Modelling rates of gasification of a char particle in chemical looping combustion

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Abstract

Rates of gasification of lignite char were compared when gasification with CO_2 was undertaken in a fluidised bed of either (i) an active Fe-based oxygen carrier used for chemical looping or (ii) inert sand. The kinetics of the gasification were found to be significantly faster in the presence of the oxygen carrier, especially at temperatures above 1123 K. An analytical solution assuming pseudo-binary diffusion of species was developed to account for external and internal mass transfer and for the effect of the looping agent. The model also included the effects of the evolution of the pore structure at different conversions. The results are compared with a full numerical model using the Stefan–Maxwell equations. Excellent agreement was observed between the rates predicted by the two models and those observed experimentally at $T \leqslant 1123$ K. At 1173 K, the pseudo-binary model predicted slightly higher rates than the full numerical solution. It was found that a significant share of the error of the predicted rates with the analytical solution was caused by an underestimation of intraparticle diffusional resistance rather than by assuming a pseudo-binary system external to the particle. Both models suggested that the presence of Fe_2O_3 led to an increase in the rate of gasification because of the rapid oxidation of CO by the oxygen carrier to CO_2. This resulted in the removal of CO and maintained a higher mole fraction of CO_2 in the mixture of gas around the particle of char, *i.e.* within the mass transfer boundary layer surrounding the particle. This effect was most prominent at $\sim$20% conversion when (i) the surface area for reaction was a maximum and (ii) because of the accompanying increase in porosity, intraparticle resistance to gas mass transfer within the particle of char had fallen, compared with that in the initial particle.

1. Introduction

In the chemical looping combustion of coal and char, solid fuel must be gasified in pure CO_2 or steam, or mixtures thereof, *in situ* with particles of a solid oxygen carrier, typically a transition metal oxide, which oxidises the resulting synthesis

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Nomenclature

A_{2ck_1}	Pre-exponential factor for the rate constant $2ck_1$, mol s^{-1} g^{-1} bar^{-1}
A_{2ck_1}	Pre-exponential factor for the rate constant $2ck_2$, mol s^{-1} g^{-1}
A_{k_{-1}/k_1}	Pre-exponential factor for the rate constant k_{-1}/k_1, -
c	Concentration of active sites per unit mass of carbon, g^{-1}
C_T	Total concentration in the fluidized bed, mol m^{-3}
$D_{B,ab}$	Molecular diffusivity, involving species a in b, m^2 s^{-1}
D_{eq}	Effective diffusivity in a fluidised bed $= D_m \varepsilon_{mf}$, m^2 s^{-1}
D_m	Constant mean diffusivity, m^2 s^{-1}
E_j	Activation energy for the rate constant j, kJ mol^{-1}
$f(X)$	Relative change in the surface area available for reaction over conversion, -
J_a	Total flux of species a, mol m^{-2} s^{-1}
k	Reaction rate constant, mol s^{-1} m^{-3} bar^{-1}
k_1	Rate constant for the reaction of CO with iron oxide (Fe$_2$O$_3$), s^{-1}
k_1, k_{-1}	Rate constants of gasification per active site, mol s^{-1} bar^{-1}
k_2	Rate constant of gasification per active site, mol s^{-1}
K_i	Adsorption equilibrium constant of i-th species, bar^{-1}
K_p	Equilibrium constant for the overall gasification reaction C + CO$_2$ = 2CO, -
L	Thickness of catalyst (=char), m
p_i	Partial pressure of gaseous species i, bar
$p_{i,bulk}$	Partial pressure of gaseous species i at the bulk or particulate phase, bar
$p_{i,s}$	Partial pressure of gaseous species i at the surface of the particle, bar

r_g	Reaction rate of carbon per gross volume, mol s^{-1} m^{-3}
R_p	Initial radius of a char particle, m
R	Universal gas constant, kJ mol^{-1} K^{-1}
R'_g	Rate of gasification of char per unit mas of sample, mol s^{-1} g^{-1}
$R'_{g,0}$	Intrinsic rate of gasification of char at zero conversion, mol s^{-1} g^{-1}
T	Temperature, K
X	Conversion of carbon, -
y_i	Mole fraction of species i, -
$y_{i,bulk}$	Mole fraction of species i in the fluidising gas (or bulk phase), -
$y_{i,s}$	Mole fraction of species i at the surface of the particle, -

Greek letters

α	Parameter defined in Eq. (19), -
δ	Thickness of the mass transfer boundary layer, m
ε_o	Initial porosity of the char, -
ε_{mf}	Void fraction in a bed, -
λ	Correction factor in Eq. (19), -
ϕ^*	Reduced Thiele modulus $= \phi_M/\phi_c$, -
ϕ_c	Critical Thiele modulus, -
ϕ_M	Modified Thiele modulus defined in Eq. (17) -
η_{in}	Effectiveness factor of the extent of mass transfer limitations within the particle, -
ρ_e	Density of a particle of char before reaction, kg m^{-3}
σ_r	Dimensionless radius, defined as r/R_p, -
τ^2_{ext}	Tortuosity factor of the region around the particle of pellet, -
τ^2_{in}	Tortuosity factor of the particle, -
υ_a	Stoichiometric coefficient of species a
ω	Parameter defined in Eq. (16), -

gases and volatile matter. Generally, gasification is much slower than the reactions between synthesis gases and the metal oxide [1–4]. A consequence of a slow rate of gasification is that the inventory of char in the system becomes substantial, making separation of the particles of fuel and oxygen-carrier problematic [1–9] prior to re-oxidising the carrier with air and so causing CO$_2$ to contaminate the resulting depleted stream of air.

In a chemical-looping reactor, gasification will occur with a high [CO$_2$] and, or, [H$_2$O], whilst CO and H$_2$, which inhibit gasification, are consumed by reaction with the oxygen carrier [10–12]. Thus,

rates of gasification should be faster in a chemical-looping system than in a normal gasifier. Here, we investigate, experimentally and theoretically, the effect of iron oxide on the rate of gasification of lignite char by CO$_2$:

$$C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)} \quad \Delta H^0_{1173K} = +173 \text{kJ mol}^{-1}$$
$$(1)$$
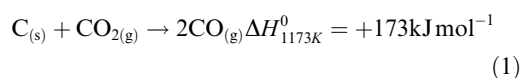
This is accompanied by Reaction (2), in Table 1, giving a net enthalpy of +95.8 kJ mol^{-1} for complete conversion of the char. Reaction (2) occurs at 1173 K provided $p_{CO}/p_{CO2} > 1.5 \times 10^{-5}$ [13]