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Mathematical models for description of hydrodynamics, mass and heat transfer in microreactor systems

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Abstract

Over the last decades the increased use of microreactors in all types of industries is observed. This phenomenon is based on the advantages that the microreactor systems can achieve in term of better process control, more efficient heat transfer and handling of hazardous chemicals. During this time mathematical models that describe flow inside microchannels have emerged ranging from Navier-Stokes equations to simplified mathematical models for laminar and segmented flows. The aim of this review is to present current studies in term of mathematical models that are nowadays commonly used for the description of hydrodynamics, mass and heat transfer in microreactor systems.

Keywords: microreactors, mathematical models, hydrodynamics, mass and heat transfer

1. Introduction

When talking about mathematical modelling in microreactors nowadays most people almost instantly think about computational fluid dynamics (CFD) and the results that are presented as a colourful pictures or moving simulations. CFD, as Zawawi et al. [1] explained, provides numerical approximation of Navier-Stokes equations that are used to describe flow conditions and is commonly used since the middle of last century [2,3]. Primarily used for water flow, pressure and velocity simulations today there is no industry which does not use CFD for the modelling of different systems ranging from micro scale (flow in microreactors) to macro scale (ocean currents and weather forecast) [4]. The main problem today is which software to use since the last two decades emerged with more than a few options that are user friendly like ANSYS, Open FOAM, PowerFLOW, SimScale, Comsol Multiphysics, Autodesk CFD, FLOW-3D and others. All of the mentioned software's come with build in Navier-Stokes equations and some even have extensive libraries with prebuild materials and objects. The main drawback still is the computer speed for solving the vast number of equations simultaneously which depending on the model quality can range from few hundreds for very simple models to few millions which are used for more demanding processes. The example of one CFD simulation for the purification of biodiesel which was obtained with the use of Comsol Multiphysics software is presented in Fig. 1. In this case microdevice with two Y-shaped inlets was used, where deep eutectic solvent (DES) was introduced in upper channel and row biodiesel in lower channel at the same flow rates. Based on the calculated Reynolds numbers laminar regime of flow was observed and thus this system was described as a laminar two-phase flow system. As seen in Fig. 1a the very fine grid was used in order to get the more precise model especially at the boundaries of two phases for the calculation of velocities of two phases.

This sort of models like one presented in Fig. 1b can give insight into the problems that may occur during the ex-

perimental phase and one can test different shapes of microreactors in order to find the most suited one for certain chemical or biochemical process. As often discussed one of the main problems with working with microreactors is the clogging. By using this approach clogging can be predicted and even avoided with the use of different flow rates or microreactor shape.

More details about Navier-Stokes equations, initial and boundary conditions and the use of simplified models which can be used to describe flow in microreactors are presented below.

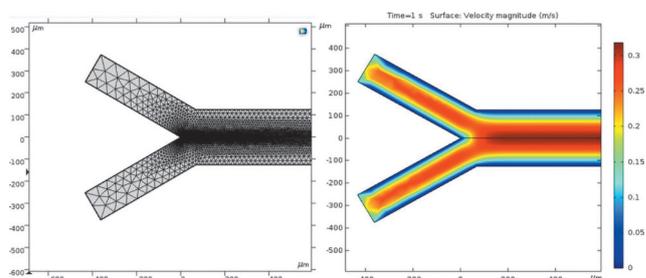


Fig. 1. CFD simulation of velocity profile in microsystem (a) grid used for the simulation, (b) velocity profile

2. Modelling of the flow in a microreactor

Microreactors are suitable for conducting processes in a single-phase and multiphase systems. When talking about reactions in multiphase systems it is important to ensure good mixing and good mass transfer of matter. In these systems the reaction rate is affected by concentration of reactants and with transfer between phases [5]. By applying micro precision engineering technologies, it is possible to construct reaction systems that ensure the intensification of mixing through effective heat and mass transfer. To ensure the optimal process conditions in a microreactor systems it is necessary to analyse the hydrodynamic and heat and mass transfer conditions.

The Navier – Stokes equation [6] can be used to describe the flow conditions in microreactors. For multiphase systems, these equations are obtained using the second Newton's laws for fluid flow [7]. If there is a gas phase in the system Navier-Stokes equation for compressible fluids is used (Eq. 1):

$$\rho \cdot \left(\frac{\partial v_i}{\partial t} + v_j \cdot \frac{\partial v_i}{\partial x_j} \right) = - \frac{\partial p}{\partial x_i} + \rho \cdot g_i + \frac{\partial}{\partial x_k} \left[\mu \cdot \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} - \frac{2}{3} \cdot \delta_{ik} \cdot \frac{\partial v_j}{\partial x_j} \right) \right] \quad (1)$$

where v_i is the component of the flow velocity in the x direction, ρ is the fluid density, μ is the dynamic viscosity, p is the pressure, g is the acceleration of the force of gravity, t is the time and δ_{ij} is the Kronecker symbol. For the complete definition of the system, the mass conservation equation is also required (Eq. 2):

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i} (\rho \cdot v_i) = 0 \quad (2)$$

To describe the flow of liquid in microreactors, Navier-Stokes equation for incompressible fluids is applied (Eq. 3):

$$\frac{\partial v_i}{\partial t} + v_j \cdot \frac{\partial v_i}{\partial x_j} = - \frac{1}{\rho} \cdot \frac{\partial p}{\partial x_i} + g_i + \frac{1}{\rho} \cdot \frac{\partial}{\partial x_j} \left(\mu \cdot \frac{\partial v_i}{\partial x_j} \right) \quad (3)$$

When talking about fluid flow in pipes (as for microchannels), it is possible to simplify the Navier-Stokes equation, assuming that the flow is stationary and there is a constant pressure drop (Eq. 4):

$$q = \frac{\Delta p}{L} \cdot \frac{\pi \cdot d^4}{128 \cdot \mu} \quad (4)$$

The above expression is known as the Hagen-Poiseuille flow, where L and d are the length and the diameter of microchannels. The Hagen-Poiseuille flow is characterized by maximum velocity in the middle of the microchannel and minimum velocity on the walls. According to Plazl and Lakner [8] at laminar flow conditions, the velocity profile fully developed in the least dimensions ($[W, -W]$) can be described as a function of y position only (Eq. 5):

$$v_x(y) = v_{max} \left[1 - \left(\frac{y}{W} \right)^2 \right] \quad (5)$$

2.1. Liquid-liquid flow profiles in a microreactor

Liquid-liquid two-phase systems have found application from extractions, reactive extractions, polymerizations, to multiphase catalysis [9]. Despite its great industrial importance, many details regarding the processes of mass transfer in these systems are still poorly understood. This is especially true for heterogeneous reactions in which there is a “competition” between the mass transfer and the chemical reaction [10].

Depending on the experimental conditions, several flow profiles may be formed in the liquid-liquid system in the microreactors; segmented (Taylor) flow, bubble flow, parallel flow or annular flow [11]. Segmented and parallel flow profiles are most commonly developed (Fig. 2) [12].

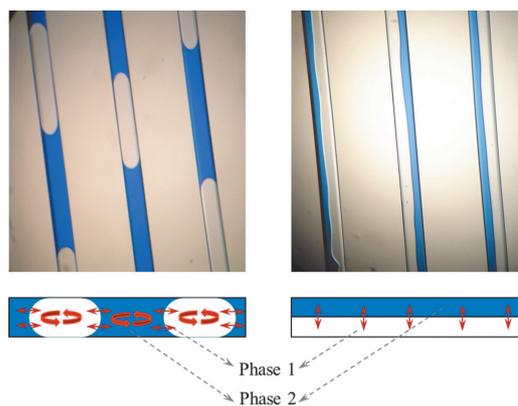


Fig. 2. Liquid-liquid system flow profiles in a microreactor

The development of segmented flow occurs by introducing two immiscible liquids into a microreactor. The main characteristic of this flow profile is a series of alternating segments of two phases, each segment being considered as a separate sub-volume. Segmented flow in the liquid-liquid system provides intense mass transfer within and between segments [13]. The mass transfer for liquid-liquid segmented flow takes place through two mechanisms: convection within a segment and diffusion between two segments [14]. The most important forces that describe segmented flow in a liquid-liquid system are most easily analysed by placing them in the ratios of dimensionless numbers (Table 1).

Jurinjak Tušek et al. [15] analysed slug flow in seven systems of organic solvents (chloroform, dichloromethane, diethyl ether, ethyl acetate, ethyl acetate, ethyl acetoacetate, hexane and toluene) and aqueous phase in a microreactor. Influence of linear flow velocity on slug lengths was explored for microreactor systems. Physical and chemical properties of the selected organic solvents were considered. To predict the slug length of both organic and aqueous phase non-linear regression model, linear regression model and artificial neural network model were proposed. The obtained results show that although quite simple and statistically not precise enough, regression models describe qualitatively the organic solvent-aqueous phase two-phase system with low accuracy. When true nonlinear models with neural networks were applied, high significance ($R^2 = 0.9$) of statistical predictions for the slug lengths were achieved.

3. Mass transfer in a microreactor

The basic equation used to describe the mass transfer in the case of incompressible fluids is derived from the general equation describing convection and diffusion (Eq. 6) [7]:

$$\frac{\partial c}{\partial t} + v_i \cdot \frac{\partial c}{\partial x_i} = \frac{\partial}{\partial x_i} \left(D \cdot \frac{\partial c}{\partial x_i} \right) - r \quad (6)$$

where c represents the concentration, v the flow rate, D the molecular diffusivity, and r the rate of the chemical/biochemical reaction. Simple analysis of the mass transfer in microchannels is performed by defining the value of Peclet's dimensionless number (Eq. 7):

$$Pe = \frac{v \cdot L}{D} \quad (7)$$

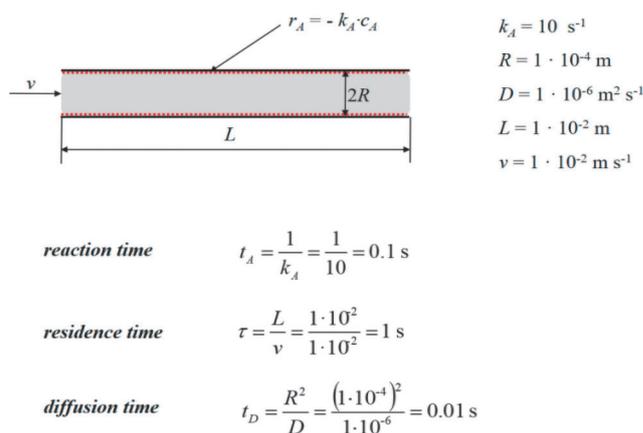
Table 1. Important dimensionless numbers for describing liquid-liquid segmented flow in a microreactor [14]

| Dimensionless numbers | Description |
|---|--|
| $Ca = \frac{\mu \cdot v}{\sigma}$ | ratio of viscous force to surface tension |
| $m = \frac{c_1^*}{c_2^*}$ | ratio of soluble saturation concentrations in phases 1 and 2 |
| $Fo = \frac{t \cdot D}{r^2}$ | ratio of real time to time needed to reach steady state |
| $Pe = \frac{d^2 \cdot v}{D \cdot L}$ | ratio of mass transfer by convection and molecular diffusion |
| $Re = \frac{v \cdot \rho \cdot d}{\mu}$ | ratio of inertial and viscous force |
| $D_R = \frac{D_1}{D_2}$ | solubility diffusivity ratio in phases 1 and 2 |
| $\mu_R = \frac{\mu_1}{\mu_2}$ | viscosity ratio of soluble substance 1 and 2 |

For most chemical and biochemical processes, especially those taking place in multiphase systems, diffusion is a limiting step [16]. By reducing the dimensions of the reactor, the characteristic distance that the molecules must pass is reduced, leading to a significant shortening of the diffusion time. Microchannels are characterized by small values of the Reynolds numbers (values generally below 100) and flow is usually laminar. Under laminar flow conditions phase mixing depends only on the diffusion of molecules from one phase to another. Diffusion process in microchannel take place according to Fick's law which correlates the dynamic change of concentration and the product of diffusion coefficient and concentration gradient. Small molecules, characterized by higher values of diffusion coefficients, can quickly diffuse and distribute between phases even at short residence times. Opposite to that, large molecules like enzymes or whole cells slowly diffuse and remain largely in the phase at which they are introduced into the microsystem [17].

The diffusion time is particularly interesting for diffusion process in a microreactor channels. Since diffusion time is the ratio of the square of the path and the diffusion coefficient, by reducing the size of the process equipment of a microreactor results in the very short time needed for the molecule to diffuse in the process space (Fig. 3).

The application of diffusion to processes carried out in microreactors can be divided into several main groups (*i*) cell extraction from suspensions, (*ii*) mass transfer with a stable concentration gradient, (*iii*) protein deposition and (*iv*) improving fluid mixing with the aim of more intensive diffusion of solvents. When microreactors are used to investigate the kinetics of reactions, the rate of the reaction should not be affected by the mass and energy transfer in order to obtain intrinsic kinetics [18] or the effect of diffusion needs to be taken into account [19].

**Fig. 3.** Characteristic times for microreactor system

When substrate and enzyme suspension were fed through the Y-shape inlet of the microreactor formation of laminar flow in the microreactor channel was observed. The two streams, the enzyme suspension and the substrate solution, which both have a laminar flow profile, are not mixed by convection. Namely, molecular diffusion takes place between them. The substrate is a smaller molecule, so it diffuses faster into the enzyme stream, while diffusion of the enzyme into the substrate phase is much slower. The reaction takes place where both, the substrate and the enzyme are present, respectively. Hexanol oxidation catalysed by NAD^+ dependent alcohol dehydrogenase from baker's yeast in a microreactor was modelled by Tušek et al. [20] as a pseudo homogeneous process with the double substrate Michaelis-Menten rate expression. In comparison with kinetic parameters estimated in the cuvette, 30-fold higher maximum reaction rate and relatively small change in the saturation constants is observed for the kinetic parameters estimated in the continuously operated tubular microreactor. Kinetic measurements performed in a microreactor shown results without product inhibition which could be explained with hydrodynamic effects (all experiments were performed in the slug flow regime) and continuous removal of inhibiting products. Šalić et al. [21] estimated kinetic parameters of the mathematical model for the NAD^+ regeneration performed in a microreactor. The influence of acetaldehyde, ethanol, NADH and NAD^+ concentrations on the reaction rates were measured. The negative effect of both products on the reaction rate was not observed for kinetics measurement performed in a microreactor which is a consequence of investigated concentration range and continuous mode of operation. Also, Jurinjak Tušek et al. [22] estimated parameters of double substrate Michaelis-Menten kinetic model describing laccase catalysed catechol oxidation based on an individual experiment performed in a microreactor. For the estimation of kinetic parameters, the concentrations of one reactant were varied, while the second was kept constant in saturation. The estimated value for the maximum reaction rate detected in a microreactor was approximately two-fold higher than the one observed in a cuvette. This effect can be explained by taking into account the high surface area-to-volume ratio in a microreactor, and short diffusion paths that ensure fast mass transfer, and make the reaction performed in the microreactor faster.

4. Simulation of chemical and biochemical processes in a continuous flow microreactor

In order to simulate chemical and biochemical processes in a continuous flow microreactor a coupled system of convection-diffusion reaction in combination with hydrodynamics has been developed. Many studies describing mathematical simulations of microfluidic systems are available: (i) 3D model for description of the mass transfer of a single steroid from water into ethyl acetate considering convection in the flow direction and diffusion in all directions [23], (ii) 2D model of laccase catalysed L-DOPA oxidation in a microchannel considering convection in the flow direction and diffusion in two directions [24], 2D model of laccase catalysed catechol oxidation in a microreactor [22] (iii) 2D model of polyphenols extraction in aqueous two-phase system [25]. All mentioned models are based on the rectangular microchannel cross-section (Fig. 4).

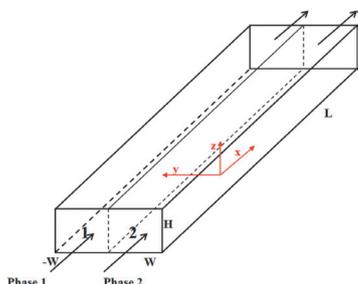


Fig. 4. Scheme of the microchannel used for development of mathematical models for different microsystems

The mathematical model for steady-state conditions in a microextractor (polyphenols extraction in aqueous two-phase system) [25] was composed of dimensionless partial differential equations for polyphenols concentrations in PEG an AMS phase and corresponding boundary and initial conditions (Eq. 8-9):

- Polyphenols concentration in PEG phase:

$$\begin{aligned}
 v \cdot \frac{\partial \gamma_{\text{polyphenols,PEG}}}{\partial \xi} &= \frac{D_{\text{polyphenols/PEG}}}{W} \cdot \left(\frac{\partial^2 \gamma_{\text{polyphenols,PEG}}}{\partial \xi^2} + \frac{\partial^2 \gamma_{\text{polyphenols,PEG}}}{\partial \psi^2} \right) \\
 \gamma_{\text{polyphenols,PEG}}(0, \psi) &= 0 & 1 \leq \psi \leq 0 \\
 \frac{\partial \gamma_{\text{polyphenols,PEG}}}{\partial \xi} \left(\frac{L}{W}, \psi \right) &= 0 & 1 \leq \psi \leq 0 \\
 \gamma_{\text{polyphenols,PEG}}(\xi, 0) &= \frac{D_{\text{polyphenols/AMP}}}{D_{\text{polyphenols/PEG}}} \cdot \frac{\partial \gamma_{\text{polyphenols,AMP}}(\xi, 0)}{\partial \psi} & 0 < \xi < \frac{L}{W} \\
 \frac{\partial \gamma_{\text{polyphenols,PEG}}(\xi, 1)}{\partial \psi} &= 0 & 0 < \xi < \frac{L}{W}
 \end{aligned} \quad (8)$$

- Polyphenols concentration in AMS phase:

$$\begin{aligned}
 v \cdot \frac{\partial \gamma_{\text{polyphenols,AMP}}}{\partial \xi} &= \frac{D_{\text{polyphenols/AMP}}}{W} \cdot \left(\frac{\partial^2 \gamma_{\text{polyphenols,AMP}}}{\partial \xi^2} + \frac{\partial^2 \gamma_{\text{polyphenols,AMP}}}{\partial \psi^2} \right) \\
 \gamma_{\text{polyphenols,AMP}}(0, \psi) &= \gamma_{\text{polyphenols,AMP},i} & 0 \leq \psi \leq 1 \\
 \frac{\partial \gamma_{\text{polyphenols,AMP}}}{\partial \xi} \left(\frac{L}{W}, \psi \right) &= 0 & 0 \leq \psi \leq 1 \\
 \gamma_{\text{polyphenols,AMP}}(\xi, 0) &= K_p \cdot \gamma_{\text{polyphenols,PEG}}(\xi, 0) & 0 < \xi < \frac{L}{W} \\
 \frac{\partial \gamma_{\text{polyphenols,AMP}}(\xi, 1)}{\partial \psi} &= 0 & 0 < \xi < \frac{L}{W}
 \end{aligned} \quad (9)$$

where v represents linear velocity, ξ and ψ represent independent dimensionless variables $\xi = x/W$, $\psi = y/W$, x and y are coordinated in the length (L) and microchannel width ($2W$). $D_{\text{polyphenols/PEG}} = 2.37 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and $D_{\text{polyphenols/AMP}} = 2.20 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ are diffusion coefficients for polyphenols in PEG and AMP phases. The molecular diffusion coefficients for polyphenols were calculated using the Hyduk-Laudie empirical correlation (Eq. 10):

$$D_{\text{polyphenols/PEG(AMP)}} = \frac{13.26 \cdot 10^{-9}}{\eta_{\text{PEG(AMP)}}^{1.14} \cdot V_{m,\text{polyphenols}}^{0.589}} \quad (10)$$

where $V_{m,\text{polyphenols}}$ is molar volume of gallic acid as standard for polyphenolic compounds, and η is water dynamic viscosity of prepared solution of PEG (AMP).

The goal of solving listed differential equations is to find a function (or a discrete approximation of a function) and boundary conditions along the boundary of a given domain, which satisfy the given relations between different derivations in a given region of space and/or time. It is very difficult to obtain a solution that satisfies the differential equation in the whole area of consideration. Therefore, numerical methods based on the discretization of a continuous system were used where the differential equations were replaced by a system of algebraic equations. The three most common methods for numerically solving partial differential equations are: (i) finite difference method, (ii) finite element method and (iii) finite volume method. Jurinjak Tušek et al. [23] described the simple method for solving partial differential equation of the diffusion and convection in a microreactor. Partial differential equations were solved by approximating microreactor with two parallel plug flow reactors (Fig. 4) in order to investigate application of simple numerical approximations for solving the system of partial differential equations.

5. Conclusion

The variety and complexity of process taking place in microreactor systems pose major challenges to the modelling approaches. To precisely describe the process in microreactors hydrodynamics, mass transfer and chemical/biochemical kinetics have to be taken into account and efficient computational tool should be used to get reliable simulation results.

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