Mathematical modeling of coke purification in a moving bed reactor

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We present a mathematical model for simulating the steady-state behavior of a moving bed reactor used for the coke purification. This reactor operates in a counterflow gas-solid mode where impurities are removed due to high temperature . The model describes most of the physico-chemical phenomena occurring into the reactor by coupling a gas and solid phases through the Eulerian-Eulerian model. The equations are solved by a commercial numerical code STAR-CD. The results obtained with an industrial reference set of operating parameters are discussed. Then, the influence of some of those operating parameters is studied with the help of the model

Introduction

Moving bed reactors are widely used in chemical and metallurgical industries. They are applied in coal gasification/1,2/, solid waste pyrolysis/4/, organic synthesis/5/, for organization of an adsorption and separation processes/6/. Important are high-temperature applications such as iron ore reduction/8/, and calcination of limestone /3 /. Current paper considers a process of graphitized coke purification in moving bed reactor. Sufficiently high temperature (above 2000 K) is required to release the inorganic impurities from the graphitized particle. The particles have almost spherical shape with diameter about 5 mm.

Fig. 1 schematically presents this moving bed reactor, which is divided into three zones:

- A preheating zone, in which graphite particles, fed at the top of the reactor, descend by gravity and are exposed to a counterflow of high-temperature N_2. This zone is supplied with nitrogen from three plasma torches, located at 120 degrees around circumference.
- A heating zone, which permits the solid particles to reach temperature necessary to start the release of inorganic impurities.
- A cooling zone (heat-recovery zone), where the descending graphite particles are cooled down by a counterflow of cold nitrogen, injected from the supply channel inside the flow splitting cap. The heat which is removed from solid particles is returned back into the heating zone. A proper control of the temperature in the reactor is a major requirement to achieve a constant quality of the production, i.e. well-purified graphite powder. On the other side, high energy input into the reactor makes the process very sensible to economic parameters, and heat recovery is very important to make the process economically viable. Numerical simulation appears to be an adequate and powerful tool for controlling and optimizing the process.

Therefore, a mathematical model for simulating the moving bed reactor in the steady state has been developed. The paper describes the different physicochemical phenomena occurring in the reactor, the assumptions and the equations for solid and gas flow, heat transfer, and chemical reactions in the reactor.

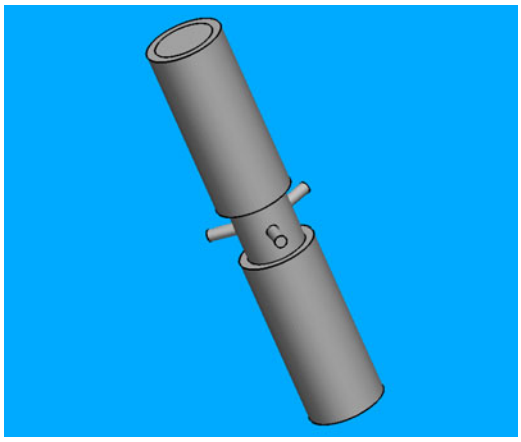

Fig. 1. Schematic representation of the moving bed reactor with 3 plasma jet inlets. Raw material enters from the top; counter-current cold gas enters from the bottom.

The finite volume method is used for solving the mass, momentum and energy balances. Commercial code STAR-CD was used.

A computation was first carried out for an industrial reference set of operating parameters to test the numerical model; then, some parameters were varied in order to better understand the behavior of the reactor.

2. Mathematical modeling

2.1. Kinetics of the chemical reactions

In general case, the removal of impurity from solid coke particle involves diffusion through the crystal lattice and diffusion through the boundary layer on the surface of the particle. For the given particle diameter these two processes were described by macrokinetic expression:

$$\frac{dC_{imp}}{dt} = K_0 \cdot T^{a1} \cdot e^{-\frac{E_a}{RT}} \qquad (1)$$

where K_0, a_1 and E_a are experimentally defined constants.

This approach avoids calculating the mass transfer in each graphite particle and is sufficiently accurate to account for the various resistances.

2.2. Modeling of the moving bed

The flow of solids in the moving bed reactor is characterized by high mass ratio solid-fluid. Modeling of dense granular flow motion accompanied by heat transfer in general case should be considered in the framework of the kinetic theory of interpenetrating flows /9 /, which also is based on the Eulerian approach. In the Eulerian multi-phase model, the phases are treated as interpenetrating continua coexisting in the flow domain. Equations for conservation of mass, momentum and energy are solved for each phase. The share of the flow domain occupied by each phase is given by its volume fraction and each phase has its own velocity, temperature and physical properties. Interactions between phases due to differences in velocity and temperature are taken into account via the inter-phase transfer terms in the transport equations. In order to reduce amount of computations and make model equations feasible for solution in reasonable time, some assumptions have to be made. Because the moving bed reactor exhibits symmetry in angular direction, only 1/72 part of reactor was modeled. Symmetry boundary conditions were applied on the sides of the “slice”.

Following assumptions, based on experimental observations of the cold flow model, were accepted:

for gas flow:

1) steady, turbulent, non-isothermal, non-compressible flow;
2) the gas thermophysical properties are functions of temperature and pressure;
3) gas exchange heat (by convection, conduction and radiation) with walls of reactor and particles;

for moving bed flow:

1) particles exchange momentum with gas and vice versa;
2) (particles exchange heat (by convection, conduction and radiation) with gas and vice versa;
3) particles exchange heat by radiation with each other;
4) flow of the granular material (graphite particles) is laminar
5) The shape of the granular flow corresponds to the pattern, given in Fig.1.

For our conditions the conservation equations are written in the following form /10/:

Conservation of mass

$$\frac{\partial}{\partial x_j}\left(\rho u_j\right) = S_m \qquad (2)$$

Conservation of momentum:

$$\frac{\partial}{\partial x_j}\left(\rho u_j u_i - \tau_{ij}\right) = \frac{\partial p}{\partial x_i} + S_i \qquad (3)$$

Conservation of energy:

$$\frac{\partial}{\partial x_j}\left(\rho u_j h - F_{h.j}\right) = \frac{\partial}{\partial x_j}\left(u_j p\right) - p\frac{\partial u_j}{\partial x_j} + \tau_{ij}\frac{\partial u_i}{\partial x_j} + S_h \qquad (4)$$

$$h = c_p T - c_p^0 T_0 + \sum m_m H_m \qquad (5)$$

In the equations above t is time, x_i is the Cartesian coordinate (i=1,2,3), u_i is the fluid velocity component in the direction x_i, p is the piezometric pressure, ρ is the density, τ_{ij} is the stress tensor component, S_m - mass source; S_i - momentum source components, h is the enthalpy, T is the temperature, $F_{h,j}$ is the diffusional energy flux in the direction x_j. Here, h is the static enthalpy, T – temperature; m_m-mass fraction of mixture constituent m, H_m-heat of formation of constituent m; Σ-summation over all mixture constituents; c_p-mean constant-pressure specific heat at temperature T; c^0_p- reference specific heat at temperature; F_{hj}-diffusional energy flux in direction; S_h-energy source term.
For turbulent flow u_i, p, and other dependant variables, including τ_{ij}, we assume that their ensemble average values are (for Newtonian fluids):

$$\tau_{ij} = 2\mu s_{ij} - \frac{2}{3}\mu \frac{\partial u_k}{\partial x_k}\delta_{ij} - \overline{u_i' \cdot u_j'} \cdot \overline{\rho} \qquad (6)$$

where μ is the molecular dynamic viscosity, and δ_{ij}, the 'Kronecker delta', is unity when i=j and zero otherwise, s_{ij} is the rate of strain tensor, given by:

$$s_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \qquad (7)$$

For turbulent flow the diffusional energy flux in the direction x_j can be expressed as:

$$F_{h.j} = k\frac{\partial T}{\partial x_j} - \overline{u_j' h'} \cdot \overline{\rho} \qquad (8)$$

For turbulence modeling, closures for the terms with pulsation components of velocity and enthalpy are written as:

$$-\overline{\rho} \cdot \overline{u_j' u_i'} = 2\mu_t s_{ij} - \frac{2}{3}\left(\mu_t \frac{\partial u_k}{\partial x_k} + \rho k\right)\delta_{ij} \qquad (9)$$

$$\overline{\rho} \cdot \overline{u_j' h'} = \frac{\mu_t}{\sigma_{h,t}} \cdot \frac{\partial h}{\partial x_j} \qquad (10)$$

$$k = \frac{\overline{u_i' \cdot u_i'}}{2} \qquad (11)$$

where k is the turbulent kinetic energy, μ_t is the turbulent viscosity, $\sigma_{h,t}$ is the turbulent Prandtl number (assumed 0.7). The turbulent viscosity μ_t is linked to the turbulent kinetic energy k and dissipation rate ε via equation (12):

$$\mu_t = f_\mu \frac{C_\mu \rho k^2}{\varepsilon} \qquad (12)$$

where f_m is an empirical coefficient, taken as unity. Transport equations for the turbulent kinetic energy k and its dissipation rate ε are used in the form of the Low Reynolds Number k-ε Model (STAR-CD Manual, 2006).

In current model we assumed that behaviour of gas and moving bed can be described by Navier-Stokes equations. Gas phase and moving bed were considered as two separate interpenetrating fluids. Each of these fluids has its own set of thermophysical properties (thermal conductivity, density, viscosity, specific heat). The momentum exchange between the fluids was described by incorporating into the momentum conservation equations terms for momentum exchange based on the porosity model of Ergun /11/. The pressure drop in the gas passing through the bed is evaluated from:

$$dP_i = -(a.V_i^2 + b.V_i).dx_i \qquad (13)$$

where dP_i - pressure drop in one of 3 directions in Cartesian coordinates;
dx_i - elementary distance;
V_i - component of velocity vector;
a and b - variable coefficients (functions of temperature).

Equations for coefficients a and b are given below:

$$a = 1.75 \cdot \frac{(1-\varepsilon)}{\varepsilon} \cdot \frac{\rho}{\phi \cdot d_p} \qquad (14)$$

$$b = 150 \cdot \frac{(1-\varepsilon)^2}{\varepsilon} \cdot \frac{\mu}{(\phi \cdot d_p)^2} \qquad (15)$$

where

ε - bed porosity
ρ - gas density (function of gas temperature),
φ - sphericity of particles in the bed,
μ - gas viscosity (function of gas temperature),
d_p - diameter of particle
To define sphericity φ from known porosity ε, the graph from the Levenshpile book /11, page 64/ was used. For the particles in the bed, experimentally measured porosity value was equal to 0,53 which gives sphericity value 0,7.

The heat exchange between gas and particles was modelled through the calculation of corresponding source term in right-hand side of energy balance equation. The source term in each cell of the grid was calculated according to the equation:

$$S = h \cdot A \cdot (T_g - T_p) \qquad (16)$$

where h - heat transfer coefficient between gas and particle, W/m^2
A - surface area of the particles in the cell
T_g - gas temperature in the cell
T_b - particle temperature.

Correlation of Rowe and Claxton /12/ was used for calculation of heat transfer coefficient in the moving bed

$$Nu = A \cdot B \cdot Re^n \cdot Pr^{0.333} \qquad (17)$$

where: $Nu = h \cdot D_p \cdot K_g$
$Re = V_p \cdot D_p \cdot \rho_p / \mu_g$
$Pr = \mu_g / (C_{pg} \cdot K_g)$
$A = 2 / [1 - (1 - \varepsilon)^{0.333}]$
$B = 2 / (3 \cdot \varepsilon)$
K_g - thermal conductivity of gas
μ_g - viscosity of gas
C_{pg} - specific heat of gas
ρ_p - density of the particle
D_p - particle diameter
ε - porosity (voidage) of the bed.

Exponent n is defined by equation (18):

$$4.65 \cdot Re^{(-0.28)} = (2 - 3n)/(3n - 1) \qquad (18)$$

Radiative and conductive heat transfer between coke particles was modelled using approach of effective thermal conductivity. According to the work of Gabor and Botterill /13/, the thermal conductivity of porous media (coke particles) was calculated from equation (19):

$$k_r = \frac{1-\varepsilon}{\frac{1}{k_p} + \frac{1}{k_r^0}} + \varepsilon \cdot k_r^0 \qquad (19)$$

where k_p is solid coke thermal conductivity and k_r^0 is radiant conductivity through the porous media. It is defined by equation (20):

$$k_r^0 = 0.229 \cdot \varepsilon_r \cdot \varepsilon \cdot d \cdot \frac{T^3}{10^6} \qquad (20)$$

where ε_r - emissivity of particles,
ε - porosity,
d - average diameter of particles,
T - particle temperature, K
k_p - coke particle conductivity.
The effective thermal conductivity was calculated from the equation:

$$k_e = 5.8 \cdot k_{gas} + k_r \qquad (20a)$$

where k_{gas} is thermal conductivity of pure gas.

2.3. Transport properties.

Gas phase specific heat capacity, viscosity, and thermal conductivity were taken as functions of temperature and pressure.
Movement of granular material in the bed is treated as a pseudoplastic fluid, and the Bingham fluid model is applied as its shear stress-shear rate relationship/7 /. The effective viscosity η_{eff} of the Bingham fluid is determined by shear stress τ and the sheer rate γ:

$$\eta_{eff} = \begin{cases} \eta + \frac{\tau_0}{\gamma} & for\ \tau > \tau_0 \\ \infty & for\ \tau \le \tau_0 \end{cases} \qquad (21a)$$

2.4. Boundary conditions

For solid particle flow, axial boundary conditions are the known input flow rates and compositions. No radial boundary condition is needed.

For gaseous species, axial boundary conditions are the known input flow rates, compositions and pressure. The radial flux is equal to zero on the symmetry axis and at the walls.
The input temperatures of solid and gaseous species are known. At each wall surface, heat is exchanged by convection and radiation.

2.5 Mesh organization

The mesh consists of about 200000 cells for the whole reactor,80000 cells occupy granular flow region and the same amount occupies porous material zone in gas flow.

3. Results and discussion

3.1. Laboratory reactor case.
For the model validation purposes, a laboratory reactor with co-current flow of gas and granular material was built and tested. The comparison of total heat losses, exit gas temperature and final concentration of impurities is given in the Table 1.

Table 1

	Total heat losses, kW	Exit gas temperature, ºC	Impurity concen-tration, mass. %
Measured	50.5	1200	0.020
Calculated	51.1	1230	0.022

3.2. Pilot plant reactor.

The reference case parameters for pilot plant reactor are given in the Table 2.

Table 2.

Parameter	Value
Plasma temperature, K	4500
Plasma flow rate, g/s	18
Cold gas flow rate, g/s	26.4
Coke flow rate, g/s	21.0

The results of calculations are summarized in the following axial temperature distributions graphs.

Axial gas temperature and impurity concentration in the solid particle for reference case process parameters are shown on the Fig.2.

In Fig.3 influence of the coke mass flow rate is shown. The 30% increase in the flow rate brings the coke temperature in heating down by almost 400 C and shifts reaction zone bounded by isotherm 2000 C closer to the outlet of the reactor.

The total residence time in the reactor is about 8 hours; however, only 20 minutes are required to remove the impurities from the coke particle below the required level.

4. Conclusion

The mathematical modeling of a moving bed reactor for the coke purification has been presented.
The developed numerical model simulates the steady-state operation of the reactor. The main physical, chemical and thermal phenomena occurring are taken into account. Eulerian-Eulerian approach was used to model movement of granular flow, heat and mass transfer in the reactor. The sensitivity of the impurity concentration in the solid coke particle to the process parameters was investigated.
First, results were obtained for a reference set of operating parameters. They show the ability of the model to represent the removal of inorganic impurities from coke particle in the reactor and compare well to experimental data. Then, simulations were carried out to study cases where parameters such as the flow rate of raw material and flow rate of cold gas are varied. The final mass fraction of impurities appears to be not very sensible to these variations unless they exceed values when the temperature in reaction zone drops below 2000 C.

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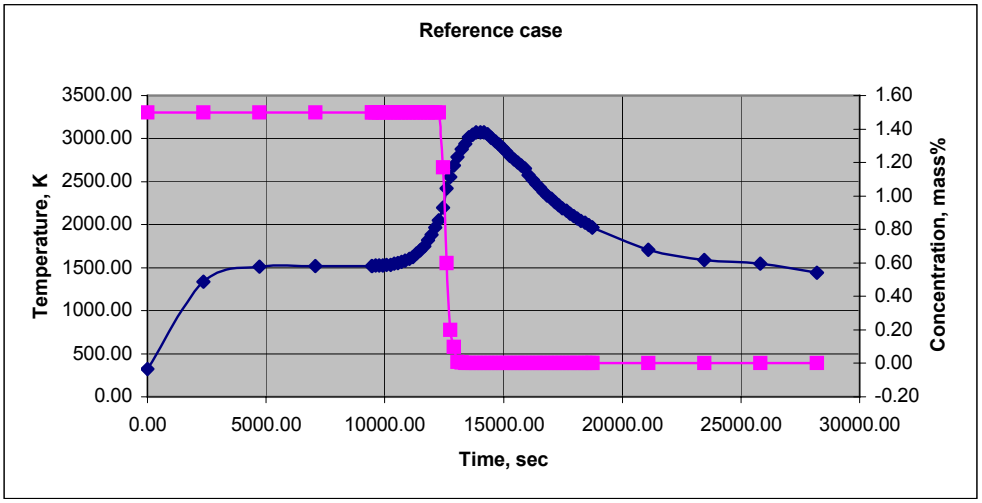

Fig. 2. Reference case: axial gas temperature (blue) and impurity concentration in the coke particle (pink).

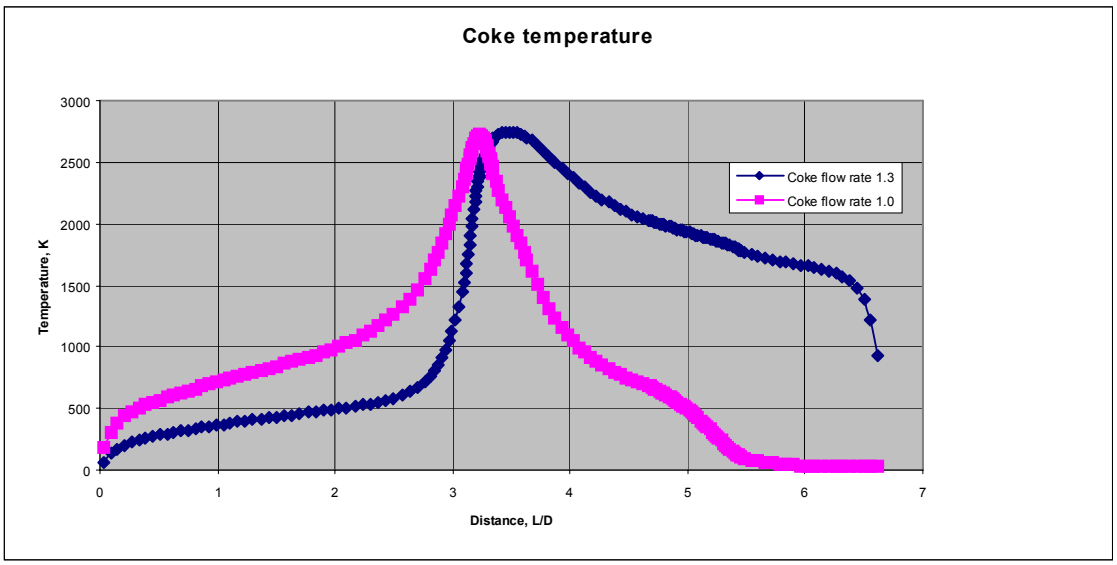

Fig. 3 Influence of the coke flow rate 30% increase on axial coke temperature.