

Development of a Computer Code for Numerical Simulation of Reactive and Catalytic Two-Phase Flows with Detailed Chemistry

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Abstract

The development of a computer code for reactive two-phase flows is presented. The code combines detailed simulation of the hydrodynamics (on basis of a volume-of-fluid method) with detailed description of chemistry. As a first step toward verification and validation, we study two one-dimensional multispecies diffusion-reaction problems in single and multiphase conditions with known analytical solutions. Both, the multicomponent diffusion model and the effective diffusivity model give similarly accurate solutions. For computing the species diffusivities, the latter model is recommended since it is computationally less expensive as it does not involve a matrix inversion.

KEY WORDS

Computation Multiphase Fluid Dynamics, Chemical Kinetics, Catalytic Reaction

1. Introduction

Catalytic monolith reactors are widely used for gas phase processes such as exhaust gas cleaning in automotive catalytic converters. They also offer a number of distinct advantages for heterogeneously catalyzed gas-liquid flows, e.g. for Fischer–Tropsch synthesis. The respective physico-chemical processes combine phenomena on the continuum level (two-phase flow) with those on the molecular level (diffusion and chemical reaction in the pores of the washcoat) and cover thus a wide range of length and time scales. The interaction between the two-phase flow hydrodynamics, the transport of heat and mass of the various species in the bulk phases and across the interface, and the chemical kinetics are hardly understood.

The ultimate goal of the present project is the development of a computer code for detailed numerical simulations of heterogeneously catalyzed chemical reactions in gas-liquid flows in a single channel of a monolith reactor. Therefore, we work on coupling two numerical codes, one for gas-liquid flows and one for reaction kinetics. The interface evolution of the

two-phase flow and the associated heat and mass transport in the fluid phases is described by the computer-code TURBIT-VOF [1]. This code has been used to investigate the slug flow of two immiscible fluids in a straight square mini-channel [2] and to study the gas-liquid mass transfer of a dilute species in such flows qualitatively [3]. Also, the influence of a simple first-order homogenous/heterogeneous reaction on mass transfer was investigated. In order to describe the chemical kinetics of multiple species with catalytic reactions at the channel wall (washcoat) in much more detail, we coupled routines of the DETCHEM package [4] into TURBIT-VOF. DETCHEM constitutes a package of software tools specifically designed for the modeling and simulation of reacting flows, in particular to heterogeneous systems such as catalysis, materials synthesis, and fuel cells.

In the present paper, we describe the application of the coupled models for two isothermal one-dimensional test cases. The first test case comprises multispecies diffusion-reactions within a gas phase, where we compare two different diffusivity models

(multicomponent model and effective diffusivity model). In the second test case, we study a multiphase reaction-diffusion problem near a planar gas-liquid interface.

2. Numerical method

Governing equations

The in-house code TURBIT-VOF solves the non-dimensional two-phase Navier-Stokes equation with surface tension term by a PLIC volume-of-fluid method on a regular staggered Cartesian mesh [5]. All spatial derivatives are approximated by central differences. For time integration, an explicit third-order Runge-Kutta scheme is employed. For simulation of mass transfer phenomena, we employ a non-dimensional single-field formulation (similar to that for the hydrodynamics). Thus, for each species $i = 1, 2, \dots, n$ a single transport equation for the mixture concentration

$$c_{m,i} \equiv \frac{fc_{1,i} + (1-f)Hc_{2,i}}{c_{\text{ref},i}} \quad (1)$$

is solved, which is valid in the entire computational domain [3]. This mixture concentration involves the volume fraction of the continuous phase, f , the species concentration in phase 1 and 2, and the dimensionless species Henry number defined as the ratio of equilibrium concentration on both sides of the interface

$$H_i \equiv \frac{c_{1,i}^{\text{eq}}}{c_{2,i}^{\text{eq}}} \quad (2)$$

A numerical advantage of this formulation is that the concentration $c_{m,i}$ is continuous at the interface. Disadvantageous is, that it requires special measures to ensure the continuity of the mass fluxes across the interface and that the method is not conservative. To ensure the continuity of the mass flux across the interface, a special weighting of the diffusivities in mesh cells containing both phases is performed for evaluation of the diffusive term in the mixture concentration transport equation. Details of the computation of this mixture diffusivity in interfacial mesh cells (which follows an approach first suggested by Davidson and Rudman [8]) are given in [3].

Multicomponent diffusion models

For describing multicomponent diffusion systems, the multicomponent diffusion model can be used to determine the diffusivities of the species. This model is based on the Maxwell-Stefan equation and is mainly used when the diffusivity needs to be considered precisely, e.g. without dilution. The one-dimensional diffusion flux along the z -direction is given by

$$\mathbf{j} = -\mathbb{B}^{-1} \cdot \frac{\partial \mathbf{c}}{\partial z} \quad (3)$$

Here, the diffusion flux vector, concentration vector and diffusivity matrix are defined as follows

$$\mathbf{j} = (j_1, j_2, \dots, j_n)^T, \quad \mathbf{c} = (c_1, c_2, \dots, c_n)^T \quad (4)$$

$$B_{ii} = \frac{c_i}{D_{in}} + \sum_{\substack{k=1 \\ i \neq k}}^n \frac{c_k}{D_{ik}}, \quad B_{ij} = -c_i \left(\frac{1}{D_{ij}} - \frac{1}{D_{in}} \right) \quad (5)$$

This multicomponent model includes the diffusivity matrix to deal with the diffusivities among all species and implies large computational costs. To reduce the effort, the effective diffusivity model has been suggested as an alternative [6]. The diffusive flux of the effective diffusion model is

$$j_i = -D_{i,\text{eff}} \frac{\partial c_i}{\partial z} \quad (6)$$

where the diffusivity of species i is given by

$$D_{i,\text{eff}} = (1 - c_i) / \left(\sum_{\substack{j=1 \\ j \neq i}}^n \frac{c_j}{D_{ij}} \right) \quad (7)$$

Thus, the computationally costly matrix inversion is eliminated and the diffusivity for each species can be easily obtained. This model is widely used even though it has inherent limitations for vanishing minor fluxes [7]. In our first test case, we will compare the two diffusion models for a ternary diffusion system.

Flux balance at the reactive wall

The basis for the coupling of TURBIT-VOF and DETCHEM is the balance between the diffusive and the reactive fluxes at the channel wall

$$\mathbb{D} \cdot \frac{\partial \mathbf{c}}{\partial z} = -\mathbb{K} \cdot \mathbf{c} \quad (8)$$

where

$$K_{ii} = k\nu_i, \quad K_{ij} = 0 \quad (9)$$

represents the matrix of reaction constants. The near-wall diffusive fluxes in the fluid domain are calculated by TURBIT-VOF, while the reactive fluxes at the wall are determined by DETCHEM. TURBIT-VOF provides the concentration at cell-centered positions, whereas DETCHEM requires the concentration at the wall. For this purpose, we linearly extrapolate for each species the two wall-closest cell-centered concentration values from TURBIT-VOF to the wall position

$$c_m|_{\text{wall}} = c_{m,k=1} - \frac{c_{m,k=2} - c_{m,k=1}}{z_{k=2} / z_{k=1} - 1} \quad (10)$$

Here, the subscript k denotes the mesh cell index in direction normal to the wall.

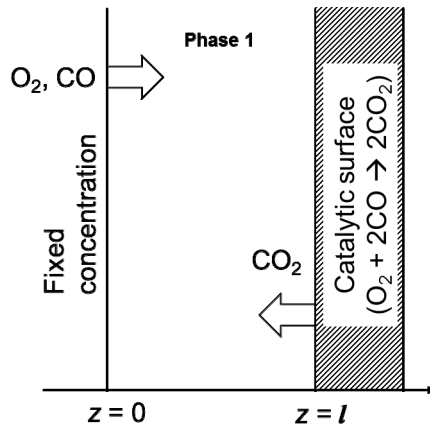


Fig. 1 Sketch of the single-phase diffusion-reaction problem with 1-step surface reaction.

3. Multispecies diffusion-reaction problem in a single phase

As first validation case for a diffusion-reaction phenomenon, we consider the CO oxidation in gaseous phase. The number of species, n , is three for this case (O_2 , CO , CO_2). For steady state without homogeneous reaction, we can replace the Maxwell Stefan equation by the convection diffusion equation

$$\nabla \cdot (k_{\text{tot}} \mathbf{c}) = \nabla \cdot (\mathbb{D} \cdot \nabla \mathbf{c}) \quad (11)$$

where

$$k_{\text{tot}} = k \sum_{i=1}^n \nu_i \quad (12)$$

is the total molar flux. Thus, from the stoichiometry, we know the boundary conditions (Eq. 8) for the convection flux (Eq. 11). Here, all molar fluxes are uniform across the domain.

Under the assumption that the diffusivities between CO-CO_2 ($D_{\text{CO-CO}_2}$) and $\text{O}_2\text{-CO}_2$ ($D_{\text{O}_2\text{-CO}_2}$) are identical, the Maxwell-Stefan equation can be solved analytically [9].

Fig. 1 shows the schematic description for the reaction of carbon monoxide and oxygen at a catalytic surface. The mixture composition at the left wall (at $z = 0$) is presumed known, and the species are transferred by reactive flux at the catalytic surface (at $z = l$). The temperature and pressure are independent of position and the reaction coefficient is set constant for this case.

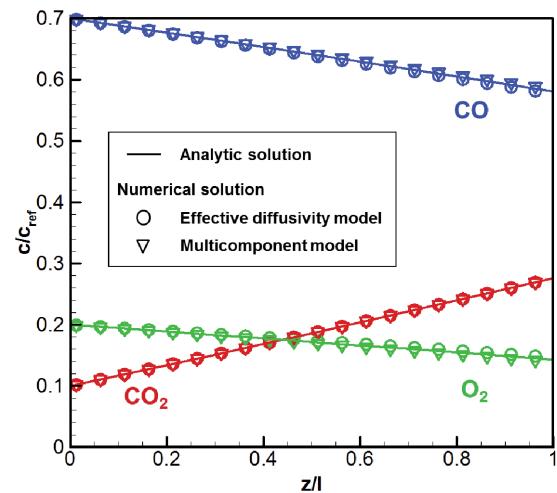


Fig. 2 Concentration profiles of effective diffusivity model (solid line), multicomponent model (dashed line) and analytic solution (symbol).

In Fig. 2, we compare the concentration profiles for the two different diffusion models computed by TURBIT-VOF with the analytic solution of Bird et al. [9]. For the numerical solution, 40 equidistant mesh cells in z -direction are used. The reaction rate of CO-oxidation is usually a function of temperature and concentrations. However, in this example the reaction rate is set constant ($k = 10^{-4} \text{ mol/m}^2\text{s}$) for simplicity. The concentrations of reactant CO and O_2 decrease

linearly along the z -axis while that of the product CO_2 is increasing. The numerical solutions of TURBIT-VOF for the two different diffusion models are in good agreement with the analytic solution. The results of the multicomponent model are slightly closer to the analytic solution but the effective diffusivity model can also make a good compliance and reduce the calculation effort without much loss of accuracy. The diffusivities of the two models are compared in **Fig. 3**. D_{11} and D_{22} in multicomponent model denote the diffusivities of species 1 and 2, respectively, and have same meaning as D_{1m} and D_{2m} in the effective diffusivity model.

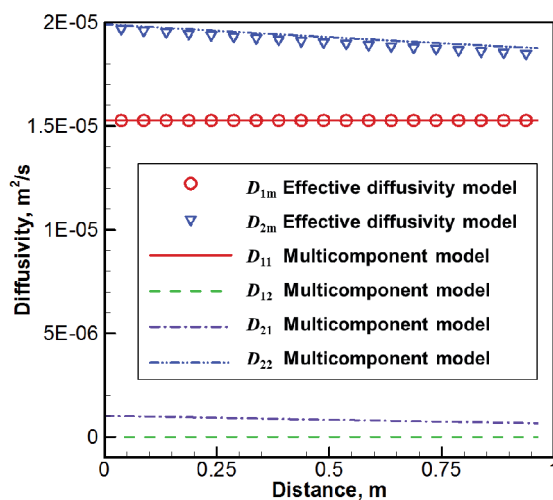


Fig. 3 Comparison of the diffusivities of effective diffusivity model (symbol) and multicomponent model (line), ($1 = \text{CO}_2$, $2 = \text{O}_2$, $m = \text{mixture}$).

D_{12} and D_{21} appear only in the multicomponent model, and account for the influence from the other species. D_{1m} and D_{11} shown in **Fig. 3** are identical and D_{12} is zero. This is caused by the assumption mentioned in the paragraph following **Eq. 12**. However, D_{2m} is different from D_{22} with existence of small value of D_{21} , which means there is a slight influence of species 1 on the diffusion of species 2. These differences of diffusivities can cause different concentration profiles but here the magnitude of the difference is negligible (cf. **Fig. 2**).

4. Multiphase reaction diffusion in the vicinity of a planar interface

The second test case considers the validation for a two-phase diffusion-reaction problem with a planar interface; see the sketch in **Fig. 4**. The phase interface is placed in the center of the

domain (at $z_{\text{int}} = l/2$). The boundary condition for the left wall (at $z = 0$) is set to the fixed concentration while the surface reaction takes place at the right wall (at $z = l$). Kenig and Gorak [10] provided the film model based approach for the multicomponent mass transfer in liquid-gas mixture. They considered diffusion with homogeneous and heterogeneous reactions on basis of the Non-Equilibrium Stage Model (NEQ) [11]. In the present study, only a heterogeneous reaction is considered and the computational results are compared with the non-equilibrium stage model with interfacial flux derived by Kenig and Gorak [10]. We varied the position of the interface with respect to the mesh cells and checked that it does not affect the solution.

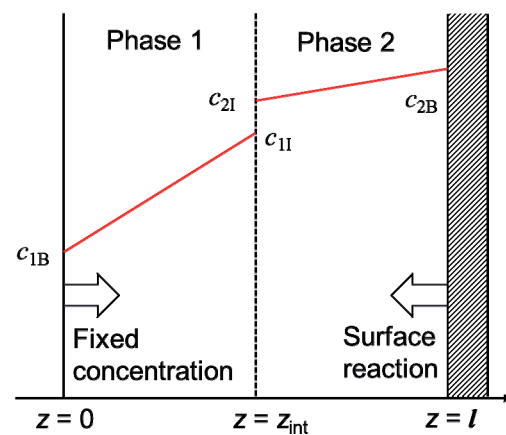


Fig. 4 Sketch of the two-phase test case with phase interface in the middle of domain.

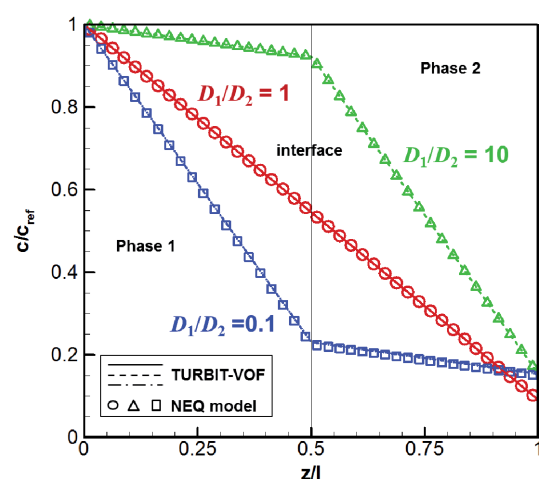


Fig. 5 Concentration profiles of TURBIT-VOF (lines) and non-equilibrium stage model (symbols) for different diffusivity ratios ($H = 1$, $k = 10 \text{ m/s}$).

Fig. 5 shows the results for three different values of the diffusivity ratio between both phases for a fixed value of the reaction rate and a Henry number of unity. When the diffusivity ratio is unity, the diffusivities of two phases are identical, which means it is the same condition as a single phase. On the other hand, the concentration gradient at the interface changes when the diffusivity ratio is not unity. High diffusivity makes the species diffuse well and therefore the gradient of species is low, see left side of green dashed line or right side of blue dash-dot line in **Fig. 5**. When the diffusivity is low, the results are contrary to the case when the diffusivity is high. The numerical results are in good agreement with the non-equilibrium stage model.

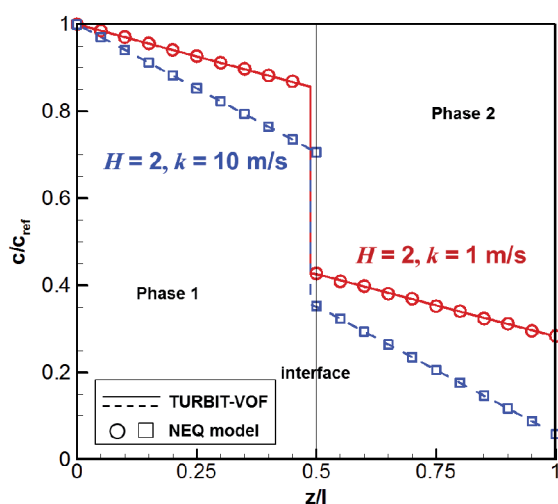


Fig. 6 Concentration profiles of TURBIT-VOF (lines) and non-equilibrium stage model (symbols) with respect to reaction constants.

Next, we investigated the effect of the reaction rate for fixed values of the diffusivity ratio (unity) and the Henry number ($H = 2$). **Fig. 6** displays the respective concentration profiles for two different values of the reaction constant ($k = 1$ m/s, 10 m/s). With increase of the reaction rate, the reactive flux to the right wall is increasing, which makes the species consumption at the right wall increasing. As the value of the Henry number is equal to 2, the ratio of concentration at the interface is 2, and a concentration jump occurs at the phase interface. Henry number is determined by Henry's law and is limited to sufficiently diluted solutions. In practice, Henry number varies with different species and

depends on the thermodynamic conditions.

5. Conclusions

In the present study, the multispecies diffusion with heterogeneous reaction has been validated for single phase and two-phase including planar interface in the middle of domain. The species equation in TURBIT-VOF has been extended for multispecies diffusion and is coupled with the DETCHEM package through the reactive flux. The results of implemented species formulations are in very good agreement with analytic solutions for different values of the diffusivity ratio, Henry number and reaction rate.

For multispecies diffusion, two widely used models have been compared for single-phase conditions. In conclusion, the effective diffusivity model gives reasonable solutions, which do not differ much from the multicomponent model and fit well as compared to analytic solutions. Consequently, we will use the effective diffusivity model for further investigations, since it is sufficiently accurate with less computational effort. The interface diffusivity calculation in the single-field species formulation of TURBIT-VOF [3] has been well verified with non-equilibrium stage model. This study is a pre-study to validate the implemented formulation before starting the next step simulation, namely the flow and mass transfer of Taylor bubbles in mini-channels with multistep surface reactions.

Acknowledgment

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Nomenclature

Symbol	Description	Unit
c	concentration	mol/m ³
D	diffusivity	m ² /s
f	liquid volume fraction	-
H	Henry number	-
j	molar flux	mol/m ² s
k	reaction constant	m/s
l	length of domain	m
n	number of species	-
Greek letter		
ν	stoichiometric number	-
Subscripts		
eff	effective	
eq	equilibrium	
i	index of species	
int	interface	
m	mixture	
ref	reference	
1	phase 1	
2	phase 2	

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