obtained by using CFD package of COMSOL Multiphysics. This research deals with the design of suitable microreactors for the catalytic oxidation of volatile organic compound (VOCs), using propane as a model molecule. The microreactor considered consists of eleven parallel channels, in which an Au/Cr/γ-Al$_2$O$_3$-catalyzed combustion reaction takes place. Each channel is 0.5 mm diameter and 100 mm long.

The catalytic microreactor was simulated for temperatures between 563 K and 663 K and inlet flow velocities between 0.05 and 1 m/s. As expected, the propane conversion increased quickly with increasing temperature for a fixed inlet flow velocity. For a fixed temperature, the propane conversion increased as the inlet flow velocity decreased. The simulated results have revealed that higher conversion rates of propane can be achieved by decreasing inlet gas velocity from 1 m/s to 0.01 m/s and increasing temperature from 593 K to 663 K

Optimum inlet gas velocity for propane conversion of 99.99 % was between 0.05 m/s and 0.1 m/s.

Keywords: Volatile organic compound oxidation, Catalytic microreactor design, modeling, propane, CFD.

1. Introduction

Microreactors are devices containing open paths for fluids with characteristic dimensions in the range of 100 – 500 μm and have multiple channels where the chemical transformations occur (W. Ehrfeld, et al, 1999). Different reactions have been used to illustrate the advantages of performing chemical reactions in microreactors, which are particularly suited for highly exothermic, endothermic and fast reactions. Their small reaction volume allows handling of dangerous reactions such as with explosive or toxic components, compared to conventional chemical reactors. Due to the small channel dimensions, microreactors have a high surface-to-volume ratio for kinetically controlled reactions and high heat and mass transfer rates (Ehrfeld et al, 1999). The small dimensions of the microchannels allow short radial diffusion time leading to a narrow residence time distribution (RTD) (Rouge et al, 2000). What is more, the scale-up can be easily performed just by multiplying the number (numbering-up) of the microreactors units without changing the channel's geometry. Catalyst material is usually deposited on the wall of the reacting channels for catalytic microreactor (Zanfir et al., 2003).

The objective of this project is to develop a suitable microreactor model for VOC catalytic oxidation using the CFD package of COMSOL Multiphysics. Propane oxidation over a catalyst (Au/Cr/γ-Al$_2$O$_3$) was chosen as a model reaction.

$$C_3H_8 + 5O_2 \Rightarrow 3CO_2 + 4H_2O \qquad (1)$$

The microreactor considered consists of eleven parallel channels, in which an Au/Cr/γ-Al$_2$O$_3$-catalyzed oxidation reaction takes place. Each channel is 0.5 mm diameter and 100 mm long. The first design step was the selection of the most suitable microreactor geometry. This was based on cold flow (without reaction) and the simulation results were obtained by using the CFD module of COMSOL Multiphysics. Four different geometries had been proposed (see Figure 1) and simulated in 2D (see Figure 2) to evaluate the fluid behaviour in the microchannels. The design of a microreactor relies on having uniform flow distribution in all parallel microchannels for optimum yield and product selectivity. Relative standard deviation was used as a measure of the quality of the flow distribution in the microchannels. As defined by (Delsman., et al, 2004):

$$\sigma = \frac{1}{\bar{F}} \sqrt{\frac{\sum_{n=1}^{n}(f - \bar{F})^2}{n - 1}} \qquad (2)$$

where f is the flow rate per channels, $\bar{F}$ the mean flow rate, n is the number of channels, and σ is the relative standard deviation.

Consequently, a larger value of the relative standard deviation will correspond to a less uniformly distributed flow over the channels. The reason is that non-uniformity of flow distribution of fluid among the channels introduces dispersion, leading to loss in conversion and selectivity in catalytic microreactor (Commenge, et al, 2002). It also leads to increase in pressure drop over the microreactor.

Type A1   Type A2   Type A3   Type A4
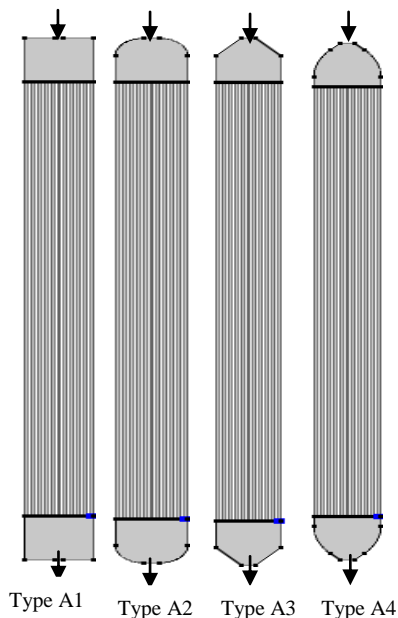
Figure 1. Four proposed geometries

The so called A2 geometry gave the optimum Flow distribution from laminar to transitional regime (the lowest relative standard deviation). The second step involved the simulation of the selected microreactor geometry for propane oxidation. The A2 geometry was modified in a 3D model to further investigate the catalytic oxidation of the model VOC. The catalytic reaction takes place at the surface of microchannel wall.

2. Use of COMSOL Multiphysics

The four proposed microreactors geometries were developed in COMSOL v4.3b and a single phase laminar compressible flow was simulated in cold flow (without reaction) at normal temperature and pressure. This approach calculates the flow field using the incompressible form of the Navier-Stokes and continuity equations. Owing to the intense computational demands, 2D model was use to accurately study the flow behavior in the microchannels. A 3D model was use to study the catalytic oxidation at steady state and atmospheric pressure. No slip boundary condition is imposed on all internal walls. $Au/Cr/\gamma$-Al_2O_3 catalyst was assumed to uniformly be deposited onto the wall layer of the microchannels. Meshing was performed by the default triangular and tetrahedral meshing algorithm available in COMSOL Multiphysics with a mesh size of 0.01mm. The flow rates in each channel were determined using COMSOL post processing. This model shows the catalytic oxidation of propane (VOCs) in a microreactor. The reactant (propane) is transported from the fluid bulk to the catalytic surfaces at the reactor wall, where it reacts. A space-independent model is set up to analyze the reaction using the reaction engineering interface. The known reaction kinetics is incorporated to solve the space-dependent model of the microreactor because all the interfaces with chemical engineering module include fields for defining arbitrary reaction kinetics.

The physics user interface supports simulation of transport by convection and diffusion in 1D, 2D and 3D. The dependent variable is the molar concentration; c.

Figure 1 and 2 shows the four proposed geometries created using CFD package of COMSOL Multiphysics in 2D.

3. Governing Equations

The flow in the microchannel is laminar and given by the Navier-Stokes equations. The Navier-Stoke equations, solved by default in all the single phase flow interfaces are the compressible formulation of the momentum equation:

$$\rho\frac{\partial u}{\partial t} + \rho u \cdot \nabla u = -\nabla p + \nabla \cdot (\mu(\nabla u + (\nabla u)^T) - \frac{2}{3}\mu(\nabla \cdot u)I) + F$$

$$\dots (3)$$

And the continuity equations:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0 \qquad (4)$$

Where ρ is the solution's density (kg/m^3), μ dynamic viscosity of the fluid (Ns/m^2), u is the velocity vector (m/s), I denote the identity matrix, F is the volume force vector (N/m^3), T is the absolute temperature (K) and p is pressure (Pa). This equation is applicable for incompressible as well as compressible flows where the density varies. The flow in this microreactor is assumed compressible because the Mach number (Ma) is less than 0.3.

The boundary conditions imposed on the momentum balance are no slip at the reactor walls:

$$u = U_0 \qquad \text{inlet}$$

$$\boldsymbol{u} = 0 \qquad \text{walls}$$

No slip boundary condition for a stationary solid wall, that is, that the fluid at the wall is not moving. The outlet boundary conditions describing fluid flow at an outlet are the **pressure**, and **no viscous stress**. The **pressure** condition prescribes only a Dirichlet condition for the pressure:

$$p = p_0 \qquad \text{outlet}$$

This boundary condition is physically equivalent to a boundary that is adjacent to a large container (inlets) or exiting into a large container (outlets).

The flow in the microreactor is driven by a pressure drop. The pressure at the inlet, p is slightly higher than that at the outlet, where the pressure is set to atmospheric pressure. The **No Viscous Stress** condition specifies vanishing viscous stress on the outlet.

$$\left(\mu (\nabla u + (\nabla u)^{\mathrm{T}}) - \frac{2}{3}\mu (\nabla \cdot u)I) \right)n = 0$$

In the 3D microreactor model, reactions occur at the catalytic surfaces located at the walls. The channel walls are however coated with Au/Cr/γ-Al$_2$O$_3$ catalyst. So that as propane gas flows through the reactor, oxidation reactions occur at the catalytic surfaces. A space-dependent model is generated and flux is applied for the surface reaction to the catalytic surface. For an ideal gas, laminar flow and transport of

diluted species is used to solve for the convection and reaction of the chemical species. The inlet concentrations and flow density is derived from the partial pressures. The calculated flow field serves as input to the transport of dilute species interface, to describe the convective mass transport. The use of parameters and variables helps to define a more complex rate expression in COMSOL.

The kinetics of propane oxidation for the catalyst systems Au/Cr/γ-Al$_2$O$_3$ using partial pressures can be represented by Equation 1.

$$r_{C_3H_8} = \frac{k_{O_2}k_{C_3H_8}P_{C_3H_8}P_{O_2}}{k_{O_2}P_{O_2} + 5k_{C_3H_8}P_{C_3H_8}} \qquad (5)$$

Equation 5 was used by (Lin, Jiunn-Nan and Ben-Zu, Wan, 2004), when they investigated the combustion of propane at different temperatures. It was derived using the Mas-Van Krevelen mechanism for reduction-oxidation.

Where k_{O_2} and $k_{C_3H_8}$ are rate constants in the reduction-oxidation mechanism, P_{O_2} and $P_{C_3H_8}$ are the partial pressures of oxygen and propane, and $r_{C_3H_8}$ is reaction rate of propane.

The Arrhenius expression for the temperature dependence of k_{O_2} and $r_{C_3H_8}$ is:

$$k_{O_2} = A_{O_2} \exp\left(\frac{-Ea_{O_2}}{RT} \right) \qquad (6)$$

$$k_{C_3H_8} = A_{C_3H_8} \exp\left(\frac{-Ea_{C_3H_8}}{RT} \right) \qquad (7)$$

Where A is the Arrhenius constant, $E_{a.}$ is the activation energy, R is the gas constant and T is the temperature in K.

The transport of diluted species user interface assumes chemical species transport through diffusion and convection and implements the mass balance equation. The interface assumes that all species present are dilute, and that their concentration is small compared to a solvent fluid or solid.

The mass transfer in the reactor domain is given by the stationary convection and diffusion equation:

$$\frac{\partial c}{\partial t} + u \cdot \nabla c = \nabla \cdot (D\nabla c) + R \qquad (8)$$

Where D denotes the diffusion coefficient (m^2/s), c is the species concentration (mol/m^3), u is the velocity vector (m/s) and R is the reaction rate expression for the species (mol/(m^3.s)). The first term on the left-hand side of Equation 8 represent the accumulation or consumption of the species. The second term on the left hand side accounts for the convective transport due to a velocity field u. This field can be obtained from coupling the transport of diluted species user interface to one that describes fluid flow (CFD or momentum balance). The first term on the right-hand side of Equation 8 accounts for the diffusion transport (interaction between the dilute species and solvent). Finally, the second term on the right-hand side of Equation 8 represents a source, or sinks term, usually due to a chemical reaction.

In the microchannel, the boundary condition for an inflow is set as (concentrations):

$$c = c_{in} \qquad (9)$$

Resolving a parabolic or laminar flow profile for the 2D model requires at least more than two elements across each channel. The 2D model was resolved with a refined mesh with five elements across each channel. The default element type for laminar flow is a linear element, so a number of linear segments are resolved due to the curved nature of the profile. Mesh is built to optimally resolve the laminar flow in the channels. First by modifying the geometry to introduce an extra rectangle (channel), in order to introduce a boundary "edge" along the top and bottom faces of each channel. Then an edge mesh is built for the channel inlets with a maximum element size of 1.25×10^{-5} m per channel. Mapped mesh is then used in the channel domains to achieve a rectangular element that have a long aspect ratio since flow is likely to have a similar profile down the channels. This uses a default mesh size of fluid dynamics and coarse that is inherited from the global size node of COMSOL Multiphysics. Mesh is completed using a free triangular mesh on the remaining domains with fluid dynamics and extra-fine on the boundaries and coarse in

the bulk. The fluid flow rates inside the channels were calculated by integrating across the normal component of the exit velocity. Since the flow is stationary and compressible, it then guarantees that the flow into a channel and out is equivalent. This accounts for the fact that the velocity is non-uniform (laminar profile) across the cross-section. To derive the flow rate in each channel I have used a "Derived Values => line integration of velocity field, y component" in COMSOL. Solving the fluid flow at higher velocities (10 m/s - 100 m/s) the computation becomes highly non-linear, and the non-linearity of the computation can be thought of as a function of the Reynolds number. This can be solved by using a continuation sweep to incrementally increase the Reynolds number. In the 3D model, a good resolution of the flow is obtained by meshing the inlet faces of the channels using a free triangular mesh with suitably fine size settings to get a good resolution of the flow across section. A swept mesh on the channel domains and a free tetrahedral mesh on the inlet and outlet domains (manifolds). For the flow study to resolve the laminar profile within the channels, a suitable custom maximum element size of 0.01 m was used on the planes in the free triangular mesh for the 3D model.

Propane fractional conversion, X is an important characteristic for the catalytic oxidation and is defined as:

$$X = \frac{C_{(C_3H_8)_{in}} - C_{(C_3H_8)_{Out}}}{C_{(C_3H_8)_{in}}} \qquad (10)$$

Where C is the concentration in mol/m^3

4. Results

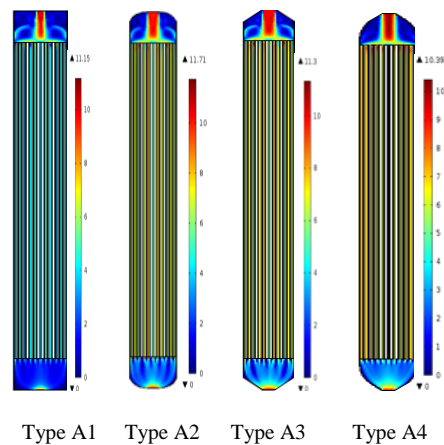Type A1   Type A2   Type A3   Type A4

Figure 2. CFD simulation of the four proposed geometries, showing the contour plot of velocity distribution in 2D

4.1. Effect of inlet velocity

This was tested by calculating a relative standard deviation of the flow rates at various velocities for each geometry as seen in Figure 3. Type A1geometry showed different results than those of the other geometries. For type A2, A3, and A4, for inlet velocities higher than 30 m/s, it was found that the deviation became constant. For type A1 the deviation continued to increase until approximately 90 m/s and then became constant.
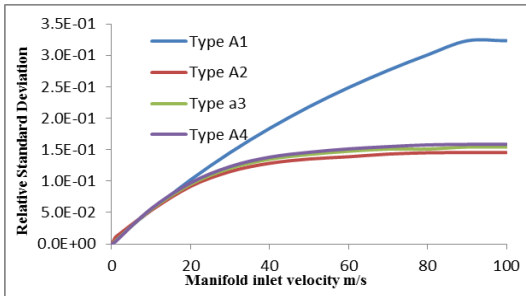
Figure 3. Relative standard deviation of the flow distribution as a function of the inlet manifold velocity as calculated for the 4 geometries

4.2. Effect of inlet velocity on flow distribution inside the microchannels

This was tested by calculating the normalized flow rates and plotting the normalized flow rate against the channel number as seen in Figure 4. Normalized flow rate is calculated by dividing the actual flow rate per channel by the mean flow rate. For all geometries there was an effect on the "outer" channels located furthest away from the manifold inlet. The flow was less for these
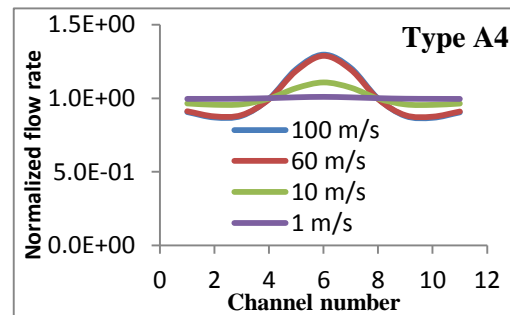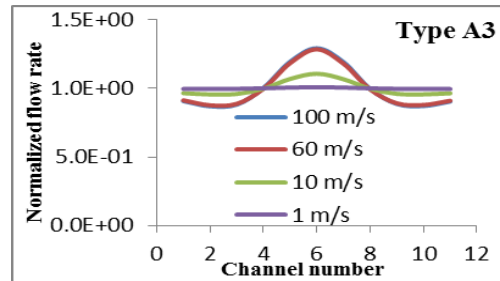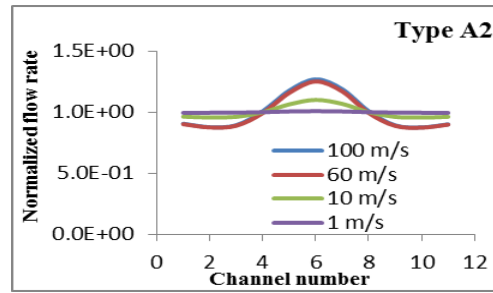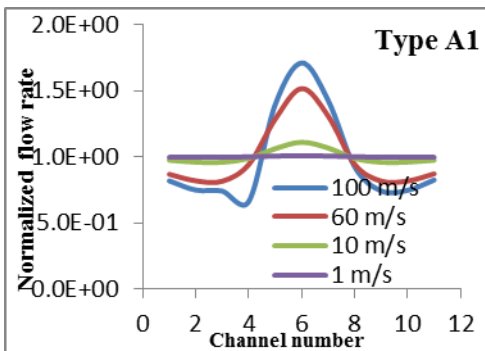

Figure 4. Flow distribution over the channels, calculated at an inlet velocity of 1 m/s, 10 m/s, 60 m/s, and 100 m/s

channels compared to the inner channels near the inlet. The highest flow rates occurred for the centre channels. This was particularly pronounced for type A1 which has a much narrowed active inlet area compared to type A2, A3, and A4 respectively. This produced a more steep parabolic profile in the centre channels compared to type A2, A3, and A4 as seen in Figure 4. At inlet velocities below 10 m/s, a constant flow rate is found, which means that the flow distribution is independent of flow rate. All the geometries (Type A1, A2, A3, and A4) gave similar results in this regime. In this region where the flow distribution is independent of the flow rate, the flow field is determined by wall friction. At an inlet velocity of 60 m/s and above, inertial forces become important.

## 4.2. Catalytic oxidation of propane

The next step was to modify geometry A2 into a 3D model to further investigate the catalytic oxidation of VOCs. Simulation results are shown in Figure 5, 6 and 7.
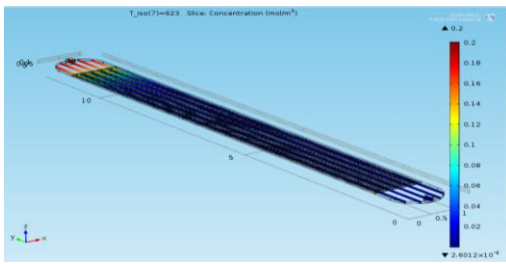
Figure 5. Concentration gradient of propane oxidation over Au/Cr/γ-Al2O3 in the microreactor at inlet velocity of 0.01 m/s
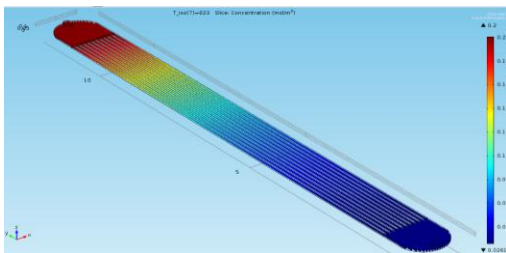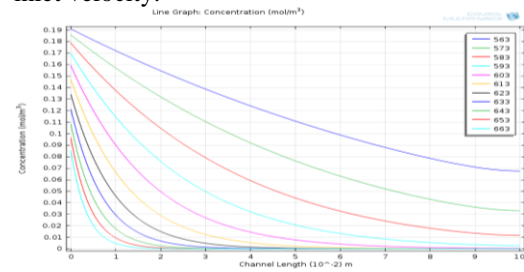

Figure 6. Concentration gradient of propane oxidation over Au/Cr/γ-A$_{l2}$O$_3$ in the microreactor at inlet velocity of 0.1 m/s
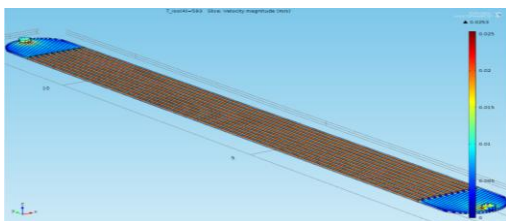
Figure 7. Velocity profile of the laminar flow field in the microreactor at temperature of 593 K

4.3. Effect of gas inlet velocity on propane concentration

When the reactant inlet velocity is increase, it means that the residence time of reactants is decreased, and the total propane conversion decreases as shown in Figure 7, 8, 9 and 10. Residence time is important parameters for catalytic oxidation of propane, because it determines 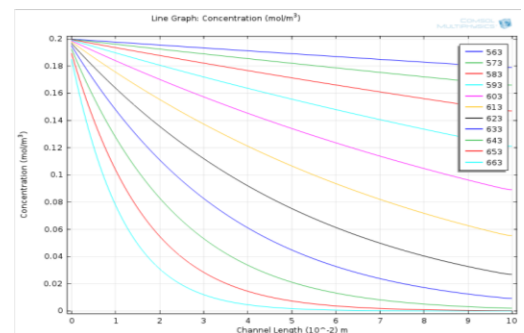the reactor productivity. The 3D simulation result shows that propane concentration is decreasing by increasing gas inlet velocity.
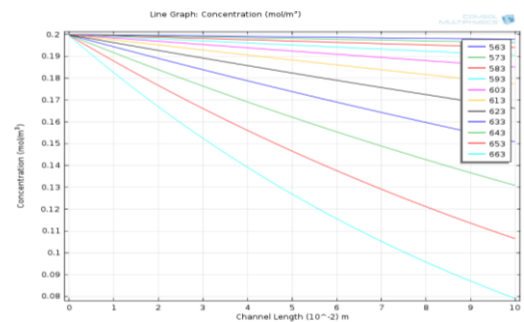

Figure 8. Propane concentration gradient along a channel at a velocity of 0.01m/s
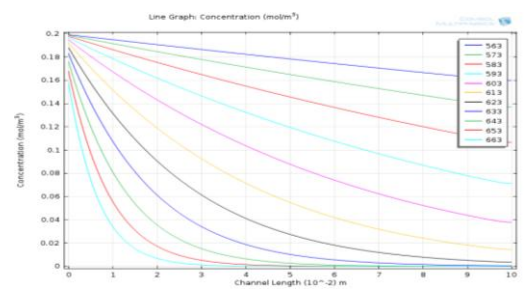
Figure 9. Propane concentration gradient along a channel at a velocity of 0.05m/s

Figure 10. Propane concentration gradient along a channel at a velocity of 0.1m/s

Figure 11. Propane concentration gradient along a channel at a velocity of 1m/s

4.4. Effect of temperature on propane conversion

Since both reaction rate and species diffusivities depend on temperature, increasing the temperature from 593 K to 663 K has a significant influence on the conversion of propane as shown in Figure 7 to 16. This increase in temperature also affects the flow in the microchannels.

The combustion of the propane is a strongly exothermic reaction with a high negative value of standard Gibbs free energy over a significant temperature range. In standard terms to increase the equilibrium fractional conversion of propane the reaction temperature should be reduced. For the exothermic reaction, if the temperature is increased the equilibrium conversion should be reduced. For this reaction (equation 1) the standard Gibbs free energy does reduce as temperature increases but even at higher temperature (593 K - 663 K) the equilibrium fractional conversion can be calculated as > 99.9%.

An examination of the Arrhenius equations (equation 5 and 6) indicates that the rate constants increase with temperature. The effect of this should be that as the reaction temperature increases the reaction rate should increase and the rate of approach to the equilibrium fractional conversion should increase. These predictions are consistent with the behaviour shown in (Figures 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, and 16). The rate at which the equilibrium conversion is approached consistently increases as the temperature increases. The increasing reactant velocity decreases the residence time in the reactor as indicated previously .This has the effect of increasing the point in the reactor where the equilibrium fractional conversion is approached but all the results obtained in the simulation in terms of velocity and temperature changes are consistent with the effects described.
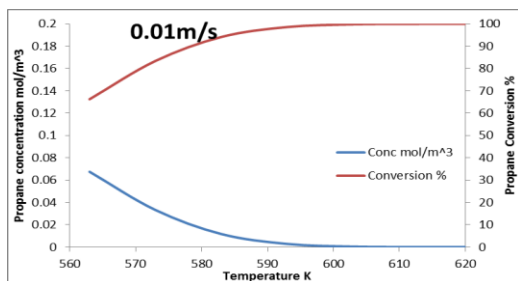

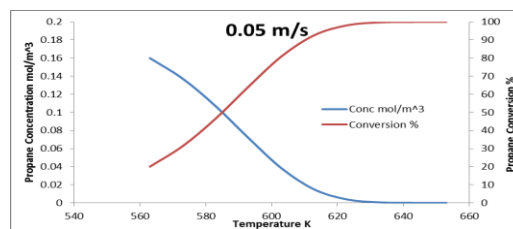**Figure 12**. Propane concentration and conversion against temperature at a velocity of 0.01m/s

Figure 13. Propane concentration and conversion against temperature at a velocity of 0.05m/s
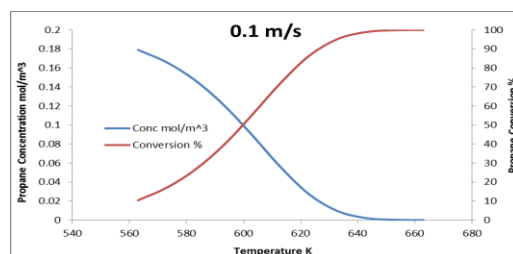

Fugure 14. Propane concentration and conversion against temperature at a velocity of 0.1m/s
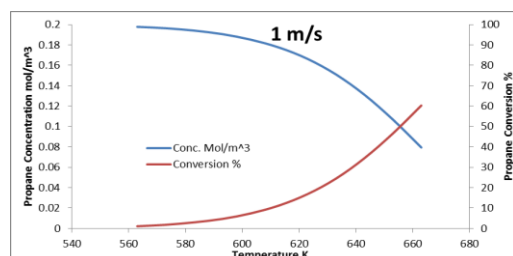

Figure 15. Propane concentration and conversion against temperature at a velocity of 1m/s
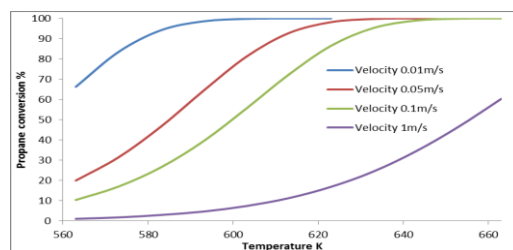

Figure 16. Propane conversion and conversion against temperature at a velocity of 0.01, 0.05, 0.1, and 1 m/s

5. Conclusions

The use of a steady-state COMSOL Multiphysics model for the simulation of propane catalytic oxidation in a microreactor was demonstrated in this paper. The effect of three important parameters namely the manifold

shape, the inlet velocity, and temperature for a cold flow (non-reaction) on fluid flow uniformity and with reaction was investigated for an 11 channel microreactor. Distributions of fluid flow over the microchannels with 4 different manifold geometries have been calculated using a 2D CFD module of COMSOL Multiphysics.

The flow behaviour has been assessed based on the relative standard deviation of the flow rates from a mean. Simulation results indicate two flow regimes depending on the inlet velocity for the 4 geometries.

For all geometries at low flow rates (below 10 m/s), the flow distribution appears to be completely determined by wall friction. In this regime all 4 geometries yielded similar results. For operation below this velocity the flow distribution appears to be independent of flow rate (as seen in Figure 4 for an inlet velocity of 1 m/s). At flow rates above a transitional velocity (60 m/s for type A2, A3, and A4 and 90 m/s for type A1), inertial effects start to influence the flow distribution with a constant relative standard deviation. Geometries A2, A3, and A4 show a similar trends; for type A1 a different effect is observed, the relative standard deviation continues to increase until it appears to level off at a higher velocity. It appears that the observed effect is linked to the nature of the flow regime in the manifold. A plot of relative standard deviation of flow rates against inlet manifold velocity, showed a significant difference between geometries A1, and A2, A3, A4. The relative standard deviations are in order of magnitude, less for type A2, A3, and A4. Type A2 gave the optimum flow distribution from laminar to transitional with the lowest relative standard deviation.

The 3D simulation results showed that the propane concentration decreases by increasing the gas inlet velocity. By increasing the temperature from 593 K to 663 K increase the conversion rate. The simulated results have revealed that higher conversion rates of propane can be achieved by decreasing inlet gas velocity from 1 m/s to 0.01 m/s and increasing temperature from 593 K to 663 K

Optimum inlet gas velocity for propane conversion of 99.99 % was between 0.05 m/s and 0.1 m/s.

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