

**A phenomenological model of gas-solid reactions for
populations of particles with intrinsic dynamics**

by

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A phenomenological model of the dynamics of gas-solid reaction in fluidized bed reactors is constructed. The model is of a diffusion- advection type with intrinsic dynamics of particles population. A discussion of the applicable simplifications in the model is given.

KEYWORDS: reaction-diffusion systems, gas-solid reactions, fluidized-bed reactors.

1. Introduction

Gas-solid reactions are involved in numerous chemical processes like iron oxide reduction, (extraction of metals from ores), combustion of solid fuel, coal gasification and burning of refuse, to give only a few examples. They may be conducted in a variety of technological installations, such as reactors with fixed, moving or fluidized bed, rotating kilns and cyclones, in particular. For all these installations a multitude of small solid particles is brought into contact with flowing gas. Since the particles are numerous, their reactions with gas and the resulting changes in properties cannot be considered on an individual basis. Instead, one must consider the evolution of certain randomly distributed properties for ensembles of particles.

The main characteristic of particles that affects the reactor dynamics is their reactivity, usually expressed in terms of an active surface, which in turn may depend on physical sizes and conversion levels. The ensembles over which the statistical properties are calculated may be localized (like in fixed bed), and then these statistics are position-dependent, or they may encompass the whole mixed

population of particles (like in fluidized beds), and then the statistics are solely time-dependent.

The evolution of the statistical properties of particle population in reactor interacts essentially with some other processes including chemical reactions, gas flows, diffusion, transport and thermal phenomena. There are many publications devoted to problems of reactor dynamics, e.g.[6], [11], [21]. Although several of the factors affecting the process development are taken there into account, but as usual the statistical description of particles is considered only in static approximation.

In this paper we propose to treat the statistics of particle population as an additional state variable. This variable is to be incorporated into the governing equations of the model. To be more specific, we have considered the case of fluidized bed reactor with a simple particle population consisting of full balls that reacted only at the outer surface; the distribution of diameters was the only important characteristics for that population. The model does not fully reflect complex nature of hydrodynamic flows around the population of particles. Rather than treating hydrodynamic variables as components of the state of process, we include them in parametrized form.

The approach we propose may easily be extended to other space-dependent properties of particles, in particular to conversion levels for porous particles.

The work was motivated by a study on fluidized bed coal gasifiers partially supported by the Research Program CPBP-01.16-7.5.

2. Structure of the reactor and simplifying assumptions

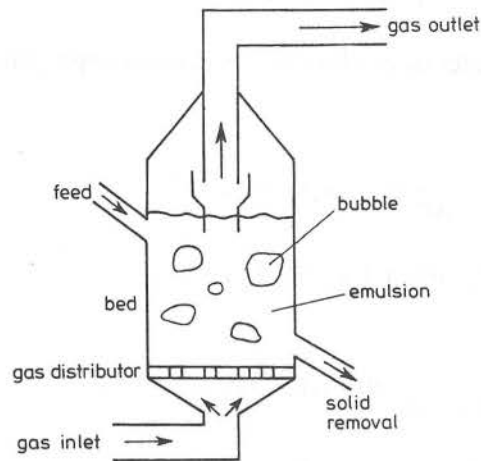
Following the available literature [11], [18], [21] we have assumed that a typical fluidized bed reactor consists of:

- a chamber containing the fluidized bed,
- a feeder for supplying solid pellets,
- a fluidizing gas inlet,
- a drain for removing partially reacted particles,
- an outlet for gaseous products.

In order to develop the appropriate numerical simulation procedures, we assume a number of simplifying hypotheses, similarly as in [11]:

- A1.** A fluidized bed contains only emulsion and bubble phases. The transition region near gas inlet is neglected. The bubble and emulsion phases are uniformly mixed.
- A2.** The surplus gas flows through the bed only in bubbles. It means that the emulsion preserves a fixed gas-solid ratio, corresponding to the critical fluidization stage.

A3. The emulsion phase is perfectly mixed, i.e. the statistical properties of solid particles are the same in any point of the bed.

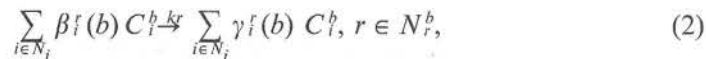
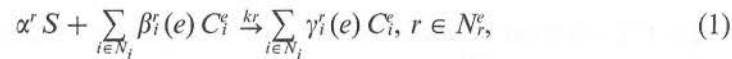


Rys. 1

A schematic form of such a reactor is shown in Fig.1.

3. Chemical reactions

Let us first introduce a few notation. We shall assume that the reactor contains a certain number N_i of active gaseous ingredients and their concentrations un emulsion and bubble phases are C_i^e , C_i^b respectively. Let S denote the solid component, and A_s the active surface of solid particles per mol. The chemical processes taking place in the reactor may be represented as:



where N_r^b , N_r^e are sets of reactions in bubble and emulsion phases (some of them may overlap). The integers $\beta_i^e(e)$, $\beta_i^b(b)$, $\gamma_j^e(e)$, $\gamma_j^b(b)$, α^r denote stoichiometric coefficients of reactions.

For any gas ingredient let us introduce now the generic sets of reactions:

$$P^e(i) = \{r \mid \gamma_i^e(e) > 0\}, \quad P^e(i) \subset N_r^e,$$

$$P^b(i) = \{r \mid \gamma_i^b(b) > 0\}, \quad P^b(i) \subset N_r^b \quad (3)$$

and similar sets of reactions where it is consumed:

$$K^e(i) = \{r \mid \beta_i^r(e) > 0\} \quad K^e(i) \subset N_r^e$$

$$K^b(i) = \{r \mid \beta_i^r(b) > 0\}, \quad K^b(i) \subset N_r^b. \quad (4)$$

Then we can write down the rates of production for gases in appropriate phases, denoted by R_i^e and R_i^b .

$$R_i^e = \sum_{r \in P^e(i)} \frac{1}{\gamma_i^r(e)} \theta(\alpha^r) A_S k_r \prod_{j \in N_i} (C_j^e)^{\beta_j^r(e)}, + \\ - \sum_{r \in K^e(i)} \theta(\alpha^r) A_S k_r \prod_{j \in N_i} (C_j^e)^{\beta_j^r(e)}, \quad (5)$$

$$R_i^b = - \sum_{r \in P^b(i)} \frac{1}{\gamma_i^r(b)} \theta(\alpha^r) A_S k_r \prod_{j \in N_i} (C_j^b)^{\beta_j^r(b)} + \\ - \sum_{r \in K^b(i)} \theta(\alpha^r) A_S k_r \prod_{j \in N_i} (C_j^b)^{\beta_j^r(b)}, \quad (6)$$

where

$$\theta(\alpha^r) = \begin{cases} 1 & \text{if } \alpha^r > 0 \\ 0 & \text{if } \alpha^r = 0 \end{cases}$$

Coefficients k are the reaction's rate constants given by

$$k_r = k_{r0} \cdot \exp(-E_r / RT). \quad (7)$$

Eqns (5), (6) must be accompanied by a similar rate of change for the reacting solid component of the bed,

$$R_S = - \sum_{r \in N_r^e(r,i)} \theta(\alpha^r) A_S k_r \prod_{j \in N_i} (C_j^e)^{\beta_j^r(e)}, \quad (8)$$

Further we shall treat the reactor as a dynamical system with state variables consisting of

$$\tilde{C} = (\tilde{C}^b, \tilde{C}^e), T$$

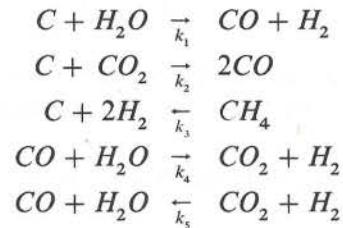
and certain statistics of particles that determine A_S . Eqns. (5) (6) (8) taken together yield the system

$$R_i^b = R_i^b(\tilde{C}^b, T),$$

$$R_i^e = R_i^e(\tilde{C}^e, T, A_s), \quad (9)$$

$$R_s = R_s(\tilde{C}^e, T, A_s).$$

In the above formulation the description of a reactor is rather abstract. To become more specific let us take a coal gasifier with fluidized bed fed by hot steam (appr. 1000 K) as an example. The reactions are [11]:

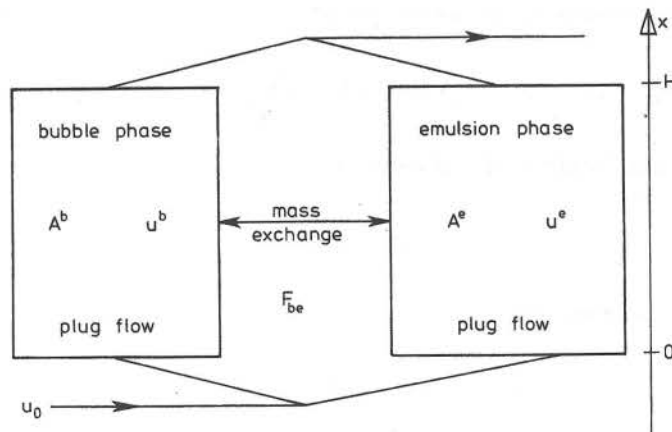


with the sets of indices

$$N_f^e = \{1,2,3,4,5\}, N_f^b = \{4,5\}.$$

4. Gas flow and advection-diffusion processes

For the reactor we consider a part of the hydrodynamic model is based on results of [11], [21] and the discussion in [5]. Although the setting is rather simple, it should be sufficient enough for describing low-pressure installations. As shown in Fig.2, the gas flow is split into two practically independent branches that correspond to the emulsion and bubble phases.



Rys. 2

Two principal parameters of the flow are:

- u_{mf} : minimal gas velocity necessary for fluidization,
- ε_{mf} : gas fraction in the emulsion phase,

both are obtained experimentally as a rule. Our goal here is to determine the flow in each phase, i.e. u^b , u^e , A^b , A^e , the exchange coefficient F_{be} and the bed height H .

Knowing ε_{mf} , we may compute the bed height corresponding to the critical fluidization condition:

$$H_{mf} = \frac{W}{A(1 - \varepsilon_{mf})\rho} \quad (10)$$

Further on, using empirical relationships established in [13], [21], we have the characterization of bubbles by their minimal diameter

$$D_{bo} = 0.00376(U_o - u_{mf})^2, \quad (11)$$

maximal diameter,

$$D_{bm} = 0.652A(U_o - u_{mf})^{0.4}, \quad (12)$$

and the distribution of diameters along the height of the bed (x-axis in Fig. 2),

$$D_b(x) = D_{bm} - (D_{bm} - D_{bo}) \exp(-0.3x / D). \quad (13)$$

The next step consists in approximating the bubbles by „equi-diametric” ones that correspond to the height $x = H / 2$,

$$\bar{D} = D_b(H / 2), \quad (14)$$

and computing the gas velocity in bubble phase,

$$u^b = u_o - u_{mf} + 0.711 \sqrt{g \bar{D}_b}. \quad (15)$$

This yields the volume fraction of bubble phase,

$$\delta = (u_o - u_{mf}) / u_b, \quad (16)$$

the gas velocity in emulsion phase,

$$u^e = u_{mf}(1 - \delta), \quad (17)$$

and finally the bed height,

$$H = H_{mf}(1 - \delta). \quad (18)$$

The empirical value of exchange coefficient is taken as

$$F_{be} = 0.11 / \bar{D}_b. \quad (19)$$

The whole construction just completed can be summarised as follows: the bed height given as an implicit function of the bed weight, incoming gas velocity and constant parameters u_{mf} , ε_{mf} :

$$\Phi(H, W, u_o, u_{mf}, \varepsilon_{mf}) = 0. \quad (20)$$

Equation (20) must be solved with respect to H .

Having the characteristics of gas flow, we may write down the diffusion-advection equations governing the transport of gaseous substances in the bed:

$$\begin{aligned} \frac{\partial C_i^b}{\partial t} &= -u^b \frac{\partial C_i^b}{\partial x} + D_i^b \frac{\partial^2 C_i^b}{\partial x^2} - F_{be}(C_i^b - C_i^e) + R_i^b, \\ \frac{\partial C_i^e}{\partial t} &= -\frac{u^e}{\varepsilon_{mf}} \frac{\partial C_i^e}{\partial x} + \frac{D_i^e}{\varepsilon_{mf}} \frac{\partial^2 C_i^e}{\partial x^2} + \frac{\delta}{1 + \delta} \frac{F_{be}}{\varepsilon_{mf}} (C_i^b - C_i^e) + \frac{R_i^e}{\varepsilon_{mf}}, \end{aligned} \quad (21)$$

$$x \in (0, H), t > 0, i \in N_i$$

As the emulsion phase is well mixed, by assumption

$$D_i^e \gg D_i^b. \quad (22)$$

System (21) is to be complemented by the boundary conditions:

$$\begin{aligned} x = 0 : \quad C_i^e - \frac{D_i^e}{u^e} \frac{\partial C_i^e}{\partial x} &= C_{i0}, \\ C_i^e - \frac{D_i^e}{u^e} \frac{\partial C_i^e}{\partial x} &= C_{i0}, \\ x = H : \quad \frac{C_i^b}{\partial x} &= 0, \\ \frac{\partial C_i^e}{\partial x} &= 0, \end{aligned} \quad (23)$$

and initial conditions for $t = 0$:

$$C_i^b = C_i^b = C_{i0}. \quad (24)$$

The above conditions mean that the reactor is fed by gas of constant composition, and no chemical reaction takes place above the bed.

5. Thermal energy flow

The heat effects inside the bed are produced by two sources: Q_{vol} — heat released by volume reactions in gas and Q_{surf} — heat released by gas-solid reactions on surfaces of particles. The intensities of both effects are proportional to the appropriate reactions rates. Let us split the reactions into the corresponding sets:

$$\begin{aligned} N_r^v &= \{r \in N_r^e \mid \alpha^r = 0\} \cup N_r^b, \\ N_r^s &= \{r \in N_r^e \mid \alpha^r > 0\}. \end{aligned} \quad (25)$$

The heat production rates may then be expressed as:

$$Q_{vol} = \sum_{r \in N_r^v} (-\Delta H_r) k_r \prod_{i \in N_i} (C_i^*) \beta_i^{s_i}, \quad (26)$$

$$Q_{surf} = S \sum_{r \in N_r^s} (-\Delta H_r) k_r \prod_{i \in N_i} (C_i^e) \beta_i^{s_i}, \quad (27)$$

Besides, there occur the following thermal effects:

- heat exchange gas-reactor walls, characterised by heat transfer coefficient h_{gw} ,
- heat exchange solid particles-walls, characterised by h_{sw} ,
- heat exchange between solid and gas phases, h_{sg} ,
- heat transport by advection and diffusion.

In the first stage we shall separately consider heat transfer in the solid and gas phases, with the gas phase encompassing both bubbles and gas contained in emulsion. Hence, the gas fraction in the bed is given by

$$\varepsilon = \delta + \frac{A^e}{A} \varepsilon_{mf}. \quad (28)$$

In further reasoning, we shall partially use results from [12], [17], [6]. The mean gas velocity in both phases may be calculated as

$$u_g = (\delta u^b + \varepsilon_{mf} \frac{A^e}{A} u^e) / \varepsilon, \quad (29)$$

and the solids velocity

$$u_s = u^e. \quad (30)$$

For low-pressure reactor the influence of pressure and velocity on the internal energy of the gas is negligible, what greatly simplifies the equations.

Let us now introduce some notations more:

C_{ig} — generalised concentration of i -th gas component,

$$C_{ig} = (C_i^b + \varepsilon_{mf} \frac{A^e}{A} C_i^e) / \varepsilon; \quad (31)$$

I_g — internal energy of gas,

$$I_g = T_g \cdot \sum_{i \in N_j} C_{ig} \frac{\partial h_i}{\partial T}; \quad (32)$$

I_s — internal energy of solid,

$$I_s = c_s T_s; \quad (33)$$

T_g, T_s — temperatures of gas and solids, respectively.

In practice, partial derivatives $\frac{\partial h_i}{\partial T}$ (the specific heats of gases) can be assumed constant over some temperature ranges (cf. [11]).

Finally, if the thermal effects in gas and solids are treated separately, we must consider the division of the heat flux produced by surface reactions into two streams Q_{surf}^g and Q_{surf}^s , going into gas and solid phases, respectively:

$$Q_{surf} = Q_{surf}^g + Q_{surf}^s. \quad (34)$$

In the above notation, the energy balance for an elementary volume of the bed admits the characterisation:

rate of energy accumulation =
 heat stream from volumetric reactions Q_{vol}
 + heat stream from surface reactions Q_{surf}^g or Q_{surf}^s
 – heat loss through reactor walls
 + balance of advective streams
 + balance of diffusive streams
 + heat stream through interphase boundary.

This gives rise to the following coupled pair of differential equations:

$$\varepsilon \frac{\partial I_g}{\partial t} = Q_{vol} + Q_{surf}^g - \varepsilon \frac{\Pi D}{A} h_{wg} (T_g - T_w) +$$

$$- \varepsilon u_g \frac{\partial I_g}{\partial x} + \varepsilon K_g \frac{\partial^2 T_g}{\partial^2 x} - Sh_{gs}(T_g - T_s), \quad (35)$$

$$(1 - \varepsilon) \rho_s \frac{\partial I_s}{\partial t} = Q_{surf} - (1 - \varepsilon) \frac{\Pi D}{A} h_{ws}(T_s - T_w) + \\ - (1 - \varepsilon) u_s \rho_s \frac{\partial I_s}{\partial x} + (1 - \varepsilon) K_s \frac{\partial^2 T_s}{\partial^2 x} + Sh_{gs}(T_g - T_s), \quad (36)$$

with $\varepsilon \in (0,1)$ representing the phase ratio.

Unfortunately, some of the parameters that enter (35), (36) are non-measurable. In particular this concerns the way Q_{surf} is decomposed into two parts and heat transfer coefficients h_{wg} , h_{gs} , h_{ws} . The only measurable coefficient specifies the global heat transfer between the bed and walls. In this connection, we shall further assume that the gas and solids have the same temperature throughout,

$$T_g = T_s = T. \quad (37)$$

This hypothesis is approximately correct provided that solid particles are small enough to contribute to heat transfer faster than their movement in the bed.

Upon combining (35) and (36) in (37) we end up with a single equation for temperature distribution in the bed:

$$\frac{\partial}{\partial t} (\varepsilon I_g + (1 - \varepsilon) I_s \rho_s) = \varepsilon Q_{vol} + Q_{surf} - \frac{\Pi D}{A} h_{wb}(T - T_w) + \\ - \frac{\partial}{\partial x} (\varepsilon u_g I_g + (1 - \varepsilon) + (\varepsilon K_g + (1 - \varepsilon) K_s) \frac{\partial^2 T}{\partial^2 x}), \quad (38)$$

accompanied by initial conditions

$$T = T_o \text{ for } t = 0, x \in [0, H], \quad (39)$$

and boundary conditions encompassing the heat exchange between solids and bed:

$$\text{for } x = 0: \quad T = T_o,$$

$$\text{for } x = H: \quad (\varepsilon K_g + (1 - \varepsilon) K_s) \frac{\partial T}{\partial x} = W_{in} \rho_s I_s^{in}(T_1) - W_{out} \rho_s I_s^{in}(T). \quad (40)$$

Let us notice that equation (38) is nonlinear, because I_g represents a combination of $C_i^h \cdot T$ and $C_i^e \cdot T$.

6. Evolution of particle population

Throughout this section we shall assume that the emulsion phase contains pure reacting solid in the form of nonporous particles. Their diameters diminish in the course of reactions. In such a case the active surface of solids per unit volume of emulsion may be expressed as

$$S = \alpha A_S \quad (41)$$

where α — constant factor.

In turn, the active surface of solids per unit mass A_S , depends on the distribution of particle diameters. This contributes to the coupling between the distribution of particle diameters and reaction intensities.

The ideas for the following derivations are partially adopted from [3], [4], where a class of simplified models of reacting particle populations have been studied.

All solid particles in the bed may be classified into two groups: reacting particles and inert particles which contribute only to the mass of the bed. We shall be concerned solely with reacting particles. Therefore, two effects must be accounted for: evolution of their diameters distribution and the total mass change. By using the distribution of absolute numbers of particles as a function of radius we can combine both effects in a single equation. So instead of using the radii distribution $p(r)$, $r \in [0, r_{max}]$ we shall use function $N(r)$ that satisfies the equality

$$\int_0^{r_{max}} N(r) dr = N_S, \quad (42)$$

where N_S — the total number of reacting particles.

According to the formula (8), the local rate of mass change for solid particles may be rewritten as

$$R_S = -A_S R'_S(\tilde{C}^e, T). \quad (43)$$

For uniform balls of the radius r , the area A_S is given by

$$A_S(r) = \frac{3}{\rho_s r}. \quad (44)$$

Since the solids in emulsion phase are well-mixed, the total mass change rate due to reactions is:

$$\bar{R}_S = -A_S \bar{R}'_S(\tilde{C}^e, T),$$

where

$$\bar{R}'_S = A^e \int_0^H R'_S(\tilde{C}^e, T) dx.$$

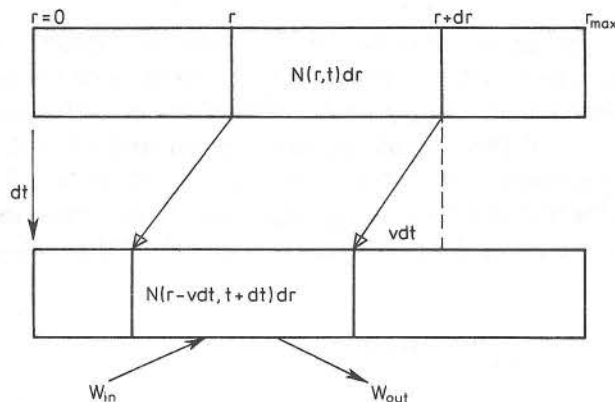
Due to (44), for ball-shaped particles the rate of shrinking for particles radii is equal

$$v = \frac{1}{3} r \bar{R}'_S A_S(r), \quad (45)$$

hence, eventually,

$$v(\tilde{C}^e, T) = \bar{R}'_S / \rho_s, \quad (46)$$

Then the balance of particle number with radii in the interval $[r, r + dr]$ may be written as (see Fig. 3):



Rys. 3

$$N(r - v dt, t + dt) dt = N(r, t) dt + N_{in}(r) dr dt - \frac{W_{out}}{W} N(r, t) dr dt. \quad (47)$$

Hence $N(r, t)$ satisfies the differential equation

$$\frac{\partial N}{\partial t} = v \frac{\partial N}{\partial r} - \frac{W_{out}}{W} N + N_{in}(r), \quad r \in [0, r_{max}], \quad (48)$$

with initial condition $N(r, 0) = N_o(r)$.

In general, the transport equation (48) has to be solved on the whole line $x \in (-\infty, \infty)$. However, since v is always positive, we may extend the functions $N_{in}(r)$, $N_o(r)$ by 0 outside the interval $[0, r_{max}]$ and solve (48) only in this interval.

In some cases the characteristics of particles fed into reactor are given in terms of radii distribution. We then use formula

$$Wp(r) = \frac{4}{3}\Pi\rho_s r^3 N(r), \quad (49)$$

where W — mass of a given portion of solids.

Let us also notice that the function $N(r,t)$ takes on extreme values and requires scaling. The normalising factor is defined as a hypothetic number of particles in the bed if all of them had the same radius $\frac{1}{2}r_{max}$: then

$$N_0 = \frac{6W}{\Pi\rho_s r_{max}^3}. \quad (50)$$

The corresponding normalised variables are

$$n(r,t) = \frac{1}{N_0} N(r,t). \quad (51)$$

Given the functions $n(r,t)$, it is easy to determine the active surface of solids per unit volume of emulsion phase

$$S(t) = \frac{4\Pi N_0}{HA(1-\delta)} \int_0^{r_{max}} n(r,t) r^2 dr. \quad (52)$$

Some discussion is needed concerning the feeding rate W_{in} . According to (20), in order to stabilise the bed height we have to maintain its weight. This implies the requirement

$$W_{in} = 4\Pi\rho_s v N_0 \int_0^{r_{max}} n(r,t) r^2 dr + W_{out}, \quad (53)$$

which must be imposed (e.g. by using a certain controller with current bed height as an input).

Eventually, the complete, normalised model of particles evolution can be given the form:

$$\begin{aligned} \frac{\partial n}{\partial t} &= v \frac{\partial n}{\partial r} - \frac{W_{out}}{W} n + \frac{3W_{in}}{4\Pi r^3 \rho_s N_0} P^{in}(r), \\ n(r,0) &= n_0(r), \quad r \in [0, r_{max}], \end{aligned} \quad (54)$$

$$W_{in}(n, \tilde{C}^e, T) = 4\pi\rho_s v N_0 \int_0^{r_{max}} n(r,t) r^2 dr + W_{out},$$

$$v = v(\tilde{C}^e, T).$$

7. Transformations of the model

The general model of reactor we have introduced consists of equations (20) (21) (38) (54). Taken together they form the system:

$$\Phi(H, W, u_0, u_{mf}, \varepsilon_{mf}) = 0,$$

$$\frac{\partial \tilde{C}_i}{\partial t} = -\frac{\partial}{\partial x}(\tilde{u} \tilde{C}_i) + \frac{\partial}{\partial x} \left(D_i \frac{\partial \tilde{C}_i}{\partial x} \right) + f_i(\tilde{C}, T, n), \quad i \in N_i,$$

$$\frac{\partial}{\partial t} E(\tilde{C}, T) = -\frac{\partial}{\partial x} E_u(\tilde{C}, T) + K \frac{\partial^2 T}{\partial x^2} + f_T(\tilde{C}, T, n), \quad (55)$$

$$\frac{\partial n}{\partial t} = v(\tilde{C}, T) \frac{\partial n}{\partial r} + g(\tilde{C}, T, n), \quad x \in [0, H], \quad r \in [0, r_{max}],$$

with boundary and initial conditions (23) (24) (39) (40). Here:

$$\tilde{C}_i = [C_i^b, C_i^e], \quad \tilde{u} = [u^b, u^e / \varepsilon_{mf}],$$

$$D_i = \text{diag}(D_i^b, D_i^e / \varepsilon_{mf}), \quad \tilde{C} = (\tilde{C}_1, \dots, \tilde{C}_{N_i}),$$

$$E(\tilde{C}, T) = \varepsilon I_g + (1 - \varepsilon) I_{s\rho_s},$$

$$E_u(\tilde{C}, T) = \varepsilon u_g I_g + (1 - \varepsilon) u_s I_{s\rho_s},$$

$$K = \varepsilon K_g + (1 - \varepsilon) K_s,$$

and f_i, f_T, g represent the remaining terms on the right-hand sides of equations.

There are three ways of simplifying such a model. One involves the assumption of isothermal conditions in the reactor, based on physico-chemical consideration. The next two consist in mathematical operations of averaging along the x-axis and transition to the stationary state ($t \rightarrow \infty$). For nonlinear functions, as in our case, the averaging operation imposes an additional error.

All kinds of models we have introduced may be classified in a diagram shown in Fig.4. Making the models isothermal requires only removing the energy equation, so we shall not discuss them separately.

T T=const	nonstationary	stationary
space dependent	M_{11}^n M_{11}^i	M_{12}^n M_{12}^i
averaged	M_{21}^n M_{21}^i	M_{22}^n M_{22}^i

Rys. 4

The most general model M_{11}^n is described by equs. (55). Upon applying the averaging operation

$$\overline{(\bullet)} = \frac{1}{H} \int_0^H (\bullet) dx$$

and taking into account boundary conditions we get from them the system including transport equation for $n(r,t)$ and ordinary differential equations:

$$\begin{aligned} \Phi(H, W, u_o, u_{mf}, \varepsilon_{mf}) &= 0, \\ \frac{d\bar{C}_i}{dt} &= F_i(\bar{C}, \bar{T}, n), \quad i \in N_i, \\ \frac{d}{dt} E(\bar{C}, \bar{T}) &= F_T(\bar{C}, n), \\ \frac{\partial n}{\partial t} &= v(\bar{C}, \bar{T}) \frac{\partial n}{\partial r} + g(\bar{C}, \bar{T}, n), \quad x \in [0, H], \quad r \in [0, r_{max}], \end{aligned} \quad (56)$$

with suitable initial conditions for \bar{C} , \bar{T} and n . This constitutes the model M_{21}^n .

Taking the other path, i.e. passing to the stationary state involves assuming all time derivatives equal zero. This operation changes character of the model, which takes on the form:

$$\begin{aligned} \Phi(H, W, u_o, u_{mf}, \varepsilon_{mf}) &= 0, \\ -\frac{d}{dx}(\tilde{u} \tilde{C}_i) + \frac{d}{dx} \left(D_i \frac{d\tilde{C}_i}{dx} \right) + \tilde{f}_i(\tilde{C}, T, n) &= 0, \quad i \in N_p, \end{aligned}$$

$$-\frac{d}{dx}E_u(\tilde{C}, T) + K\frac{d^2T}{dx^2} + f_T(\tilde{C}, T, n) = 0, \quad (57)$$

$$v(\tilde{C}, T)\frac{dn}{dr} + g(\tilde{C}, T, n) = 0, \quad x \in [0, H], \quad r \in [0, r_{max}],$$

with appropriate boundary conditions at $x = 0$, $x = H$, and $r = r_{max}$. Here we have a two-point boundary value problem for a system of ordinary differential equations (for \tilde{C} and T) and the one-sided boundary problem for ordinary differential equation for n . This constitutes a model M_{12}^n .

The simplest model M_{22}^n may be obtained in two ways: by averaging M_{12}^n or making M_{21}^n stationary. It has the form

$$\Phi(H, W, u_o, u_{mf}, \varepsilon_{mf}) = 0,$$

$$F_i(\tilde{C}, T, n) = 0, \quad i \in N_p, \quad (58)$$

$$F_T(\tilde{C}, T, n) = 0,$$

$$v(\tilde{C}, T)\frac{dn}{dr} + g(\tilde{C}, T, n) = 0, \quad r \in [0, r_{max}],$$

with additional constraint $n(r_{max}) = 0$. This is a system containing algebraic equations for \tilde{C} , T and ordinary differential equation for n .

Each type of models described above requires a different solution techniques. The classification given above and in Fig. 4 is intended as an aid in choosing a strategy for solving the modelling problem in case of a particular reactor and chemical process. Besides, the models of different types may serve for mutual checks of solution accuracy.

There are several theoretical questions of mathematical nature concerning the general model (55) and its simplified versions. The very first problem is that of the well-posedness. Indeed, let us note that system (55) contains free boundaries, as a matter of fact. There exist several phases whose geometric evolution is by no means a priori prescribed.

Our approach to the model is equivalent with imposing regularisation on equations, based on replacing sharp phase separation by boundary layers, where all involved phases coexist in equilibrium (with phase ratio varying smoothly), cf. [14].

Within such setting, the existence of solutions is ensured by the standard results on semilinear parabolic systems with smooth coefficients, [8], [10].

Other questions of concern are related to:

- global stability and asymptotic behaviour of solutions,
- their invariance properties.

As far as the stability questions are concerned, one usually obtains the possibility of multiple steady states, [8]. Since we are mostly involved with transient stages of the process, we do not explore further this line.

Of relevance for us are, instead, the invariance aspects. In particular, to acquire physically reasonable results, we must provide non-negativeness of all state components. Fortunately, the arguments developed by Henry [8] for parabolic systems that describe combustion processes (see Chapters 6.1 and 10.2) apply to our model, yielding invariance properties and the desired non-negativeness as a consequence.

Let us note that for simplified versions of the model (56) through (58) one still faces the possibility of multiple steady states. A discussion of these questions, based on computational experiments, will be given in a forthcoming paper [22].

Notation:

A	— reactor cross-section area, [m^2]
A_S	— the active surface of particles per unit mass, [m^2/kg]
C_i^b, C_i^e	— concentration of i -th gas in bubble and emulsion phases, [$kmol/m^3$]
C_{ig}	— average concentration of i -th gas in the reactor, [$kmol/m^3$]
D_i^b, D_i^e	— gas diffusion coefficients in bubble and emulsion phases, [m^2/s]
D_{b0}, D_{bm}	— minimal and maximal bubble diameters, [m]
\bar{D}	— mean bubble diameter, [m]
E_r	— activation energy for r -th reaction, [$kJ/kmol$]
F_{be}	— gas exchange coefficient between bubble and emulsion phases, [$1/m$]
H	— bed height, [m]
H_{mf}	— bed height corresponding to the minimal fluidization velocity, [m]
ΔH_r	— enthalpy change for r -th reaction, [$kJ/kmol$]
I_S, I_g	— internal energy of gas and solids, [kJ/kg]
k_r	— frequency factor for r -th reaction, [m/s] for gas-solid reaction, [$m^3/kmol \cdot s$] for gas-gas reaction
$n(r, t)$	— normalised number of reacting particles with radius r at the moment t
N_0	— normalising factor for $n(r, t)$
Q_{vol}, Q_{surf}	— heat energy production for volume reactions, [$kJ/m^3 \cdot s$], and surface reactions, [$kJ/m^2 \cdot s$]
R	— universal gas constant
R_i^b, R_i^e	— rate of production for i -th gas in bubble and emulsion phases, [$kmol/m^3 \cdot s$]
R_S	— rate of change for the mass of reacting solids in bed, [kg/s]

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Received, July 1988.

Fenomenologiczny model reakcji gaz-ciało stałe dla populacji cząstek z wewnętrzną dynamiką

W pracy przedstawiono model dynamiki reakcji gaz-ciało stałe w reaktorach ze złożem fluidalnym. Model ten ma charakter układu adwekcyjno-dyfuzyjnego z wewnętrzną dynamiką populacji cząstek. Przedyskutowano możliwe metody uproszczenia modelu.

Феноменологическая модель реакции газ-твердое тело для совокупности частиц с внутренней динамикой

В работе представлена модель динамики реакции газ-твердое тело в реакторах с кипящим слоем. Эта модель носит характер адвективно-диффузионной системы с внутренней динамикой совокупности частиц. Рассмотрены возможные методы упрощения модели.

