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EULERIAN THREE-PHASE FLOW MODEL APPLIED TO TRICKLE-BED REACTORS

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The majority of publications and monographs present investigations which concern exclusively two-phase flows and particulary dispersed flows. However, in the chemical and petrochemical industries as well as in refineries or bioengineering, besides the apparatuses of two-phase flows there is an extremely broad region of three-phase systems, where the third phase constitutes the catalyst in form of solid particles (Duduković et al., 2002; Martinez et al., 1999) in either fixed bed or slurry reactors. Therefore, the goal of this study is to develop macroscopic, averaged balances of mass, momentum and energy for systems with three-phase flow. Local instantaneous conservation equations are derived, which constitute the basis of the method applied, and are averaged by means of Euler's volumetric averaging procedure. In order to obtain the final balance equations which define the averaged variables of the system, the weighted averaging connected with Reynolds decomposition is used. The derived conservation equations of the trickle-bed reactor (mass, momentum and energy balance) and especially the interphase effects appearing in these equations are discussed in detail.

Keywords: multiphase flow, averaging procedure, trickle-bed reactor conservation equations

1. INTRODUCTION

Multiphase flows take place in a number of processes connected with various industrial sectors, such as chemical and pharmaceutical industry, food manufacturing, processes of environmental protection, power engineering (conventional and nuclear power plants), heat transfer systems (evaporators, condensers, driers, spray cooling towers etc.). Therefore, the problems concerning multiphase flows became one of the main interests in many engineering disciplines with investigations directed towards the development of a theoretical background of this physical phenomenon and, in consequence, to create possibilities of their broad application in optimal design of this type of systems.

From the mathematical point of view multiphase flow can be considered as a region divided into one-phase subregions with moving and continuously changing interfaces.

The mechanics of continuous systems constitutes a well founded theoretical background for the development of models describing the one-phase flow based on the conservation principles of mass, momentum and energy, supplemented by appropriate constitutive relations, which determine the thermodynamic state of the system investigated, the transport phenomena of mass, momentum and energy as well as the kinetics of chemical reactions taking place in the system. Equations thus obtained form a system of instantaneous, local equations which define the one-phase flow model describing the thermodynamic and transport properties of the variables of the system analysed.

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Formulation of the multiphase flow based on local, instantaneous, one-phase equations is in principle a boundary value problem of multiple and continuously changing boundaries. Unfortunately, such a method of integration of a set of differential equations encounters insurmountable mathematical and numerical difficulties and becomes completely unrealistic for practical application. The attempts at developing a multiphase flow model as a result of an appropriate compilation of the local, instantaneous equations did not lead to satisfactory results, either.

This led to the necessity of elaborating a macroscopic model of multiphase flow by means of applying appropriate averaging methods with respect to the local, instantaneous equations. This approach yields averaged values of flow parameters and physicochemical properties. Simultaneously, this method of averaging eliminates local, instantaneous fluctuations of flow variables and allows the application of a mesh of larger dimensions and longer time steps. It requires, however, additional relationships in order to close an analysed system of differential equations . These relationships are mostly empirical and demand additional experimental data to be verified.

In the last four decades investigations, both theoretical and experimental focused on the development of a general and exact quantitative description of the multiphase flow have been considerably intensified (Boemer et al., 1995; Boure and Delhaye, 1982; Delhaye and Achard, 1977; Drew, 1983; Gidaspow, 1986; Ishii and Hibiki, 2011; So, 1990; Enwald et al., 1996; Lyczkowski et al., 2010).

However, a considerable majority of the publications (if not all) present investigations which concern exclusively two-phase flows and, particularly, dispersed flows e.g. bubbling gas in liquid, liquid droplets in gas or solid particles in gas or liquid. Similarly, the general classification of multiphase flows proposed by Ishii and Hibiki (2011) also includes only two-phase flows (gas – liquid, solid particles – liquid or gas), assembling them in three groups depending on the geometry of interfaces. It has also to be stressed that the software Fluent Users Guide 6.1.22 concerns, in principle, only dispersed two-phase flows, presenting methods of solutions of the flow equation either by the discrete phase model applying the Lagrange formulation or by the Eulerian two-phase model. Therefore, the above listed constitutive relations and transfer laws which determine the interphase action are valid solely for the dispersed flow in form of droplets and bubbles or solid particles.

However, in the chemical and petrochemical industries, besides apparatuses with two-phase flow there is an extremely broad region of three-phase systems where the third phase is a catalyst in form of solid particles (Duduković et al., 2002; Martinez et al., 1999). These are slurry reactors, in which fine particles of a catalyst are suspended in a very well mixed two-phase system of gas and liquid (Shah, 1979). Similarly, there is a very broad range of processes carried out in three-phase fixed-bed reactors (called trickle-bed reactors) where the concurrently flowing phases (gas and liquid) are brought into contact with solid catalyst particles in order to perform the desired chemical transformation (Satterfield, 1975; Bartelmus et al., 1998, Burghardt et al., 1999).

Direct application of the methods of solution elaborated for two-phase flows in analyzing three-phase systems encounters difficulties because of the problem with identifying phases in the latter class of systems. For instance, the software Fluent Users Guide 6.1.22 defines as the primary or basic phase the continuous phase and the dispersed phase as the secondary phase. The introduction into these systems of a third phase especially catalyst particles in a fixed bed, requires artificial numerical operations.

Therefore, the aim of this study is to develop macroscopic, averaged balances of mass, momentum and energy for systems with the three-phase flow in as general a form as possible, allowing the user to extend them to any number of phases. In these considerations the methods of averaging have been applied which were described in cited references.

In order to develop the averaged balance equation of three-phase flow, the following procedure was employed:

1. Development of local, instantaneous balance equations of three-phase flow, together with jump conditions at the interfaces
2. Averaging of the local, instantaneous equations thus obtained
3. Defining the averaged macroscopic constitutive and transfer relationships
4. Derivation of a system of partial differential equations which define the macroscopic, averaged model of three-phase flow
5. Adaptation of the model to the trickle –bed reactor. Special attention has been devoted to the definition of the interphase actions which play a key role in a trickle-bed reactor.

2. LOCAL INSTANTANEOUS ONE-PHASE EQUATIONS

Let us consider a control volume situated in the analysed system which comprises all three phases ($k = 1, 2, 3$), separated by the interfaces moving with velocity $\vec{v}_I$ (Fig. 1).
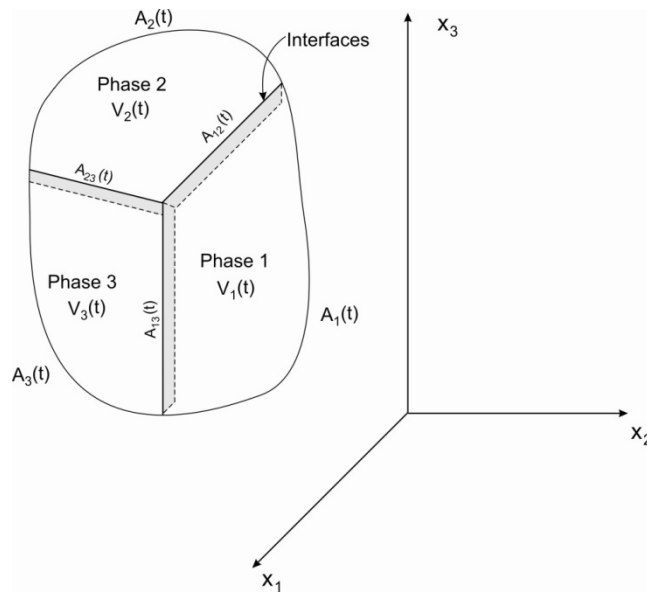

Fig. 1. Scheme of the control volume

The balance is performed for the conserved variable ψ_k ($k = 1, 2, 3$) referred to unit mass representing a scalar quantity which can be the concentration of a species in the fluid mixture e.g. the mass fraction in the mass balance or the total energy of the mixture in the energy balance as well as vector quantity defining the fluid mixture velocity in the momentum balance. The three basic principles of conservation of mass, momentum and energy can thus be expressed by means of a single balance equation for the variable ψ_k. The balance concerns the control volume as a whole, thus only transport of the variable ψ_k through the boundaries of the control volume is taken into account (Delhaye and Achard, 1977). This enables us to obtain the jump conditions at the interfaces. In the Cartesian coordinate system the balance can be presented as

$$\sum_{k=1}^{3}\left(\frac{d}{dt}\int_{V_k(t)} \rho_k\psi_k dV \right) = \sum_{k=1}^{3}\left(-\int_{A_k(t)} \rho_k\psi_k\left(\vec{v}_k \cdot \vec{n}_k\right)dA - \int_{A_k(t)} J_k \cdot \vec{n}_k dA + \int_{V_k(t)} \rho_k S_k dV \right) \qquad (1)$$

In this equation $\vec{n}_k$ is the unit vector normal to the interface directed out of the phase k, $\vec{v}_k$ is the velocity of phase k and ρ_k the density. J_k is a generalised molecular flux of the variable ψ_k and can be a vector quantity representing the mass flux in the mass balance, or the heat flux in the energy balance as well as a tensor defining the momentum flux equated to the viscous stress tensor in the momentum balance. S_k is a source term characterised by a scalar quantity comprising the rate of chemical reactions

in the mass balance and physical energy sources such as work performed by the body forces, the heat of radiation and heat effects generated by chemical reactions in the energy balance as well as a vector quantity defining the body force in the momentum balance.

The dependence between the flux J_k as well as the source terms S_k and their driving forces composed of state variables, concentration, temperature, pressure and fluid velocities, which form the constitutive closure laws depend on the particular analysed system and will be discussed in detail in the second part of the study referred to the trickle-bed reactors. Simultaneously, special attention will be devoted to transfer closure laws, which are empirical equations obtained mostly on the basis of experiments and define the interactions between phases occurring at the interfaces.

In Eq. (1) the surface tension is not included because the capillary forces in the trickle-bed reactors are negligible in comparison to the pressure gradient in each phase and the interface drag force, although they play a significant role in estimation of the onset of the pulsing flow (Jiang et al., 2001; Grosser et al., 1988).

The ordinary time derivative, Eq. (1), takes also into account changes of the variable ψ_k in the control element caused by the displacement of the interface, and can be included into the balance by means of the Leibniz theorem

$$\frac{d}{dt}\int_{V_k(t)} (\rho_k \psi_k) dV = \int_{V_k(t)} \frac{\partial}{\partial t} (\rho_k \psi_k) dV + \sum_{\substack{p=1\\p\neq k}}^{3} \int_{A_{kp}} \left(\rho_k \psi_k \left(\vec{v}_I \cdot \vec{n}_{kp}\right)\right) dA \quad k = 1, 2, 3 \qquad (2)$$

Similarly, the convection and diffusion terms were transformed using the Gauss theorem

$$\int_{V_k(t)} \nabla \cdot (\rho_k \psi_k \vec{v}_k) dV = \int_{A_k(t)} \rho_k \psi_k \left(\vec{v}_k \cdot \vec{n}_k\right) dA + \sum_{\substack{p=1\\p\neq k}}^{3} \int_{A_{kp}(t)} \rho_k \psi_k \left(\vec{v}_k \cdot \vec{n}_{kp}\right) dA \quad k = 1, 2, 3 \qquad (3)$$

$$\int_{V_k(t)} \nabla \cdot J_k dV = \int_{V_k(t)} \vec{J}_k \cdot \vec{n}_k dA + \sum_{\substack{p=1\\p\neq k}}^{3} \int_{A_{kp}} \vec{J}_k \cdot \vec{n}_{kp} dA \quad k = 1, 2, 3 \qquad (4)$$

Introducing Eqs. (2), (3) and (4) into the balance equation (1) and performing appropriate transformations whereby the surface integrals are separated from the volume integrals, the following relationship is obtained

$$\sum_{k=1}^{3} \left(\int_{V_k(t)} \left(\frac{\partial}{\partial t} (\rho_k \psi_k) + \nabla \cdot (\rho_k \psi_k \vec{v}_k) + \nabla \cdot J_k - \rho_k S_k \right) dV \right) =$$
$$= \sum_{\substack{k=1\\p\neq k}}^{3} \sum_{p=1}^{3} \left(\int_{A_{kp}(t)} \left(\dot{m}_{kp} \psi_k + J_k \cdot \vec{n}_{kp} + \dot{m}_{pk} \psi_p + J_p \cdot \vec{n}_{pk} \right) dA \right) \qquad (5)$$

Eq. (5) must be satisfied for any values of $V_k(t)$ and $A_{kp}(t)$, giving as a result the local, instantaneous, one-phase equation

$$\frac{\partial}{\partial t} (\rho_k \psi_k) + \nabla \cdot (\rho_k \psi_k \vec{v}_k) + \nabla \cdot J_k - \rho_k S_k = 0 \quad k = 1, 2, 3 \qquad (6)$$

together with the boundary conditions at the interface called jump conditions

$$\dot{m}_{kp} \psi_k + J_k \cdot \vec{n}_{kp} + \dot{m}_{pk} \psi_p + J_p \cdot \vec{n}_{pk} = 0 \quad k = 1, 2, 3; p = 1, 2, 3; k \neq p \qquad (7)$$

3. AVERAGED EQUATIONS OF THREE-PHASE FLOW

3.1. Methods of averaging

The use of averaging procedures in two-phase flow theory has been extensively analysed by Ishii and Hibiki (2011) and Delhaye and Achard (1977).

Averaging methods applied can be classified depending on the character of flow in three different groups: ensemble averaging Euler's averaging and the Lagrange averaging, all containing subgroups for different variables based on which the averaging is performed. The most general averaging procedure is the ensemble average given by the relation:

$$\langle f(\bar{r},t)\rangle = \int_S f(\bar{r},t)\,dP(\mu) \tag{8}$$

where $f(\bar{r},t)$ defines a physical quantity which can be a scalar, vector or tensor and determines its value in space $\bar{r}$ and time t, $P(\mu)$ is the probability density function observing process μ and S the set of all possible realisations (Drew and Lahey, 1993; Ishii and Hibiki, 2011). Thus, the ensemble average is the statistical mean of any observed physical quantity at a given position and time over a number realisations. It demands, however, the knowledge of the probability density function which can be estimated by performing additional experiments and is therefore used only in exceptional cases.

Time and spatial averages can be considered as approximations of the ensemble average and valid if there is a clear separation between small and large time or space scales and flow is treated as pseudohomogeneous. This is an application on the local scale of the ergodicity hypothesis which states that if a flow is stationary and homogeneous the ensemble time and volume averages are equivalent.

The important group of Euler's averages is commonly applied, as it is strictly connected with the Eulerian description of physical phenomena, where time and space variables are independent variables in relationships determining changes of physical quantities. Moreover, the local, instantaneous equations derived in the previous chapter fully correspond to this manner of description of physical phenomena. The Lagrange average is directly related to the description of various phenomena by means of the Lagrange formulation, which analyses the movement of a single particle in terms of the so-called "material coordinates" instead of space coordinates, and is therefore mainly used to investigate dispersed systems of low concentrations of particles.

Therefore, the most frequently used Eulerian averages are the volume average and the time average. The volume average is estimated in the volume around the point $\vec{r}$ in time t, while the time average is estimated at point $\vec{r}$ over a time interval Δt. The volume average is defined as

$$\langle f(\vec{r},t)\rangle_V = \frac{1}{\Delta V}\int_{\Delta V} f(\vec{r},t)\,dV \tag{9a}$$

fulfilling the following restrictions (Whitaker, 1969; 1989):
  characteristic dimension of phases,
 $\ll$ characteristic dimension of averaging volume,
 $\ll$ characteristic dimension of physical system.

The time average is given by

$$\langle f(\vec{r},t)\rangle_t = \frac{1}{\Delta t}\int_{\Delta t} f(\vec{r},t)\,dt \tag{9b}$$

According to Delhaye and Archard (1977), the time interval must satisfy the following conditions:

time scale of flow fluctuations,
<< time interval of averaging,
<< time scale of mean flow fluctuations.

Both Eulerian averages, i.e. the volume and the time average treat the multiphase system as quasicontinuous. Consequently, the choice of an appropriate average depends on the type of the multiphase system considered. It has to be pointed out that the dynamic characteristic of a dispersed flow system depends on the interactions of the solid state particles, gas bubbles, and liquid droplets between themselves as well as with the surrounding, continuous fluid phase. In contrast, in separated flow systems this characteristic is connected with the structure and dynamics of the interfaces which undergo wave changes. This structure influences considerably the fluxes of mass, momentum and energy at the interface. Therefore, for dispersed flow systems both the volume average and the time average lead to almost identical results. For a fixed bed, where solid particles do not move, the average concentration of particles at a fixed point can take either a constant value or zero, whereas the volume average gives the correct value.

Thus, in the following considerations the volume average is used, although in the majority of publications cited the time average was used.
- The characteristic scales which fulfil the conditions of the volume averaging in the trickle-bed reactor can be characterised as follows.
- The single phase equations of gas and liquid are regarded as local instantaneous equations valid in a "point" and time.
- The "point" is viewed as a space and time large enough to eliminate microscopic, molecular motions, but simultaneously small enough to exhibit still the properties of the continuum and avoid macroscopic changes in the flow.
- The scale of this flow can be presented by estimating the values of gas and liquid holdups which are parts of fixed bed porosity and are placed in the range of a few millimeters.
- The volume of averaging encompasses averaged gas and liquid flows as well as the solid catalyst phase in form of a system where the interpenetrating, continuous media are bounded by interphase actions also called a jump conditions. The scale of this volume is much larger than the scale of local instantaneous equations eliminating fluctuations of flow variables.
- The characteristic dimensions of a physical system are comparable with dimensions of a fixed bed in a reactor.

The following properties of the average will be necessary in further considerations;

$$\langle f + g \rangle = \langle f \rangle + \langle g \rangle \tag{10}$$

$$\langle \langle f \rangle g \rangle = \langle f \rangle \langle g \rangle \tag{11}$$

$$\left\langle \frac{\partial f}{\partial t} \right\rangle = \frac{\partial \langle f \rangle}{\partial t} \tag{12}$$

$$\langle \nabla f \rangle = \nabla \langle f \rangle \tag{13}$$

$$\langle \nabla \cdot f \rangle = \nabla \cdot \langle f \rangle \tag{14}$$

3.2. Development of macroscopic, averaged flow equations

In the procedure of averaging physical quantities over the volume of the control element which contains all the three phases it is necessary to locate individual phases in specified parts of the control

element. To this end a function called a phase indicator is introduced (Ishii and Hibiki, 2011) and defined as follows

$$L_k(\vec{r},t) = \begin{cases} 1 & \text{if} \quad \vec{r} \in k \\ 0 & \text{if} \quad \vec{r} \notin k \end{cases} \tag{15}$$

It is worth mentioning that the volume average of the function L_k which comprises numerous experiments $L_k = 0$ and $L_k = 1$, gives the volume average of the phase k with respect to the volume of the control element and thus the volume fraction of the phase

$$\langle L_k \rangle = \frac{1}{V} \int_V L_k dV = \alpha_k \tag{16}$$

and

$$\sum_{k=1}^{3} \alpha_k = 1 \tag{17}$$

The first step in the averaging procedure is to multiply the local, instantaneous equation (6) by the function L_k, and then to estimate the volume averages of its terms. This leads to the following equation

$$\left\langle L_k \frac{\partial}{\partial t}(\rho_k \psi_k) \right\rangle + \left\langle L_k \nabla \cdot (\rho_k \psi_k \vec{v}_k) \right\rangle + \left\langle L_k \nabla \cdot J_k \right\rangle - \left\langle L_k \rho_k S_k \right\rangle = 0 \quad k = 1, 2, 3 \tag{18}$$

Employing the following rules of the differential calculus

$$\frac{\partial}{\partial t}\langle L_k f_k \rangle = \left\langle L_k \frac{\partial f_k}{\partial t} \right\rangle + \left\langle f_k \frac{\partial L_k}{\partial t} \right\rangle \tag{19}$$

$$\nabla \langle L_k f_k \rangle = \langle L_k \nabla f_k \rangle + \langle f_k \nabla L_k \rangle \tag{20}$$

$$\nabla \cdot \langle L_k f_k \rangle = \langle L_k \nabla \cdot f_k \rangle + \langle f_k \cdot \nabla L_k \rangle \tag{21}$$

in Eq. (18), the general form of the averaged balance of the variable ψ_k is obtained

$$\frac{\partial}{\partial t}\langle L_k \rho_k \psi_k \rangle + \nabla \cdot \langle L_k \rho_k \psi_k \vec{v}_k \rangle + \nabla \cdot \langle L_k J_k \rangle - \langle L_k \rho_k S_k \rangle$$
$$= \langle \rho_k \psi_k (\vec{v}_k - \vec{v}_I) \cdot \nabla L_k \rangle + \langle J_k \cdot \nabla L_k \rangle \qquad k = 1, 2, 3 \tag{22}$$

Let us now analyse the values of the gradient ∇L_k. This gradient is equal to zero inside the phase k as $L_k = 1$ in the whole region of this phase. Similarly, in the region outside the phase k this quantity also equals zero. Thus, any change of this gradient can only take place at crossing the interface, where the function L_k undergoes a step change from the value $L_k = 1$ for $\vec{r}_k \in k$ to $L_k = 0$ for $\vec{r}_k \notin k$. Therefore, the gradient ∇L_k assumes an infinitely large value at the interface and can be defined by the following relation

$$\nabla L_k = \frac{\partial L_k}{\partial n_I} \vec{n}_k \tag{23}$$

which, introduced into Eq. (22) leads to the following equation

$$\frac{\partial}{\partial t}\langle L_k \rho_k \psi_k \rangle + \nabla \cdot \langle L_k \rho_k \psi_k \vec{v}_k \rangle + \nabla \cdot \langle L_k J_k \rangle - \langle L_k \rho_k S_k \rangle = \left\langle \left(\overset{\bullet}{m}_k \psi_k + J_k \cdot \vec{n}_k \right) \frac{\partial L_k}{\partial n_I} \right\rangle \quad k = 1, 2, 3 \tag{24}$$

As the quantity $\partial L_k / \partial n_I$ assumes an infinitely large value at the interface, it can be expressed by Dirac's delta function

$$\frac{\partial L_k}{\partial n_I} = -\delta_{kI} = -\delta_k (\vec{v}_k - \vec{v}_I) \tag{25}$$

Consequently, the average over the volume V yields the quantities $\overset{\bullet}{m}_k$ and J_k at the interface. They form the terms of interphase mass, momentum and energy exchange or, generally, interphase actions (transfer closure laws) introduced into the macroscopic balance of the variable ψ_k as a result of the averaging of local instantaneous equations. They are, as has been mentioned in the Introduction, empirical relationships and have to be estimated experimentally.

The gradient of the phase indicator is also used to average the local, instantaneous jump condition (7) at the interface

$$\left\langle \left(\overset{\bullet}{m}_{kp} \psi_k + J_k \cdot \vec{n}_{kp} \right) \frac{\partial L_k}{\partial n_{kp}} \right\rangle + \left\langle \left(\overset{\bullet}{m}_{pk} \psi_p + J_p \cdot \vec{n}_{pk} \right) \frac{\partial L_p}{\partial n_{pk}} \right\rangle = 0 \quad k = 1, 2, 3; p = 1, 2, 3; p \neq k \tag{26}$$

As interactions between the phases are introduced into the averaged flow equation (24) (right-hand side of this equation), the jump conditions at the interface (26) form restrictions imposed onto the averaged balance equations.

The right-hand side of the averaged balance equation (24) represents interphase actions in a global manner, in the sense that it defines the sum of interactions of the phase k with other phases through all its interfacial surfaces. In order to introduce a differentiation of interphase actions with regard to the transport of variables through different interfaces one has to select these actions by means of jump conditions. This leads to the following expression

$$N_{kI} = \left\langle \left(\overset{\bullet}{m}_k \psi_k + J_k \cdot \vec{n}_k \right) \frac{\partial L_k}{\partial n_I} \right\rangle = \left\langle \sum_{\substack{p=1 \\ p \neq k}}^{3} \left(\overset{\bullet}{m}_{kp} \psi_k + J_k \cdot \vec{n}_{kp} \right) \frac{\partial L_k}{\partial n_{kp}} \right\rangle \quad k = 1, 2, 3 \tag{27}$$

Unfortunately, the averaged balance equation (24) cannot be used directly to determine the functions which define the physical quantities appearing in these equations, as they present the averages of products of these quantities. Thus, it is necessary to convert these equations into a form which would contain products of averages of physical quantities. To this end Drew and Lahey (1993) as well as Ishii and Hibiki (2011) proposed the weighting averaging procedure connected with the Reynolds decomposition for ensemble averages and time averages.

Therefore, the dependent variable $f(\vec{r}, t)$ is presented in the following form

$$f = \langle f \rangle^W + f' \tag{28}$$

where $\langle f \rangle^W$ is the weighted average and f' the fluctuating deviation from this average.

Generally, the weighted average of a dependent variable (a scalar, vector or tensor) is

$$\langle f \rangle^W = \langle W f \rangle / \langle W \rangle \tag{29}$$

where W is an arbitrary weighting factor. In order to transform the average of the products of variables into the product of their averages two types of weighting are used. In the first type the phase indicator L_k is used as the weighting factor (phase average), whereas in the second the product of the phase indicator L_k and the density of the fluid ρ_k (mass weighted average) are employed

$$\langle f_k \rangle^{L_k} = \frac{\langle L_k f_k \rangle}{\langle L_k \rangle} \tag{30}$$

$$\left\langle f_k \right\rangle^{L_k \rho_k} = \frac{\left\langle L_k \rho_k f_k \right\rangle}{\left\langle L_k \rho_k \right\rangle} \tag{31}$$

The averaged density of phase k is obtained by applying the phase average

$$\left\langle \rho_k \right\rangle^{L_k} = \rho_k^{L_k} = \frac{\left\langle L_k \rho_k \right\rangle}{\left\langle L_k \right\rangle} = \frac{\left\langle L_k \rho_k \right\rangle}{\alpha_k} \tag{32}$$

Applying the phase average in a similar way, the averaged value of the molecular flux can be obtained

$$\left\langle J_k \right\rangle^{L_k} = J_k^{L_k} = \frac{\left\langle L_k J_k \right\rangle}{\left\langle L_k \right\rangle} = \frac{\left\langle L_k J_k \right\rangle}{\alpha_k} \tag{33}$$

Using relation (28), let us separate flow velocity into the weighted average and the fluctuating deviation, based on the average

$$\vec{v}_k = \left\langle \vec{v}_k \right\rangle^{L_k \rho_k} + \vec{v}_k^{\,\prime} = \vec{V}_k + \vec{v}_k^{\,\prime} \tag{34}$$

In a similar way, the variable ψ_k can be presented as

$$\psi_k = \left\langle \psi_k \right\rangle^{L_k \rho_k} + \psi_k^{\,\prime} = \Psi_k + \psi_k^{\,\prime} \tag{35}$$

It has to be pointed out that

$$\left\langle \vec{v}_k^{\,\prime} \right\rangle^{L_k \rho_k} = 0 \tag{36}$$

as well as

$$\left\langle \psi_k^{\,\prime} \right\rangle^{L_k \rho_k} = 0 \tag{37}$$

Introducing relations (34) and (35) into Eq. (24) gives

$$\frac{\partial}{\partial t} \left\langle L_k \rho_k \left(\Psi_k + \psi_k^{\,\prime} \right) \right\rangle + \nabla \cdot \left\langle L_k \rho_k \left(\Psi_k + \psi_k^{\,\prime} \right)\left(\vec{V}_k + \vec{v}_k^{\,\prime} \right) \right\rangle + \nabla \cdot \left\langle L_k J_k^{L_k} \right\rangle$$
$$= \left\langle L_k \rho_k S_k \right\rangle + N_{kI} \qquad k = 1, 2, 3 \tag{38}$$

Averaging every term of Eq. (38) leads to the final form of the averaged three-phase flow equation (see the Appendix)

$$\frac{\partial}{\partial t} \left(\alpha_k \rho_k^{L_k} \Psi_k \right) + \nabla \cdot \left(\alpha_k \rho_k^{L_k} \Psi_k \vec{V}_k \right) = -\nabla \cdot \left(\alpha_k \left(J_k^{L_k} + J_k^{f} \right) \right) + \alpha_k \rho_k^{L_k} S_k^{L_k \rho_k} + N_{kI} \quad k = 1, 2, 3 \tag{39}$$

in which the averaged term of interphase interactions (27) is given by

$$N_{kI} = \sum_{\substack{p=1 \\ p \neq k}}^{3} -\left(\overset{\vee}{m}_{kp} \Psi_k + \overset{\vee}{J}_{kp} \right) \tag{40}$$

In this equation $\overset{\vee}{m}_{kp}$ represents the averaged value of the interphase convective mass flux per unit volume, while $\overset{\vee}{J}_{kp}$ is the averaged interphase molecular flux per unit volume defined by

$$-\overset{\vee}{J}_{kp} = -\left\langle J_k \cdot \vec{n}_{kp} \frac{\partial L_k}{\partial n_{kp}} \right\rangle = \overset{\vee}{J}_{pk} \tag{41}$$

Mass fluxes $\overset{\vee}{m}_{kp}$ can take positive or negative values. Following Eq. (40), for positive values of $\overset{\vee}{m}_{kp}$

the mass flux leaves phase k. Thus, it is directed from phase k to one of the phases p. For negative values of $\overset{\vee}{m}_{kp}$ the direction of the mass flux is from phase p into phase k.

Among the p phases in contact with the phase k there are p_1 phases where the mass flux is directed from phase p into phase k and p_2 where it leaves phase k ($p_1+p_2=p$). Thus, Eq. (40) can be rewritten as

$$N_{kI} = \sum_{\substack{p_1 \\ p_1 \neq k}} \overset{\vee}{m}_{pk} \, \Psi_p - \sum_{\substack{p_2 \\ p_2 \neq k}} \overset{\vee}{m}_{kp} \, \Psi_k + \sum_{p=1}^{3} \overset{\vee}{J}_{pk} \ (p_1+p_2=p); \quad k = 1, 2, 3 \tag{42}$$

4. CONSERVATION EQUATIONS IN TRICKLE-BED REACTORS

As mentioned in the Introduction, the majority of chemical reactors operating in a number of industrial sectors involve predominantly multiphase reactor technology in order to transform selected raw materials into desired products (e. g. bulk chemicals, syngas and natural gas conversion, fine chemicals, pharmaceuticals and petroleum products). A three phase reactor called "trickle-bed reactor" plays a very important and special role. In the TBR, which includes a fixed bed of catalyst particles, two phases flowing concurrently down (gas and liquid) are brought into contact with a solid catalyst to carry out the required chemical transformation. As the reactants of chemical reactions taking place in the catalyst pellet occur both in the gas phase and in the liquid phase, a very important role in trickle-bed processes is played by the transport phenomena of mass and energy between the gas, the liquid, and the catalyst surface. They influence considerably solutions of model equations and, therefore, have to be carefully selected in order to safeguard the accuracy of numerical results.

In order to close a system of averaged macroscopic partial differential equations of three-phase flow, additional equations are needed. These equations define two types of closure laws: constitutive and transfer laws.

Constitutive laws relate fluxes and sources in the bulk of fluid phases to their driving forces composed of state variables. Transfer laws are empirical equations obtained mostly on the basis of experiments, and define interactions between phases occurring at the interface. The selection of appropriate closure laws is crucial for the accurate modeling of a reactor process.

4.1. Mass balance[*]

In order to obtain the averaged mass balance of component i in the phase k, the variable Ψ_k in Eq. (39) is set equal to the mass fraction of component i in this phase

$$\Psi_k = Y_k^i \tag{43}$$

It is assumed that the generalised flux J_k is equal to the diffusional flux of component i in the phase k and, therefore, is a vector quantity (constitutive closure law)

$$J_k = \bar{J}_k^i \tag{44}$$

defined by the relationship

$$\bar{J}_k^i = -\rho_k D_k^{ij} \nabla Y_k^i \tag{45}$$

which is rigorous for binary mixtures. For multicomponent mixtures the generalised Fick's law is

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[*] In the present considerations the superscripts denoting the weighting factor have been omitted.

usually used (Taylor and Krishna, 1993)

$$\vec{J}_i = -\rho_k \sum_{j=1}^{n-1} \overset{\vee}{D}_k^{ij} \nabla Y_j \qquad (46)$$

where the multicomponent diffusion coefficients $\overset{\vee}{D}_k^{ij}$ are functions of the composition of the fluid mixture and the binary diffusion coefficients of mixture's components. An alternative is to use an approximate equation defining the effective diffusion coefficient of the component D^{ief} (Bird, Stewart, Lighfoot, 1960).

The term of interphase interactions (42) takes the form

$$N_{kI} = \sum_{\substack{p_1 \\ p_1 \neq k}} \overset{\vee}{m}_{pk} Y_p^i - \sum_{\substack{p_2 \\ p_2 \neq k}} \overset{\vee}{m}_{kp} Y_k^i + \sum_{p=1}^{3} \overset{\vee}{J}_{pk}^i \qquad (p_1 + p_2 = p); \quad k = 1, 2, 3 \qquad (47)$$

where $\overset{\vee}{m}_{pk} Y_p^i$ is the average convective mass flux per unit volume of component i from phase p into phase k. Similarly, $\overset{\vee}{J}_{pk}^i$ is the interphase diffusional flux from phase p into phase k.

The source term expresses the production of component i as a result of R_k homogeneous chemical reactions taking place in the phase k (constitutive closure law)

$$\alpha_k \rho_k S_k = \alpha_k \rho_k M_k^i \sum_{r=1}^{R_k} v_{rk}^i r_{rk} \qquad (48)$$

Finally, the averaged mass balance of component i in the phase k can be presented as

$$\frac{\partial}{\partial t}\left(\alpha_k \rho_k Y_k^i\right) + \nabla \cdot \left(\alpha_k \rho_k Y_k^i \vec{V}_k\right) = -\nabla \cdot \left(\alpha_k \vec{J}_k^i\right) +$$

$$+ \alpha_k \rho_k M_k^i \sum_{r=1}^{R_k} v_{rk}^i r_{rk} + \sum_{p_1} \overset{\vee}{m}_{pk} Y_p^i - \sum_{p_2} \overset{\vee}{m}_{kp} Y_k^i + \sum_{\substack{p=1 \\ p \neq k}}^{3} \overset{\vee}{J}_{pk}^i \qquad (p_1 + p_2 = p); \ k = 1, 2, 3; \ i = 1, 2, \ldots n \quad (49)$$

The diffusion mass flux at the interface is defined by means of empirical relationships which use mass transfer coefficients determined experimentally (transfer closure law)

$$\overset{\vee}{J}_{pk}^i = K_{pk}^i \left(Y_p^i - \frac{Y_k^i}{H_{pk}^i}\right) \qquad (50)$$

The dependence of the overall mass transfer coefficient K_{pk}^i on the mass transfer coefficients in individual phase is given by the equation

$$\frac{1}{K_{pk}^i} = \frac{1}{k_k^i} + \frac{H_{pk}^i}{k_p^i} \qquad (51)$$

where H_{pk}^i is the approximate slope of the equilibrium curve of component i between phases p and k.

Mass transfer coefficients are usually presented in the form of empirical correlations of dimensionless numbers, which determine particular mass transfer process. These correlations can be found in monographs on mass transfer (Sherwood et al, 1975; Cussler, 1997; Taylor and Krishna, 1993) for various structures of packings and phases as well as in numerous publications specially devoted to trickle-bed reactors (Dwivendi and Upadhyah, 1977; Fukushima and Kusaka, 1977; Tan and Smith, 1980; Goto and Smith, 1975; Iliuta et al., 1999; Dudukowic et al., 1996). Among the cited references of

particular importance is the study by Iliuta et al. (1999). The authors employ a wide – ranging data base (3200 measurements) for correlations of liquid and gas-side mass transfer coefficients. The correlations have been elaborated by using a combination of artificial neural network and dimensional analysis.

In processes with very low liquid flow rates the outer catalyst's surface may not be fully wetted and then an additional transfer closure law has to be used which determines the wetting efficiency of the bed (Al-Dahhan and Dudukovic, 2006).

As the mass balance (49) concerns homogeneous phases detailed explanation demands the stationary solid phase composed of porous catalyst particles. The catalyst particle is a very complex geometrical structure usually characterised by pore size distribution. As intraparticle transport limitations often play an important role in the design of chemical reactors, the relationship between the structure of the porous medium and the transport phenomena is crucial in modelling of processes taking place in the catalyst particle. In the majority of mathematical models of transport phenomena in porous media the pellet is assumed to be pseudohomogenous and isotropic representing a monodispersed pore size distribution with a mean pore diameter. Therefore the parameters in used models are effective values like e.g. bulk diffusivity

$$D_s^{ijef} = \frac{\varepsilon}{\tau} D_s^{ij} \tag{52}$$

or Knudsen diffusivity

$$D_s^{iKef} = \frac{\varepsilon}{\tau} D_s^{iK} \tag{53}$$

where ε is the mean porosity of the particle and τ the tortuosity of pores forming transport channels for reagents to and from the active centres of the catalyst.

However, it has to be noticed that the pore size distribution of a catalyst pellet can in some cases range from micropores to macropores, thus representing a two-modal distribution. As mentioned before the choice of an appropriate relationship defining the molecular mass flux $\vec{J}_s^i$ is crucial for accurate modelling of phenomena taking place in the catalyst pellet. In many models mass transport in a porous, granular catalyst is described by the Fick's law

$$J_s^i = -\rho_s D_s^{ief} \nabla Y_s^i \tag{54}$$

assuming D_s^{ief} to be constant and defined by the equation

$$\frac{1}{D_s^{ief}} = \frac{1}{D_s^{ijef}} + \frac{1}{D_s^{Kief}} \tag{55}$$

However, this equation is valid only in two quite special cases:
- when mass transport is controlled by Knudsen diffusion, i.e. pressure is low or the diameter of the catalyst pore is comparable with the free path of gas molecules.
- when an isomerisation reaction is taking place on catalyst surfaces, thereby giving rise to equimolar binary diffusion.

In all other cases, Eq (55) has to be replaced by a more general equation for multicomponent mass transport. According to many authors the dusty gas model (Jackson, 1977; Mason and Malinauskas, 1983) is consirered to be the most general model.It combines bulk diffusion defined by Maxwell-Stefan relations and Knudsen diffusion. Additional mass flux of component i is generated by viscous flow of the reaction mixture which is caused by the pressure gradient in the catalyst pellet according to the Darcy's law. This mass flux is added to the combined diffusion flux defining in this way a total mass

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flux $\vec{N}_i$ of the component which in consequence leads to the elimination of the mixture velocity $\vec{V}_s$ from the averaged mass balance (49).

The following equation defines the dusty gas model

$$\frac{\vec{N}_s^i}{D_s^{Kief}} + \sum_{j=1}^{n} \frac{y_s^j \vec{N}_s^i - y_s^i \vec{N}_s^j}{D_s^{ijef}} = -\frac{P}{RT}\nabla y_s^i - \frac{y_s^i}{RT}\left(1 + \frac{B_0 P}{\mu_s D_s^{Kief}}\right)\nabla P \qquad i = 1, 2, \dots n \qquad (56)$$

where B_0 is the permeability factor of the porous pellet.

Summation of the above equation over all components i yields the pressure gradient in the pellet which introduced into Eq. (56) leads to the final form of the dusty gas model

$$\frac{\vec{N}_s^i}{D_s^{Kief}} + \sum_{j=1}^{n} \frac{y_s^j \vec{N}_s^i - y_s^i \vec{N}_s^j}{D_s^{ijef}} =$$

$$-\frac{P}{RT}\nabla y_s^i - \frac{y_s^i}{RT}\left(1 + \frac{B_0 P}{\mu_s D_s^{Kief}}\right) \frac{\displaystyle\sum_{j=1}^{n} \frac{\vec{N}_s^j}{D_s^{Kjef}}}{1 + \frac{B_0 P}{\mu_s} \displaystyle\sum_{j=1}^{n} \frac{y_s^j}{D_s^{Kjef}}} \qquad i = 1, 2, \dots n \qquad (57)$$

In order to obtain relations in the form of the generalized Fick's law for multicomponent mixtures, the above equations have to be inverted with respect to the concentration gradients (Burghardt and Patzek, 1983) or the separately calculated value of the total mass flux N_s^i in the porous pellet can be introduced into the mass balance of the catalyst phase (49).

Finally the averaged mass balance of component i in the catalyst phase can be presented as

$$\frac{\partial}{\partial t}\left(\alpha_s \rho_s Y^i\right) = -\nabla \cdot \left(\alpha_s M_s^i \vec{N}_s^i\right) + f_s \alpha_s \rho_s M_s^i \sum_{r=1}^{R_s} v_{rs}^i \eta_{rs} r_{rs} + \sum_{p_1} \dot{m}_{ps} Y_p^i - \sum_{p_2} \dot{m}_{sp} Y_s^i + \sum_{p=1}^{3} \overset{\vee}{J}_{ps}^i \quad (58)$$

where f_s is the wetting efficiency of the catalyst pellet (Al-Dahhan and Dudukovic, 2006) and η_{rs} the effectiveness factor of the r-th reaction.

The effectiveness factor for the first or pseudo-first order reaction can be calculated by means of analytical formulae given in a monographs on chemical reaction engineering (Froment and Bischoff, 1990). For a nonlinear kinetics of a single reaction (e.g. Langmuir-Hinshelwood kinetics) one can use the approximate formulae given in (Haynes jr., 1998; Burghardt and Bartelmus, 2001).

For a multicomponent and multireaction system the set of differential equations defining the mass and energy transport in the porous catalyst pellet must be integrated in order to estimate the effectiveness factor for every reaction. A coherent numerical procedure to solve this problem has been presented by Burghardt and Patzek (1993).

The interphase mass flux of component i is calculated by the equation

$$\overset{\vee}{J}_{ps}^i = k_{ps}^i \left(Y_p^i - Y_s^i\right) \qquad (59)$$

In cases when the mass transfer resistance is negligibly small the concentrations of the species in the catalyst phase become nearly equal to those in the p-phases in contact with the catalyst phase. As a result, the term characterising heterogeneous reaction rates in Eq. (58) can be substituted into the balance Eq. (49) of these p-phases replacing the homogenous reaction terms. As a result, the mass balance of the catalytic phase can be eliminated which considerably simplifies the computations.

4.2. Continuity equation

The continuity equation can be obtained by summing up Eq. (49) over all the components $i=1, 2,…n$ of the phase k, taking into account the following relationships

$$\sum_{i=1}^{n} Y_k^i = 1 \tag{60}$$

$$\sum_{i=1}^{n} \vec{J}_k^i = 0 \tag{61}$$

and transforming the reaction source term in the following way

$$\sum_{i=1}^{n} \alpha_k M_k^i \sum_{r=1}^{R_k} v_{rk}^i r_{rk} = \alpha_k \sum_{r=1}^{R_k} r_{rk} \sum_{i=1}^{n} v_{rk}^i M_k^i = 0 \tag{62}$$

This term becomes equal to zero because $\sum_{i=1}^{n} v_{rk}^i M_k^i = 0$ is the stoichiometric equation of the r-th reaction in phase k.

The continuity equation then takes the following form

$$\frac{\partial}{\partial t}(\alpha_k \rho_k) + \nabla \cdot (\alpha_k \rho_k \vec{V}_k) = \sum_{p_1} \overset{\vee}{m}_{pk} - \sum_{p_2} \overset{\vee}{m}_{kp} \qquad (p_1+p_2=p); \; k = 1, 2, 3 \tag{63}$$

The right-hand side of this equation presents the convective mass exchange between the phases, which can occur in condensation and evaporation. If there is no convective mass exchange between phases, the classical continuity equation is obtained

$$\frac{\partial}{\partial t}(\alpha_k \rho_k) + \nabla \cdot (\alpha_k \rho_k \vec{V}_k) = 0 \tag{64}$$

4.3. Momentum balance

This balance can be derived from Eq. (39) by setting

$$\Psi_k = \vec{V}_k \tag{65}$$

and equating the molecular flux to the stress tensor

$$J_k = -\vec{\vec{\pi}}_k = P_k I - \vec{\vec{\tau}}_k \tag{66}$$

in which $\vec{\vec{\tau}}_k$ is the viscous stress tensor representing the molecular momentum flux defined by the strain-stress relations (constitutive closure law)

$$\vec{\vec{\tau}}_k = \mu_k \left(\nabla \vec{V}_k + (\nabla \vec{V}_k)^T\right) + \left(\chi_k - \frac{2}{3}\mu_k\right)\nabla \cdot \vec{V}_k I \tag{67}$$

In this equation μ_k is the shear and χ_k the bulk viscosity, usually neglected in calculations because of the lack of reliable values.

According to Eqs (41) and (66) the interphase molecular momentum exchange is given by

$$\overset{\vee}{J}_{pk} = \vec{R}_{pk} = \left\langle -\vec{\vec{\pi}}_p \cdot \vec{n}_{pk} \frac{\partial L_p}{\partial n_{pk}} \right\rangle \tag{68}$$

which determines interphase friction force, pressure changes and other interphase effects and has to be estimated experimentally. It is subject to the following conditions

$$\vec{R}_{pk} = -\vec{R}_{kp} \quad \text{and} \quad \vec{R}_{kk} = 0 \tag{69}$$

The source term is equated with the body force (constitutive closure law)

$$S_k = \vec{g}_k \tag{70}$$

Thus, the averaged momentum balance can be presented as

$$\frac{\partial}{\partial t}\left(\alpha_k \rho_k \vec{V}_k\right) + \nabla \cdot \left(\alpha_k \rho_k \vec{V}_k \vec{V}_k\right) =$$

$$-\alpha_k \nabla P_k + \nabla \cdot \left(\alpha_k \vec{\vec{\tau}}_k\right) + \alpha_k \rho_k \vec{g}_k + \sum_{p_1} \overset{\vee}{m}_{pk} \vec{V}_p - \sum_{p_2} \overset{\vee}{m}_{kp} \vec{V}_k + \sum_{\substack{p=1 \\ p \neq k}}^{3} \vec{R}_{pk} \qquad k = 1, 2, 3 \tag{71}$$

If there is no convective mass exchange, the term expressing interphase actions represents only interaction forces between the phases *p* and *k*, and is usually defined as (transfer closure law)

$$\vec{R}_{pk} = F_{pk}\left(\vec{V}_p - \vec{V}_k\right) \tag{72}$$

where F_{pk} is the volumetric coefficient of the interphase momentum exchange determined experimentally.

Among numerous studies (Al-Dahhan et al., 1997; Al-Dahhan and Duduković, 1994; Szlemp et al., 2001; Wammes et al., 1991; Bartelmus, 1993; Burghardt et al., 1995) there are three models which provide values of coefficients of the interphase momentum exchange F_{pk}. These include the relative permeability model of Saez and Carbonell (1985), the single slit model of Holub et al. (1992) and the two-fluid phase interaction model of Attou et al. (2000). The form of the relationship which defines interaction forces between the phases has been developed from the Ergun equation.

The relative permeability model as well as the slit model neglect the interphase force between the gas and liquid phases, thus assuming zero drag force at the gas – liquid interface. Obviously, this can only be true for very low flow rates of both phases. Thus only the two-fluid phase interaction model provides formulae for the coefficients of interphase momentum exchange which determine all the interaction forces in a three-phase flow system (gas, liquid, solid particles). The exchange coefficients F_{pk} defined by the equations proposed by Attou et al. (2000) are presented below:

- gas-liquid momentum exchange coefficient:

$$F_{GL} = \alpha_G \left[\frac{E_1 \mu_G (1 - \alpha_G)^2}{\alpha_G^2 d_p^2} \left(\frac{\alpha_S}{1 - \alpha_G}\right)^{0.667} + \frac{E_2 \rho_G (V_G - V_L)(1 - \alpha_G)}{\alpha_G d_p} \left(\frac{\alpha_S}{1 - \alpha_G}\right)^{0.333} \right] \tag{73}$$

- gas-solid momentum exchange coefficient:

$$F_{GS} = \alpha_G \left[\frac{E_1 \mu_G (1 - \alpha_G)^2}{\alpha_G^2 d_p^2} \left(\frac{\alpha_S}{1 - \alpha_G}\right)^{0.667} + \frac{E_2 \rho_G V_G (1 - \alpha_G)}{\alpha_G d_p} \left(\frac{\alpha_S}{1 - \alpha_G}\right)^{0.333} \right] \tag{74}$$

- liquid-solid momentum exchange coefficient:

$$F_{LS} = (1 - \alpha_S) \left[\frac{E_1 \mu_L \alpha_S^2}{\alpha_L^2 d_p^2} + \frac{E_2 \rho_L V_L \alpha_S}{\alpha_L d_p} \right] \tag{75}$$

The constants E_1 and E_2, called the Ergun constants, are determined experimentally for a dry bed, using only gas flow through the bed.

The drag force exerted by the fluid (gas and liquid) on the catalyst phase is balanced by the gravity force and the interactions between particles and between particles and walls of the reactor. Thus, an established equilibrium between the drag force, gravitational force and contact forces and torques between neighboring particles as well as particle and walls holds the catalyst phase stationary and therefore the momentum balance for this phase is omitted.

4.4. Energy balance

The variable ψ_k represents the total energy which includes the internal energy and the kinetic energy

$$\Psi_k = E_k = u_k + \frac{1}{2}V_k^2 = u_k + K_k \tag{76}$$

The flux J_k comprises the molecular heat flux (heat conduction) and the energy flux generated by the mechanical effect which represents the work performed by the stress tensor $\vec{\vec{\pi}}_k$ (constitutive closure law)

$$J_k = \vec{q}_k - \vec{\vec{\pi}}_k \cdot \vec{V}_k \tag{77}$$

The heat flux is given by the relation (constitutive closure law)

$$\vec{q}_k = -\lambda_k \nabla T_k \tag{78}$$

where λ_k is the heat conductivity.

The source term determines physical heat sources, such as the work performed by body forces or heat of radiation, as well as heat effects generated by chemical reactions taking place in phase k. Thus,

$$S_k = \vec{g}_k \cdot \vec{V}_k + S_k' + \sum_{r=1}^{R_k} \Delta H_{rk} r_{rk} \tag{79}$$

The total energy balance takes the following form

$$\frac{\partial}{\partial t}\left(\alpha_k \rho_k E_k\right) + \nabla \cdot \left(\alpha_k \rho_k E_k \vec{V}_k\right) = -\nabla \cdot \left(\alpha_k \vec{q}_k\right) - \nabla \cdot \left(\alpha_k P_k \vec{V}_k\right)$$
$$+ \nabla \cdot \left(\alpha_k \vec{\vec{\tau}}_k \cdot \vec{V}_k\right) + \alpha_k \rho_k \vec{g}_k \cdot \vec{V}_k + \alpha_k \rho_k S_k' - \alpha_k \rho_k \sum_{r=1}^{R_k} \Delta H_{rk} r_{rk} + N_{kI} \qquad k = 1, 2, 3 \tag{80}$$

In order to eliminate the kinetic energy from the total energy balance (Eq. 80) the kinetic energy balance (Eq. 81) has been subtracted from Eq. (80)

$$\frac{\partial}{\partial t}\left(\alpha_k \rho_k K_k\right) + \nabla \cdot \left(\alpha_k \rho_k K_k \vec{V}_k\right) = -\nabla \cdot \left(\alpha_k P_k \vec{V}_k\right) + \alpha_k P_k \nabla \cdot \vec{V}$$
$$+ \alpha_k \rho_k \vec{g}_k \cdot \vec{V}_k + \nabla \cdot \left(\alpha_k \vec{\vec{\tau}}_k \cdot \vec{V}_k\right) - \alpha_k \vec{\vec{\tau}}_k : \nabla \vec{V} \tag{81}$$

and enthalpy has replaced the internal energy

$$h_k = u_k + P_k v_k \tag{82}$$

the thermal energy balance is finally obtained

$$\frac{\partial}{\partial t}\left(\alpha_k \rho_k h_k\right) + \nabla \cdot \left(\alpha_k \rho_k h_k \vec{V}_k\right) = \frac{D}{Dt}\left(\alpha_k P_k\right) - \nabla \cdot \left(\alpha_k \vec{q}_k\right) + \alpha_k \vec{\vec{\tau}}_k : \nabla \vec{V}_k$$

$$+ \alpha_k \rho_k S'_k - \alpha_k \rho_k \sum_{r=1}^{R_k} \Delta H_{rk} r_{rk} + \sum_{p_1} \overset{\vee}{m}_{pk} h_p - \sum_{p_2} \overset{\vee}{m}_{kp} h_k + \sum_{\substack{p=1 \\ p \neq k}}^{3} \overset{\vee}{Q}_{pk} \qquad k = 1, 2, 3; \ p_1 + p_2 = p \quad (83)$$

where h_k is the specific enthalpy of phase k and $\overset{\vee}{Q}_{pk}$ defines the heat exchange between the phases p and k per unit volume (transfer closure law)

$$\overset{\vee}{Q}_{pk} = U_{pk}\left(T_p - T_k\right) \qquad (84)$$

U_{pk} is the volumetric overall heat transfer coefficient which depends on heat transfer coefficients in individual phases as estimated experimentally, while $D(\alpha_k P_k)/Dt$ is the substantial derivative of pressure in the phase k

$$\frac{D(\alpha_k P_k)}{Dt} = \frac{\partial(\alpha_k P_k)}{\partial t} + \vec{V}_k \cdot \nabla(\alpha_k P_k) \qquad (85)$$

The term $\alpha_k \vec{\vec{\tau}}_k : \nabla V_k$ in Eq. 83 (which represents energy dissipated as a result of viscous friction) is usually neglected in computations, because its value is extremely small in comparison to other terms and begins to be comparable only at very high fluid velocities (which generate large velocity gradients) or for fluids of very high viscosities. Similarly, the term expressing the heat of radiation S'_k is important only in processes at very high temperature and therefore is not taken into account while modelling processes in trickle-bed reactors.

Heat transfer coefficients in individual phases can be taken from the VDI Heat Atlas (Verein Deutscher Ingenieure, 2010) which provides a wide range of such correlations for various packing structures of a fixed bed. There is also the possibility of using the formulae for mass transfer coefficients estimated for a trickle-bed reactor based on the heat – mass transfer analogy and substituting the Nusselt number for the Sherwood number and the Schmidt number for the Prandtl number.

For further analysis of thermal energy balance it is more convenient to write the left hand-side of this balance somewhat more compactly using the substantial derivative derived by exploiting the continuity equation. The thermal energy balance takes then the following form:

$$\alpha_k \rho_k \frac{Dh_k}{Dt} = -\nabla \cdot \left(\alpha_k \vec{q}_k\right) + \frac{D}{Dt}\left(\alpha_k P_k\right) - \alpha_k \rho_k \sum_{r=1}^{R_k} \Delta H_{rk} r_{rk} + N_{kI} \qquad (86)$$

For most engineering calculations it is desirable to express the thermal energy balance (Eq. 86) in terms of fluid temperature T_k. As the specific enthalpy is a function of temperature and pressure i.e.

$$dh = \frac{\partial h_k}{\partial T_k} dT_k + \frac{\partial h_k}{\partial P_k} dP_k = C_p dT_k + \left[\nu_k - T_k\left(\frac{\partial \nu_k}{\partial T_k}\right)_{P_k}\right] dP_k \qquad (87)$$

substituting this relation into Eq. (86) leads finally to thermal energy balance in terms of T_k applied to trickle-bed reactors:

$$\alpha_k \rho_k \frac{DT_k}{Dt} = -\nabla \cdot \left(\alpha_k \vec{q}_k\right) + P_k \frac{D\alpha_k}{DT} + \alpha_k \left(\frac{\partial \ln \nu_k}{\partial \ln T_k}\right) \frac{DP_k}{Dt}$$

$$- \alpha_k \rho_k \sum_{r=1}^{R_k} \Delta H_{rk} r_{rk} + \sum_{p_1} \overset{\vee}{m}_{pk} h_p - \sum_{p_2} \overset{\vee}{m}_{kp} h_k + \sum_{\substack{p=1 \\ p \neq k}}^{3} \overset{\vee}{Q}_{pk} \qquad (88)$$

The parameters in the heat balance of the catalyst phase (83) are effective values. Thus, the effective conductivity of this phase is a function of the conductivity values of both the solid phase and of the gaseous mixture in pores and the particle porosity (Verein Deutscher Ingenieure, 2010). The velocity of the gaseous mixture in pores is usually neglected thus the thermal energy balance for the catalyst phase is presented as

$$\frac{\partial}{\partial t}\left(\alpha_s \rho_s h_s\right) = -\nabla \cdot \left(\alpha_s \vec{q}_s\right) - \alpha_s \rho_s \sum_{r=1}^{R_k} \Delta H_{rs} \eta_{rs} r_{rs}$$
$$+ \sum_{p_1} \dot{m}_{ps} h_p - \sum_{p_2} \dot{m}_{sp} h_s + \sum_{\substack{p=1 \\ p \neq s}}^{3} \overset{\vee}{Q}_{ps} \qquad k=1, 2, 3; \; p_1+p_2 = p \qquad (89)$$

Similarly, as in the analysis of the mass balances of components, if heat transfer resistance is negligibly small the thermal energy balance for the catalyst phase can be neglected and the term characterising reactions' heat effects substituted into the *p* balances in contact with the catalyst phase.

5. CONCLUSIONS

In this study a method of developing averaged, macroscopic equations of three-phase flow is presented. Basic equations of the method are local, instantaneous balance equations, which rigorously describe flow dynamics of each of the three phases, together with interfacial boundary conditions called jump conditions. The variable ψ_k per unit mass chosen as the independent variable represents a scalar or vector quantity which can be the concentration of a species in the fluid mixture, the total energy of the mixture as well as the vector quantity defining the fluid mixture velocity and thus includes the three conservation equations of mass, momentum and energy.

A macroscopic model of three-phase flow was formulated by means of appropriate averaging methods with respect to the local, instantaneous equations which determine the averaged values of flow parameters and physicochemical properties.

As it is assumed that the averaged model should also encompass separated flows, Euler's volume average was employed although in most publications the time average is used which is better adapted to dispersed flows. As a result of averaging the terms of interfacial transport of mass, momentum and energy the transfer closure laws i.e. the so-called relationships of interphase interactions are introduced into the balance equation for the variable ψ_k. These relationships are mostly empirical and have to be estimated experimentally. The method of weighted averaging together with the Reynolds decomposition is used to derive the final form of the averaged balance equations which define averaged variables of a system. This set of differential equations together with jump conditions fully defines the averaged three-phase flow.

Substituting the mass fraction of component *i* in the phase *k*, the velocity of phase *k* or the total energy of phase *k* for Ψ_k, the averaged balances of mass, momentum and energy, respectively, are derived. The averaged conservation equations in a trickle-bed reactor (mass, momentum, energy) are developed and discussed in detail, especially with respect to the relationships which define transfer closure laws i.e. interaction between phases.

SYMBOLS

A	surface area, m^2
B$_0$	permeability factor, m^2

C	molar density, kmol m^{-3}
D^{ij}	binary diffusion coefficient, m^2 s^{-1}
D^{ki}	Knudsen diffusion coefficient, m^2 s^{-1}
$\check{D}_{ij}$	multicomponent diffusion coefficient, m^2 s^{-1}
d_p	particle diameter, m
E_1, E_2	Ergun constants (-)
E	total energy, kJ kg^{-1}
F_{pk}	coefficient of interphase momentum transfer, kg m^{-3} s^{-1}
ΔH_r	heat effect of r-th reaction, kJ kmol^{-1}
h_k	specific enthalpy, kJ kg^{-1}
J_k	generalised molecular flux of
	- mass, kg m^{-2} s^{-1}
	- momentum, (kg m s^{-1}) m^{-2} s^{-1}
	- energy, kJ m^{-2} s^{-1}
$\breve{J}_{pk}$	generalised interphase molecular flux of
	- mass, kg m^{-3} s^{-1}
	- momentum, (kg m s^{-1}) m^{-3} s^{-1}
	- energy, kJ m^{-3} s^{-1}
$\vec{J}_{pk}^{\,i}$	diffusional flux of component, kg m^{-2} s^{-1}
$\breve{J}_{pk}^{\,i}$	interphase diffusional flux of component i, kg m^{-3} s^{-1}
K_k	kinetic energy, kJ kg^{-1}
k_{pk}^{i}	mass transfer coefficient, kg m^{-3} s^{-1}
k_{pk}^{q}	heat transfer coefficient, W m^{-3} K^{-1}
$L_k(\vec{r},t)$	phase indicator (-)
M_k^i	molar mass of component i, kg kmol^{-1}
$\dot{m}$	convective mass flux, kg m^{-2} s^{-1}
$\dot{m}_{kp}$	interphase convective mass flux $\left(= \rho_k(\vec{v}_k - \vec{v}_l)\cdot\vec{n}_{kp}\right)$, kg m^{-2} s^{-1}
$\check{m}_{kp}$	averaged interphase convective mass flux per unit volume, kg m^{-3} s^{-1}
N_S^i	total molar flux in the catalyst phase, kmol m^{-2} s^{-1}
N_I	interphase interaction term
$\vec{n}_k$	unit vector normal to the interface and directed out of phase k (-)
P	pressure, Pa
q_k	heat flux, kJ m^{-2} s^{-1}
$\check{Q}_{pk}$	interphase heat flux, kJ m^{-3} s^{-1}
$\vec{R}_{pk}$	interphase molecular momentum flux, (kg m s^{-1}) m^{-3} s^{-1}
r_{rk}	reaction rate of r-th reaction in phase k, kmol kg^{-1} s^{-1}
U	overall heat transfer coefficient, W m^{-3} K^{-1}
u_k	internal energy, kJ kg^{-1}
V	volume, m^3
$\vec{V}$	the weighted average fluid velocity, ms^{-1}
$\vec{v}$	velocity, ms^{-1}
$\vec{v}_I$	displacement velocity of the interface, m s^{-1}
v_k	specific volume, m^3 kg^{-1}

Y_k^i	mass fraction of component i in phase k (-)
y_k^i	mole fraction of component i in phase k (-)

Greek symbols

α_k	volume fraction of phase k
δ_{kI}	Dirac's delta function (-)
χ_k	bulk viscosity, Pa s
μ_k	shear viscosity, Pa s
v_{rk}^i	stoichiometric coefficient of component i of the r-th reaction in phase k (-)
$\vec{\vec{\pi}}_k$	stress tensor in phase k, N m^{-2}
ρ_k	density, kg m^{-3}
$\vec{\vec{\tau}}_k$	viscous stress tensor in phase k, N m^{-2}
ψ_k	generalised variable (scalar or vector)

Subscripts

k=1, 2, 3	phase
kp	interface between phases p and k
I	interface

Superscripts

i	component
V	quantity per unit volume

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APPENDIX

The procedure of averaging Eq. (38) is performed by analyzing separately its individual terms.

Term I of the left-hand side

$$\frac{\partial}{\partial t}\left\langle L_k \rho_k \Psi_k + L_k \rho_k \psi'_k \right\rangle = \frac{\partial}{\partial t}\left(\Psi_k \left\langle L_k \rho_k \right\rangle\right) + \frac{\partial}{\partial t}\left\langle L_k \rho_k \psi'_k \right\rangle = \frac{\partial}{\partial t}\left(\alpha_k \rho_k^{L_k} \Psi_k\right) \qquad (A1)$$

as according to Eq. (37), the second expression in (A1) equals zero.

Term II of the left-hand side

$$\nabla \cdot \left\langle L_k \rho_k \Psi_k \vec{V}_k \right\rangle + \nabla \cdot \left\langle L_k \rho_k \Psi_k \vec{v}'_k \right\rangle + \nabla \cdot \left\langle L_k \rho_k \psi'_k \vec{V}_k \right\rangle + \nabla \cdot \left\langle L_k \rho_k \psi'_k \vec{v}'_k \right\rangle$$
$$= \nabla \cdot \left(\Psi_k \vec{V}_k \left\langle L_k \rho_k \right\rangle\right) + \nabla \cdot \left(\Psi_k \left\langle L_k \rho_k \vec{v}'_k \right\rangle\right) + \nabla \cdot \left(\vec{V}_k \left\langle L_k \rho_k \psi' \right\rangle_k\right) + \nabla \cdot \left(L_k \rho_k \psi'_k \vec{v}'_k\right) \qquad (A2)$$

The second and third expression in (A2) are equal to zero, according to Eq. (36) and (37). The last expression represents the flux of variable ψ_k caused by the fluctuation of velocity $\vec{v}'_k$ and variable ψ'_k, and is presented as the phase average of the product of fluctuating variables (similarly as the molecular flux).

$$\nabla \cdot \left\langle L_k \rho_k \psi'_k \vec{v}'_k \right\rangle = \nabla \cdot \left(\alpha_k J_k^f\right) \qquad (A3)$$

Finally, the second term of the left hand side takes the following form

$$\text{Term II} = \nabla \cdot \left\langle \alpha_k \rho_k^{L_k} \Psi_k \vec{V}_k \right\rangle + \nabla \cdot \left(\alpha_k J_k^f\right) \qquad (A4)$$

Term I of the right-hand side

Averaging the source term in a similar way gives

$$\left\langle L_k \rho_k S_k \right\rangle = \alpha_k \rho_k^{L_k} S_k^{L_k S_k} \qquad (A5)$$

Introducing Eqs (A1), (A4) and (A5) into Eq. (38) leads to the averaged balance equation of the variable ψ_k (46).