Mathematical modelling of the agglomeration in a reactive porous medium with variable permeability

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Abstract. When processing low-grade fuels, such as waste and biomass, the problems associated with bed agglomeration often arise. In this work, one of the variants of the agglomeration model is proposed, in which local permeability decreases as a result of the physicochemical process caused by heating, and the agglomeration centers (particles of the melting material) are randomly distributed in a two-dimensional porous medium. A relatively simple model allows the study of the development of thermohydrodynamic inhomogeneities in the fixed granular bed and evaluation of its hydraulic resistance at different fractions of melting material.

1. Introduction
The problems of thermal utilization of municipal solid waste are associated with low technical and environmental efficiency of their combustion. A high proportion of noncombustible components, moisture content and mechanical instability of the fuel lead to high underburning and formation of harmful pollutants. To solve these problems, it is necessary to study thermophysical processes in the burning bed of waste.

One of the main components of the waste is a mixture of polymeric materials, whose thermal decomposition and burning can lead to a local decrease in the permeability of the fuel bed due to softening and melting the particles at the heating stage, as well as softening and melting ash at the intensive burning stage. Both mechanisms are similar to each other. Due to temperature fluctuations, agglomerates can form in the bed that are sintered pieces of fuel that burn out much more slowly than individual particles. In a number of experimental studies, the formation of agglomerates during combustion and gasification of biomass [1, 2], peat [3, 4], and plastics [5] was studied.

The development of mathematical models of the agglomerates formation is of great interest. In the present work, it is assumed that the formation of agglomerates is associated with the flow of plastic mass distributed in the bed, which leads to a lack of a gaseous oxidizing agent in some regions of the bed, decrease of burnup and temperature, and formation of a densified region with reduced permeability [6]. To study these processes, mathematical modelling of transfer processes in porous media in two dimensions could be used. Similar mathematical models were proposed in [7] for investigation of moving-bed waste incineration process; in papers [8, 9] for studying the thermal regimes of porous media with complex geometry and gravitational convection.

2. Formulation of the model
A two-dimensional rectangular region of porous medium (a fixed bed of fuel particles), through which a gaseous reactant flows, is considered. The height of the region is $Z$ and width is $Y$. A one-stage endothermic reaction proceeds on the surface of the particles. The system of equations is written as follows:

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial z}\left(D_{g}\frac{\partial C_i}{\partial z}\right) + \frac{\partial}{\partial y}\left(D_{g}\frac{\partial C_i}{\partial y}\right) - U\frac{\partial C_i}{\partial z} - V\frac{\partial C_i}{\partial y}$$

$$c_{s}\rho_{s}\frac{\partial T_s}{\partial t} = \frac{\partial}{\partial z}\left(\lambda_{s}\frac{\partial T_s}{\partial z}\right) + \frac{\partial}{\partial y}\left(\lambda_{s}\frac{\partial T_s}{\partial y}\right) + \alpha S(T_g - T_s) + Q_{m}m'$$

$$c_{g}\rho_{g}\frac{\partial T_g}{\partial t} = \frac{\partial}{\partial z}\left(\lambda_{g}\frac{\partial T_g}{\partial z}\right) + \frac{\partial}{\partial y}\left(\lambda_{g}\frac{\partial T_g}{\partial y}\right) - c_{g}\rho_{g}U\frac{\partial T_g}{\partial z} - c_{g}\rho_{g}V\frac{\partial T_g}{\partial y} - \alpha S(T_g - T_s)$$

$$U = -\frac{k_{D}}{\mu}\frac{\partial P_g}{\partial z}; \quad V = -\frac{k_{D}}{\mu}\frac{\partial P_g}{\partial y}$$

$$P_g = \frac{\rho_{g}RT_c}{M'g}$$

$$P_g|_{z=0} = P_{out} + \Delta P; \quad P_g|_{z=Z} = P_{out}$$

$$\frac{\partial f}{\partial y}|_{y=0} = \frac{\partial f}{\partial y}|_{y=Y} = 0; \quad f = \{T_g, T_s, P_g, C_i\}$$

$$\frac{\partial T_g}{\partial z}|_{z=Z} = 0; \quad \frac{\partial C_i}{\partial z}|_{z=Z} = 0$$

$$c_{g}\rho_{g}U|_{z=0} = c_{g}T_g\rho_{g}U|_{z=0} - \Pi\lambda_{g}\frac{\partial T_g}{\partial z}$$

$$C_iU|_{z=0} = C_iU|_{z=0} - \Pi D_{s}\frac{\partial C_i}{\partial z}$$

$$\lambda_{g} = a_{1} + b_{1}\sqrt{T}$$

$$\mu = \mu_{0}\left(\frac{T}{T_0}\right)^{2/3}$$

$$\lambda_{s} = a_{1} + b_{1}T + c_{1}\sigma T$$

Here $T_g$ is gas temperature, $T_s$ is solid phase temperature, $c_p$ is heat capacity, $C_i$ is gas component concentration, $P_g$ is gas pressure, $y$ and $z$ are spatial coordinates, $U$ and $V$ are velocity components in $z$ and $y$ directions. Boundary conditions for temperature and concentrations on walls ($y = 0$ and $y = Y$) and outlet ($z = Z$) are Neumann conditions, inlet boundary conditions ($z = 0$) are Danckwerts conditions; boundary conditions for inlet and outlet pressure are Dirichlet conditions. Pressure, gas density and components concentrations are connected by state equation. The pressure drop $\Delta P$ was selected in such a way as to provide reasonable gas flow rates through a cold porous medium. It is assumed that $\Delta P$ is kept constant, however, the problem can be posed in a more general form, when the pressure drop is a function of time or flow characteristics in the selected area, for example, temperature or flow rate measurements at the outlet of the bed (in this way, control methods can be constructed [10]). We consider the effect of natural convection to be insignificant. Transfer coefficients are determined according to the following recommendations [11, 12].
A numerical algorithm for solving the system of equations is compiled based on [8, 13-16]. The two-dimensional problem splits into a set of one-dimensional in both directions. One-dimensional transport problems are solved by splitting into physical processes: first, the problem of piezoconductivity in a porous medium is solved; then the diffusion-convection problem is solved for a given velocity field, and mass flows can be determined. After this, the problem of heat transfer is solved taking into account advection flows. To coordinate the solutions of these subtasks, the method of simple iteration over temperature fields is used.

A feature of the problem statement is a random discrete arrangement of foci of agglomeration (melting plastic particles). For a given concentration level of plastic weight fraction \( w_P \), a random matrix of zeros and ones equivalent to a two-dimensional grid is formed such that the average value of all elements is equal to \( w_P \). Unit-containing cells change their local permeability coefficient when heated to the melting temperature. It is supposed that the kinetics of melting is determined by the rate of heating:

\[
 r_m = \frac{\sum q_i}{Q_m} \left( \sum q_i > 0 \right)
\]

Here \( r_m \) is the mass melting rate, kg/s; \( q_i \) is the heat flux between the current cell and the \( i \)-th neighboring cell, W; \( Q_m \) is the thermal effect of the melting, J/kg. At each step, a balance is drawn between the solid and molten phases, as a result of which we find the degree of phase transformation of the substance in cell \( X \). The problem posed in this way can be considered as a two-dimensional Stefan problem in porous media with discrete sinks.

The local permeability coefficient \( k_D \) depends on \( X \) as follows:

\[
 \lg(k_D) = X \lg(k_{D,\min}) + (1 - X) \lg(k_{D,\max})
\]

Coefficients \( k_{D,\min} \) and \( k_{D,\max} \) differ from each other by several orders of magnitude, which makes it possible to simulate realistically the change in permeability during critical phenomena [17].

Since the melting components are distributed randomly in the porous medium, we are faced with the problem of percolation in a porous medium [18, 19]. When mixing bulk solids, the melting particles are distributed among the thermally stable (hard) particles. When heated by input gas, polymer particles soften, melting mass swell and fill voids, blocking the porous channels between the particles (and inside them). As a result, the permeability of the porous medium is patchy; however, the flow characteristics averaged over different configurations can have quite clear dependences on the content of the melting particles. This problem will be investigated below for a several number of examples.

3. Results and discussion

Let us consider an isothermal section of a porous medium with dimensions of 25x15 cm. The porous space is filled with gas at the same temperature as the solid phase at atmospheric pressure. The characteristic average particle size is 1 cm. Hot gas is supplied from below at a temperature of 600 K at a speed of 10 cm/s (on the cold section). The heating of the solid phase causes physicochemical transformations; therefore the gas path through the section becomes tortuous: the effective cross section decreases, the gas flow through the section (under constant pressure drop) decreases. In this case, it is of interest not only the stationary filtration regimes, but also the dynamics of the flow during the interaction of heat transfer with the physicochemical transformation. In the calculations, the following values of the spatial and temporal grid steps were used: \( h_y = h_z = 5 \times 10^{-3} \) m, \( \tau = 1 \times 10^{-2} \) s. Agglomeration centers distribution was randomly generated for each calculation. Fraction of agglomerating (melting) particles \( w_P \) is varied from 0 to 20% (up to 75 particles for selected region).

The condition for the phase transition to occur is expressed as follows: the softening of the melting material occurs stepwise at a temperature of 473 K, the thermal effect is endothermic (-100 kJ/kg). An example of the calculation is shown in figure 1, which shows the instantaneous fields of gas temperature and local permeability after 1000 s after the start of heating. It can be seen from figure 1
that even with a small fraction of agglomeration centers \((w_P = 2\%)\), the gas flow becomes inhomogeneous in cross section. Gaps of permeability form a discontinuous form of the heating front, and the random nature of their location can lead to overlapping of a section through consecutive overlays. Such a picture is characteristic of a two-dimensional flow, but qualitatively, most likely, it will also be observed for the three-dimensional case.

The inhomogeneities observed in the calculation resemble “viscous fingers” that are widely known display of the Saffman–Taylor instability. Similar phenomena are also observed for the combustion front in porous media [20]. The difference, however, is that in the case presented here, the heterogeneities are associated not with the internal dynamic laws of the filtration flow, but with the inherent heterogeneity, stochasticity of the initial conditions in which the system is placed. Such stochasticity, however, is typical of a number of practically interesting processes, for example, associated with the energy and technological processing of low-grade fuels (biomass, wastes).

Figure 1. Modelling results for \(w_P = 2\%\): (a) temperature field, K; (b) locations with decreasing permeability.

When studying the combustion of mixtures with agglomeration centers, these inhomogeneities will generate thermohydrodynamic instabilities, which are observed in the form of burnouts and hot spots. These phenomena lead to inefficient combustion and, among other things, can lead to the formation of harmful pollutants (such as, for example, aromatic products of thermolysis and incomplete oxidation of synthetic polymers [21]). Naturally, depending on the current bed configuration, different variants of the development of the flow can be obtained.
Figure 2. Dependence of output gas flowrate on time for $w_p = 2\%$.

The main indicator of agglomeration is a decrease in gas flow through the bed with a constant pressure drop. Therefore, further we will be interested in the total gas flow through the upper boundary. Thus, it is possible to reduce (with a certain degree of approximation) the development of a complex two-dimensional flow to the dynamics of a single variable (of particular interest). Figure 2 shows the dynamics of the total gas flow rate $G_{out}$: the dashed lines correspond to different random configurations at $w_p = 2\%$. The general trend toward a decrease in flow rate over time is associated with the heating of the porous medium: it follows from the formula for the viscosity coefficient $\mu$ that when the gas is heated from 300 to 600 K, its viscosity will increase by 1.5 times (the coefficient in the Darcy equation will decrease by the same amount), while density will decrease by 2 times. Thus, even with constant permeability of the medium after complete heating, the gas flow rate should decrease by 3 times: this is precisely the trend observed in the calculations. The presence of agglomeration centers additionally reduces gas flowrate, so the main interest is not so much an absolute decrease in flowrate as a dynamics of relative flowrate, $G_{out}/G_{out}^0$ (i.e. in comparison with a non-disturbed, uniform porous system).

Figure 3. Dependence of relative average output gas flowrate on time for $w_p$ in the range 0-20\%. 
Figure 2 shows that the initial section (of the order of the first 100 s) is the same for all variants: the
temperature of the porous medium does not yet reach the softening temperature. Then, depending on
how close the agglomeration centers are to the lower boundary of the site, permeability decreases with
different rates: in some cases, a stepwise drop in flow rate is observed after 500 s, in others it remains
smooth almost until the end of the site heating. After multiple numerical experiments, one can obtain
the average flow characteristics (the solid curve in figure 2) and compare them with the characteristics
of the flow in a medium without agglomeration centers. Figure 3 shows the dynamics of flowrate at
the upper boundary of the site, assigned to the corresponding flow rates with zero content of melting
material. Depending on the fraction of the melting material, one can observe a transition from a
smooth, almost linear decrease in flowrate over time (at fractions \(w_P\) of 1-5%) to a sharp decrease that
is close to exponential (at \(w_P\) of 10-20%).

It is also possible to construct the dependence of the total flow rate at the upper boundary on the
fraction of the melting material \(w_P\) (figure 4): this dependence has a sharp drop at 5–10%, then the
drop becomes slower, and at \(w_P = 20\%\) the gas flow is very close to zero after 2000 s. Experimental
works [22-24] show that, at fixed-bed combustion of polymer-containing wastes, the range of plastic
content 10-20\% is often marked as a boundary between the regions of stable and unstable combustion
modes. The values obtained in this paper (5-10\%) are underestimated, which may be due to the
roughness of the two-dimensional model: in real thermal devices, filtration flow develops in three
dimensions. However, the fact of the existence of different stochastic dynamic filtration regimes in
such systems is interesting. It is possible that further expansion of the model (addition of three-
dimensional geometry, chemical heat sources due to heterogeneous oxidation, etc.) will give a more
accurate picture of the phenomena under consideration.

4. Conclusions
Model of two-dimensional non-isothermal filtration in stochastic porous medium is proposed to
simulate permeability changes in polymer-containing mixed granular materials. To this end, melting
phenomenon introduced in the model as a local permeability decreasing process. Results of multiple
simulations allow an estimate of the influence of melting component (polymer) fraction \(w_P\) on
filtration regimes. According to calculation results, there is a range of \(w_P\) (between 5\% and 10\%)
where a sharp decrease in the output gas flowrate is observed. Further work could be concerned with
three-dimensional problem and implementation of more detailed description of physical and chemical processes (pyrolysis, combustion etc.).

Acknowledgments
This work was supported by Russian Foundation for Basic Research (project number 19-08-00744) and was carried out using equipment of the multi-access scientific centre ”High Temperature Circuit”.

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