Sulfur retention by ash during coal combustion. Part I.
A model of char particle combustion

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Abstract: A model for the combustion of porous char particles as a basis for modeling the process of sulfur retention by ash during coal combustion is developed in this paper. The model belongs to the microscopic intrinsic models and describes the dynamic behavior of a porous char particle during comustion, taking into account temporal and spatial changes of all important physical properties of the char particle and various combustion parameters. The parametric analysis of the enhanced model shows that the model represents a good basis for the development of a model for the process of sulfur retention by ash during coal combustion. The model enables the prediction of the values of all parameters necessary for the introduction of reactions between sulfur compounds and mineral components in ash, primarily calcium oxide.

Keywords: dynamic model, char combustion, sulfur retention by ash.

INTRODUCTION

During coal combustion, sulfur is converted into gaseous pollutants and solid compounds in the ash. The process that encompasses reactions between gaseous sulfur compounds and base oxides in coal ash, due to which a part of the sulfur remains in the ash, is termed sulfur self-retention (self-capture, self-absorption). The interest for this process was enhanced with the introduction of fluidized bed combustion (FBC) technology since the temperatures and other conditions are favorable for sulfur self-retention.

Sulfur self-retention is influenced by various factors which depend upon the coal characteristics and combustion conditions. The most investigated coal characteristics are the molar Ca/S ratio[1–5] and the $(CaO+MgO+Na_2O+K_2O)/S$ ratio[4–6] in coal, the coal particle size,[2,3] as well as the content of sulfur forms in coal and coal rank.[5] The combustion conditions, *i.e.*, temperature, residence time of ash particles, excess air ratio, and other operating and construction characteristics relevant for sulfur self-retention, are largely influenced by the type of combustor.[5]

The overall process of coal combustion takes place in two successive steps: devolatilization and char combustion. The process of devolatilization is significantly

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shorter and, due to the reducing conditions and lower temperatures, the process of sulfur self-retention during devolatilization is not significant. Our investigations[7,8] have shown that it is possible to predict the amount of sulfur that remains in char, after devolatilization, using a correlation which was tested using our own data as well as data found in the literature.

Sulfur self-retention occurs mostly during char combustion mainly due to the reaction of SO_2 with CaO, termed as sulfation reaction. This reaction is heterogeneous and its kinetics, apart from the available surface for the reaction, depends on the temperature and gas concentrations inside the char particle, primarily SO_2. The values of these parameters and their variation with time and along the char particle radius cannot be determined experimantally. Thus, it was necessary to model the process of char combustion as a basis for a model of the process of sulfur self-retention.

CHAR PARTICLE COMBUSTION MODEL

There are two main groups of mathematical models of char combustion: global models and models of intrinsic reactivity. Global models usually take into account external mass transfer and chemical kinetics related to the external surface of the coal/char particles.[9,10] They assume quasi steady-state conditions and all equations are analytically solved.

Models of intrinsic reactivity are suitable for investigations of some specific phenomena related to the combustion of char particle. There are two kinds of these mathematical models: macroscopic and microscopic. Both of these types of models describe processes inside the porous char particle, taking into account parameters which are neglected in global models, such as: heat and mass transfer inside the char particle and its porosity and internal surface area. The difference between these two types of intrinsic models lies in the level of analysis of processes inside the char particle. The macroscopic models usually assume homogenous characteristics of the char particle, uniform temperature and quasi steady-state conditions.[11–13]

The applied model belongs to the microscopic intrinsic models of char particle combustion.[14–17] The mathematical model describes the dynamic behavior of a porous char particle during combustion, *i.e.*, spatial and temporal changes of all the important physical properties of the char particle (porosity, internal specific surface area, thermal conductivity) and parameters (temperature, gas concentrations, effective diffusivity, conversion degree).

The main assumptions of the model are:

– The shape of the char particle is spherical and there is no fragmentation nor attrition.

– Distribution of all considered matter and the values of all thermal and physical properties are intially the same throughout the particle volume.

– The main mechanisms of heat transfer inside the char particle are conduction and radiation, while mass transfer is achieved by molecular diffusion, taking into account porosity and pore tortuosity. The convective heat and mass transfer inside the char particle

is neglected and the pressure inside the char particle is assumed to be constant and equal to the surrounding pressure.

– The influence of the particle surroundings is taken into account *via* the boundary conditions.

Chemical reactions during char particle combustion

It is assumed that the main reactions of combustion are:

Reaction 1: $(x+y)C + (x/2+y)O_2 \rightarrow xCO + yCO_2$

Reaction 2: $CO + (1/2)O_2 \rightarrow CO_2$
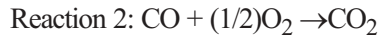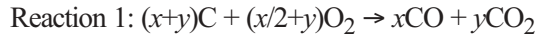
Reaction 1 is a heterogeneous reaction of oxidation of solid carbon that takes place both on the surface of the pores and on the surface of the char particle and its rate is:

$$\Re_1 = A_1\, X_{02}\, \exp\!\left(\frac{-E_1}{R_g\, T}\right) \tag{1}$$

The values of the activation energy and the pre-exponential factor[18] are $E_1 = 179.4$ kJ/mol and $A_1 = 254.16$ mol/m^2 s. The primary mole CO/CO_2 ratio (Reaction 1) is defined by[19]:

$$\gamma = \frac{x}{y} = \frac{CO}{CO_2} = 2512\, \exp\!\left(\frac{-51880}{R_g\, T}\right) \tag{2}$$

Reaction 2 is a homogeneous reaction of oxidation of CO that takes place inside the pores and its rate is defined as:

$$\Re_2 = \frac{dc_{CO}}{d\tau} = A_2\, c_{CO}\, c_{O_2}^{0.5}\, c_{H_2O}^{0.5}\, \exp\!\left(\frac{-E_2}{R_g\, T}\right) \tag{3}$$

The activation energy for this reaction[20] is $E_2 = 55.695$ kJ/mol. The pre-exponential factor A_2 is a model parameter and is fitted for various chars, according to ones own experimental data.[21]

It is assumed that the only product of combustion of sulfur compounds in char is SO_2 and theat the rate of its formation is proportional to the rate of carbon conversion:

$$\Re_3 = \frac{\partial c_{SO_2}}{\partial \tau} = \frac{\partial c_C}{\partial \tau} = \frac{S_{CC}}{C_{fix}} = \frac{M_C}{M_S} \tag{4}$$

Heat and mass balance and boundary conditions

Heat and mass balance, which determine the temperature and concentration profile of the gaseous compounds (O_2, CO_2, CO, SO_2) along the radius of the char particle are described by the following partial differential equations:

$$C_{p,v} \frac{\partial T}{\partial \tau} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \lambda_{eff} \frac{\partial T}{\partial r} \right) + \quad\quad (5)$$

$$\sum (C_{p,j} N_j) \frac{\partial T}{\partial r} - \Delta H_1 \Re_1 S - \Delta H_2 \Re_2 \varepsilon - \Delta H_3 \Re_3 S$$

$$\frac{\partial c_j}{\partial \tau} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_{eff} \frac{\partial c_j}{\partial r} \right) + v_{1,j} \Re_1 S + v_{2,j} \Re_2 \varepsilon + v_{3,j} \Re_3 S \quad\quad (6)$$

where $j = 1$–4 ($O_2 - 1$, $CO_2 - 2$, $CO - 3$, $SO_2 - 4$).

The boundary conditions are defined by the following relations:

$$r = 0 \quad \Rightarrow \quad \frac{\partial c_j}{\partial r} = 0, \quad \frac{\partial T}{\partial r} = 0$$

$$r = R \quad \Rightarrow \quad - \left| \lambda \frac{\partial T}{\partial r} \right|^- = \alpha(T_s - T_a) + (1-\varepsilon)\Delta H_1 \Re_1 + \sigma \varepsilon_r (T_s^4 - T_a^4),$$

and

$$-D_{eff,j} \left| \frac{\partial c_j}{\partial r} \right|^- = k_m (c_{j,s} - c_{j,a}) + v_{1,j} \Re_1 (1 - \varepsilon)$$

The convective mass transfer inside the char particle, which could arise due to the non-equimolar nature of Reactions 1 and 2 and due to the effect of temperature variations, is neglected in the mass balance Eq. (6). This simplification, commonly used in modeling char particle combustion,[17,22] could lead to slightly erroneous predictions of gas concentrations, but should not have any significant effect on the general process of combustion, since it is diffusion controlled. On the other hand, in processes like devolatilization, i.e., processes in which the build-up of gaseous products is significant, the convective mass transfer must be taken into account.[22] The convective heat and mass transfer between the char particle and its surrounding is taken into acount via the above boundary conditions.

Supplementary expressions, for defining the thermal and physical properties of char and gaseous compounds, as well as heat and mass transfer, have been given in a previous paper.[21]

Solution procedure

The initial conditions (temperatures and gas concentrations), based on the presumed values after devolatilization, are given as input data to the model. The initial temperature of the char particle is constant along the radius and equal to the surrounding temperature, while the O_2 concentration is near zero due to the reducing conditions inside the char particle after devolatilization. For numerical purposes, the char particle is subdivided into segments (usually more than 100) of equal volume. The numerical method of control volumes[23] is used for solving the system of partial differential Eqs. (5) and (6) in their dimensionless forms, i.e., for obtaining the values of temperatures and gas concentrations

along the char particle radius and their change in time. The degree of conversion of carbon for each char particle volume segment is defined by:

$$X_{con}(\tau, \Delta r) = \frac{1}{m_{c,0}} \int_0^\tau m_c(\Delta r) d\tau \qquad (7)$$

It is assumed that the local porosity increases proportionaly with the local degree of conversion of carbon, and thus:

$$\varepsilon = \varepsilon_0 + X_{con}(1 - Ash - \varepsilon_0) \qquad (8)$$

The change of the specific internal surface area during combustion is taken into account using the following relation[15]:

$$S = S_0(1 - X_{con})\sqrt{1 - \psi \ln(1 - X_{con})} \qquad (9)$$

PARAMETRIC ANALYSIS

As an illustration of the capabilities of the model, the profiles of temperature and gas concentrations, the most importan parameters for the process of sulfur self-retention, are shown in Fig. 1. The calculations were done using following main parameters: char
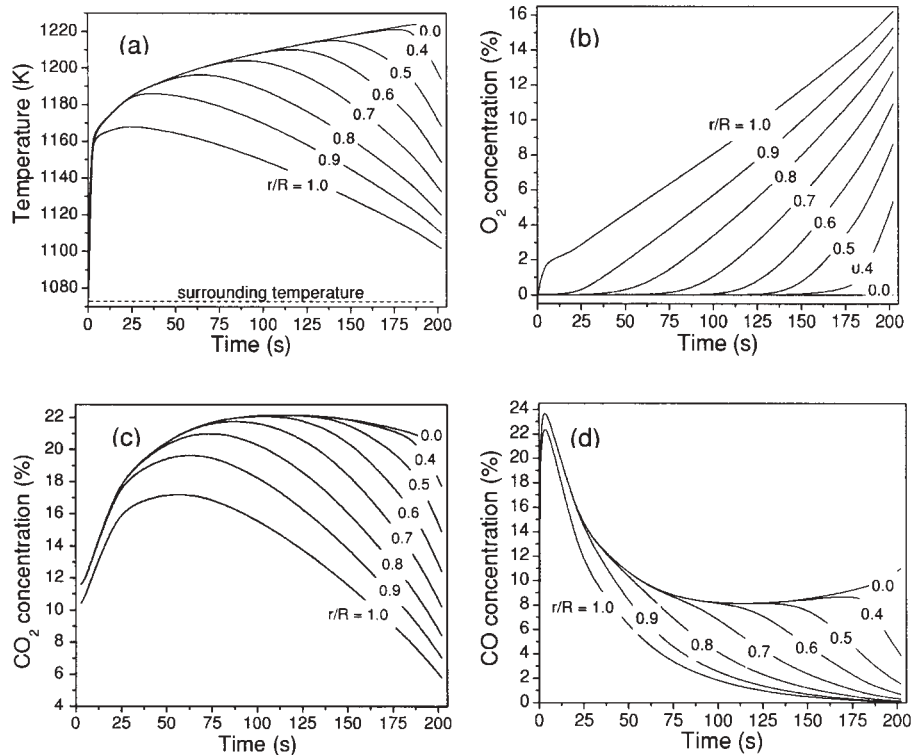

Fig. 1. Model predictions of temperature and gas concentrations inside a char particle during combustion.
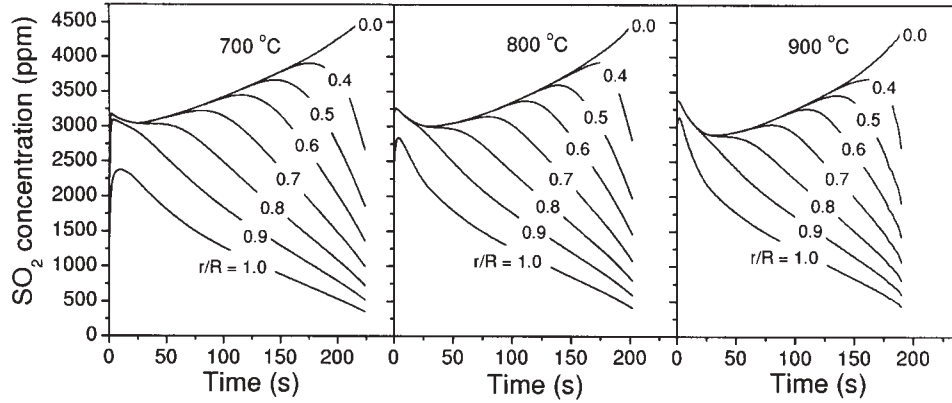
Fig. 2. Concentrations of SO$_2$ inside a char particle during combustion at different surrounding temperatures.

particle diameter 4 mm, initial porosity 50 %, initial specific internal surface area 300 m^2/cm^3, combustable content of sulfur in the char 2 %, surrounding temperature 1073 K
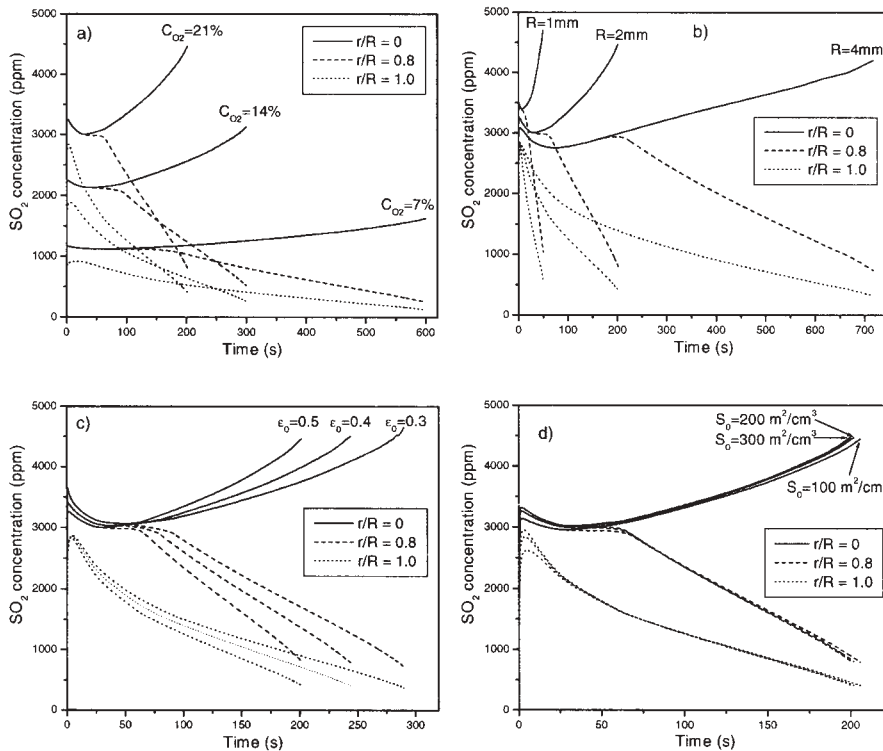

Fig. 3. The influence of the surrounding conditions and char properties on the SO$_2$ concentrations inside the char particle (the set of curves for each run can be identified by the duration of conbustion).

and surrounding O_2 concentration 21 %. It can be seen that the model predicts significant variations of temperature and gas concentration with time, as well as along the char particle radius. As the combustion progresses, the difference between these parameters in the particle center and outer surface increase, reaching near the end of the combustion the values of 120 K for temperature, 15 % for CO_2, and 11 % for CO. The very steep gradients of O_2 concentration indicate that the combustion process is diffusion controlled. A more detailed analysis of these parameters and a comparison of the model predictions with experimentally obtained data are given in a previous paper.[21] The introduction of the reactions of sulfur compounds does not significantly influence the temperature and gas concentration profiles since the sulfur content in char is relatively small.

The influence of various parameters on the SO_2 concentration inside the char particle is shown in Fig. 2 and Fig. 3. Increasing the temperature (Fig. 2) has practically no influence on the qualitative nature of the SO_2 concentration profiles. Neglecting the initial phase of combustion, the SO_2 concentration in the center increases and reaches levels above 4000 ppm, while at other places it first increases and then start decreasing as the combustion progresses. Taking also into account the temperature gradients, significant differences in the level of sulfation along the char particle radius can be expected. This analysis shows the necessity for use of these kind of models for theoretical consideration and explanation of the experimental results of complex processes such as sulfur self-retention.

The influence of the surrounding O_2 concentration, char particle radius, initial porosity and specific internal surface area on the SO_2 concentration at three locations inside the char particle is shown in Fig. 3. Decreasing the surrounding O_2 concentration from 21 % to 7 % significantly decreases the levels of SO_2 concentration as a consequence of the lower combustion rates and, in turn, lower rates of SO_2 formation. Increasing the char particle radius from 1 mm to 4 mm has a strong effect on the duration of combustion but the levels of SO_2 concentration are only somewhat lowered. The same can be said in the case of decreasing the porosity from 0.5 to 0.3, except that the effect on the duration of the combustion is not so pronounced. Changing the specific internal surface area from 100 m^2/cm^3 to 300 m^2/cm^3 has practically no influence on the combustion process and SO_2 concentration, as a consequence of the fact that combustion is diffusion controlled.

CONCLUSION

A microscopic intrinsic model of char particle combustion has been developed with the aim of forming a basis for modeling the process of sulfur self-retention. The model decreibes the dynamic behavior of a porous char particle during combustion, predicting temperatures and gas concentrations inside the particle.

Parametric analysis of the model shows that the combustion process is diffusion controlled. As the combustion progresses, significant temperature and gas concentration gradients form along the char particle radius. The most significant parameters that have an influence on the SO_2 concentration inside the char particle are the surrounding O_2 concetration and the char particle radius.

The temperature and gas concentration profiles, *i.e.* the significant spatial and temporal gradients, justify the necessity for the use of this kind of model for theoretical consideration and explanation of the experimental results of complex processes, such as sulfur self-retention.

NOMENCLATURE

A_i – Pre-exponential factor for *i*-chemical reaction, (1st – mol/m^2 s, 2nd – mol/m^{3}s)

Ash – Mass fraction of ash in char, (–)

c_j – Concentration of *j*-component, (mol/m^3)

C_{fix} – Fixed carbon content in char, (%)

C_{pij} – Specific heat capacity of *j*-component, (J/mol K)

$C_{p,v}$ – Specific heat capacity of porous char particle, (J/m^3 K)

D_{eff} – Effective diffusion coefficient, (m^2/s)

E_i – Activation energy of *i*-chemical reaction, (J/mol)

k_m – Mass transfer coefficient between char particle and its surrounding, (m/s)

m_c, $m_{c,0}$ – Current and initial mass of carbon in char particle, (kg)

M_C, M_S – Molar mass of carbon and sulfur, (kg/mol)

N_j – Molar flux of *j*-component, (mol/m^2 s)

r, R – Radius nad char particle radius, (m)

$\Re_i$ – Reaction rate of *i*-chemical reaction, (1st – mol/m^2 s, 2nd and 3rd – mol/m^3 s)

R – Gas consant, (J/mol K)

S, S_0 – Current and initial specific surface area of porous char particle, (m^2/m^3)

S_{CC} – Combustible sulfur content in char, (%)

T – Temperature (*a*-ambient, *s*-char particle surface), (K)

X_j – Mole fraction of *j*-componenet, (–)

X_{con} – Conversion degree, (–)

α – Convective heat transfer coefficient between char particle and ambient, (W/m^2 K)

ε, ε_0 – Current and initial char particle porosity, (–)

ε_r – Emissivity, (–)

λ_{eff} – Effective heat conductivity of porous char particle, (W/m K)

$\nu_{i,j}$ – Stoichiometric coefficients for *i*-reaction and *j*-component, (–)

σ – Stefan-Boltzmann constant, (W/m^{2}K^4)

τ – Time, (s)

ψ – Model parameter for the specific internal surface area evolution, (–)

ИЗВОД

ЗАДРЖАВАЊЕ СУМПОРА У ПЕПЕЛУ ТОКОМ САГОРЕВАЊА УГЉА. I. МОДЕЛ САГОРЕВАЊА ЧЕСТИЦЕ КОКСНОГ ОСТАТКА

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У раду је приказан развијени математички модел сагоревања порозне честице коксног остатка који представља основу за моделирање процеса задржавања сумпора у пепелу током сагоревања угља. Модел је заснован на микроскопском приступу и описује динамичко понашање честице коксног остатка током сагоревања. Узимају се у обзир просторне и вре-

менске промене свих значајнијих физичких карактеристика и разних параметара сагоревања. Параметарском анализом је показано да модел представља добру основу за развој модела процеса задржавања сумпора у пепелу током сагоревања угља. Модел омогућава добијање свих потребних величина за увођење реакција једињења сумпора са минералним компонентама пепела, пре свега калцијум-оксидом.

REFERENCES

1. A. P. Raymant, :Sulfur Capture by Coal Ash and Freeboard Processes During Fluidized Bed Combustion, *Proc. 10th Int. Conf. on Fluidized Bed Combustion*, San Francisco, California, **1** (1989) p. 597
2. B. Grubor, V. Manović, *Energy & Fuels* **16** (2002) 951
3. V. Manović, B. Grubor, B. Jovančićević, *Chemical Industry* **53** (1999) 107 (in Serbian)
4. A. B. Fuertes, V. Artos, J. J. Pis, G. Marban, J. M. Palacios, *Fuel* **71** (1992) 507
5. C. Sheng, M. Xu, J. Zhang, Y. Xu, *Fuel Process. Technol.* **64** (2000) 1
6. V. R. Gray, *Fuel* **65** (1986) 1618
7. V. Manović, "Influence of Combustion Conditions and Coal Characteristics on Sulfur Retention in Ash", *Ms Thesis*, Chemistry Faculty, University of Belgrade (2000) (in Serbian)
8. V. Manović, B. Grubor, Behavior of Sulfur Forms During Devolatilization of Coal, *Proc. 3rd Sypm. of South-East European Countries (SEEC) on Fluidized Beds in Energy Production, Chemical and Process Engineering and Ecology*, Sinaia, Romania, (2001) p. 57
9. M. Avedesian, J. Davidson, *Trans. Inst. Chem. Engrs.* **51** (1973) 121
10. R. Chakraborty, J. Howard, *J. Inst. Energy*, March (1981) 48
11. I. W. Smith, "The Combustion Rates of Coal Chars; A. Review", *Proc. 19th Symposium on Combustion*, (1982) p. 1045
12. R. Tyler, *Fuel* **65** (1986) 235
13. H. Tseng, T. Edgar, *Fuel* **68** (1989) 114
14. G. Simons, "The Pore Tree Structure of Porous Char", *Proc. 19th Symposium on Combustion*, (1982) p. 1067
15. S. Bhatia, D. Perlmutter, *AIChE J.* **26** (1980) 379
16. A. Bliek, J. Lont, W. Swaaij, *Chem. Eng. Sci.* **41** (1986) 1895
17. D. Hsuen, S. Sotirchos, *Chem. Eng. Sci.* **44** (1989) 2639
18. I. W. Smith, *Fuel* **57** (1978) 409
19. J. Arthur, *Trans. Faraday Soc.* **47** (1951) 164
20. J. Scholer, "Ein Gesamtmodell für Dampferzeugeranlangen mit zirkulierender Wirbelschichtfeuerung", *Ph. D. Thesis*, Siegen University, Germany, 1992
21. M. Ilić, S. Oka, B. Grubor, *Thermal Science* **2** (1998) 61
22. C. Chen, T. Kojima, *Fuel Process. Technol.* **53** (1997) 49
23. S. V. Patankar, *Numerical Heat Transfer and Fluid Flow*, Hemisphere Publishing Corp., USA, 1980.