THE MATHEMATICAL SIMULATION OF A FLUIDIZED-BED REACTOR

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The authors examine the problem of the mathematical simulation of heterogeneous processes in a fluidized-bed reactor.

The theoretical analysis of the fluidized-bed process is complicated, in the first place, by our ignorance of the hydrodynamic situation in the reactor. It is precisely the hydrodynamics that determine the trajectories of the suspended polymer particles (we are considering the process of polymer chlorination in a fluidized bed), but since, other things being equal, the trajectory of a particle uniquely determines the degree of chemical reaction, two problems naturally arise.

1. Determination of the trajectories of the particles.
2. Determination of their degree of chlorination.

As far as we know, the first problem has not yet been solved; therefore we are obliged to assume some hydrodynamic situation in the reactor. On the basis of the published data [2], we will assume that the particle mixing process is described by the convective diffusion equation

$$\frac{\partial m}{\partial t} = D_{\text{eff}}\frac{\partial^2 m}{\partial x^2} + w\frac{\partial m}{\partial x}, \quad 0 \leqslant x \leqslant H, \ 0 \leqslant t < \infty, \quad (1)$$

with the corresponding initial and boundary conditions

$$m(x, 0) = \delta(x - 0),$$
$$\frac{\partial m}{\partial x}(H, t) = 0, \quad \frac{\partial m}{\partial x}(0, t) + \frac{w}{D_{\text{eff}}} m(0, t) = 0, \quad (2)$$

since all the particles introduced into the equipment at zero time will be initially concentrated around the inlet to the apparatus at the point x = 0.

Wiener [3] and Kolmogorov [4] have shown that a knowledge of equations of this type is sufficient to determine the probability distribution of the particle trajectories, or, as it is said, to introduce a measure in trajectory space. It is obvious a priori that not all trajectories are equiprobable. For example, it is improbable that all the particles introduced into the reactor at zero time will immediately leave it. It is also improbable that, if the process is continuous, all the particles will remain in the reactor for an indefinite time.

On the other hand, it is obvious that in such processes it is not enough to know the particle distribution with respect to dwell time in order to give a unique answer to the question of the degree of chlorination. For example, suppose a certain chlorine volume concentration profile has been established in the reactor; then, as may be seen in the figure, even though two trajectories begin and end at the same time $(0, t_0)$ (i.e., the corresponding particles remain in the reactor for the same period of time), they may still travel through different parts of the reactor with different chlorine concentrations C* and hence may be differently chlorinated.

These simple considerations demonstrate the necessity for taking the particle trajectories into account. The measure introduced in trajectory space has many of the properties of the length of a segment. For example, it makes sense to speak of the integral over trajectory space. In particular, all the bounded and continuous functionals (i.e., functions in which the role of independent variable is played by the trajectory, e.g., the amount of chlorine absorbed by a particle with a given trajectory) are integrable with respect to this measure.

We will now construct a mathematical model of the process. From the technical standpoint it makes sense to consider only the stationary process in the following two variants:

I. The concentration of chlorine in the gas phase C*(x) is kept at a given level along the entire length of the reactor.

II. The concentration of chlorine at the reactor inlet C*(0) is given for a known fluid flow rate.

In both problems it is required to determine the chlorine content of the polymer particles leaving the equipment.

We will consider variant I. In this case there are three possibilities.

1. The process at an individual grain proceeds in a region intermediate between the intradiffusional and the kinetic. In this case we have the following equations for the mass balance inside the granule (for simplicity the temperature inside the granule is assumed constant):

$$\frac{\partial C}{\partial t} = D\,\Delta C - f(C, n),$$
$$\frac{dC_1}{dt} = f(C_1, n),$$
$$\frac{dn}{dt} = \psi(C_1, \gamma); \quad (3)$$

the corresponding boundary and initial conditions are

$$C(0, r) = 0, \quad \frac{\partial C}{\partial r}(t, 0) = 0, \quad C(t, R) = C^*(x),$$
$$C_1(0, r) = 0, \quad n(0) = n_0. \quad (4)$$

For a particle with fixed trajectory x(t) the boundary condition takes the form C(t, R) = C*(x(t)), i.e., the content of free and bound chlorine in the particle at any moment, and in particular when it leaves the reactor, is in fact determined exclusively by the particle trajectory; consequently, the distribution of the product with respect to degree of chlorination is determined by the measure in trajectory space.

2. The process on an individual polymer granule proceeds in the kinetic region. (This can be achieved by reducing the size of the granule.) In this case the concentration of free chlorine in the particle pores may be assumed not to depend on the distance to the boundary of the particle (the variable coordinate is the radius) and is equal to the concentration of chlorine in the gas phase at that point of the reactor where the particle happens to be located. Of course, this assumption is permissible only at relatively small particle velocities, at which equalization of the free chlorine concentrations inside the particle proceeds more rapidly than variation of the concentration of chlorine in the gas phase at the boundary of the particle due to its motion. In practice this situation is observed at small values of the mixing coefficient D_{eff} and a small linear particle velocity w. Then the last two equations of system (3) with the corresponding initial conditions $C_1(0) = 0$, $n(0) = n_0$ are sufficient to describe the material balance inside the polymer granule. Here, C_1 does not depend on r and is constant over the entire volume of the particle. Of course, the amount of bound chlorine in the particle also depends on the particle trajectory, which is immediately evident from Eqs. (3).

3. The process at the individual granule proceeds in the intradiffusional region. This means that the rate of supply of free chlorine, determined by internal diffusion, is much lower than the rate of the chlorine addition reaction. Consequently, the entire chlorine addition process proceeds at the interface between a surface film of chlorine-saturated polymer and the rest of the polymer which is chlorine-free. In this case the rate of the process is determined by the rate of diffusion of free chlorine through the saturated polymer film, and the rate of growth of the film is determined by the rate of variation of the amount of added chlorine and the chlorine saturation concentration. Mathematically, the process is described as follows: the equation of diffusion of free chlorine through the film is

$$\frac{\partial C}{\partial t} = D\Delta C \qquad (5)$$

with the initial condition

$$C(0, r) = 0$$

and the boundary conditions

$$C(t, R) = C^*\left(x(t)\right),$$
$$C\left(t, R_{in}(t)\right) = 0, \qquad (6)$$

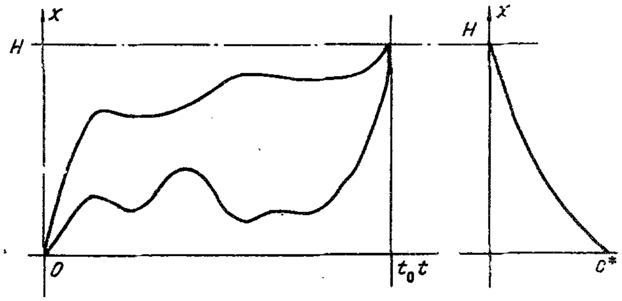
where $R_{in}(t)$ is the inside boundary of the saturated film.

The equation for the inside boundary is

$$\frac{dR_{in}}{dt} = D\frac{\partial C(t, r)}{\partial r}\frac{1}{4\pi C_{sat} R_{in}^2} \qquad (7)$$

at the point $r = R_{in}(t)$. Here, C_{sat} is the saturation concentration.

Thus, in this case it is necessary to solve the equation of diffusion in a spherical ring with variable inside boundary $R_{in}(t)$, the value of $R_{in}(t)$ being found from Eq. (7). The chlorine content of the particle also depends on the trajectory; this relation is found from one of boundary conditions (6).



Trajectories of particles with the same residence time. The curve on the right represents the chlorine distribution along the reactor.

In all these cases the measure in trajectory space determines the particle distribution function with respect to degree of chlorination. Moreover, in order to maintain a given concentration profile of gas-phase chlorine it is necessary to supply a certain amount of chlorine along the length of the reactor, this amount being determined from the chlorine material balance equation for an element of reactor volume; the quantity of chlorine absorbed from this volume by the particles depends on the measure in trajectory space. Further details of the material balance equation and methods of numerical solution are given below.

Let us consider variant II. The chlorine concentration at the equipment inlet $C^*(0)$ is given. Chlorine is not made up along the length of the reactor. Here again three cases are possible, but we will consider only case 1.

For the individual particle we have Eqs. (3) with boundary conditions (4). We construct the material balance equation for an element of the reactor volume. We denote by $q_\tau(\bar{x}, x, t)$ the amount of chlorine absorbed by a single particle introduced into the equipment at time τ (the so-called τ-particle) with trajectory $\bar{x}(t)$ in the reactor zone from $\zeta = 0$ to $\zeta = x$ in time t. It is obvious, for example, that $q_\tau(\bar{x}, H, t-\tau) = 4\pi\int_0^R C(r, t-\tau)r^2dr$; then the amount of chlorine absorbed by that particle in the reactor zone (x, x + dx) in time (t, t + dt) is given by

$$q_\tau(\bar{x}, x+dx, t+dt) - q_\tau(\bar{x}, x+dx, t) -$$
$$- q_\tau(\bar{x}, x, t+\Delta t) + q_\tau(\bar{x}, x, t) =$$
$$= \frac{\partial^2 q_\tau(\bar{x}, x+\Theta_1\Delta x, t+\Theta_2\Delta t)}{\partial x\,\partial t}\Delta x\Delta t.$$

The amount of chlorine absorbed in the zone (x, x + Δx) in time (t, t + Δt) by all the τ-particles is expressed by the integral of this functional over trajectory space with measure μ_T defined by Eq. (1):

$$\Delta x \Delta t \int\limits_{[X]} \frac{\partial^2 q_\tau}{\partial x\, \partial t} (\bar{x}, x + \Theta_1 \Delta x, t + \Theta_2 \Delta t)\, d\mu_\tau.$$

For the stationary case the chlorine material balance equation has the form

$$\frac{dC^*}{dx} V = \int\limits_{-\infty}^{t} \left[\int\limits_{[X]} \frac{\partial^2 q_\tau}{\partial x \partial t} (\bar{x}, x, t)\, d\mu_\tau \right] d\tau,$$

where V is the volume rate of supply of gas phase. Thus, for the stationary case the mathematical model of the process is represented by a system of equations of the form

$$\frac{\partial C(t, r)}{\partial t} = D \Delta C - f(C, n),$$

$$\frac{dC_1}{dt} = f(C, n),$$

$$\frac{dn}{dt} = \psi(C_1, \gamma),$$

$$\frac{\partial C^*}{\partial x} V = \int\limits_{-\infty}^{t} \left[\int\limits_{[X]} \frac{\partial^2 q_\tau}{\partial x\, \partial t} (\bar{x}, x, t)\, d\mu \right] d\tau$$

with the corresponding boundary and initial conditions

$$C(0, r) = 0, \ \frac{\partial C}{\partial r}(t, 0) = 0, \ C(t, R) = C^*(x),$$

$$C_1(0, r) = 0, \ C^*(0) = C_0^*, \ n(0) = n_c.$$

We will now turn to certain questions connected with the solution of such problems.

VARIANT I

The gas-phase chlorine concentration profile over the height of the reactor is maintained by means of a distributor. It is required to determine the density function of the product with respect to chlorine content for a given chlorine concentration profile. At the same time, of course, the following extremal problem arises: to determine the "optimal" chlorine concentration profile in some sense, i.e., the profile such that the product is most uniform in composition (for example, this profile corresponds to the minimum variance of the distribution function).

VARIANT II

The concentration of chlorine in the gas supplied to the equipment (the gas is supplied from below) is given. In this case some concentration profile is established over the height of the reactor in the stationary regime. The problem consists in determining this profile and the distribution function (in the same way as in problem I). At the same time, two extremal problems arise: a) to achieve maximum chlorine conversion, b) to achieve a chlorine supply such that the product is uniform.

We will determine the algorithm of the numerical solution. Since in both cases in order to solve this problem we need to know the particle trajectories, we shall first discuss a method of trajectory construction.

We select a time interval Δt. At the instant $t_k = k\Delta t$ let the particle be in position x_k. Then the probability distribution for its position at the instant t_{k+1} is given by the solution $\psi_{k+1}(\Delta t, x)$ of Eq. (1) with boundary conditions (2) and the initial condition $\delta(x - x_k)$.

We then construct a random number generator which makes it possible to determine x_{k+1} from a given distribution function. In this way we construct the particle trajectory, noting that $x_0 = 0$ always. The trajectory ends at $x_k = H$. Obviously, the smaller Δt, the more accurately the trajectory will be constructed. Moreover, we assume that over the entire interval Δt from the instant t_k the particle is in position x_k, i.e., we approximate the trajectories with step functions.

SOLUTION OF PROBLEM I

Let the particle have a trajectory x(t), constructed by the method described above. We solve Eq. (5) on the interval $[t_k, t_{k+1}]$ with the corresponding initial and boundary conditions

$$C_k(t_k, r) = C_{k-1}(t_{k-1} + \Delta t, r),$$

$$\frac{\partial C_k(0, t)}{\partial r} = 0, \quad C_k(t, R) = C^*(x_k).$$

The chlorine content of the particle when it leaves the equipment is

$$q = \int\limits_0^R 4\pi r^2 C_{N-1}(t_{N-1} + \Delta t, r)\, dr,$$

where N is the number of steps for the given trajectory.

Having computed q for a sufficient number of particles, we obtain some approximation of the particle distribution function with respect to the degree of chlorination. The extremal problem consists in finding the function $C^*(x)$ that minimizes the variance D of the particle distribution function with respect to the degree of chlorination for a given mean value of the chlorine content of the particles. Approximating $C^*(x)$ with a step function, we find that $D = D(x_1, x_2, \ldots, x_n)$, i.e., the problem reduces to minimization of a function of n variables, which is not very complicated, but a rather clumsy computational task.

SOLUTION OF PROBLEM II

This can be reduced to a sequence of problems I: We assign the arbitrary profile $C^*_1(x)$. We solve the modified problem I, but in addition we calculate how much chlorine is "captured" by all the particles introduced at time τ from the interval $[x_k, x_{k+1}]$.† In view of the stationarity of the process this amount of

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†By this we understand particles introduced into the reactor during the interval from t to t + Δt.

chlorine is equal to the amount absorbed in that interval by all the particles in the interval $[x_k, x_{k+1}]$ during time Δt (correct to a multiplier). We denote this amount of chlorine, referred to unit volume of a reactor of length $[x_k, x_{k+1}]$, by q_k. This quantity shows what the difference $C^*_{k+1} - C_k$ should be. Knowing $C^*_1(0)$, we can construct the function $C'^*_1(x)$. As the second approximation we take the function $C^*_2 = \alpha C'^*_1 + \beta C'^*_1$, where α and $\beta > 0$, $\alpha + \beta = 1$. The choice of α and β is based on considerations relating to accelerated convergence of the iteration process. This process is repeated until

$$|C^*_n - C^*_{n-1}| < \varepsilon.$$

The particle distribution function with respect to chlorine content is obtained automatically in the last step. The optimization problem formulated for this case above is similarly solved.

NOTATION

$m(x, t)$ is the mass of particles in a unit volume; H is the height of the reactor; t is the time; x is the coordinate along the reactor; D_{eff} is the mixing coefficient; $C(t, r)$ is the free chlorine concentration in the particle; r is the coordinate along the particle radius; n is the free radical concentration; C_1 is the bound chlorine concentration; γ is the power of the source; $C^*(x)$ is the concentration of chlorine in the gas phase; w is the particle velocity; D is the diffusion coefficient.

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