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Numerical investigation of stratified flow-parallel reaction microchannel system: A deterministic approach

Rahul Antony, Giri Nandagopal M S, Rangabhashiyam S,
Anu N & Selvaraju N*

Department of Chemical Engineering National Institute of
Technology Calicut 673 601, Kerala, India
E-mail: selvaraju@nitc.ac.in

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A deterministic based analytical model has been developed to study the mass transfer characteristics between the reactants in a liquid- liquid parallel flow microchannel reactor. Since each phase is continuous and parallel to each other, the interface between the phases is well defined. Convection and diffusion mass transfer mechanisms with a third order reaction is considered for the design of single dimensional deterministic model. The model is developed by considering the transport phenomena of the system and solved with the help of pdepe solver in Matlab 7.6.0. The effects of residence time with various concentration profiles are discussed. The study reveals that the concentrations of desired and undesired products mainly depend on the flow velocity and concentration gradient of the reactants. The time required for the equilibrium is inversely proportional to the pseudo mass transfer coefficient of the system.

Keywords: Microfluidics, Parallel Reactor, Liquid-liquid flow, Deterministic model.

The manipulation of fluids in channels with dimensions of tens of micrometres - Microfluidics- has emerged as a distinct new field. Microfluidics has great potential to influence subject areas from chemical synthesis and biological analysis to optics and information technology¹. But the field is still at the budding stage of development.

The surface to volume ratio will be extremely high due to smaller characteristic dimensions in the Microchannel devices and this will provide many advantages over conventional type reactors such as: a) Enhanced heat and mass transport rates²; b) Safe environment for toxic or hazardous chemicals³; c.) Effective control possible for the process²; d) Energy efficient and less by-products²; e) On demand, on site synthesis of chemicals is possible⁴ and f) No strict limit in size reduction or expansion of plant components since any production capacity is achievable by means of parallel operation⁵.

The technology development in these days is sailing towards the innovation of miniaturised objects like microelectronic chips, nano robots, mobile phones etc. In case of chemical engineering and technology, micro reactors are revolutionary concept for the trendy change in chemical industries. Batch reactors are very strenuous to carry out menacing reactions like nitration etc. Also the micro scale sample production and precise reaction control can be possible with micro reactors. This in turn will reduce the wastage of chemicals¹.

Single phase flows inside the microchannels has been commonly used in electronic equipments as heat sinks. Because of the higher heat transfer rates in microchannel fluid flows, wide research works have been carried out by focussing in this field^{6,7}. Microchannel two phase flows are found to have more applications compared to single phase flows. Most of the applications involving chemical reactions (reactors, mixers etc) microchannel two phase flows are involved. The two phase reaction may be either liquid-liquid flows or liquid-gas flows⁸⁻¹¹. In liquid-liquid flow study in microchannels, reactants should be immiscible or should use immiscible carrier fluids for the reactor for easy separation of the product¹².

Two phase liquid-liquid flow regimes can be generally classified in to five categories: droplet flow, slug flow, parallel flow, annular flow and churn flow. The flow patterns for liquid- liquid flows in microchannel were first investigated by Taylor, 1961¹³ and Bretherton, 1961¹⁴. Since then, two phase flow patterns and its mass transfer properties have been investigated extensively^{15,16}. In micro reactors the commonly preferred flow regime is stratified flow and slug flow because of the prediction chances and easy product separation. In the present work, the change in concentration with respect to the reactant's residence time for the parallel flow in a micro reactor has been developed. Analytical model is implemented with the help of 'pdepe solver' in Matlab 7.6.0. The numerical model, and its results obtained are explained in the following sections.

Computational Model

Problem definition

The following assumptions are made to develop the one dimensional computational model for the

study of mass transfer with reaction in liquid-liquid stratified flow:

- Channel mass transfer between the junction and outlet is considered and excluded the junction zone, outlet droplet zone and sampling bottle mass transfer zones.
- Both reactants are Newtonian, incompressible and viscous liquids.
- No effect of channel shape and gravitational force on mass transfer.
- Velocity across the cross section is uniform.
- The system is unsteady and considered no slip.

The schematic representation for the possible internal circulation in parallel flow is indicated in Fig. 1. When a segment of a fluid pass through the capillary channel, internal circulations¹⁷ within the slug will arise and this depends on the prevalent physical properties of fluid and the channel. The shear between the wall surface and slug axis produces internal circulations within the segment and which reduces the thickness of boundary layer at the phase interface thereby enhances the diffusive penetration. When the flow pattern is slug, internal circulation has more effect on the mass transfer¹⁸. But when it is parallel flow, the path of the movement of internal particles in the slug will be higher and nearly infinity as shown in Fig. 1 and convection due to the internal circulation is negligible. But the convection due to liquid flow velocity is higher in the channel¹⁹. For parallel flow reactor, the main driving force for mass transfer is diffusion at the interface between aqueous and organic phase reactants. The objective of this

work was to develop a prototype model for the mass transfer with reaction in a parallel flow micro reactor.

Parallel reactor

A CFD developed diagram for the stratified (parallel) flow in microchannel is displayed in Fig. 1. The direction of flow is also indicated in the Fig. 1. Parallel flow is commonly known as stratified flow. In this type of flow the both phases will be separated by an undisturbed horizontal interface and flows parallel to each other. Compared to other flow regimes, parallel flow is having a greater advantage in the design of micro reactor as its separation is easy. The occurrence of stratified flow is reported by Dessimoz *et al.* (2008)²⁰ and Zhao *et al.* (2006)²¹ and the formation of this regime gets affected when gravity is negligible and the density difference between the two phases is small²².

The general form of parallel reaction is:



An isothermal parallel reaction is considered here and reactants A and B are considered as two reactants with organic and inorganic behaviour. T shaped microreactor is considered for the study. A and B are given as the two inlets for the channel. Outputs of the reaction are considered as C and D and immiscible. Interstitial fluid velocity in axial direction is considered as U. When parallel flow is formed in the system, there is an interface between the two phases where the transport of particles takes place. The example for this type of reaction is the alkaline hydrolysis reaction between n-butyl acetate

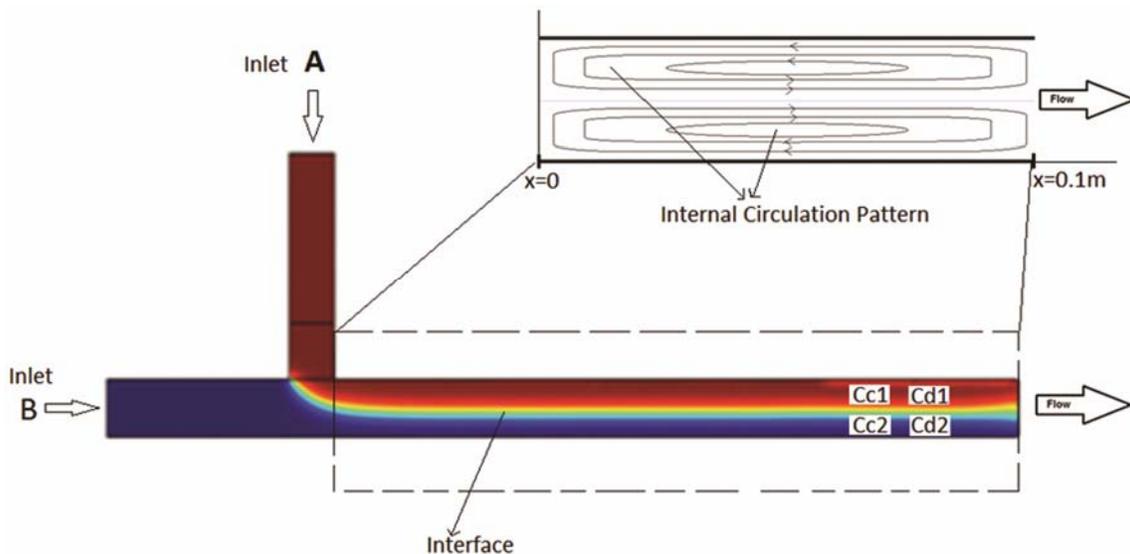


Fig. 1—Stratified flow generation in A T- Junction microreactor and Internal circulation pattern.

(reactant A) and sodium hydroxide (reactant B) and which produces n-butanol and sodium acetate.

Parallel Reaction considered for the present simulation is:



Boundary and initial conditions

In deterministic sense, two types of boundaries exist for the microchannel namely the 'open' and 'closed' boundary. In open boundaries, continuity of concentration is maintained and particles can freely traverse to either side of the boundary²³. This is not the case with 'closed' inlet and outlet boundaries, in which, particles enter and exit the system at once. We considered the Danckwerts boundary conditions²⁴ in this case, where continuity of concentration is lost at the origin:

$$UC_i \Big|_{x=0^-} = UC - D_A \frac{\partial C}{\partial x} \Big|_{x=0^+} \quad \dots (4)$$

where, C_i is the inlet concentration of the chemical, which can generally be a function of time. If the system length 'L' and the system are closed at the exit, then the exit boundary condition is:

$$\frac{\partial C_i}{\partial x} \Big|_{x=L} = 0 \quad \dots (5)$$

The initial conditions which considered for finding out the solution are listed below in Table 1. Here the maximum concentration is represented with value 1 and minimum with 0.

Mass transfer with reaction

The mass transfer in microchannel is due to diffusion or convection or both. The chemical reaction term can be represented as either source or sink term in the convection-diffusion equation depending on the kinetics of the chemical reaction.

Table 1—Initial conditions considered for execution of the code

Variables (mol/L)	Value
C_{A1}	1
C_{B1}	0
C_{C1}	0
C_{D1}	0
C_{A2}	0
C_{B2}	1
C_{C2}	0
C_{D2}	0

Rate equations are different for the products and in the present work it is considered as:

$$r_C = k_C C_A^2 C_B \quad \dots (6)$$

$$r_D = k_D C_A C_B^2 \quad \dots (7)$$

Difference in rate laws provides a scope for using stratified flow. First reaction which gives the desired product will be dominant in the phase where there is more A and the second one will occur in the phase where there is more B. Therefore, mainly C will be produced in one phase and D in the other. Since both phases are immiscible, separation of the desired and undesired products becomes much easier. Since the surface tension is higher the two phases will be separated by a thin film of both fluids.

Simultaneous convection, diffusion and reaction in stratified microchannel flow systems can be expressed mathematically by the eight equations Eq. 8 to Eq. 15 and are derived from the laws based on the mass transfer and reaction between two fluids. The convection-diffusion- reaction equations of each species are executed parallel and the updated concentrations were used as the initial data for the system of partial differential equations:

$$\frac{\partial C_{A1}}{\partial t} = D_A \frac{\partial^2 C_{A1}}{\partial x^2} - U \frac{\partial C_{A1}}{\partial x} - k_C C_{A1} C_{B1}^2 - k_D C_{A1}^2 C_{B1} - k_m (C_{A1} - C_{A2}) \quad \dots (8)$$

$$\frac{\partial C_{A2}}{\partial t} = D_A \frac{\partial^2 C_{A2}}{\partial x^2} - U \frac{\partial C_{A2}}{\partial x} - k_C C_{A2} C_{B2}^2 - k_D C_{A2}^2 C_{B2} - k_m (C_{A2} - C_{A1}) \quad \dots (9)$$

$$\frac{\partial C_{B1}}{\partial t} = D_A \frac{\partial^2 C_{B1}}{\partial x^2} - U \frac{\partial C_{B1}}{\partial x} - k_C C_{A1} C_{B1}^2 - k_D C_{A1}^2 C_{B1} - k_m (C_{B1} - C_{B2}) \quad \dots (10)$$

$$\frac{\partial C_{B2}}{\partial t} = D_A \frac{\partial^2 C_{B2}}{\partial x^2} - U \frac{\partial C_{B2}}{\partial x} - k_C C_{A2} C_{B2}^2 - k_D C_{A2}^2 C_{B2} - k_m (C_{B2} - C_{B1}) \quad \dots (11)$$

$$\frac{\partial C_{C1}}{\partial t} = D_A \frac{\partial^2 C_{C1}}{\partial x^2} - U \frac{\partial C_{C1}}{\partial x} + k_C C_{A1} C_{B1}^2 - k_m (C_{C1} - C_{C2}) \quad \dots (12)$$

$$\frac{\partial C_{C2}}{\partial t} = D_A \frac{\partial^2 C_{C2}}{\partial x^2} - U \frac{\partial C_{C2}}{\partial x} + k_C C_{A2} C_{B2}^2 - k_m (C_{C2} - C_{C1}) \quad \dots (13)$$

$$\frac{\partial C_{D1}}{\partial t} = D_A \frac{\partial^2 C_{D1}}{\partial x^2} - U \frac{\partial C_{D1}}{\partial x} + k_D C_{A1}^2 C_{B1} - k_m (C_{D1} - C_{D2}) \quad \dots (14)$$

$$\frac{\partial C_{D2}}{\partial t} = D_A \frac{\partial^2 C_{D2}}{\partial x^2} - U \frac{\partial C_{D2}}{\partial x} + k_D C_{A2}^2 C_{B2} - k_m (C_{D2} - C_{D1}) \quad \dots (15)$$

The above equations correlate the concentration changes in each phase with respect to time. The system depends on the microchannel length, x . The derived equations are partial differential equations of order two. Each and every concentration inside the channel depends on each other and any changes in one concentration will cause the change of concentrations of other phases.

Results and Discussion

The system is solved with the parameter values given in Table 2 and is collected from the literature²³.

The change in concentrations according to the time is considered to study here. The change in residence time according to the mass transfer coefficient is also analyzed. In Fig. 2, the concentrations of desired and undesired products in the first phase from the microfluidic parallel reaction are shown with the input concentration of A in both phases. The graph indicates the mass transfer and reaction between the

reactants in the channel. The concentration of C_{A1} (or C_{a1}) is taken as 1 when reaction starts at $x=0$ and $t=0$. As time increases, concentration C_{A1} decreases and C_{A2} (or C_{a2}) increases and attains equilibrium state in the channel (Considered there is no reverse reaction). From the Fig. 2 it is clear that the input concentrations of A in both phases attain equilibrium after sometime and when C_{A1} decreases C_{C1} and C_{D1} increases. This time the concentration of desired and undesired products reaches the maximum value. The reaction rate can be varied by changing the physical parameters of the channel such as, area, length etc.

Similar to the first phase, at the same time concentration of C_{B1} (or C_{b1}) is decreases from its maximum value 1 and attains equilibrium with C_{B2} (or C_{b2}). This is because of the mass transfer and reaction between the two phases. In Fig. 3 the concentrations of desired and undesired products in second phase are given with input B concentrations in both phases. From Fig. 3 and Fig. 4, it is clear

Table 2—Parameter values considered for the model²³

Parameters	Value
D_A (m ² /s)	9.450×10^{10}
k_m	0.650
k_C	100
k_D	0.5×100
L (m)	0.1

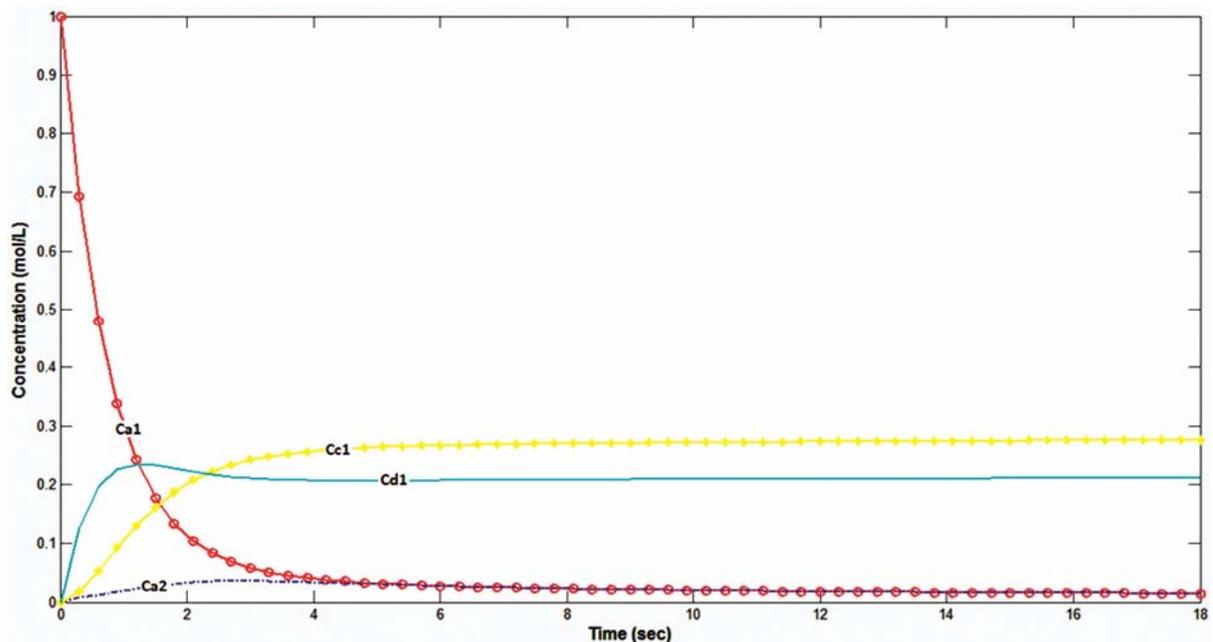


Fig. 2—Plot of phase 1 desired and undesired concentrations at $k_m=0.650$, $U=0.03$.

that when concentrations of A and B decreases, the product concentration increases. The concentrations of desired and undesired products can be vary by changing the velocity of the fluids and the pseudo mass transfer coefficient, k_m .

It has been observed that, the mass transfer coefficient (k_m) increases as the time required for

attaining equilibrium decreases and this in turn lead to an efficient reaction shown in Fig.4. In future, the model can be improved by incorporating the microchannel hydrodynamics such as shape of the channel, hydrophobic effects, etc. and by introducing fluid properties such as viscosity, slip conditions etc. to this work.

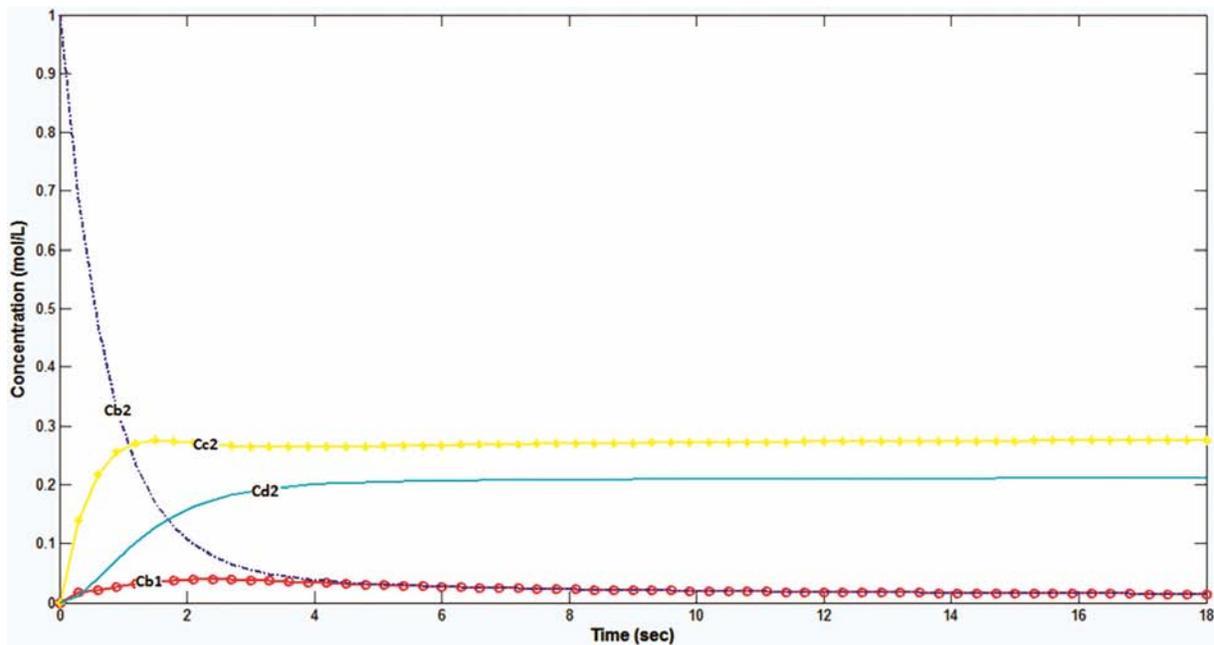


Fig. 3—Plot of phase 2 desired and undesired concentrations at $k_m=0.650$, $U=0.03$.

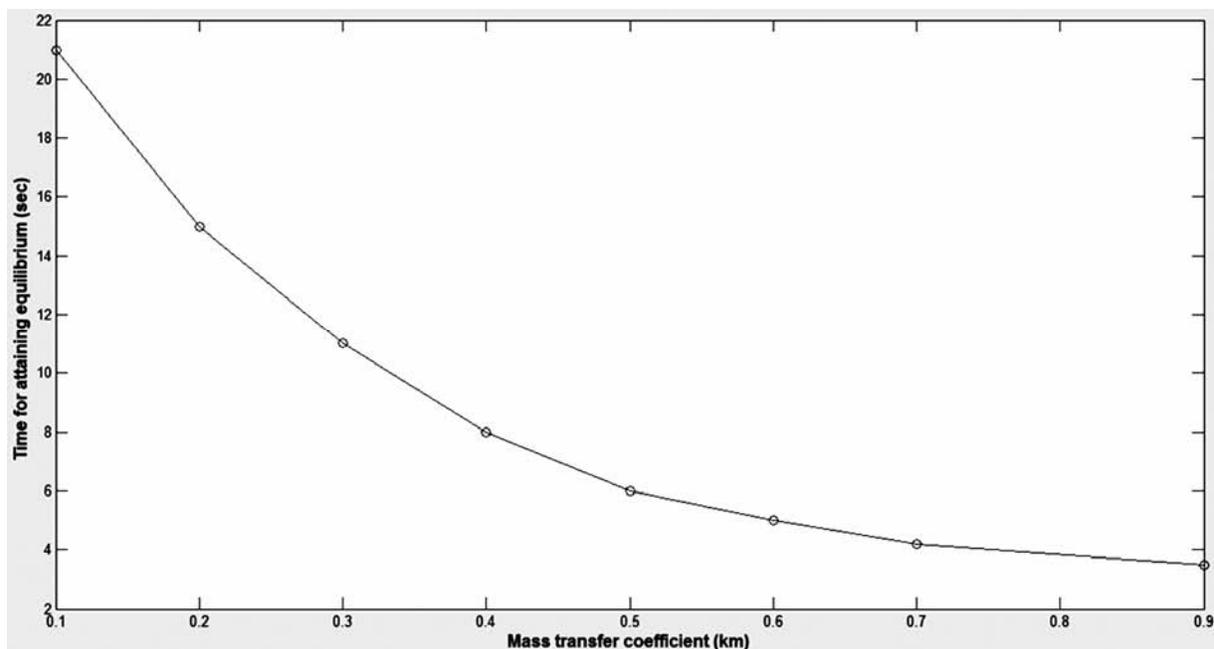


Fig. 4—Dimensionless mass transfer coefficient (k_m) vs time to attain equilibrium (s).

Conclusion

The behaviour of the microreactors can be studied by using simplified models which incorporate the essential physics. This model can be used to get a good estimate of the microreactors performance. A deterministic one dimensional model has been developed to simulate the mass transfer with chemical reaction for the liquid-liquid parallel flow microchannel reactor by considering the unsteady state condition. The variation of concentration according to the residence time is simulated. Several simulations are carried out to evaluate the model. It has been observed that mass transfer in the microreactor is mainly depends on the flow velocity and the concentration difference between the reactants in two phases. These models give us a reliable quantitative estimate of the microchannel system performance and the present work shows a promising methodology to evaluate the microreactor performance and thus save time for the computational work. This work can be extended to different flow regimes in microchannels and can be used to develop a two dimensional model for the system.

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Nomenclature

U = Interstitial fluid velocity in axial direction (m/s)
 D_A = Diffusion coefficient (m^2/s)
 k_C = Reaction rate constant for the reaction which causes the desired product as output.
 k_D = Reaction rate constant for the reaction which causes the undesired product as output.
 k_m = Dimensionless pseudo mass transfer coefficient
 C_{A1} = Concentration of Chemical A at Phase 1 (mol/L)
 C_{A2} = Concentration of Chemical A at Phase 2 (mol/L)
 C_{B1} = Concentration of Chemical B at Phase 1 (mol/L)
 C_{B2} = Concentration of Chemical B at Phase 2 (mol/L)
 C_{C1} = Concentration of Chemical C at Phase 1 (mol/L)

C_{C2} = Concentration of Chemical C at Phase 2 (mol/L)
 C_{D1} = Concentration of Chemical C at Phase 1 (mol/L)
 C_{D2} = Concentration of Chemical C at Phase 2 (mol/L)
 r_C = Reaction Rate for C product formation
 r_D = Reaction Rate for D product formation
 L = Length of the Microchannel (meter)
 t = Time (seconds)

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