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STOCHASTIC APPROACH TO CHEMICAL REACTORS MODELING

MODELE STOCHASTYCZNE REAKTORÓW CHEMICZNYCH

Abstract

Applicability of the Kolmogorov's equations for mathematical simulation of gases purification under low temperature plasma tubular reactor was considered. Comparison of the obtained results with other simulation methods and experimental data was performed.

Keywords: stochastic modeling, Kolmogorov's equations, gas purification, low temperature plasma

Streszczenie

W pracy przedstawiono możliwość zastosowania równań Kołmogorowa do matematycznego modelowania oczyszczania gazów w niskotemperaturowym, plazmowym reaktorze rurowym. Przedstawiono porównanie wyników zaproponowanej symulacji z wynikami innych metod i eksperymentów.

Słowa kluczowe: modelowanie stochastyczne, równania Kołmogorowa, oczyszczanie gazów, plazma niskotemperaturowa

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1. Introduction

At the mathematical modeling already at the step of problem statement the problem of concrete approach to modeling choice always appears. In that case we do not speak so much about mathematical methods of modeling as about which abstraction level it is necessary to use for sufficient description of physical nature of phenomena under study. The sufficiency here means a compromise accomplishment of requirements to model such as adequacy, universality and economy. But if at the mathematical model creation of any concrete phenomena the satisfactory agreement between all requirements to the model can be achieved then the description of group objects connected, for example, with the technological relationship only becomes quite difficult task in the frame of single approach. The chemical technological processes are an example of such group of modeling objects. These objects include processes in dispersion and continuous media, heat, diffusion and mechanical processes, chemical kinetics etc.

Attempts have been made repeatedly to propose more or less universal approach unified for whole processes groups. Some of them were sufficiently successful. So, the determinate approach based on an application of substance transfer equation (Umov's equation) is a classical one [1]. The fundamental dependencies of continuum dynamics, heat and mass transfer are the special cases of that equation [2, 3]. These dependencies use the methods of partial differential equations and elements of field theory. It is necessary to point out that models being used to describe the process in study at continuous space and time. It is a positive property of such approach. On the other hand, the application of the classical determinate transfer equations without essential simplifications results in substantial calculating difficulties, especially, for multidimensional non-stationary tasks. These difficulties has not been overcome till now in spite of existence of powerful computers.

The attempts have been made repeatedly to simplify the phenomena physical picture to make easier the mathematical operations with models without prejudice to modeling quality. Thus, cell models are widely used at reactors modeling that is, in fact, the spatial discretization of object [4]. The task solutions of transfer with variable coefficients when model assumes a space division on a number of zones within which the task is believed to be linear and for agreement on boundaries the boundary conditions are used are other example [3].

Recently, numerous attempts of application for technological processes modeling of stochastic approaches appeared. In particular, interesting results of discrete Markov's chains theory elements application for the description of a number of technological processes (bulk solids treatment, heat and mass transfer) have been obtained [5–7].

The aim of present paper is the demonstration of stochastic approach possibilities to modeling based on the Kolmogorov's equations application.

2. Modeling object

Let us consider the tubular reactor for gas purification with the application of low temperature plasma of dielectric barrier discharge (DBD) as the modeling object.

The reactor (Fig. 1) had a coaxial geometry. The reactor body was made from a Pyrex tube which also acted as the dielectric barrier. The alternative high voltage of industrial

frequency was applied between internal metal electrode and cylindrical external one located on a glass reactor body. A gas mixture containing the carbon monoxide admixture and technical grade oxygen as the main plasma forming gas inputted to a ring gap between internal surface of glass tube and internal electrode. The discharge action resulted to gas purification from CO during the gas movement along the discharge axis.

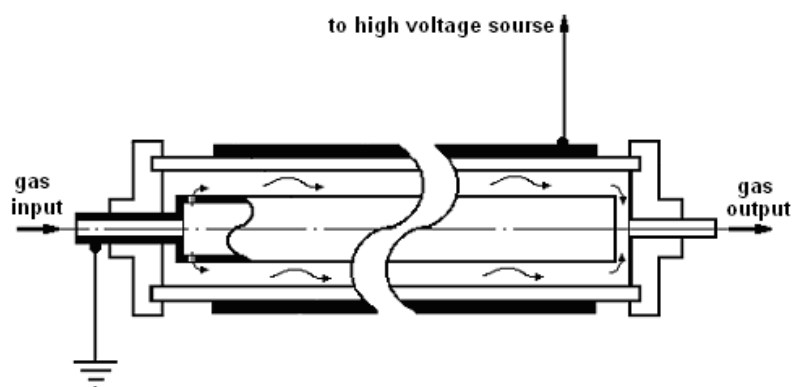


Fig. 1. The scheme of the DBD reactor for gas purification

Rys. 1. Schemat reaktora DBD do oczyszczania gazu

The atomic oxygen and ozone forming under discharge excitation were the active species which react with polluting components transforming them into less toxic substances.

3. Conventional approach to modeling

The conventional classical approach to mass transfer process modeling accompanied by a volume chemical reaction usually assumes the application of fundamental equation describing the concentration field in a moving reacting medium [2]

$$\frac{\delta C}{\delta t} + C \cdot \text{div}(\bar{\mathbf{v}}) + \bar{\mathbf{v}} \cdot \text{grad}C = D \cdot \nabla^2 C + \gamma \quad (1)$$

where: C is the substance concentration; v is the medium velocity; D is the diffusion coefficient; γ is the volume powder of source (sink) of substance mass; t is the time.

The volume powder value characterizes a substance amount forming or consuming per time unit due to chemical reaction.

For the equation (1) solution it is necessary to add the equations of medium movement (2) and flow continuity (3) to it

$$\frac{\partial(\rho\bar{\mathbf{v}})}{\partial t} + \text{div}(\rho\bar{\mathbf{v}}\bar{\mathbf{v}}) = -\text{div}\bar{\boldsymbol{\sigma}} \quad (2)$$

$$\frac{\partial\rho}{\partial t} + \rho \cdot \text{div}(\bar{\mathbf{v}}) + \bar{\mathbf{v}} \cdot \text{grad}\rho = 0 \quad (3)$$

where ρ is the medium density; σ is the stress tensor.

As is easy to see that the problem in such statement is rather complicated. Therefore, some assumptions are made at the process modeling. Because the tubular type reactors length is essentially higher than the diameter the process is considered as one dimensional omitting the cross diffusion. Beside that, the medium is considered as an incompressible. That assumption is often not valid under the gas mixture study. Nevertheless, such assumptions allow to simplified essentially the mathematical statement of problems and result the task in single partial differential equation

$$\frac{\partial C}{\partial t} + v \cdot \frac{\partial C}{\partial x} = D \cdot \frac{\partial^2 C}{\partial x^2} + \gamma \quad (4)$$

Such equation with appropriate initial and boundary conditions describes the non-stationary mass transfer process with chemical reaction for the tubular type reactor and allows to study the local concentrations profile in that device.

Nevertheless, practical application of given models has shown that the problem of correct statement of boundary condition appears in this case. In particular, at the modeling substances concentrations are known at the reactor input only. But concentrations values are not enough for task solution. It is necessary to use additional assumptions about the process proceeding. It is often believed that the reactor length is enough for process finishing [8]. That assumption means that the concentration gradient equals zero at the reactor output and the task becomes completely definite.

It is necessary to note that the introduction of simplifying assumptions can distort the process real picture.

4. Stochastic approach to modeling

Let the reactor volume be divided into several elementary cells along its length. The gas entering for purification passes through these cells in series. The substance amount change into the each elementary cell depends on the following parallel proceeding processes:

- substance coming in the cell due to its diffusion and macroscopic movement of a medium,
- substance consumption in the cell due to a reaction,
- removal of the substance non-reacting part from the cell with the media movement and with the diffusion.

We will assume that pollutant concentration is the stochastic variable which can take the value in the range from initial concentration up to zero. Otherwise, it means that the reactor is a system possessing the ensemble of probable states. Let the number of possible states be limited with the finite value n .

The reactor state ($i = 1, 2, \dots, n$) will be denoted as S_i whereas $C_i(t)$ will be the probability of S_i state realization at a time moment t . It is easily to show that in this case the $C_i(t)$ value means the same that relative (normalized) concentration of pollutant in the i -cell.

The characteristics of forces acting on a system we will denote the following way. The parameter λ characterizes the intensity of processes transferring the system to the S_j ($j > i$) state. The parameter μ characterizes the intensity of processes transferring the system to the S_k ($k < i$)

state. We will suppose that in common case these parameters depend on the S_i . Obviously, the system can transfer from S_i state to the one of the neighboring states S_{i+1} or S_{i-1} only at a quite small range of time Δt .

Therefore, the gas purification process in the reactor can be described with the graph (transfer diagramm) shown in Fig. 2.

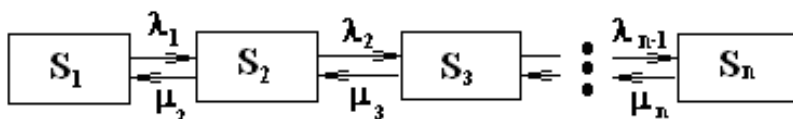


Fig. 2. The graph for gas purification process in a reactor

Rys. 2. Schemat procesu oczyszczania gazu w reaktorze

The probability change $C_i(t)$ over small range Δt directly following time t is

$$\Delta C_i(t) = \lambda_{i-1} \cdot \Delta t \cdot C_{i-1}(t) - \lambda_i \cdot \Delta t \cdot C_i(t) - \mu_i \cdot \Delta t \cdot C_i(t) + \mu_{i+1} \cdot \Delta t \cdot C_{i+1}(t)$$

Dividing this equation by Δt and finding the limit at $\Delta t \rightarrow 0$, we obtain

$$\frac{dC_i(t)}{dt} = \lambda_{i-1} \cdot C_{i-1}(t) - (\lambda_i + \mu_i) \cdot C_i(t) + \mu_{i+1} \cdot C_{i+1}(t) \quad (5)$$

The equation (5) is not valid at the $i = 1$ and $i = n$ because in these cases the probabilities $C_{i-1}(t)$ or $C_{i+1}(t)$ lose meaning. Therefore, it is necessary to analyze the appropriate equation with special way. For example, at the $i = 1$ the system can change the S_2 state on the S_1 one. Then

$$\frac{dC_1(t)}{dt} = -\lambda_1 \cdot C_1(t) + \mu_2 \cdot C_2(t) \quad (6)$$

The equations (5), (6) allow to determine the system state change with respect to time at given initial conditions and known intensity parameters λ_i and μ_i .

Applying given equations for modeling the state of reactor with substance consumption it can be indicated that under constant flow of purifying gas and constant parameters of chemical reaction the λ and μ parameters can be considered as the constants which independent on the current system state and number of possible states n . In that case the λ will be the normalized intensity of media flux whereas the μ will be the normalized intensity of substance consumption. In this case the normalization means the dividing intensities mentioned above by total amount of consuming substance coming to the reactor. It is necessary to note that intensity of substance consumption (μ) characterizes proceeding, at least, two parallel processes – a substance consumption in the cell due to reaction and a removal of non-reacting substance part with the media flux and with the diffusion.

In that case the state of reactor being modeling can be described by the Kolmogorov's equations for the Markov's chains with continuous time that is by following system of equations

$$\begin{cases} \frac{dC_1(t)}{dt} = -\lambda \cdot C_1(t) + \mu \cdot C_2(t) \\ \frac{dC_k(t)}{dt} = \lambda \cdot C_{k-1}(t) - (\lambda + \mu) \cdot C_k(t) + \mu \cdot C_{k+1}(t); \quad k = 2, 3, \dots, n-1 \\ \frac{dC_n(t)}{dt} = \lambda \cdot C_{n-1}(t) - \mu \cdot C_n(t) \end{cases} \quad (7)$$

The following condition has to fulfill strictly

$$\sum_{k=1}^{k=n} C_k(t) = 1 \quad (8)$$

For the stationary conditions the differential equation system by A.N. Kolmogorov transforms to the algebraic system of equations

$$\begin{cases} -\lambda \cdot C_1 + \mu \cdot C_2 = 0 \\ \lambda \cdot C_{k-1} - (\lambda + \mu) \cdot C_k + \mu \cdot C_{k+1} = 0; \quad k = 2, 3, \dots, n-1 \\ \lambda \cdot C_{n-1} - \mu \cdot C_n = 0 \end{cases} \quad (9)$$

Obtained mathematical models (7) and (9) together with the condition (8) allow to find probable states of system from n elementary cells modeling considering reactor in stationary (9) or transition (7) regimes. The relative concentration in the last cell C_n characterizes the substance amount at the reactor output.

5. Experimental verification

The adequacy of models proposed can be studied by calculated data comparison with experimental results obtained on the laboratory set up the scheme of which was shown in Fig. 1. The reaction zone length was 122 mm, the internal diameter was 20 mm, the square of the ring gap was 1,7 cm². The discharge voltage was varied in the range of 10–16 kV. The model gas mixture containing the carbon oxide (CO) of 1,2 vol.% was inputted into reactor. The gas mixture flow was changed from 0,2 up to 1,4 cm³/s. The carbon oxide losses due to the reaction depended on the operating voltage on reactor electrodes. These losses were calculated on the base of dependencies given in the study [9]. The change range of losses was from 0,065 to 0,084 mg/(L×s). Coefficients of model (7)–(9) λ and μ were calculated from constructive parameters of the experimental set up and conditions of experiment accomplishing. The coefficient λ depending on model mixture flow and normalized on a total amount of substance changed in the range of 0,0037–0,0252 s⁻¹ at the considered conditions. The coefficient μ was in the range of 0,0041–0,0258 s⁻¹.

The comparison of experimental and calculated data is given in the Tables 1, 2. Here, the equations system (9) added with the condition (8) was used. The number of cells was taken of 10. The output concentration was calculated as S_{10} state probability multiplied by input concentration. In the same Tables the data calculated on the conventional model (1)–(3) simplified according to assumptions described above are given. Tables include experimental data obtained at various voltages applied to electrodes.

Table 1

The carbon monoxide concentrations at the reactor output under the voltage of 12 kV

Gas flow [cm ³ /s]	Carbon monoxide concentration [g/m ³]				
	Experimental value	Calculation on the (1)–(3) model		Calculation on the (8)–(9) model	
		Value	Error, [%]	Value	Error, [%]
0,29	9,7	9,2	5,15	9,6	1,03
0,33	10,6	10	5,66	10,1	4,72
0,51	11,7	11,6	0,85	11,6	0,85
0,65	11,8	12,4	5,08	12,2	3,39
0,91	12,52	13,1	4,63	12,9	3,04
1,00	13,4	13,3	0,75	13,1	2,24
1,21	13,4	13,6	1,49	13,4	0,00
1,40	13,5	13,8	2,22	13,6	0,74

Table 2

The carbon monoxide concentrations at the reactor output under the voltage of 14 kV

Gas flow [cm ³ /s]	Carbon monoxide concentration [g/m ³]				
	Experimental value	Calculation on the (1)–(3) model		Calculation on the (8)–(9) model	
		Value	Error, [%]	Value	Error, [%]
0,29	8,6	8,8	2,33	8,6	0,00
0,33	9,1	9,6	5,49	9,2	1,10
0,51	10,2	11,4	11,76	10,9	6,86
0,65	10,4	12,2	17,31	11,6	11,54
0,91	11,1	13	17,12	12,5	12,61
1,00	11,3	13,2	16,81	12,7	12,39
1,21	11,9	13,5	13,45	13	9,24
1,40	12,6	13,7	8,73	13,3	5,56

The analysis of data listed in the tables indicates that there is a correlation between experimental and calculated data. Moreover, results show that the model proposed describes the process better (errors are less).

Also, the approach proposed allows to study the transition regime of reactor operating, in particular, changing with respect to time the concentration of reacting substance at the reactor output under the concentration stepwise impulse at the reactor input.

One of the examples of calculation on the model (7) together with condition (8) is presented below. Model parameters corresponded to mixture flow of 0,51 cm³/s and voltage of 15 kV. Initial conditions for system (7) were

$$C_1(0) = 15, \quad C_i(0) = 0 \quad i = 2, 3, \dots \quad (10)$$

The model time was calculated from mixture flow and reactor volume. Results of modeling are presented in Fig. 3.

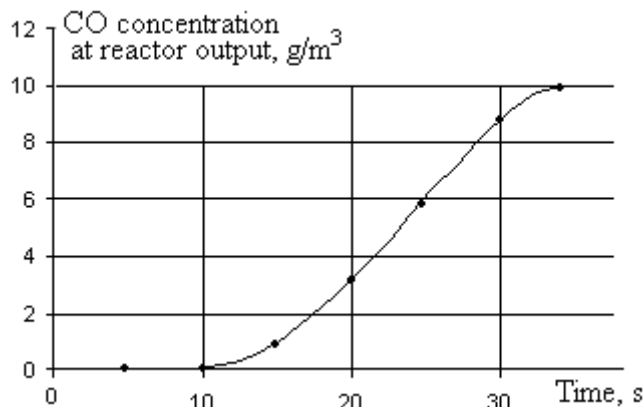


Fig. 3. The concentration change at reactor output with respect to time

Rys. 3. Zmiana koncentracji na wyjściu z reaktora

6. Conclusion

Thus, the proposed stochastic approach utilizing the Kolmogorov's equation for the tubular reactor modeling can be applied parallel with conventional methods based on the classical transfer equations.

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