Comparative study of four alternative models for CO oxidation around a burning coal char particle

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ABSTRACT

The steady state combustion of a quiescent char particle is investigated by means of a detailed model which accounts for heterogeneous oxidation and gasification, as well as homogeneous reactions (GRI-Mech 3.0) in the particle's boundary layer. First, the way and extent in which the mass and energy transfer are altered due to the oxidation of CO are examined by comparison with the predictions of a single-film model in the case of anthracite particles within 60–1000 μm. Then, four alternative descriptions of the gas phase (single-film, double-film, global kinetics and detailed kinetics) are evaluated for two coals of very different reactivity towards O_2 and CO_2, at low and high O_2 concentration and in the same broad range of sizes. The overall influence of the CO conversion modeling on the particle burning rate and temperature (i.e. whether the reduction in O_2 surface concentration or the heat and CO_2 provided by the flame dominate over each other) is found to depend on the conditions considered. The single-film approach reasonably fits the predictions of the most complete model in all cases (and especially in the pulverized-coal size range), whereas the double-film hypothesis and the global kinetics generally overestimate the effects of the flame on the consumption rates and the particle temperatures.

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1. Introduction

Extensive work has been and still is being accomplished to model coal conversion computationally. The actual mechanism of coal combustion is complex; in a very simplified scheme, when a coal particle is heated a rapid release of moisture and volatiles is followed by a char conversion step, which includes heterogeneous and homogeneous reactions at the surface(s) and in the surroundings of the particle, respectively. It is still under controversy to what extent homogeneous reactions influence the mass and heat transfer through the boundary layer and, as a consequence, the particle reaction rate and temperature. It is commonly accepted that for small particles (say, <100 μm) the single-film model, in which the CO conversion reactions in the boundary layer are neglected, is applicable, while large particles (>1–2 mm) are assumed to burn according to the double-film theory, i.e. CO oxidation occurs in an infinitely thin flame around the particle [1,2].

The single-film limit has been widely applied in the past (e.g., [1,3–5]) some double-film modeling works are also available in the literature [6–9], most of them focused on the combustion of large particles. On the contrary, limited work has been performed without *a priori* assumptions regarding the reaction rate and the location of the CO oxidation zone. Mon and Amundson [10] investigated the combustion of a coal char particle surrounded by a reactive boundary layer by applying the global kinetic parameters provided by Howard et al. [11] for the homogeneous CO–O_2 reaction; apparent kinetics were used for the heterogeneous C–O_2 and C–CO_2 reaction. This model was later modified by Sotirchos and Amundson [12] to consider also pore diffusion and intrinsic kinetics for the heterogeneous reactions; in this work, the O_2–CO_2 molar fraction and gas temperature profiles for a large (~1000 μm) and a small (~100 μm) particle respectively resembled those of the infinitely fast homogenous kinetics (i.e. double-film) and the single-film models later presented by the same research group [9]. Makino and Law [13] solved the combustion of a spherical carbon particle in a similar way, considering the surface oxidation and gasification reactions and the same global kinetics for the gas-phase reaction; by varying the pre-exponential factor for the CO-to-CO_2 reaction they found intermediate burning rates between those for the two limiting regimes already mentioned. The effect of this CO conversion was also investigated by Mitchell et al. [14] by means of a more detailed mechanism (18 adsorption–desorption reactions at the external surface, 25 homogeneous reactions). Their results comparing the burning rates and particle temperatures with and without CO oxidation supported the applicability of the single-film model for particles in the pulverized-coal size range (50–300 μm) reacting under low oxygen concentrations

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Nomenclature

A_c — frequency factor for heterogeneous oxidation (kg m^{-2} s^{-1} Pa^{-n})

a_E — weighting coefficient for the east node temperature in the discretized energy balance equations

A_g — frequency factor for heterogeneous gasification (kg m^{-2} s^{-1} Pa^{-n})

a_P — weighting coefficient for the main node temperature in the discretized energy balance equations

a_P^0 — weighting coefficient for the transient term in the discretized energy balance equations

a_W — weighting coefficient for the west node temperature in the discretized energy balance equations

C — char content (kg of char/kg of particles)

Cp_g — gas specific heat (J kg^{-1} K^{-1})

Cp_p — particle specific heat (J kg^{-1} K^{-1})

D_i — mass diffusivity of the species i (m^2 s^{-1})

d_p — particle diameter (m)

E_c — activation energy for oxidation (J mol^{-1})

E_g — activation energy for gasification (J mol^{-1})

h — heat transfer coefficient (J m^{-2} s^{-1} K^{-1})

H_c — heat of heterogeneous combustion (J kg^{-1})

H_g — heat of heterogeneous gasification (J kg^{-1})

$\dot{m}_C$ — overall burning rate (kg C m^{-2} s^{-1})

n_i — mass flow rate of species i (kg m^{-2} s^{-1})

n_j — apparent reaction order with respect to O_2 or CO_2

Nu — Nusselt number

P_j — partial pressure of O_2 or CO_2 (Pa)

q_c — heat of heterogeneous oxidation (J m^{-2} s^{-1})

q_{conv} — convective heat flow towards the particle (J m^{-2} s^{-1})

q_g — heat of heterogeneous gasification (J m^{-2} s^{-1})

q_{rad} — heat flow towards the particle by radiation (J m^{-2} s^{-1})

R — universal gas constant (J mol^{-1} K^{-1})

r — radial coordinate (m)

R_j — carbon consumption rate by oxidation or gasification (kg C m^{-2} s^{-1})

r^* — normalized radial coordinate ($2r/d_p$)

r_x^* — dimensionless radial coordinate at which x% CO has been converted to CO_2

$S_{g,i}$ — gas-phase reactions source term for the mass balances of species i (kg$i$ m^{-3} s^{-1})

$S_{g,T}$ — gas-phase reactions source term for the gas energy balance (J m^{-3} s^{-1})

$S_{het,i}$ — consumption or generation of O_2, CO or CO_2 through heterogeneous reactions (kg m^{-2} s^{-1})

t — time (s)

T — temperature (K)

T_w — temperature used to evaluate the radiative term (K)

U — unburnt fraction (Eq. (9))

u — flow velocity (m/s)

W_g — molecular mass of the gas (g mol^{-1})

W_i — molecular mass of species i (g mol^{-1})

X_i — molar fraction of the species i

Y_i — mass fraction of the species i

$v_{i,c}$ — mass-based stoichiometric ratio of species i in oxidation (kg i released/kg C reacted)

$v_{i,g}$ — mass-based stoichiometric ratio of species i in gasification (kg i released/kg C reacted)

ρ_g — gas density (kg m^{-3})

ρ_p — particle density (kg m^{-3})

λ_g — gas thermal conductivity (W m^{-1} K^{-1})

λ_p — char particle thermal conductivity (W m^{-1} K^{-1})

σ — Stefan-Boltzmann constant (W m^{-2} K^{-4})

ε — particle emissivity

α_T — relaxation weighting factor to obtain an initial guess for the temperature profile

α_Y — relaxation weighting factor to obtain an initial guess for each mass fraction profile

$[CO]$ — CO concentration (mol m^{-3})

$[H_2O]$ — H_2O concentration (mol m^{-3})

$[O_2]$ — O_2 concentration (mol m^{-3})

ΔH_{CO-CO_2} — Entalpy of Howard's global reaction for the CO conversion (J kg CO^{-1})

Subscripts

bulk — bulk gas

c — refers to oxidation

CO — carbon monoxide

CO_2 — carbon dioxide

g — refers to gasification

gas — refers to the gas-phase

i — species

j — refers to O_2 (or oxidation) or CO_2 (or gasification)

O_2 — oxygen

p — particle

s — particle surface

Superscripts

0 — initial time

k — time step

(up to 12%). Finally, Adomeit and co-workers [15,16] performed theoretical investigations on the rate of carbon oxidation for finite gas-phase reaction rates as well as for the two limiting cases of non-existent and infinitely fast homogeneous reaction; according to these authors, both the single-film and double-film predictions failed to reproduce well the experimental results of Matsui et al. [17] on carbon consumption rates. Also, the effect of water vapor concentration on the combustion rate was further analyzed for the continuous-film case by using both an 18-reaction gas-phase mechanism and the global kinetic parameters determined by Howard et al. [11]; CO conversion in the boundary layer was found to be catalyzed by the moisture present in the bulk gas.

The works mentioned so far correspond to studies on conventional combustion atmospheres (i.e. N_2-rich). Hecht et al. [18] studied the effects of the chemistry in the boundary layer as well as gasification on the char burning rate in oxy-combustion conditions (i.e. with CO_2 as the main carrier) with the help of the Surface Kinetics in Porous Particles (Skippy) code, which was originally developed by Ashman and Haynes [19] and allows calculating the species concentrations and temperature profiles across a porous particle and the boundary layer around it. Their results for an isolated 130 μm particle showed both the significant impact of homogeneous reactions in O_2-enhanced environments and the non-negligible influence of the gasification reaction, especially when predicting particle temperatures.

Very recently, Hecht et al. [20] have published a comparative study of the performance of the above mentioned Skippy code and two simplifications (single-film and double-film approaches) to evaluate the errors associated to the use of the latter in the case of a subbituminous char in the pulverized size range (60–135 μm). They concluded that the single-film is an appropriate model to describe pulverized char combustion under both conventional and