1D Mathematical Model of Coke Combustion

Robert Straka and Tadeusz Telejko

Abstract—We describe behavior of the moving coke bed combustion in a cupola furnace, based on balance equations for big coke particles and oxygen enriched blast. The undergoing chemical reactions are described by the Arrhenian kinetics (reaction rate proportional to $e^{-\frac{E}{RT}}$ for homogeneous reactions) as well as diffusion limited rate chemistry for heterogeneous reactions on the coke surface. We also consider the heat transfer among solid and gas phases and furnace water jacket. The system of PDEs is discretized using the finite volume method (FVM) and time integration is performed via Euler explicit scheme together with point-implicit preconditioning of species balance equations. Simulation results are compared with experimental ones.

Index Terms—coke combustion, reactive flow modeling, heterogeneous combustion

I. INTRODUCTION

COMBUSTION of large particles constitutes one of the major problems in modeling of industrial scale combustion. The rate of combustion is limited by two competing processes, the kinetic limited and the diffusion limited combustion. While kinetic limited combustion is the case for small particles and homogeneous reactions in the gas phase, the diffusion limited combustion takes place during surface heterogeneous reactions on the large particles. Main products of such reactions are carbon dioxide and carbon monoxide whose concentrations in exhaust gases are to be controlled and in the latter case limited to the minimum. When coke burns, extensive amounts of carbon monoxide can be released in flue gases due to e.g. Boudouard reaction. However in some cases this is necessary part of industrial process (as in the case of a blast furnace) in other cases this is strictly unwanted. We develop a 1D model of large coke particles combustion in a cupola furnace, together with essential chemical reactions and heat and mass transfer relations which can be further used for simulation of other industrial processes where the coke combustion is main source of heat and emissions. Model itself is based on heat and mass balance laws for counter current tubular reactor. Comparison of simulated and experimental results shows good agreement [1] and the model was incorporated into the bigger project of rock melting cupola simulation tool [2].

II. MATHEMATICAL MODEL

Moving bed consists of two phases, flue gases and solid coke particles, for the solid phase we have following mass and heat balances:

$$\frac{\partial \varepsilon_s \rho_s u_s}{\partial x} = S_{rs},$$

$$\frac{\partial \varepsilon_s \rho_s h_s}{\partial t} + \frac{\partial \varepsilon_s \rho_s u_s h_s}{\partial x} = S_{hs},$$

where ε_s is solids' volume fraction ($\varepsilon_s = 1 - \varepsilon_g$ where ε_g is void fraction), ρ_s is particle density of coke, u_s is descent velocity (which is constant for all particles at given time), S_{rs} is mass source term due to coke combustion and gasification, h_s is specific enthalpy of coke particles and S_{hs} is energy source term due to combustion, gasification and heat transfer to the surrounding gas and walls. For flue gases we have mass, heat and components' mass fractions balances:

$$\frac{\partial \varepsilon_g \rho_g}{\partial t} + \frac{\partial \varepsilon_g \rho_g u_g}{\partial x} = S_{rg},$$

$$\frac{\partial \varepsilon_g \rho_g h_g}{\partial t} + \frac{\partial \varepsilon_g \rho_g u_g h_g}{\partial x} = S_{hg},$$
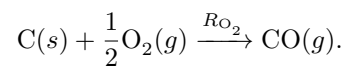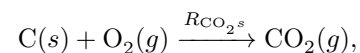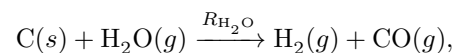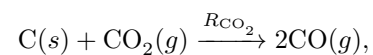
$$\frac{\partial \varepsilon_g \rho_g u_g Y_j}{\partial t} + \frac{\partial \varepsilon_g \rho_g u_g Y_j}{\partial x} = S_{Y_j},$$

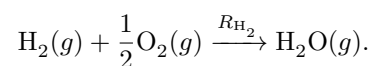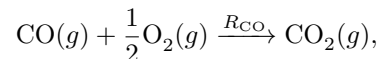$$j \in \{O_2, CO_2, H_2O, CO, H_2\},$$

where ρ_g is gas density, u_g is actual velocity, S_{rg} is mass source term due to coke combustion and gasification, h_g is specific enthalpy, S_{hg} is energy source term due to combustion and heat transfer to the coke particles and walls, Y_j is mass fraction of j-th component of flue gas and S_{Y_j} is source term due to homogeneous reactions in flue gases. Gas phase is considered to be in a state of plug flow, and its superficial velocity is computed from known blast volumetric flux, rate of combustion and barotropic condition inside the cupola furnace.

Chemical reactions considered in the model are:

1) Heterogeneous gasification of fuel

$$C(s) + CO_2(g) \xrightarrow{R_{CO_2}} 2CO(g),$$

$$C(s) + H_2O(g) \xrightarrow{R_{H_2O}} H_2(g) + CO(g),$$

$$C(s) + O_2(g) \xrightarrow{R_{CO_2 s}} CO_2(g),$$

$$C(s) + \frac{1}{2}O_2(g) \xrightarrow{R_{O_2}} CO(g).$$

2) Homogeneous combustion

$$CO(g) + \frac{1}{2}O_2(g) \xrightarrow{R_{CO}} CO_2(g),$$

$$H_2(g) + \frac{1}{2}O_2(g) \xrightarrow{R_{H_2}} H_2O(g).$$

3) Water gas shift

$$CO(g) + H_2O(g) \xrightarrow{R_w} CO_2(g) + H_2(g).$$
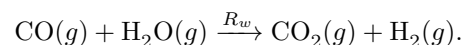
Heterogeneous reactions take place in the vicinity of the coke particles creating thin film, away from this film homogeneous combustion of carbon monoxide and hydrogen occurs together with water gas shift reaction. Combination of source terms R_* yields the overall source terms S_{rs}, S_{rg} and S_{Y_j}

for appropriate phase and specie, these terms are described in the following section.

Heat transfer among gas, particles and walls is given by following relations:

$$
\begin{aligned}
S_{hg} &= -\sum_k \eta_k \Delta H_k R_k - S_{\mathrm{h,het}} + a_s h_{gs}(T_s - T_g) \\
&\quad + a_s \sigma e_s(T_s^4 - T_g^4) + Q_{\mathrm{gw}},
\end{aligned}
$$

$$
\begin{aligned}
S_{hs} &= -\sum_k (1 - \eta_k) \Delta H_k R_k + S_{\mathrm{h,het}} \\
&\quad - a_s h_{gs}(T_s - T_g) - a_s \sigma e_s(T_s^4 - T_g^4) + Q_{\mathrm{sw}},
\end{aligned}
$$

where first terms are due to chemical reactions with η_k being portion of energy ΔH_k released by homogeneous reaction R_k transferred to gas phase, $S_{\mathrm{h,het}}$ is energy released from heterogeneous reactions, third terms is combined convective and conductive heat transfer h_{gs} between gas and particles surface a_s with T_g gas- and T_s solid temperatures, next terms provide radiative heat exchange between gas and solid (effective emissivity of coke e_s is assumed to be 0.9) and last terms represent heat losses to walls, $\sigma = 5.67 \cdot 10^{-8}$ is Stefan-Boltzmann constant. Note that summing up those two equations and dropping first and last terms yields zero, i.e. non-chemical energy is conserved in the model when the system is adiabatically insulated. Energy exchange term for heterogeneous reactions reads:

$$
\begin{aligned}
S_{\mathrm{h,het}} &= R_{\mathrm{O_2}}(M_{\mathrm{O_2}} h_{\mathrm{O_2}}(T_g) - 2M_{\mathrm{CO}} h_{\mathrm{CO}}(T_s)) \\
&\quad + R_{\mathrm{CO_2}s}(M_{\mathrm{O_2}} h_{\mathrm{O_2}}(T_g) - M_{\mathrm{CO_2}} h_{\mathrm{CO_2}}(T_s)) \\
&\quad + R_{\mathrm{CO_2}}(M_{\mathrm{CO_2}} h_{\mathrm{CO_2}}(T_g) - 2M_{\mathrm{CO}} h_{\mathrm{CO}}(T_s)) \\
&\quad + R_{\mathrm{H_2O}}(M_{\mathrm{H_2O}} h_{\mathrm{H_2O}}(T_g) - M_{\mathrm{H_2}} h_{\mathrm{H_2}}(T_s) \\
&\quad - M_{\mathrm{CO}} h_{\mathrm{CO}}(T_s)).
\end{aligned}
$$

Overall heat transfer coefficient h_{gs} is given by relation [3]:

$$
h_{gs} = 1.061 \delta_{h_{gs}} \left(d_s \rho_g \frac{u_g}{\mu_g} \right)^{-0.41} \rho_g u_g c_{p,g} \mathrm{Pr}_g^{-2/3},
$$

where $\delta_{h_{gs}}$ is a correction coefficient established during validation, μ_g is gas dynamic viscosity, $c_{p,g}$ is gas specific heat and Pr_g is Prandtl number. Particle diameter d_s, surface area a_s and volume fraction ε_s change during combustion and gasification and are computed from:

$$
\begin{aligned}
d_s &= d_{s,\mathrm{in}} \sqrt[3]{\frac{\varepsilon_s \rho_s u_s}{(\varepsilon_s \rho_s u_s)_{\mathrm{in}}}}, \\
a_s &= \frac{6\varepsilon_s}{\phi_s d_s}, \\
\varepsilon_s &= \frac{\rho_{s,\mathrm{bulk}}}{\rho_s},
\end{aligned}
$$

where ϕ_s is sphericity of coke particles. Non-conserved energy terms due to interaction with surrounding walls are:

$$
Q_{\mathrm{sw}} = A\sigma(\xi_s e_s T_s^4 - e_w T_{wall}^4),
$$

the correction parameter ξ_s must be determined from measurements and wall emissivity is set to $e_w = 0.85$,

$$
Q_{\mathrm{gw}} = A\sigma e_g(T_g^4 - T_{wall}^4) + A h_{gw}(T_g - T_{wall}),
$$

where heat transfer coefficient from gas to wall is given by [4]:

$$
h_{gw} = 0.07659 \frac{\lambda_g}{d_s} \frac{1 - \varepsilon_g}{\varepsilon_g} \mathrm{Re}_s^{0.815} \mathrm{Pr}_g^{-0.5} \frac{T_g}{T_{wall}}^{0.73},
$$

with λ_g gas heat conduction coefficient and Re_s is Reynolds number based on particle diameter. System of equations is accompanied with following relations:

$$
p = \rho R T_g, \quad \rho = \sum_j \rho_j, \quad h_{g/s} = \sum_j \int_{T_0}^{T_{g/s}} c_{p,j/s}(T)\mathrm{d}T.
$$

III. HETEROGENEOUS AND HOMOGENEOUS COMBUSTION

Mass source terms for balance equations are derived from stechiometric equations from previous section and read:

$$
\begin{aligned}
S_{rg} &= M_C(R_{\mathrm{CO_2}} + R_{\mathrm{H_2O}} + R_{\mathrm{CO_2(s)}} + 2R_{\mathrm{O_2}}), \\
S_{rs} &= -\frac{M_C}{C^r}(R_{\mathrm{CO_2}} + R_{\mathrm{H_2O}} + R_{\mathrm{CO_2(s)}} + 2R_{\mathrm{O_2}}), \\
S_{Y_{\mathrm{O_2}}} &= -M_{\mathrm{O_2}}\left(R_{\mathrm{O_2}} + R_{\mathrm{CO}} + R_{\mathrm{H_2}} + R_{\mathrm{CO_2}s}\right), \\
S_{Y_{\mathrm{H_2O}}} &= M_{\mathrm{H_2O}}\left(2R_{\mathrm{H_2}} - R_{\mathrm{H_2O}} - R_w\right), \\
S_{Y_{\mathrm{CO}}} &= M_{\mathrm{CO}}\left(2(R_{\mathrm{CO_2}} + R_{\mathrm{O_2}} - R_{\mathrm{CO}}) + R_{\mathrm{H_2O}} - R_w\right), \\
S_{Y_{\mathrm{CO_2}}} &= M_{\mathrm{CO_2}}\left(-R_{\mathrm{CO_2}} + 2R_{\mathrm{CO}} + R_{\mathrm{CO_2}s} + R_w\right), \\
S_{Y_{\mathrm{H_2}}} &= M_{\mathrm{H_2}}\left(R_{\mathrm{H_2O}} - 2R_{\mathrm{H_2}} + R_w\right),
\end{aligned}
$$

where M_C is molar mass of carbon and C^r is mass fraction of carbon in coke as given by ultimate analysis of fuel sample. Reactions terms are described by Arrhenian kinetic for homogeneous reactions i.e. the reaction rate k is given by:

$$
k_k^{\mathrm{hom}} = A_k \mathrm{e}^{\left(-\frac{E_k}{R_0 T}\right)},
$$

where frequency factors A_k and activation energies E_k for reactions are taken from [5]. Heterogeneous reactions are diffusion-kinetic limited i.e. their rates are evaluated as:

$$
k_k^{\mathrm{het}} = \min(k_k^{\mathrm{kin}}, k_k^{\mathrm{diff}}),
$$

where diffusion rate:

$$
k_k^{\mathrm{diff}} = \frac{\mathrm{Sh}_j D_j}{d_s}
$$

is evaluated using Sherwood number (Sh_j) correlations by Dwivedi and Upadhyay [6]:

$$
\mathrm{Sh}_j = \mathrm{Sc}_j^{1/3} \mathrm{Re}_s \left(\frac{0.765}{\mathrm{Re}_s^{0.82}} + \frac{0.365}{\mathrm{Re}_s^{0.386}} \right),
$$

where Sc_j and D_j are Schmidt number and diffusion coefficient for $\mathrm{O_2}$, $\mathrm{CO_2}$ and $\mathrm{H_2O}$ [7]:

$$
\begin{aligned}
D_{\mathrm{O_2}} &= 2.2 \cdot 10^{-4} \left(\frac{T_g}{1000} \right)^{1.75} \frac{101325}{p}, \\
D_{\mathrm{H_2O}} &= 1.6 \cdot 10^{-5} \left(\frac{T_g}{395} \right)^{1.75} \frac{101325}{p}, \\
D_{\mathrm{CO_2}} &= 2.2 \cdot 10^{-5} \left(\frac{T_g}{273} \right)^{1.75} \frac{101325}{p}.
\end{aligned}
$$

IV. NUMERICAL ALGORITHM

Furnace chamber is divided into finite control volumes and finite volume method approximation of spatial derivatives together with simple explicit Euler scheme for time derivatives is applied:

$$
\frac{\partial U}{\partial t} + \frac{\partial F}{\partial x} = S
$$

$$\frac{U_{i+1}^\tau - U_i^\tau}{\Delta \tau} + \frac{1}{|\Omega_i|}\left((\partial \Omega U)_{i+1/2} - (\partial \Omega U)_{i-1/2}\right) = S_i,$$

where following notation is used:

$$U = \begin{pmatrix} \varepsilon_g \rho_g \\ \varepsilon_g \rho_g h_g \\ \varepsilon_g \rho_g Y_{O_2} \\ \varepsilon_g \rho_g Y_{CO_2} \\ \varepsilon_g \rho_g Y_{CO} \\ \varepsilon_g \rho_g Y_{H_2} \\ \varepsilon_g \rho_g Y_{H_2O} \\ 0 \\ \varepsilon_s \rho_s h_s \end{pmatrix}, F = \begin{pmatrix} \varepsilon_g \rho_g u_g \\ \varepsilon_g \rho_g u_g h_g \\ \varepsilon_g \rho_g u_g Y_{O_2} \\ \varepsilon_g \rho_g u_g Y_{CO_2} \\ \varepsilon_g \rho_g u_g Y_{CO} \\ \varepsilon_g \rho_g u_g Y_{H_2} \\ \varepsilon_g \rho_g u_g Y_{H_2O} \\ \varepsilon_s \rho_s u_s \\ \varepsilon_s \rho_s u_s h_s \end{pmatrix}, S = \begin{pmatrix} S_{rg} \\ S_{hg} \\ S_{Y_{O_2}} \\ S_{Y_{CO_2}} \\ S_{Y_{CO}} \\ S_{Y_{H_2}} \\ S_{Y_{H_2O}} \\ S_{rs} \\ S_{hs} \end{pmatrix}.$$

When fast (chemical reactions) and slow (heat transfer, slow chemical reactions) processes are coupled, above system of equations has great disparity in Jacobian's eigenvalues which leads to extremely small time steps in order to keep positivity and accuracy of the solution. One remedy is to apply point implicit preconditioning of time derivatives of species equations [8]:

$$U_{Y_i}^{\tau+1} = U_{Y_i}^\tau + \frac{\Delta \tau}{1 + \Delta \tau \partial S_{Y_i} / \partial U_{Y_i}} [\text{Res}]_{Y_i}^\tau,$$

this technique does not affect steady-state solution which is the desired one. The above system of discretized equations is then accompanied with boundary conditions, the known volumetric flux, composition and temperature of blast at the bottom of the cupola and composition and temperature of solid fuel at the opposite side. The initial conditions must be carefully chosen to support startup of the combustion inside the cupola.

V. Results

To examine model abilities, we setup the model consistently with experiment performed by Hameedullah and Chakraborty [9] (values are given in Tab. I). Character N before m^3 stands for normal conditions i.e. volume of gas is given at pressure equal to 1 atmosphere and temperature equal to 273.15 Kelvins. A bulk density is mass of material related to the volume which the material occupies i.e. in coke filled container (so called "bed") of volume equal to 1 m^3 we have 500 kg of coal particles. During several runs, correction parameters (that cannot be measured or predicted in advance) were fine tuned until agreement between measured and computed values was established. The parameter $\delta_{h_{gs}}$ has great influence on temperature profiles as increasing heat flux to the wall decreases flue gas and coal temperatures and rather small influence on concentrations profiles (with observable effect on carbon dioxide concentrations shift). The parameter ξ_s has very strong influence on the temperature profiles in the middle of the cupola (where the highest temperatures occur) and thus observable influence on the carbon monoxide and carbon dioxide concentrations in the upper half of the cupola. Comparison of experimental data (digitally acquired from the article [9]) with computed is shown in Fig. 1. Computed values are depicted as lines, molar fractions of CO_2, CO, O_2, H_2O and H_2 together with flue gas temperature and coal particles temperature. Measured values taken from the paper [9] are denoted by symbols, there are six levels where concentrations of oxygen,

TABLE I
SIMULATION SETUP.

Hot blast volume	169.8 Nm³/h
Blast temp.	80 °C
Oxygen enrichment	0 Nm³/h
Coke bulk density	500 kg/m³_BED
Coke diameter	0.04 m
Carbon content	71.3 %
Cupola diameter	0.2 m
Cupola height	1.37 m
Wall temp.	37 °C

carbon monoxide and carbon dioxide were measured. At each level, three samples were taken at near wall, midpoint and center locations. Accuracy of the tuned model is surprisingly high.

VI. Conclusion

The complex model of coke combustion and gasification in moving bed was developed. Data from simulations were compared with experimenal data and are in good agreement. From the simulated and measured data it is clear that oxygen is consumed up to the half of the cupola with increasing concentrations of carbon monoxide and dioxide. The presence of high temperature, water molecules and oxygen keeps the concentration of carbon monoxide low. The peak temperature of flue gases is at same position as the peak carbon dioxide concentration indicating that at this point the combustion is the most intensive. After this point, oxygen is almost exhausted and carbon monoxide produced by Boudouard reaction cannot be burned to carbon dioxide, thus the concentration of carbon monoxide is increasing together with decrease in carbon dioxide concentration and temperature decrease due to endothermic nature of Boudouard reaction. Nevertheless the temperature of flue gases are too high to stop Boudouard reaction and it proceeds until the end of cupola. High temperature of flue gases and lack of oxygen also cause decrease in water and increase in hydrogen concentrations due to water gas and water gas shift reactions. The extended version of the model is used in simulation tool of rock-melting cupola. The model can be further developed and enhanced to simulate different industrial processes which involve moving bed combustion (e.g. blast furnaces) of coal particles.

References

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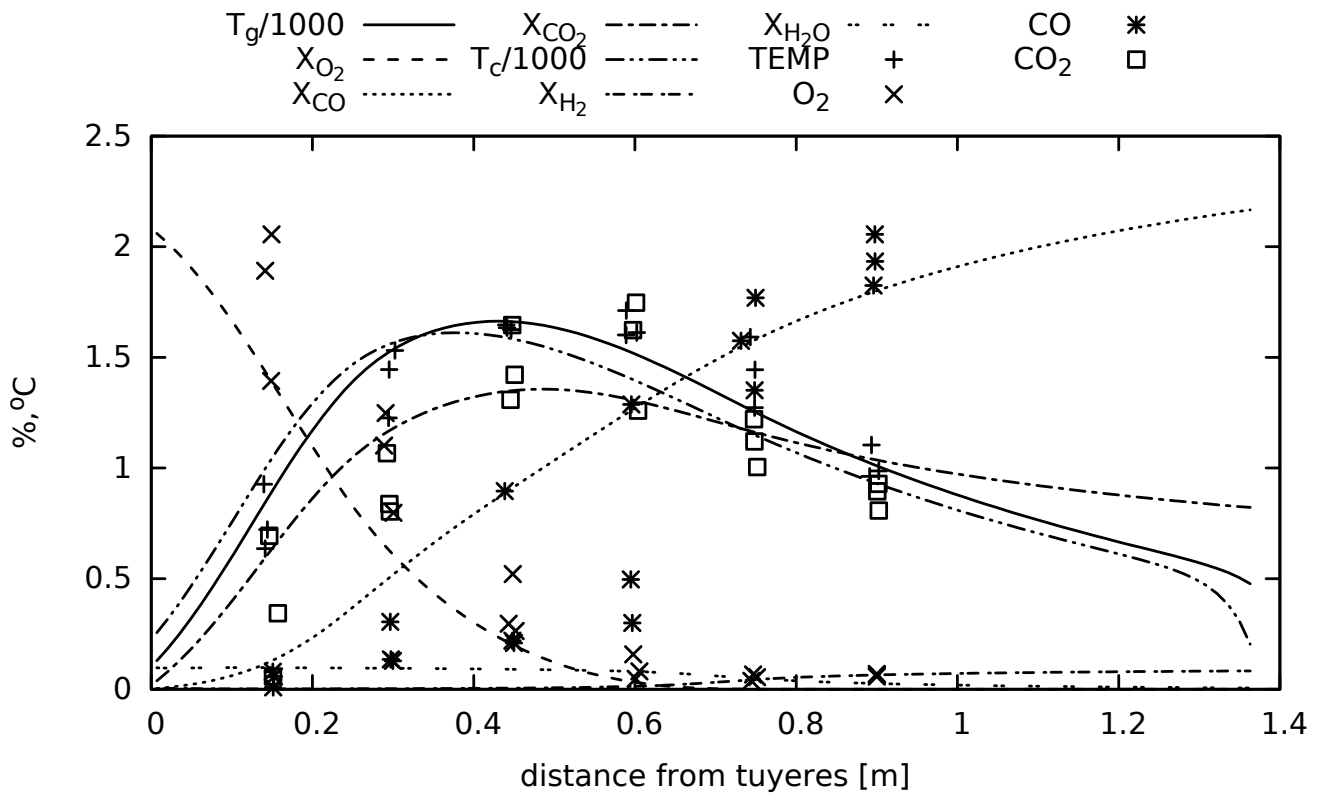
Fig. 1. Simulation results, comparison of measured (symbols) and computed (lines) values. X axis denotes position from tuyeres, Y axis is scaled to contain both temperature in Celsius and molar fractions in percents.

[9] M. Hameedullah and P. N. Chakraborty, "Combustion in a cold blast cupola," *Combustion Science and Technology*, vol. 45, pp. 129–146, 1986.