

Modelling of Gasification of a Single Coal Char Particle*

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A mathematical model of gasification of a large single coal char particle in a carbon dioxide atmosphere was developed. The model formulation took into account the heterogeneous reaction mechanism and the solid phase structure. The pre-exponential factor of the gas-solid reaction of carbon with carbon was estimated in this study whereas the values of activation energies and other model parameters were taken from literature. The model was used to fit the experimental data obtained by TG measurements that were performed using coal char particles prepared by degasification of Slovak brown coal from the coal mine Cígeľ at low and medium temperatures and at atmospheric pressure with different inlet mixtures of carbon dioxide and argon.

Combustion and gasification are the main commercial technologies of coal processing where the heterogeneous reaction between carbon and carbon dioxide takes place. A successful design and optimal operation of commercial combustors/gasifiers would not be possible without a proper understanding of the combustion/gasification reaction mechanism and kinetics. The mechanism of coal combustion/gasification consists of various processes, which proceed at various rates. This behaviour can be explained by the single coal particle history. Once the coal particle is placed into the combustion/gasification device, immediate and quick release of volatile compounds takes place. Then, a slower step of the process, namely oxidation of carbon, is started. Four main combustion reactions are assumed, which include three heterogeneous reactions of carbon oxidation and one homogeneous reaction of carbon monoxide oxidation to carbon dioxide [1, 2]. However, only the reaction of carbon with carbon dioxide is necessary for the formulation of a model of coal gasification [1].

Both more complex reaction schemes [3, 4] and models of coal combustion/gasification based on a simplified reaction scheme and for stationary conditions [4] are available in literature. This simplification is achieved by the minimization of the influence of other factors, for example, transport limitations when kinetic parameters are determined. Our task was the formulation of a model able to predict the single coal char particle behaviour during its combustion/gasification. This model includes simultaneous intraparticle diffusion and reaction, internal heat

transfer by conduction, and external heat transfer by radiation and convection.

From the chemical engineering point of view, combustion or gasification of coal char can be characterized as noncatalytic gas-solid reaction. The two limiting mechanisms, namely the homogeneous and the shell progressive one [2, 5], are used to describe this process. However, the real behaviour of the coal particle during its combustion/gasification is more complex and could be assumed as superposition of the two mechanisms mentioned above. Careful selection of the mechanism should reflect the reaction rate magnitude and the rate of intraparticle mass transport. In our previous study [1], the evidence for homogeneous mechanism of coal gasification in a wide range of temperature and carbon dioxide concentration was found.

THEORETICAL

During the model development the following assumptions were adopted:

- nonisothermal conditions,
- constant pressure,
- constant particle size during reaction,
- particle free of volatile compounds at the beginning of the process,
- increase of the particle porosity during its oxidation,
- no solid products formed in the reaction course, and
- heat exchange realized by conduction through

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the laminar layer, and by radiation.

Applying the above-mentioned assumptions, the reaction rate is given by

$$\dot{\xi} = k_{\infty} \exp\left(-\frac{E_a}{RT}\right) C_C^m C_{CO_2}^n \quad (1)$$

The mass balance for gas components ($i = 1$ for CO_2 , $i = 2$ for CO) inside the coal particle is given by the following dimensionless equation

$$\frac{\partial(\varepsilon_p Y_{si})}{\partial \tau} = \xi_i \frac{1}{\varphi^2} \frac{\partial}{\partial \varphi} \left(\left(\frac{\varepsilon_p}{\varepsilon_{p0}} \right)^{\beta} \varphi^2 \frac{\partial Y_{si}}{\partial \varphi} \right) - Th^2 \nu_i R_r \quad (2)$$

The carbon mass balance in the dimensionless form is given by

$$\frac{\partial Y_C}{\partial \tau} = -\kappa Th^2 \nu_C R_r \quad (3)$$

The enthalpy balance for the coal particle in the dimensionless form can be expressed as

$$\Xi \frac{d\theta_s}{d\tau} = \Lambda \nabla^2 \theta_s + \eta Th^2 R_r \quad (4a)$$

The initial conditions were as follows

for $t = 0$:

$$Y_{si} = Y_{si}^0 = 0 \quad (4b)$$

$$Y_C = Y_C^0 = 1 \quad (4c)$$

$$\varepsilon_p = \varepsilon_p^0 \quad (4d)$$

$$D_{esi} = D_{esi}^0 \quad (4e)$$

$$\theta_s = \theta_s^0 \quad (4f)$$

Boundary conditions applied

for $t > 0$ and $\varphi = 0$:

$$dY_C/d\varphi = dY_{si}/d\varphi = d\theta_s/d\varphi = 0 \quad (4g)$$

for $t > 0$ and $\varphi = 1$:

$$Y_{gi} = Y_{si}^S \quad (4h)$$

$$d\theta_s/d\varphi = \{B i_h (\theta_g - \theta_s^S) + E((\theta_g)^4 - (\theta_s^S)^4)\} \quad (4i)$$

During gasification/combustion both the particle internal structure and its porosity are changed. Due to the porosity variation also other parameters are changed. These changes correspond to decrease of the particle mass. Assuming the amount of other solid components negligible, the porosity variation is proportional to the changes of carbon amount in the coal particle. If the linear relation between the carbon conversion and the particle porosity is assumed [6], the porosity change could be expressed by the following dimensionless equation

$$\varepsilon_p = \varepsilon_p^0 + \psi(1 - Y_{sC}) \quad (5)$$

The effective diffusion coefficients and the thermal conductivity vary with the porosity, too. These dependences are expressed as follows

$$\frac{D_{esi}}{D_{esi}^0} = \left(\frac{\varepsilon_p}{\varepsilon_p^0} \right)^{\beta} \quad (6)$$

$$\Lambda = \frac{\lambda_u}{\lambda_u^0} = \left[1 - \left(1 - \frac{\lambda_{ua}}{\lambda_u^0} \right) (1 - Y_C) \right] \quad (7)$$

where β is equal to 2 for random pore size distribution [7]. The effective diffusion coefficient of gas components in solid phase at initial conditions can be calculated by the following equation

$$D_{esi} = \frac{D_i \varepsilon_p}{\tau_p} \quad (8)$$

The binary diffusion coefficient, D_i , was calculated using the equation from literature [8]

$$D_i = \frac{0.00143T^{1.75}}{PM_{i,Ar}^{1/2} [\Sigma_i^{1/3} + \Sigma_{Ar}^{1/3}]^2} \quad (9)$$

where

$$M_{i,Ar} = 2 \left[\frac{1}{M_i} + \frac{1}{M_{Ar}} \right]^{-1} \quad (10)$$

The values of diffusivity volumes Σ_i were taken from tables available in [1].

EXPERIMENTAL

Coal from the coal mine Cígeľ (Handlová, Slovakia) was used in our experiments. Coal char was prepared by slow degassing of the original coal particle in nitrogen up to 1100 K. Gasification experiments were carried out in an equipment described previously [9]. Atmosphere with different carbon dioxide concentrations (5–100 vol. %) in argon was used. The initial gasification temperatures varied within the range from 1000 to 1300 K. The coal particle diameter was in the range of 6–10 mm. The volumetric flow rate of the inlet feed was $100 \text{ dm}^3 \text{ h}^{-1}$. Gasification of the particle was conducted up to the desired mass of the particle (50 %–100 % of carbon burnout). The mass of the particle, temperature in the particle centre, at the particle surface, and the temperature of gas close to the geometrical surface of the particle were continuously measured.

The overall reaction rate of the coal char particle gasification depends on the accessibility of its internal surface to the gaseous reactant (CO_2). The particle internal surface accessibility for gases is closely related to the particle pore structure. In our previous work [10] we have found that during the release of volatile compounds an intraparticle pore structure is

created, in which the diffusion of gaseous reactants takes place. Therefore, the pore structure of original, devolatilized, partially and completely burnt particles was measured using the gas adsorption (SORPTOMATIC 1900, Fisons, Rodano, Milan, Italy) and mercury penetration (Porosimeter P2000, Fisons, Rodano, Milan, Italy) methods.

RESULTS AND DISCUSSION

The mathematical model represented by eqns (2–4) is a system of nonlinear differential equations, which were transformed into a set of ordinary differential equations using the orthogonal collocation method. This system was solved by Gear's method with time as independent variable.

The model was simplified applying the assumption of negligible resistance of the laminar film to the mass transfer (compared to the internal mass transfer and the reaction kinetics). Thus, the concentration of gaseous component i at the particle external surface is equal to its concentration in the gas bulk flow. The heat transfer between the coal char particle and the surrounding gas phase is assumed to occur by means of radiation and convection throughout the laminar layer. The heat transfer coefficient, α , depends on the experimental set-up, and was calculated by a semiempirical equation from literature [5]. The initial values of porosity and coal char density were measured experimentally. The coal char particle density as well as the specific heat capacity and emissivity were assumed to be independent of temperature.

Only one kinetic parameter, the pre-exponential factor, was estimated. The activation energy value ($143.0 \text{ kJ mol}^{-1}$) was published elsewhere [9], the reaction order with respect to carbon and carbon dioxide equal to their stoichiometric coefficients was assumed. The estimation of model parameter was based on the least-square method employing a modified Levenberg–Marquardt algorithm. 19 records of experimental particle mass variation *vs.* time were fitted in order to get the optimal value of the model pre-exponential factor ($1017.5 \text{ m}^6 \text{ mol}^{-1} \text{ s}^{-1} \text{ kg}^{-1}$). However, it is almost impossible to compare this value with other values available in literature. This parameter is strongly influenced by the origin and the type of coal used in experiments [11]. Moreover, the value of the pre-exponential factor could be related to other particle properties (internal surface area, surface area accessible for the reaction, particle mass, solid reactant mass, *etc.*) and depends on the form of the rate equation (reaction order).

The comparison of experimental and computed dependences of particle mass and temperature in the centre of particle *vs.* time showed a good agreement (Figs. 1 and 2, respectively). A slight difference in dependence of the particle mass decrease *vs.* time in Fig. 1 (first the computed reaction rate is higher, then

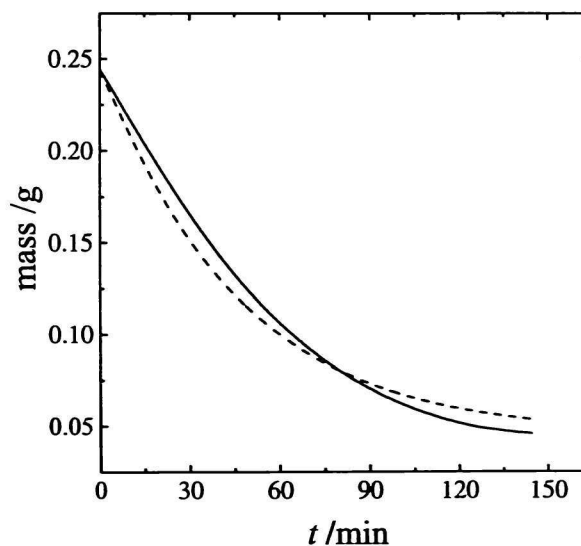


Fig. 1. Comparison of experimental (solid line) and calculated (dashed line) variation of coal char particle mass during gasification in a mixture of carbon dioxide and argon *vs.* time (content of CO_2 25 %, initial temperature 1220 K).

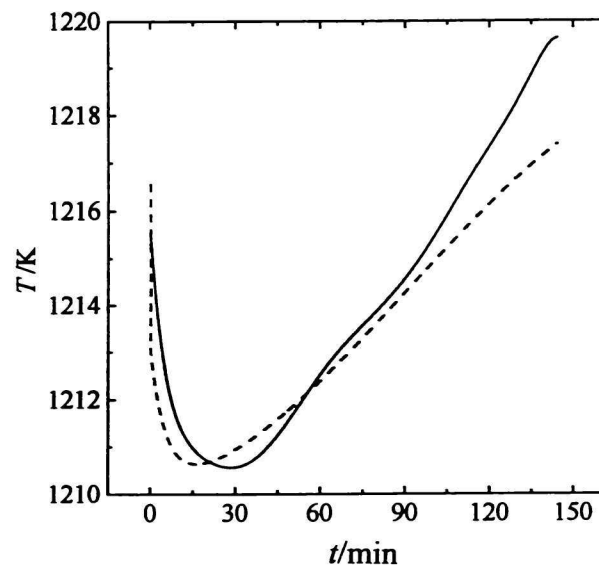


Fig. 2. Comparison of experimental (solid line) and calculated (dashed line) variation of temperature in the centre of coal char particle during gasification in a mixture of carbon dioxide and argon *vs.* time (content of CO_2 25 %, initial temperature 1220 K).

it becomes lower compared to that measured) could be explained by that the carbon reaction order was probably lower than unity.

Figs. 3 and 4 present the calculated reactant concentration profiles (C and CO_2 , respectively) inside the coal char particle at different reaction times. The approximately constant carbon concentration inside the whole particle shown in Fig. 3 confirmed the suitability of the use of the reaction-diffusion mechanism

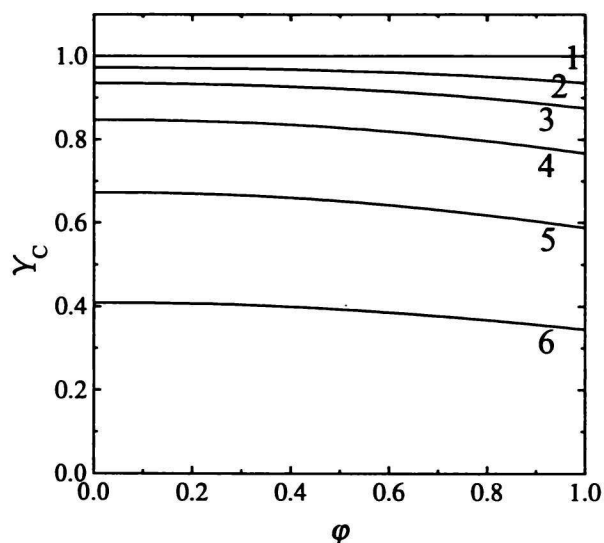


Fig. 3. Calculated carbon concentration profile inside the coal char particle at different reaction times (1. 0 min, 2. 2.5 min, 3. 5 min, 4. 10 min, 5. 20 min, 6. 2400 min).

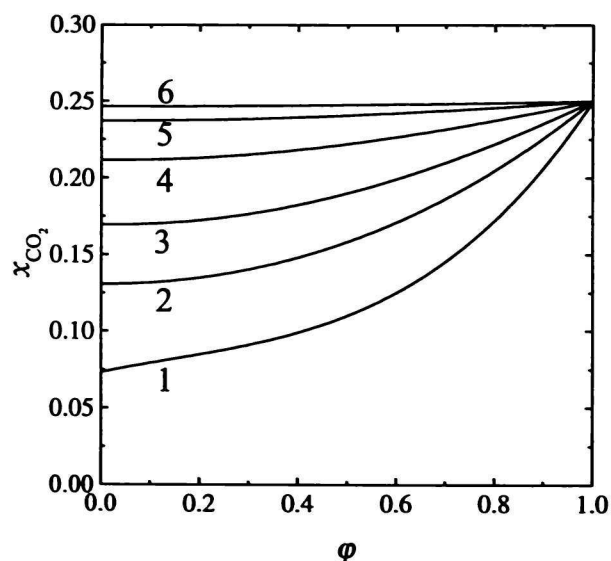


Fig. 4. Calculated mole fraction profiles of carbon dioxide inside the coal char particle at different reaction times (1. 1 s, 2. 2.5 min, 3. 5 min, 4. 10 min, 5. 20 min, 6. 2400 min).

for the coal char gasification modelling. Moreover, the carbon dioxide concentration inside the coal char particle reached the inlet CO_2 concentration already at carbon conversion of 0.3 (Fig. 4, curve 5). Therefore, it could be concluded that the intraparticle diffusion of carbon dioxide was faster than its consumption.

CONCLUSION

The main goal of this work was to develop a simple model for the prediction of the large coal char parti-

cle gasification, able to describe the variation of the coal char particle mass and the temperature inside the coal char particle with time. The value of $1017.5 \text{ m}^6 \text{ mol}^{-1} \text{ s}^{-1} \text{ kg}^{-1}$ for the only estimated parameter of the model developed in this study (the pre-exponential factor of the heterogeneous reaction between carbon and carbon dioxide) was obtained by comparison of experimental and modelled data. All other model parameters were taken from literature. The fit of experimental data by model is good. Other results (the reactant concentration and temperature profiles) confirmed the validity of our assumption that the homogeneous mechanism fits heterogeneous carbon—carbon dioxide reaction well. Based on the results we can conclude that this heterogeneous gas-solid reaction takes place within the entire volume of the large coal char particle. Computed reactant concentration profiles do not show any sharp changes and are approximately the same inside the whole coal char particle, already in the first third of the gasification process.

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SYMBOLS

Bi_h	dimensionless parameter	$= \alpha R_p / \lambda_u$	
C	molar concentration		mol m^{-3}
c_{pu}	specific heat capacity of coal char		$\text{J kg}^{-1} \text{K}^{-1}$
D_e	effective diffusion coefficient		$\text{m}^2 \text{s}^{-1}$
E_a	activation energy		J mol^{-1}
$\Delta_r H^\circ$	reaction enthalpy		J mol^{-1}
k_∞	pre-exponential factor		$\text{m}^6 \text{mol}^{-1} \text{s}^{-1} \text{kg}^{-1}$
M	molar mass		kg mol^{-1}
m	reaction order for solid reactant		
n	reaction order for gas reactant		
P	pressure		Pa
R	gas constant		$\text{J mol}^{-1} \text{K}^{-1}$
R_r	dimensionless reaction rate	$= \dot{\xi} / \dot{\xi}^0$	
R_p	particle radius		m
r	particle radial coordinate		m
Th	dimensionless parameter,	$Th^2 = R_p^2 \dot{\xi}^0 \rho_s^0 / D_{e1} C_{g1}^0$	
T	temperature		K
t	time		s
x	mole fraction		
Y_i	dimensionless concentration of the gas component	$= C_{gi} / C_{g1}^0$	
Y_C	dimensionless concentration of carbon	$= C_C / C_C^0$	

Greek Letters

α	heat transfer coefficient	$\text{W m}^{-2} \text{K}^{-1}$
β	empirical parameter	
E	dimensionless parameter	$= \sigma \varepsilon_e (T_g^0)^3 R_p / \lambda_u$
ε_e	emissivity	
ε_p	porosity of particle	

η	dimensionless parameter = $= D_{es1}^0 C_g^0 (-\Delta_r H^\circ) / \lambda_u T_g^0$	
θ	dimensionless temperature = T/T_g^0	
κ	dimensionless parameter = C_g^0 / C_C^0	
Λ	dimensionless parameter defined by eqn (7)	
λ_u	effective thermal conductivity of coal char	$W m^{-1} K^{-1}$
λ_{ua}	effective thermal conductivity of ash	$W m^{-1} K^{-1}$
ν	stoichiometric coefficient	
ρ	density	$kg m^{-3}$
v	molar volume	$m^3 mol^{-1}$
$\dot{\xi}$	reaction rate based on the mass of solid phase	$mol kg^{-1} s^{-1}$
ξ_i	dimensionless parameter = D_{esi}^0 / D_{es1}^0	
σ	Stefan—Boltzman constant	$W m^{-2} K^{-4}$
Σ	diffusivity volume	
τ	dimensionless time = $t D_{es1}^0 / R_p^2$	
τ_p	tortuosity	
φ	dimensionless radius = r/R_p	
ψ	dimensionless parameter = $C_{sC}^0 v_C$	
Ξ	dimensionless parameter = $\rho_s c_{pu} D_{es1}^0 / \lambda_u^0$	

Subscripts

Ar	argon
C	carbon
CO ₂	carbon dioxide
g	gas phase, bulk gas flow
i	number of gas component
p	particle
s	solid phase

Superscripts

S	geometrical surface of particle
0	initial condition

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