1 **Using an Experimentally-Determined Model of the Evolution of**
2 **Pore Structure for the Gasification of Chars by CO₂**

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Abstract

A pseudo-steady state model of reaction and diffusion has been constructed to model the non-isothermal gasification of single char particles by CO_2 . The model uses a Cylindrical Pore Interpolation Model for intraparticle mass transfer, Ergun's Langmuir-Hinshelwood equation for the intrinsic rate of gasification, an experimentally determined function $f(X)$ for the pore evolution as a function of the conversion X , the Stefan-Maxwell equations to describe external mass transfer and the equation of energy for energy balance. Experiments were conducted to measure rates and extent of conversion, at various temperature and for various particle sizes, of lignite char and the less reactive activated carbon. The simulation results have been compared with experimental measurements, with excellent agreement being obtained. The results show that for the gasification of chars, the experimentally determined function $f(X)$ predicts the rate of reaction of particles of various sizes well, all being at the same temperature. However, for the CO_2 gasification of char particles, at least, an $f(X)$ evaluated at one temperature does not predict experimental measurements well at other temperatures, possibly because there are contributions from multiple types of active sites within the particles. However, multiple sites are also not reflected in most published pore models.

Keywords

Modelling; Char gasification; Pore evolution;

Nomenclature

A_A, A_C, A_K	coefficients in pressure gradient equation	$\text{Pa s m g}^{-0.5} \text{ mol}^{-0.5}$
c_0	number of active sites per unit mass of carbon	g^{-1}
$C_{p,a}$	molar heat capacity of gas species a	$\text{J mol}^{-1} \text{ K}^{-1}$
$d_{b,m}$	mean bubble diameter	m
$d_{pore}, d_{pore,0}$	diameter of the pores and its initial value	m
$D(3,2)$	Sauter mean diameter	m
$D_{A,ab}$	diffusivity at arbitrary Knudsen number, for gas species a and b	$\text{m}^2 \text{ s}^{-1}$
$D_{B,ab}$	molecular diffusivity, involving gas species a in b	$\text{m}^2 \text{ s}^{-1}$
$D_{K,a}$	Knudsen diffusivity of gas species a	$\text{m}^2 \text{ s}^{-1}$
$f(X)$	surface area available for reaction	-
H_a	partial molar enthalpy of gas species a	J mol^{-1}
J_a	total molar flux of gas species a	$\text{mol m}^{-2} \text{ s}^{-1}$
k_1, k_{-1}	rate constants of CO_2 gasification per active site	$\text{mol s}^{-1} \text{ bar}^{-1}$
k_2	rate constant of CO_2 gasification per active site	mol s^{-1}
K_P	equilibrium constant	-
M_C, M_a	molecular mass of carbon and gas species a	g mol^{-1}
P	total pressure	bar
P_0	total pressure at the bulk condition	bar
p_a	local partial pressure of gas species a	bar
P_s	total pressure at the surface of the particle	bar
r	radial distance from the particle centre	m
$r_p, r_{p,0}$	radius of a char particle and its initial value	m
R	universal gas constant	$\text{kJ mol}^{-1} \text{ K}^{-1}$
$R'_{g,0}$	rate of formation of CO per unit mass of C at zero conversion	$\text{mol s}^{-1} \text{ g}^{-1}$
S_a	net rate of reaction of gas species a inside the particle	$\text{mol m}^{-3} \text{ s}^{-1}$
t	time	s
T	absolute temperature	K
T_s, T_0	temperature at the surface of the char particle and in bulk gas	K
U, U_{mf}	inlet flow velocity and its value at incipient fluidisation	m s^{-1}
U_b	bubble velocity	m s^{-1}
u_m	mass-averaged velocity of gas mixture	m s^{-1}
$X, \bar{X}$	local conversion and average of carbon, respectively	-
y_a	mole fraction of gas species a	-
Greek letters		
ε_0	initial porosity of char particle	-
ε_b	void fraction of gas bubbles in the fluidised bed	-
$\varepsilon_{bed}, \varepsilon_{mf}$	porosity of the bed and its value at incipient fluidisation	-
λ_{eff}	effective thermal conductivity of the particle	$\text{W m}^{-1} \text{ K}^{-1}$
μ_{mix}	dynamic viscosity of the gas mixture	Pa s
ρ_a	density of the gas species a	g m^{-3}
ρ_e	bulk density of a particle of char before reaction	g m^{-3}
ρ_m	skeletal density of the char particle	g m^{-3}
τ^2	tortuosity factor of the particle	-
τ_{bed}^2	tortuosity factor of the fluidised bed	-
ν_{mix}	kinematic viscosity of the gas mixture	$\text{m}^2 \text{ s}^{-1}$
γ	parameter for calculation of effectiveness factor	-
δ	external diffusion boundary layer thickness	m
η_r	dimensionless radius	-
κ_{eff}	effectiveness factor	-

ν_a	stoichiometric coefficient of gas species a	-
$\varepsilon(\bar{X})$	porosity of char particle as a function of average conversion	-
ϕ^*	modified Thiele modulus	-

Subscripts

$a, b = 1, 2, 3$	CO, CO ₂ and N ₂
s	value of the parameter at the particle surface condition

Abbreviation

BET	Brunauer–Emmett–Teller
CPIM	cylindrical pore interpolation model
DGM	dusty gas model
MPTM	mean pore transport model
OCFE	orthogonal collocation on finite element
RPM	random pore model

1 Introduction

A characteristic of most models of non-catalytic reactions between gases and solids generally is that the intrinsic rate of reaction, r , at some point within a solid particle is of the form $r = g(C_i, T, P) \times f(X)$. Here, g describes the intrinsic reaction kinetics at temperature T and total pressure P in the presence of the reacting gases, concentration C_i , and $f(X)$ is a direct function of the conversion of the particle and is correlated with the internal morphology of the particle, *e.g.* surface area, porosity, pore size distribution, particle diameter *etc.* Invariably, $f(X)$ is not a function of C_i , T , or P . This is exemplified by a recent study [1] of char gasification in a fluidised bed, where it was proposed that a simple, arbitrary function, $f(X)$, could be determined from the plot of measurements of rate *vs.* conversion of a sample of char in the kinetically controlled regime. Then in theory, the arbitrary function could be used in place of complicated – and equally arbitrary – mathematical models of pore structure to describe the change of internal morphology at a point within particles being gasified under conditions affected by intraparticle mass transfer. The objective of this paper is to investigate this approach, comparing theory with experiment.

During the gasification of a batch of char, the rate of reaction increases, from time $t = 0$, to a maximum and thereafter drops continuously with time as conversion increases. This has been attributed to the change in the pore structure of the particle during reaction. At the start, new gas-solid interface area is created as the small pores grow during gasification, but, at larger conversions, the internal area falls as large pores coalesce [2,3]. Hence, many have sought to model the change of internal pore structure with conversion during reactions. For example, Bhatia & Perlmutter [3] and Gavalas [4] developed random pore models (RPM), using different approaches, to model the total surface area at any conversion as a function of the initial morphological parameters, *e.g.* the initial porosity and surface area. Gavalas [4] reported a reasonable agreement between the model and experimental measurements of char gasification at low temperature, but observed some degree of deviation at high temperature where intraparticle diffusion limitations became significant within a char particle. Similar behaviour was also observed for the RPM of Bhatia & Perlmutter [3] in Lin & Strand [5]. Often the correlation between the total surface area, as measured by Brunauer–Emmett–Teller (BET) N_2 or CO_2 adsorption, and reactivity is weak. This is because the BET area does not account for the nature of the surface, or the concentration of active sites there [6,7]. Hence the applicability of complex mathematical models of pore structure does not always capture all the features of the reaction.

Saucedo [1,8] proposed that the ratio between the rate of reaction at any conversion and the initial rate of reaction reflects, generally, the variation in the pore structure as the reaction proceeds in the absence of

intraparticle mass transfer limitation (*e.g.* at low temperature or using small particles or with chars of low reactivity). Hence, instead of using a mathematical pore model for $f(X)$, the function $f(X)$ could be experimentally determined by $f(X) = r(X)/r(X = 0)$, whenever the rate of reaction is controlled by intrinsic kinetics. In a review of early work, Laurendeau [9] summarised that the overall kinetics of char gasification were often correlated by an expression of the form of $r = K_0 C_{\text{CO}_2}^n$ where K_0 is the overall rate constant and the order of reaction n is between 0 and 1. However, many researches [10–12] agreed that the intrinsic rate of reaction followed Ergun’s Langmuir-Hinshelwood kinetics based on the oxygen-exchange mechanism [11]. If detailed descriptions of the intraparticle and external diffusion processes and energy balance are included in the model, then it is more realistic to use the intrinsic kinetics for the reaction rate rather than using the overall kinetics.

Saucedo [1,8] took the equations for the diffusion of gaseous reactants and products within a particle of char and coupled them, locally, with an expression describing the chemical kinetics of gasification within the char in the form $r = g(C_i, T, P) \times f(X)$. Clearly, this meant that the conversion would vary across the radius of the particle. However, Saucedo [1,8] assumed that X could be replaced by its average for the particle at a particular time, $\bar{X}$, thus reducing the computational complexity of marching forward local values of X at each radial grid point.

In the present paper, Saucedo’s [1,8] problem has been solved rigorously by developing a computational model based on the local conversion within a particle. The theory has then been investigated experimentally to determine how far the use of an arbitrary $f(X)$ can be applied to the reaction of similar particles, but of different size and being gasified at conditions different to those used to determine $f(X)$.

2 Experimental

2.1 Materials

The gases used were (i) N_2 (≥ 99.9 vol%, oxygen ≤ 2 ppmv), (ii) CO_2 (≥ 99.8 vol%), and (iii) air (20.9 vol% O_2 in N_2). All gas cylinders were supplied by BOC or Air Liquide. Natural, uncrushed silica sand (fraction C, David Ball Group plc., dry), sieved to 355 – 425 μm , was used as a fluidised bed material. The density of the non-porous sand particles was $\sim 2690 \text{ kg m}^{-3}$. Two solid fuels were used: i) char particles made from a low-rank Hambach lignite coal supplied by RWE Power AG, Germany, and ii) activated carbon particles (Sorbonorit B4, Norit) used by Scott [13]. The lignite char was prepared by the pyrolysis of the parent coal in a bed of sand fluidised by pure N_2 at 1073 K [1]. The resulting char particles were sieved from the sand and recovered in four size fractions for the experiments: 0.36 - 0.50 mm, 0.60 - 1.00 mm, 1.00 - 1.40 mm and 1.70 - 2.56 mm. The

activated carbon did not require pyrolysis: it was crushed and sieved into different size fractions, 0.36 - 0.43 mm, 0.71 - 1.25 mm and 1.70 - 2.36 mm. Table 1 shows the composition and density of the particles, where the densities were estimated from the pore structure measurements by mercury intrusion porosimetry, assuming negligible volume in pores < 3 nm diameter.

[Table 1 hereabouts]

2.1.1 Analysis of pore structure

Table 2 shows the measurements from the BET analysis (TriStar 3000) and mercury intrusion porosimetry (AutoPore IV 9500), both of which produced a pore size distribution of the fuel particles. The measurements show similar values of parameters for the same fuel indicating that the pore structures of particles of different sizes are the same. Comparing the two sets of analyses, it can be concluded that most of the surface area exists in small pores ($d_{pore} < 10$ nm) while the majority of the pore volume is contained in large pores ($d_{pore} > 100$ nm). It was, of course, possible that the fuel particles had considerable unmeasured surface area and pore volume in the microporous range ($d_{pore} < 2$ nm), as the BET and mercury intrusion analyser were unable to measure pores below a diameter of 1.7 nm and 3 nm respectively. In the subsequent modelling, the mean pore diameter $d_{pore} = 4V/A$ from mercury porosimetry was used as the initial pore diameter of the fuel particles, where V was the total intrusion volume and A was the total pore area.

[Table 2 hereabouts]

2.1.2 Particle size distribution

Optical microscopy allowing a maximum measurable dimension of 1000 μm was used to measure the size distribution and the shape of the particles. Table 3 lists the main parameters obtained from measurements of the size distribution of lignite chars. No measurements were made on the activated carbon particles as their size fractions (0.71 – 1.25 mm and 1.70 – 2.36 mm) exceeded the measuring range. For the lignite chars, the mode of the main peak occurs at a size close to the Sauter mean diameter, $D(3,2)$. The values of Sauter mean diameter are larger than the upper mesh size, because the particles have large aspect ratios and pass through the sieves by their smallest dimension. In the model, the particle diameter, d_p , was calculated from the geometric mean of the sieves $d_p = (\text{lower mesh} \times \text{upper mesh})^{0.5}$. It gave values close to those given by $D(3,2) \times \psi$, where $\psi = 4\pi S_p / P^2$. Here S_p is the mean of measured area and P is the mean of measured perimeter of the particle sample.

[Table 3 hereabouts]

2.2 Apparatus and method

Batch experiments were performed in a fluidised bed contained in a quartz reactor, internal diameter 30 mm and length 460 mm, provided with a porous frit (4 mm thick, pore size +100, -160 μm) as the distributor, situated 110 mm from the base of the reactor. The pressure drop across the distributor and a 20 ml sand bed was measured to be 13 – 15 mbar at experimental conditions. The reactor was externally heated by an electric furnace (LTF 12/38/250, Lenton Ltd.). The temperature of the bed was measured by a K-type thermocouple (1.5 mm dia.) inserted into the top, with its tip 20 mm above the distributor. Flowrates of CO_2 , N_2 and air in the fluidising gas were controlled by rotameters calibrated at 293 K and 1 barg. The off-gas leaving the fluidising bed was sampled at 16.7 mL s^{-1} (STP) through a quartz tube. To prevent elutriated particles, tars and water vapour in the sampled gas entering the analysers, the gas was passed through a glass wool filter, an impinger tube submerged in ice bath and a drying tube filled with CaCl_2 in series. The volume fractions of CO_2 and CO were measured by a non-dispersive infra-red gas analyser (ABB EL3020). The arrangement of the apparatus can be found in [1,8].

In an experiment, the reactor was filled with 20 ml of silica sand and heated to the desired temperature, *viz.* 1073 – 1273 K. For gasification, the fluidising gas was typically 30 mol% CO_2 , balance N_2 . The total volumetric flowrate was 50 mL s^{-1} (STP), giving $U/U_{mf} \sim 4.2 - 5.0$, with U being the superficial velocity at the temperature of the bed and U_{mf} being the value at incipient fluidisation. The value of U_{mf} was determined by a pressure sensor measuring the pressure drop between the reactor inlet and outlet as a function of the gas flow rate at room temperature. Experimental measurements gave the flowrate at U_{mf} of 10 and 12 mL s^{-1} (STP) for 1273 and 1073 K, respectively, whereas the correlation of Wen & Yu [14] gave values of 9 and 12 mL s^{-1} (STP). About 0.05 g of fuel were added to the reactor and allowed to gasify to a point when the concentration of CO became ~ 0 . Then the reactor was purged with pure nitrogen before burning off the residual carbon in air. Each experiment was repeated at least 3 times. The mass of fuel added to the bed was chosen to be small to avoid complications arising from rate of mass transfer between the bubble and the particulate phases. The overall rate of production of CO from gasification in $\text{mol s}^{-1} \text{g}^{-1}$ is $R'_g = 2 \times [\dot{n}_{out}(y_{\text{CO},out} + y_{\text{CO}_2,out}) - \dot{n}_{in}(y_{\text{CO},in} + y_{\text{CO}_2,in})]/m_{batch}$, where m_{batch} is the initial mass of char added. The $\dot{n}_{out}$ and $\dot{n}_{in}$ are the total molar flows leaving and entering the reactor at the exit and entrance conditions, where $\dot{n}_{out}(1 - y_{\text{CO},out} - y_{\text{CO}_2,out}) = \dot{n}_{in}(1 - y_{\text{CO},in} - y_{\text{CO}_2,in})$ from the mass balance of nitrogen. The raw measurements were deconvoluted to account for the mixing and delay in the sampling line using the method described in [1,15].

3 Theoretical

The system modelled was a spherical carbon particle gasified by a stream of CO₂, diluted by N₂ in a fluidised bed reactor of silica sand particles. The only reaction occurring is:

The two principal assumptions were:

- i) The material and energy balances inside and outside the particle are in pseudo-steady state, so that the gas concentrations, total fluxes, total pressure and temperature have no time dependence. However, the balances are affected indirectly by the conversion of carbon X which does have time dependence and affects the physical properties of particles (*e.g.* porosity, pore diameter and particle size). This assumption is in line with many previous studies, where it was used to model the gasification of chars and methanation reaction [8,16–18].
- ii) The evolution of the internal morphology of a particle of char during gasification can be described by an arbitrary $f(X)$, a function of the local conversion of carbon X . Hence the reaction rate at some point within the solid can be expressed in the form of $r = g(C_i, T, P) \times f(X)$. It is assumed that $f(X)$ applies everywhere within a large particle, where rate is also affected by intraparticle mass transfer. The $f(X)$ can be obtained from plots of the experimental rate of gasification against conversion obtained from measurements in which rate is controlled *solely* by intrinsic chemical kinetics.

3.1 The kinetics of char gasification with CO₂

This research focused on gasification by CO₂ given in Eq. (1); of course, steam is also an important gasifying agent. The most widely-used reaction scheme is that of Ergun [11] in which gaseous CO₂ is adsorbed on an active site, C*, on the surface of the char followed by desorption of the CO produced:

The intrinsic rate of CO production per unit mass of carbon, $R'_{g,0}$, can be expressed as

$$R'_{g,0} = \frac{2c_0k_2(p_{CO_2} - p_{CO}^2/K_p)}{p_{CO_2} + k_2/k_1 + (k_{-1}/k_1)p_{CO}} \quad (4)$$

using Langmuir-Hinshelwood (L-H) kinetics and assuming a pseudo-steady state for the number of occupied sites C(O). Ergun [11] proposed this equation without the term p_{CO}^2/K_p . The extra term was added to allow reaction (3)

to be reversible [16]. Here c_0 is the initial number of active sites per unit mass of char, k_1 , k_{-1} and k_2 are rate constants, p_{CO} and p_{CO_2} are partial pressure of CO and CO₂, and K_P is the equilibrium constant for the overall gasification reaction (1). Both the equilibrium constant for reaction (2), given by k_{-1}/k_1 , and the combined parameter c_0k_2 were found [11] to be independent of the type of carbon used. The values of k_{-1}/k_1 and c_0k_2 were fitted by Arrhenius equations with constant activation energies of -95 kJ/mol and 247 kJ/mol respectively [11]. In fact, experiments have shown that k_2 is independent of partial pressure of CO₂, thus confirming the L-H kinetics used by Ergun [19,20].

3.2 Equations of mass balance

Using assumption ii), the rate of production of CO is $R'_{g,0} \times f(X)$. A pseudo-steady mass balance over a spherical shell at radius r gives the flux equations for CO and CO₂:

$$\frac{1}{r^2} \frac{d}{dr} (r^2 J_a) = S_a = \frac{\nu_a}{2} (R'_{g,0} \rho_e) f(X) \quad a = 1, 2, 3 \quad (5)$$

$$\rho_e = \rho_m (1 - \varepsilon) \quad (6)$$

where J_a is the total flux (*i.e.* diffusive flux + advective flux) of species a . Also S_a is the net rate of reaction of species a , in mol m⁻³ s⁻¹, inside the particle, which is positive for a net gain and negative for a net loss in species: ν_a is the stoichiometric coefficient of species a in reaction (1). The subscripts 1, 2 and 3 represent CO, CO₂, and N₂ respectively. Finally, ρ_e is the bulk density, ρ_m is the skeletal density and ε is the porosity of the particle. The total flux J_3 (diffusive flux + advective flux) of nitrogen is zero, hence:

$$J_1 + 2J_2 = 0 \quad J_3 = 0 \quad (7)$$

A material balance on carbon across a differential element gives the variation of local conversion of carbon with respect to time as a function of the carbon consumption rate S_C :

$$\left. \frac{dX}{dt} \right|_r = -M_c \left(\frac{S_C}{\rho_e} \right) = -12 \left(\frac{S_C}{\rho_e} \right) \quad S_C = S_2 = -\frac{S_1}{2} \quad (8)$$

the initial condition of which is:

$$t = 0: \quad X(r) = 0 \quad \text{for all } r \in [0, r_p] \quad (9)$$

3.3 Equations of intraparticle mass transfer

The stoichiometry of reaction (1) involves three species (CO₂, CO and N₂ as an inert gas). Here, a model of multi-component diffusion based on the Stefan-Maxwell equations within a porous media was used to describe the intraparticle diffusion. The two principal flux models for non-equimolar, multi-component mass transfer are the Dusty Gas Model (DGM) [21], and the Mean Pore Transport Model (MPTM) [22–24]. The approach used in

this work was to employ Young & Todd's [25] Cylindrical Pore Interpolation Model (CPIM), a type of MPTM. Compared to both the DGM and previous types of MPTM, the CPIM has a more rigorous treatment of continuum flow, a clearer interpolation procedure for transitional flow, and a more compact form of the working equations which helps to clarify the roles of the governing parameters. Recent studies suggest that the CPIM is well suited to modelling multi-component diffusion in both catalyst pellets [18] and in gasifying lignite char particles [8]. The governing equations are:

$$\frac{dy_a}{dr} = \frac{\tau^2 RT}{\varepsilon P} \sum_{b=1}^3 \left(\frac{y_a J_b}{D_{A,ba}} - \frac{y_b J_a}{D_{A,ab}} \right) \quad a = 1, 2, 3 \quad (10)$$

$$\frac{dP}{dr} = -\frac{\tau^2 A_A}{\varepsilon} \sum_{b=1}^3 (\sqrt{M_b} \cdot J_b) \quad (11)$$

The boundary conditions for the above equations are given at the centre ($r = 0$) and the surface ($r = r_p$) of the particle by:

$$r = 0: \quad J_a = 0 \quad (a = 1, 2, 3) \quad (12)$$

$$r = r_p: \quad y_a = y_{a,s} \quad \& \quad P = P_s \quad (13)$$

Here, y_a is the mole fraction of species a . The parameter τ^2 represents the tortuosity factor of the particle from mercury intrusion porosimetry measurements. The parameter ε is the porosity at the local point, which varies with conversion, discussed later. M_i is the molar mass of gas species i . The parameters $D_{A,ab}$ and A_A were found by interpolating between the extremes of continuum and Knudsen flow using the equations proposed by Young & Todd [25]:

$$\frac{1}{D_{A,ab}} = \frac{1}{D_{K,a}} + \frac{1}{D_{B,ab}} \quad \frac{1}{A_A} = \frac{1}{A_K} + \frac{1}{A_C} \quad (14)$$

where $D_{B,ab}$ is the molecular diffusivity calculated from the Chapman-Engskog theory using the Lennard-Jones (6-12) potential [26]. The error in the predicted binary diffusivities by this method is $\sim 7.3\%$ [27]. Finally, $D_{K,a}$ is the Knudsen diffusivity and the parameters A_K and A_C are the coefficients in the pressure gradient equation in the continuum and Knudsen regime, given by

$$D_{K,a} = \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi M_a}} \quad A_K = \frac{3}{2d_{pore}} \sqrt{\frac{\pi RT}{2}} \quad (15)$$

$$A_C = 32\mu_{mix}RT / \left(Pd_{pore}^2 \sum_{a=1}^3 (y_a \sqrt{M_a}) \right)$$

The viscosity of the gas mixture, μ_{mix} , was calculated using Chapman-Engskog theory.

The porosity, ε , changes with the local conversion of carbon, X , during reaction and can be derived from the carbon balance equation over a thin cylindrical shell inside the particle:

$$\varepsilon(X) = \varepsilon_0 + X(1 - \varepsilon_0) \quad (16)$$

It was assumed that the particle has uniform cylindrical pores of initial diameter $d_{pore,0}$; the corresponding initial porosity of the particle was ε_0 . Ignoring the small volume of crossover between pore channels, the local porosity can be estimated by $\varepsilon(r) \cdot \delta V = \pi d_{pore}^2 \sum_{i=1} L_i / 4$, where δV is the volume of a differential element between r and $r+dr$ and $\sum_{i=1} L_i$ is the sum of the length of the cylindrical pores within the element. Assuming that the enlargement of the pores during reaction occurs only in a radial direction so that the pore diameter changes while the length of the pore remains constant, then:

$$\varepsilon(r)/\varepsilon_0 = (d_{pore}/d_{pore,0})^2 \quad (17)$$

Substituting Eq. (16) into (17), the pore diameter at some time when the local conversion is X is:

$$d_{pore} = d_{pore,0} \sqrt{(\varepsilon_0 + X(1 - \varepsilon_0))/\varepsilon_0} \quad (18)$$

3.4 Equations of external mass transfer

The fluidised bed was considered to have a constant local tortuosity and porosity around the carbon particle. It was also assumed that there is no variation of total pressure with radial distance outside the char particle, since previous studies [1,8] for the gasifying system have shown that the interstitial velocity of fluidising gas is much higher than the mass average velocity of gases leaving the surface of a reacting particle. This suggests that there is no tendency to form voids or bubbles around the reacting particle in the case under consideration and that pressure variations outside the particle can be neglected. The general Stefan-Maxwell equations were used to model the external mass transfer within a diffusion boundary layer of thickness δ outside the particle:

$$\frac{dy_a}{dr} = \frac{\tau_{bed}^2 RT}{\varepsilon_{bed} P} \sum_{b=1}^3 \left(\frac{y_a J_b - y_b J_a}{D_{B,ab}} \right) \quad a = 1, 2, 3 \quad dP/dr = 0 \quad (19)$$

Here τ_{bed}^2 is the tortuosity factor of the sand bed. It was experimentally measured to be $1.34^2 = 1.80$ for a packed bed with 200 μm dia. quartz sand in [28]. The porosity of the bed, ε_{bed} , was assumed to be 0.44, the same as the porosity at incipient fluidisation used for a bubbling fluidised bed of silica sand [29]. The parameter $D_{B,ab}$ is the binary molecular diffusivity of species a and species b . The boundary conditions at the particle surface ($r = r_p$) and the edge of boundary layer ($r = r_p + \delta$) are:

$$r = r_p: \quad J_1 = J_{1,s} \quad (20)$$

$$r = r_p + \delta: \quad y_a = y_{a,bulk} \quad (a = 1, 2, 3) \quad \& \quad P = P_{bulk} \quad (21)$$

3.5 Equations of energy balance

It was assumed that the heat transfer coefficient from the bulk bed to the surface of the particle was large, so that the particle surface is close to the temperature of the bulk. It was also assumed that the radiative contribution and transpiration contributions to heat transfer were small. Inside the char particle, the energy flux, E , is

$$E = \sum_{a=1}^3 M_a J_a \left(\frac{u_m^2}{2} + \frac{H_a}{M_a} \right) - \lambda_{eff} \frac{dT}{dr} \quad (22)$$

Jackson [30] showed that the energy balance can be expressed as $\text{div}(E) = 0$, which gives:

$$\begin{aligned} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) &= \frac{1}{\lambda_{eff}} \sum_{a=1}^3 \left(H_a + \frac{u_m^2}{2} M_a \right) S_a + \frac{1}{\lambda_{eff}} \frac{dT}{dr} \sum_{a=1}^3 J_a C_{p,a} \\ &+ \frac{1}{\lambda_{eff}} \sum_{a=1}^3 M_a J_a u_m \frac{du_m}{dr} \end{aligned} \quad (23)$$

This equation makes specific allowance for the small change in momentum due to the change in mass in the gas phase as a result of the non-catalytic reaction between CO_2 and the solid. Here, $C_{p,a}$ is the molar heat capacity of species a assumed constant; λ_{eff} is the effective thermal conductivity; H_a is the partial molar enthalpy of species a at temperature T , and is calculated from standard enthalpy of formation $H_{a,f}^0$ by $H_a = H_{a,f}^0 + \int_{298}^T C_{p,a} dT$. The calculation of the thermal parameters H , C_p and λ is discussed in section 3.7. Finally, u_m is the mass-averaged velocity of the mixture which is given by $u_m = \sum_{a=1}^3 M_a J_a / \sum_{a=1}^3 \rho_a$. The boundary conditions for the internal energy balance were:

$$r = 0: \quad dT/dr = 0 \quad r = r_p: \quad T = T_s \quad (24)$$

3.6 Change of particle radius during reaction

The change of radius of the particle during the reaction occurs in two stages: i) prior to the overall conversion reaching a critical value, the particle shrinks as its density decreases, and ii) at a critical overall conversion, the particle disintegrates from the outside owing to a loss of structural integrity [4,31]. During the second stage, the change of radius is usually extremely rapid and is a complicated process occurring at a conversion close to 100%. The present study focused on the first stage. When a particle shrinks with decreasing density, the loss of elemental carbon in solid and gas phases within a char particle is equal to the net carbon

transferred out of the particle by the fluxes of CO and CO₂, at pseudo-steady conditions. This gives the following equations:

$$-\frac{d}{dt}\left(\frac{4\pi}{3}r_p^3(1-\bar{\varepsilon})\frac{\rho_m}{M_c} + \frac{4\pi}{3}r_p^3\overline{\varepsilon \cdot [C]}\right) = 4\pi r_p^2(J_{1,s} + J_{2,s}) \quad (25)$$

$$\bar{\varepsilon} = 3 \int_0^1 \eta_r^2 \varepsilon d\eta_r \quad \overline{\varepsilon \cdot [C]} = 3 \int_0^1 \eta_r^2 \varepsilon ([CO_2] + [CO]) d\eta_r \quad (26)$$

where η_r is the dimensionless radius. The above equations can be rearranged:

$$-\left(3(1-\bar{\varepsilon})\frac{\rho_m}{M_c} + 3\overline{\varepsilon \cdot [C]}\right)\frac{dr_p}{dt} + r_p\frac{\rho_m}{M_c}\frac{d\bar{\varepsilon}}{dt} - r_p\frac{d}{dt}(\overline{\varepsilon \cdot [C]}) = 3(J_{1,s} + J_{2,s}) \quad (27)$$

The initial condition is

$$t = 0: \quad r = r_{p,0} \quad (28)$$

In the Eq. (27), $d\bar{\varepsilon}/dt$ and $d(\overline{\varepsilon \cdot [C]})/dt$ can be estimated by numerically differentiating the outputs of Eq. (26). The above equation is a 1st order ODE in r_p and was solved numerically in MATLAB. In addition, Eq. (27) could be simplified to describe a shrinking core model at constant density by setting $d\bar{\varepsilon}/dt = 0$. In practice, the initial particle diameter, $r_{p,0}$, was more of a variable input around its estimated value rather than a constant owing to the uncertainties in using a mean value for the size distribution measurement.

3.7 Calculation of parameters

The Arrhenius coefficients and activation energies of the kinetic parameters $2c_0k_2$ and $2c_0k_1$ in Eq. (4), shown in Table 4, were determined from the initial rates of reaction measured at various temperatures and concentrations of CO₂ [1,8,13,15]. The values of the equilibrium constant K_p for the overall reaction (1), taken from experimental measurements on lignite chars by [1,8], were $6.3 - 100 \times 10^5$, consistent with partial pressures expressed in Pa at 1073 – 1248 K. These values were assumed to hold for the activated carbon; however, any error was not significant because p_{CO_2} is much larger than p_{CO}^2/K_p in Eq. (4).

[Table 4 hereabouts]

The equilibrium constant, involving k_{-1} and k_1 in reaction (2), was given as

$k_{-1}/k_1 = 2.4 \times 10^{-4} \exp(+95 \text{ kJ mol}^{-1}/RT)$ [11]. The errors associated with the kinetic parameters mainly came from the linear regression analysis applied on the limited number of measurements of the initial rates.

The boundary layer thickness δ was calculated from

$$Sh_{EMCD} = 2\varepsilon_{mf}(1 + r_p/\delta) \quad (29)$$

$$Sh_{EMCD} = 2\varepsilon_{mf} + 0.61(2r_p U_p / v_{mix})^{0.48} (v_{mix} / D_{B,23})^{0.33} \quad (30)$$

$$U_p = U_{mf}(1 - \varepsilon_b)\{1 - 0.5\pi L n(1 - 6\varepsilon_b/\pi)\} \quad (31)$$

where $\varepsilon_{mf} = 0.44$ was the voidage at incipient fluidisation for a bubbling fluidised bed with silica sand [29]. Also, v_{mix} is the kinematic viscosity of the gas mixture calculated using Chapman-Engskog theory and $D_{B,23}$ the binary molecular diffusivity for CO₂ and N₂. The bubble fraction, ε_b , was given by $\varepsilon_b = (U - U_{mf})/U_b = (H - H_{mf})/H$, where the bubble velocity $U_b = (U - U_{mf}) + 0.71(gd_{b,m})^{0.5}$. Here, H_{mf} was the bed height at incipient fluidisation, measured to be 0.029 m and the mean bubble diameter, $d_{b,m}$, was estimated from the correlation of Darton *et al.* [32]: $d_{b,m} = 0.54(U - U_{mf})^{0.4} H^{0.8} / (2g^{0.2})$ with H being the expanded height of the bed when fluidised at superficial velocity U . Although the correlations of Hayhurst & Parmar [29] were based on EMCD, it has been shown that they will yield the correct value of δ from Eq. (29), even for non-EMCD [33].

The thermal conductivities of the gases were calculated from $\lambda = C_1 T^{C_2} / (1 + C_3/T + C_4/T^2)$, where $C_1 - C_4$ are constants given by [27]. The effective thermal conductivity of the particle was calculated from $\lambda_{eff} = (1 - \varepsilon)\lambda_{solid} + \varepsilon\lambda_{gases}$, where $\lambda_{gases} = \sum_{a=1}^{a=3} y_a \lambda_a$. The overall thermal conductivity was largely influenced by that of the solid. The reported thermal conductivity of coal and amorphous carbon is 0.26 and 1.6 W m⁻¹ K⁻¹ respectively [27]. The thermal conductivity of graphite char at 819 K was 0.62 W m⁻¹ K⁻¹ [34]. Hence, λ_{solid} was taken to be 1.0 W m⁻¹ K⁻¹. The specific heat capacity of each gas was estimated from $C_p = E_1 + E_2 T + E_3/T^2$, where $E_1 - E_3$ are constants given by [27].

3.8 Numerical solution

The system is described by Eqs. (5) to (28). Both the intraparticle and external mass transfer models have five 1st order ordinary differential equations (ODEs) in the space domain, and hence five boundary conditions are provided. The ODE for conversion is 1st order in the time domain, hence only one initial condition is required. The energy equation is a 2nd order ODE, hence two boundary conditions are required for both the internal and external cases. The equation of change of radius is a 1st order ODE in the time domain, with an initial condition. The main difficulty in solving the system lies in efficient solution of the large system of equations. A numerical algorithm, Orthogonal Collocation on Finite Elements (OCFE) [35] was written in MATLAB to solve the model. Pseudo-steady state was assumed for all the other variables except for the conversion X . Using the initial condition in Eq. (9), the 1st order time-dependent ODE of local conversion X , Eq. (8), was solved. The value of $X(r)$ at time

$t + \Delta t$ could be calculate based on $X(r)$ and dX/dt at time t . The relevant model parameters (*e.g.* porosity and pore diameter) were updated with the new value of $X(r)$, and then the internal and external model were solved for results at time $t + \Delta t$. The iterative process was stopped when the overall conversion reached unity.

4 Results

Fig. 1 shows the raw measurements of gas concentration during the experiments for lignite char and activated carbon. There is a small peak of CO_2 after the end of the gasification in plot b), which was due to the combustion of the residual carbon with air. The figure shows that lignite char at 1173 K was completely reacted after ~ 200 s while activated carbon at 1273 K was not 100% reacted even after 750 s. Hence the reactivity of activated carbon was significantly less than that of lignite char. The figure also confirms that the fluidised bed was close to a differential reactor, because the overall change of the CO_2 concentration across the reactor was always $< 10\%$ of its input value. Hence it was reasonable, for the experiments shown in Fig. 4, to use 30% CO_2 balance N_2 as the bulk concentration in the model.

[Fig. 1 hereabouts]

4.1 Mass balance

The statistical analysis of the mass balance of carbon within the reactor is shown in Table 5, where 4 different sizes of lignite char and 3 different sizes of activated carbon were gasified at 3 different temperatures. Experiments were replicated 3 times at each condition. The table shows that an almost complete closure of the mass balance was achieved in the reactor within the accuracy of the experiments.

[Table 5 hereabouts]

4.2 Gasification of fuel particles at different temperatures

Since the model predicts the distributions of reaction rate and conversion across the radius of a particle, the overall values of rate and conversion need to be obtained from integration across the particle radius. For a distribution of the variable χ (*e.g.* S_C and X), its volume averaged value can be calculated from

$$\bar{\chi} = 3 \int_0^1 (\eta_r^2 \chi) d\eta_r, \text{ where } \eta_r \text{ is the dimensionless radius. The integral was evaluated numerically.}$$

Initially, a constant arbitrary function $f(X)$, appearing in Eq. (5), was used in the simulations at different temperatures. The $f(X)$ was determined from experimental measurements of gasification rate *vs.* conversion conducted under conditions where the reaction was controlled by intrinsic chemical kinetics. Given the high reactivity of the lignite chars, this necessitated experiments at relatively low temperatures. For example, for lignite

char, 0.60 – 1.00 mm dia. particles were gasified by 30 vol% CO₂ balance N₂ at 1073, 1123 and 1173 K. The $f(X)$ was determined from the result of experiments at 1073 K experiments, at which the effectiveness factor $\kappa_{eff} \sim 0.94$, and applied to the simulations of reaction at 1123 K (where $\kappa_{eff} \sim 0.92$) and 1173 K ($\kappa_{eff} \sim 0.82$). The calculation of the initial effectiveness factors is discussed later in section 0, with values at other conditions depicted in Fig. 8. The comparison between theory and experiment is shown in Fig. 2, which exhibits increasing disagreement between the two as temperature increases. Although the rate of gasification at the peak was over-predicted for 1123 K and 1173 K, the overall conversion vs. time matched well the experimental results for all temperatures. [Fig. 2 hereabouts]

For activated carbon, 0.36 – 0.43 mm dia. particles were gasified by 30 vol% CO₂, balance N₂ at 1173, 1223 and 1273 K. The $f(X)$ was determined from the results at 1173 K, at which $\kappa_{eff} \sim 0.97$, and applied to the simulations at 1223 K ($\kappa_{eff} \sim 0.95$) and 1273 K ($\kappa_{eff} \sim 0.92$). The comparison between the model and the experimental measurements is shown in Fig. 3. Since the reaction was stopped when the rate of gasification became very slow at high conversion, the experiments at 1173 K only had measurements of gasification rate up to an overall conversion of 0.8. Thus the $f(X)$ determined from it could not be extrapolated beyond 80% of conversion and so the figure shows no theoretical predictions beyond this point. The experimental measurements displayed initial spikes in the rate (not shown), owing to the reaction of oxygen, previously adsorbed on the surface of the fuel by exposure to air. No attempt to model this feature has been made, hence causing some discrepancies in the conversion plots as illustrated. Model and experiment matched well at 1173 K and 1223 K, but differed somewhat for 1273 K even though all three experiments were fairly close to being controlled by intrinsic chemical kinetics.

[Fig. 3 hereabouts]

It was concluded that using a constant $f(X)$ for all temperatures gave an imperfect fit between the model and the measurements for both lignite char and activated carbon. One possible cause of this could be that the particles contained multiple types of active sites, whose contributions to the overall gasification rate changed with temperature. Therefore, the $f(X)$ determined at low temperature would not correctly reflect the change of number of active sites due to changes of internal morphology. Thus, it was necessary to examine whether a constant $f(X)$ was applicable to simulating the experiments affected by intraparticle mass transfer, by using particles of different sizes, at the same temperature. Since the arbitrary function $f(X)$ was to be determined from the measurements conducted under conditions where the reaction was controlled by intrinsic chemical kinetics, at the given temperature, it necessitated using particles sufficiently small in size to evaluate the $f(X)$. So, at each temperature,

the $f(X)$ was obtained from the measurements on the smallest particles and then applied to the simulations of the larger ones.

4.3 Gasification of fuel particles of different sizes

Experiments with lignite char were performed using different sizes of particles (0.60 – 1.00 mm, 1.00 – 1.40 mm and 1.70 – 2.56 mm), at 1073 K, 1123 K and 1173 K. Additional particles with a sieve size of 0.36 – 0.50 mm were used at 1173 K, because at this temperature the kinetics are fast and lead to significant gradients in intraparticle gaseous diffusion in 0.60 – 1.00 mm dia. particles. Hence, in summary, the $f(X)$ was determined from the measurements at 1073 K on 0.60 – 1.00 mm particles, at 1123 K on 0.60 – 1.00 mm particles and at 1173 K on 0.36 – 0.50 mm particles. The derived $f(X)$ were then applied to reaction and diffusion in larger particles, at the corresponding temperature. Fig. 4 compares the overall rate of CO production vs. overall carbon conversion from both experiment (points) and theory (line) for lignite chars gasified in 30 vol% CO₂, balance N₂ at 1073 – 1173 K. Judging from the plots of conversion vs. time, there is an excellent fit between measurements and model results. The plots of rate vs. conversion show deteriorating agreement between experiments and model as the particle diameter increases. Nonetheless, the agreement between model and experiment is satisfactory.

[Fig. 4 hereabouts]

Experiments with activated carbon were performed at 1173 K, 1223 K and 1273 K, using particle sieve sizes of 0.36 – 0.43 mm, 0.71 – 1.25 mm and 1.70 – 2.36 mm. At each temperature, the $f(X)$ was determined from the experimental measurements made with particles of sieve size 0.36 – 0.43 mm and applied to the simulations of larger particles, at the corresponding temperatures. Fig. 5 shows the results. The low reactivity of activated carbon has resulted in noisy measurements and large error bars. Despite this, the figure shows excellent agreement between measurements and the model predictions up to 60% conversion. In addition, the model successfully captured the curvature of the rate as highlighted in plot e), where the rate became constant for a short while as large particles started to experience external mass transfer limitation. The rate soon dropped as pores coalesced and internal reactive surface area commenced to fall.

[Fig. 5 hereabouts]

5 Discussion

5.1 The $f(X)$ hypothesis

The original $f(X)$ hypothesis, proposed in [1,8], assumed that the variation in the rate of reaction due to pore structure changes at any temperature could be modelled by an arbitrary $f(X)$ function obtained from reaction in the absence of intraparticle gradients in gas concentration at one temperature. One implicit assumption in the original hypothesis was that the solid was homogeneous and that all the particle reacted with the same rate parameters. However, if there were multiple species of carbon (*e.g.* graphitic and amorphous), with different rate parameters and kinetics, the $f(X)$ at one temperature is likely to be different to that at another, because there would be two species with different activation energies contributing to the curve. The results in section 4.2 showed that a constant $f(X)$ function obtained from low temperature experiments was relatively poor in predicting the value and shape of the rate *vs.* conversion curve for higher temperature experiments. This strongly suggests that both the lignite char and the activated carbon contained multiple active sites.

[Fig. 6 hereabouts]

To eliminate the effect of different active sites, the lignite chars were subjected to heat treatment. Previous studies [20] have found that c_0 in Eq. (4) decreases exponentially with temperature. It was surmised that the reactivity of heat-treated chars is nearly constant because of a more homogeneous carbon structure [9]. In a previous study [36] the chars were treated at 900 – 1200 °C for 1 – 300 minutes, and it was found that their reactivity decreased considerably with increasing temperature and time. Hence the lignite char particles were heat-treated in a sand bed fluidised by a stream of pure N₂ at 1273 K for 1 hour and cooled to room temperature before gasification by CO₂. The results, in Fig. 6, showed a significant reduction of reactivity compared to Fig. 2. In order to match the initial rate of reaction at 1073 K, the activation energy of the kinetic parameter c_0k_2 was arbitrarily increased to 317 kJ/mol, a 27 kJ/mol increase due to the thermal deactivation. The figure shows an excellent fit between the model results and experimental measurements at 1073 K and 1123 K. At 1173 K, the shape of the $f(X)$ curve could no longer capture the change of the reaction rate, but it still shows a good agreement between model and experiment when conversion > 0.5. Compared to Fig. 2, the fit between model predictions and experimental measurements here is better at 1123 K but poorer at 1173 K. Fig. 7 compares the $f(X)$ curve for both normal and heat-treated lignite char particles and shows a complete change of shape of $f(X)$ curves, suggesting that thermal deactivation of active sites did change the $f(X)$ curve.

[Fig. 7 hereabouts]

Thus, it can be concluded that the model utilising $f(X)$ determined from the measurements on small particles at one temperature (Regime I) could be used for the simulation of larger particles at the same temperature (Regime II) with excellent accuracy; the existence of multiple types of active sites prevents, in accurate work, the use of $f(X)$ across temperatures due to the change of rate contributions from each species. However, even if it is applied across a range of temperatures, the agreement between model and experiment is still reasonable.

5.2 The fuel particles

The lignite chars contained very large pores and cavities that could potentially act as feeder pores to the small pores. The reacting CO_2 probably diffused quickly through the large feeder pores, but diffused more slowly into the smaller pores which contained most of the surface area. Reducing the size of a char particle, *e.g.* by grinding, would have little effect on mass transfer, until the particles were small enough to eliminate the large pores [15]. On this basis, the char particle could be viewed as an agglomerate of several small particles with large voids in between. Thus the mean particle diameter of the char particle, obtained from the particle size distribution measurement, might not be a realistic reflection of the true particle size in mass transfer. In addition, the particle diameter used in the model was estimated from the geometric mean of the sieve sizes, which introduces an approximation. Therefore, the uncertainties in initial particle diameters used in the model might be significant. In practice, changing the particle diameter had no significant effect on the predicted rate of reaction for particles in Regime I, as expected. As the reaction of the particles moved to Regime II, the change of particle diameter had a larger effect on the predicted rate, *e.g.* smaller particle diameters gave higher rates and larger diameters resulted in lower rates. Therefore, it was possible to adjust the particle diameter used in the model to match the measurements of the rate. However, the shape of the overall rate *vs.* conversion curve could not be altered by changing the particle diameter used in the model.

For lignite chars, an average of 165 nm from the measured mean pore diameters was used to give the results shown in section 4.2 and 4.3. While the pore diameter of activated carbon, 133 nm, determined by the mercury porosimetry in Table 2, did not give a good fit between experimental measurements and the model results. The value of the pore diameter for activated carbon was varied during the fitting process. As a result, a pore diameter in the relatively narrow range of 20 – 40 nm gave the best fits, as shown in Fig. 3 and Fig. 5. It should be noted that the activated carbon particles were investigated using mercury porosimetry [15], and were found to have no macro-pores. Hence, there are also uncertainties in pore diameters used in the model.

Lignite char was very reactive when gasified by CO_2 , whilst the activated carbon was much less so. Comparing the rates of reaction of the smallest particles (lignite char: 0.36 – 0.43 mm and activated carbon: 0.36 –

0.50 mm) at 1173 K, the peak rate of gasification of lignite char was ~ 10 times that of the activated carbon. Since activated carbon had ~ 5 times more BET area than lignite, this difference in rate indicated that the correlation between BET area and reactivity was poor. It also meant that the mathematical pore models predicting the rate of reaction based on total surface area would have limited application in simulating the reaction and diffusion inside the particles during char gasification. One reason for these differences in kinetics is that the lignite, a low rank coal, tends to contain more metal elements than does activated carbon. The metal impurities, especially the alkali metals, *e.g.* potassium, sodium and calcium, could catalyse the reaction of carbon. Saucedo [1] reported that calcium, presumably as CaO, was found to catalyse the rate of reaction in the later stages of conversion (*i.e.* $X > 0.4$) increasing the rate by as much as 25% over untreated char. Experiments performed in the present work, using scanning electron microscopy coupled with electron diffraction scattering (SEM-EDS), have confirmed that i) lignite char contains 0.12 wt% Na, 4.78 wt% Ca and 0.89 wt% Mg and ii) activated carbon contains 0.07 wt% Na, 0.59 wt% Ca and 0.48 wt% Mg. This confirms the higher content of potentially catalytic metals in the lignite.

5.2 Effectiveness factor

Fig. 8 shows the initial effectiveness factor calculated for each particle size at different temperatures using $\kappa_{eff} = \tanh(\gamma\phi^*/\phi^*)$, which can be applied to a catalytic reaction following a Langmuir-Hinshelwood mechanism [37]. The detailed definitions of the correction factor γ and the normalised Thiele modulus ϕ^* were summarised by [38]. The figure confirms that the smallest particles used at each temperature were all in the kinetically-controlled regime (Regime I), because their κ_{eff} was close to unity. As both the temperature and the particle size increase, the effectiveness factor drops, indicating a growing intraparticle mass transfer limitation to the rate of reaction (Regime II). As the diffusional flux increases during reaction due to growing pores, the effectiveness factor will gradually increase with conversion. To compare the model results in different regimes, three sets of theoretical predictions for the reaction of activated carbon are highlighted here: i) 0.36 – 0.43 mm dia. particles at 1173 K, $\kappa_{eff} = 0.97$ (Regime I); ii) 0.71 – 1.25 mm dia. particles at 1223 K, $\kappa_{eff} = 0.85$ (Regime II); iii) 1.70 – 2.36 mm dia. particles at 1273 K, $\kappa_{eff} = 0.51$ (well within Regime II).

[Fig. 8 hereabouts]

5.3 Local conversion

Fig. 9 shows the profiles of local conversion *vs.* dimensionless radius for the three sets of simulations, where it can be seen that the gradient of the conversion profile becomes steeper in particles experiencing severer intraparticle mass transfer limitation, as expected. Moving from a) to c), the initial gradient becomes steeper when the effectiveness factor is lower. As the overall conversion increases, the resistance to intraparticle mass transfer

falls because of the opening and coalescence of pores, hence the gradient of conversion gradually reduces. Plot b) shows that even when the effectiveness factor is as high as 0.85, there is a difference of 0.2 – 0.3 in conversion between the surface and the centre of the particle.

[Fig. 9 hereabouts]

5.4 Gas concentration and total fluxes

Fig. 10 shows three sets of simulations of the gas concentration and total fluxes with radial distance from the centre of the particle at different overall conversions. Moving vertically from a) to e), the initial gradient in concentration of gas becomes steeper, meaning that the internal mass transfer limitation is severer for bigger particles at higher temperature. At the start of the reaction ($X < \sim 0.2$), the pores open up, the porosity increases and reactive surface area grows. As a result, the rate of carbon gasification increases, which reduces the concentration of CO_2 and increases that of CO . The total fluxes of CO_2 and CO increase as a result of the higher gasification rate. As conversion increases ($X > \sim 0.2$), the pores start to coalesce with each other and the reactive surface area falls. The rate of reaction also drops, resulting in decreases in total fluxes. The concentration of CO_2 then increases while that of CO drops. Similar trends can also be observed for pressure and temperature variation, discussed in section 5.6.

[Fig. 10 hereabouts]

Moving vertically from plot a) to e), the figure also shows that the boundary layer thickness relative to the particle diameter δ/r_p reduces: a) ~ 2.12 ; b) ~ 1.36 ; c) ~ 0.83 . This is because the Sh_{EMCD} in Eq. (29) is proportional to $r_p^{0.48}/T^{0.5}$, where the temperature dependence comes from the diffusivity $D_{B,23}$, and the large increase in r_p has dominated over the relative small change in T . In addition, the gradient of external gas concentration increases as the effectiveness factor reduces as expected.

5.5 Change in particle diameter

Changes in particle diameter with conversion, calculated from Eq. (27), are shown in Fig. 11. They are compared with the curve for a shrinking core model, where $d_p/d_{p,0} = (1 - \bar{X})^{1/3}$. The highlighted area in the figure shows that all three cases had some degree of shrinking core behaviour when conversion was low. The particle of activated carbon, 1.70 – 2.36 mm dia., at 1273 K displays the shrinking core behaviour up to 30% conversion while the two other cases diverge from the shrinking core curve after a conversion of 10%. As conversion increases and pores open up, the gas concentration gradient within the particle flattens and the rate of

particle shrinking reduces. At high conversion ~ 0.8 , the rate of particle shrinking further reduces as indicated in the figure.

[Fig. 11 hereabouts]

It has been suggested that a carbon particle would start to shrink when the porosity at the surface reached ~ 0.8 during combustion in air [4]. This corresponds to a conversion of ~ 0.7 at the particle surface for activated carbon particles. However, Fig. 11 shows that all three particles start to shrink at the beginning of gasification. Looking at the conversion profiles in Fig. 9, none of the three simulations gave such a high conversion at the surface when gasification had just started.

5.6 Pressure and temperature variation

Fig. 12 shows the predicted profiles of pressure for the three sets of simulations, calculated using Eq. (11). As the rate of reaction passes through a maximum at about 15% – 20% conversion, the pressure profile reached a maximum as shown in the figure. However, the effects are slight and would be undetectable, experimentally. The magnitude of the difference in total pressure between the inside of a particle and the outside is small, e.g. a maximum $\sim 14\%$ of the bulk pressure for activated carbon gasified at 1273 K and 30% CO_2 .

[Fig. 12 hereabouts]

Since the gasification of carbon with CO_2 is endothermic, the temperature inside the particle, not shown here, will always be lower than the outside. The differences in temperature between the bulk and the centre of the particle increased with increase in particle sizes and temperature as the influence of intraparticle mass transfer became more significant, but the overall magnitude was very small. The model predicted a maximum temperature difference of $\sim 2^\circ\text{C}$ for activated carbon gasified at 1273 K and 30% CO_2 . This value is in line with the conclusion by [15] that the temperature difference between the particle and the bed was $< 4^\circ\text{C}$, when a reactive char was gasified at 1273 K in 100% CO_2 . In addition, the model showed that the temperature gradient across the particle was small, which also agrees with the isothermal assumption used in many gasification studies.

6 Conclusions

It has been proposed that a simple arbitrary function $f(X)$, determined from experimental measurements of rate vs. conversion in the kinetically-controlled regime, could be used, in place of mathematical pore models, to describe the evolution of pore structure during a reaction influenced by intra-particle gas mass transfer. A model to examine this has been constructed using the Cylindrical Pore Interpolation Model for intraparticle mass transfer,

Ergun's rate equation of gasification, the Stefan-Maxwell equations for external mass transfer and the equations of energy.

The results show that for the gasification of chars, the $f(X)$ predicts the rate of reaction of particles of various sizes well, all being at the same temperature. However, for chars and gasification at least, an $f(X)$ evaluated at one temperature does not predict experimental measurements well at other temperatures, possibly because there are contributions from multiple types of active sites within the particles. The significance of this research is that the $f(X)$ hypothesis presents a simple solution for modelling the evolution of pore structures during reactions of particles. Instead of using complicated mathematical pore models, one could determine the $f(X)$ from the experiments used for kinetic studies. This idea could be further applied to many other gas-solid reactions that involve change of pore structures during reactions. However, one needs to be aware that the presence of multiple types of active sites could lead to incorrect predictions. However, multiple sites are also not reflected in most published pore models.

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623 List of Figure Captions

624 Fig. 1. Raw measurements of gas mole fraction during gasification experiments.

625 Fig. 2. Comparison of model results with experimental measurements of the gasification of 0.60 – 1.00 mm lignite
626 char particles by 30 vol% CO₂ balance N₂. The chars were gasified at three different temperature: 1073 K (×),
627 1123 K (○) and 1173 K (□). The error bars of the experimental measurements indicate the 95% confidence
628 interval obtained from a t – distribution of three repeated measurements of each sample.

629 Fig. 3. Comparison of model results with experimental measurements of the gasification of 0.36 – 0.43 mm
630 activated carbon particles by 30 vol% CO₂ balance N₂. The chars were gasified at three different temperature:
631 1173 K (×), 1223 K (○) and 1273 K (□). The error bars attached to the experimental points indicate the 95%
632 confidence interval obtained from a t – distribution of three repeated measurements of each sample.

633 Fig. 4. Comparison of model results with experimental measurements of the gasification of lignite char by 30 vol%
634 CO₂ balance N₂ at 1073 K, 1123 K and 1173 K. Three different size fractions of lignite char were used at 1073 K
635 and 1123 K: 0.60 – 1.00 mm (×), 1.00 – 1.40 mm (○) and 1.70 – 2.56 mm (□). Additional particles with size of
636 0.36 – 0.50 mm (∇) were used for 1173 K experiments. The error bars on the experimental points indicate the 95%
637 confidence interval obtained from a t – distribution of three repeated measurements of each sample.

638 Fig. 5. Comparison of model with experiment for the gasification of activated carbon by 30 vol% CO₂ balance N₂
639 at 1173 K, 1223 K and 1273 K. Three different size fractions of activated carbon were used: 0.36 – 0.43 mm (×),
640 0.71 – 1.25 mm (○) and 1.70 – 2.36 mm (□). The on the experimental points indicate the 95% confidence interval
641 obtained from a t – distribution of three repeated measurements of each sample.

642 Fig. 6. Comparison of model results with experimental measurements of the gasification of 0.60 – 1.00 mm lignite
643 char particles, heat treated at 1273 K for 1 hour, by 30 vol% CO₂ balance N₂. The chars were gasified at three
644 different temperature: 1073 K (×), 1123 K (○) and 1173 K (□). The error bars on the experimental points indicate
645 the 95% confidence interval obtained from a t – distribution of three repeated measurements of each sample.

646 Fig. 7. The $f(X)$ function curves for the normal 0.60 – 1.00 mm lignite char particles and the heat treated (1273 K,
647 1 hour) particles fitted from the gasification measurements at 1073 K by 30% CO₂ balance N₂.

648 Fig. 8. Initial effectiveness factor of the samples: a) lignite char particles at 1073 K, 1123 K and 1173 K; b)
649 activated carbon at 1173 K, 1223 K and 1273 K. Three samples, highlighted in b), are selected for comparison.

650 Fig. 9. Local conversion profile of three different sizes of activated carbon particles gasified by 30 vol% CO₂
651 balance N₂ at various temperature.

652 Fig. 10. Model predicted profiles of gas concentration and total flux of activated carbon particles gasified by 30
653 vol% CO₂ balance N₂. Radius 0 – 1 is inside the particle; radius > 1 is outside the particle. A positive value of flux
654 means the direction of the flux is pointing outwards from the centre, and a negative value means the flux is
655 directed inwards.

656 Fig. 11. Model predicted change of particle diameter for three different sizes of activated carbon particles gasified
657 by 30 vol% CO₂ balance N₂ at various temperature.

658 Fig. 12. Model predicted pressure profiles for three different sizes of activated carbon particles gasified by 30 vol%
659 CO₂ balance N₂ at various temperature.

Table 1. Analysis of the char particles used in the experiments.

Fuel	Ultimate Analysis (wt%) ^a				Density (kg m ⁻³)	
	C	H	N	Balance	Bulk	Skeletal
Hambach lignite char	85.69	0.82	0.84	12.65	831	1310
Activated carbon	87.80	0.64	0.37	11.19	703	1076

^a From [8,13].

Table 2

Table 2. Summary of the particle characterisation results.

Fuel particles	BET analysis			Mercury intrusion porosimetry		
	BET area / m ² g ⁻¹	BJH volume / cm ³ g ⁻¹	BJH adsorption mean pore diameter / nm	Total pore area / m ² g ⁻¹	Total intrusion volume / cm ³ g ⁻¹	Mean pore diameter / nm
Lignite char, 0.60 – 1.00 mm	178	0.113	5.6	10.70	0.428	160
Lignite char, 1.70 – 2.56 mm	160	0.103	6.4	10.56	0.452	171
Activated carbon, 0.71 – 1.25 mm	1019	0.130	3.3	14.75	0.492	133
Activated carbon, 1.70 – 2.36 mm	947	0.122	3.5	n.d.	n.d.	n.d.

Table 3. Summary of particle size characterisation for lignite chars.

Parameter	355 – 500 μm	600 – 1000 μm
10% of total volume below this size, D_{10} / μm	466	856
50% of total volume below this size, D_{50} / μm	551	1070
90% of total volume below this size, D_{90} / μm	653	1268
Sauter mean diameter, $D(3,2)$ / μm	574	1100
Average high sensitivity circularity, ψ / -	0.74	0.75
$D(3,2) \times \psi$ / μm	425	825
Geometric mean diameter used in model, d_p / μm	421	775

Table 4

Table 4. Kinetic parameters used in the model.

Char particles	$A_{2ck2} / \text{mol s}^{-1}$ g^{-1}	E_{2ck2} / kJ mol^{-1}	A_{2ck1} / mol $\text{s}^{-1} \text{g}^{-1} \text{pa}^{-1}$	E_{2ck1} / kJ mol^{-1}	Reference
Lignite char	1.26×10^{10}	290	25.6	200	[1]
Activated carbon	70.6×10^6	268	116.4	236	[15]

Table 5. Yield of carbon converted to CO from the complete gasification of the fuels

Statistical parameter	Lignite char	Activated carbon
Average yield ^a of carbon in fraction of sample mass	1.01	0.98
Standard deviation in fraction of sample mass	0.05	0.07
Number of experiments × 3 replicates at each condition	36	27

^a Yield is defined as percentage of solid carbon in the chars converted into CO.

Figure 1

Figure 2

Figure 3

Figure 4(a_b)

Figure 4(c_d)

Figure 4(e_f)

Figure 5(a_b)

Figure 5(c_d)

Figure 5(e_f)

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12