Investigations of the Oxy-Fuel Coal Char Gasification Reactions Kinetics in the Isothermal Drop-Tube Furnace

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Abstract

The influence of the individual gasification reactions, with CO_2 and H_2O, occurring on the coal char particle surface during oxy-fuel combustion was addressed in this paper. The experimental results were used to derive the individual reaction kinetic parameters using ash tracer method and fitting data algorithm. Data analysis was supported by the CFD modelling providing thermal histories of the particles, i.e. temperatures and residence times. The overall char combustion model was modified in order to include the influence of the individual gasification reactions on the particle surface reaction rate and was implemented in the commercial CFD code. Numerical simulations of the oxy-fuel char gasification in drop-tube have been carried out, and results are in reasonable consistency with the experimental data.

Nomenclature

ΔH	heat of reaction, kJ/kmol,
$\dot{\boldsymbol{n}}''$	molar flux, kmol/(s·m^2),
X_C	char conversion (char burnout),
ρ	density, kg/m^3,
A	preexponential factor, (different units),
C	molar concentration, kmol/m^3,
c_p	particle specific heat capacity, J/(kg·K),
D	effective diffusion coefficient, m^2/s,
d_p	particle diameter, m,
E	activation energy, J/kmol,
f	mass fraction,
k_c	reaction rate coefficient, (different units),
k_d	mass transfer coefficient, m/s,
M	molecular mass, kg/kmol,
m	mass, kg,
p	pressure, Pa,
r	radius, m or reaction rate, kg/s,
T	temperature, K,
t	time, s,
V	volume, m^3,
y	mole fraction,
Subscripts	
∞	free stream,
C	carbon,
a	ash,
f	fluid,
g	gas species index,
i	reaction index,
p	particle,
s	surface,
0	initial state.

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1. Introduction

One of the most promising measures of the CO_2 emission abatement from coal fired power plants is oxy–fuel combustion, due to its lowest energy penalty associated with the investment and operational costs [1]. The main feature of the oxy–fuel technology is an elimination of air from the combustion system and its replacement with the mixture of recycled flue gases (mainly CO_2 and H_2O) and O_2. In consequence, the flue gas mainly comprises of CO_2, which significantly increases its removal efficiency. But this action can alter the combustion process due to different physical and chemical properties of diluents such as CO_2 and H_2O in respect to N_2 [2]. Flame and particle temperatures, heat transfer, emissions and burnout can be changed [3, 4], which can be caused by different gas properties and/or combustion mechanism.

Naredi and Pisupati [5] observed that the char burnouts are lower during oxy–fuel combustion compared to in air for 2 ranks of bituminous coal, most likely due to lower particle temperature, however the difference becomes smaller at higher temperatures, which can be explained by an increase of the gasification reaction with CO_2.

Brix *et al.* [6] have conducted char combustion experiments in EFR and found no evidence of the gasification reaction with CO_2 in a range of operating conditions, but the modelling of the process suggests that the gasification may occur where there are low concentrations of O_2, high temperatures and bigger particles.

However, Gonzalo-Tirado *et al.* [7] stated in their work that gasification reactions can contribute to the overall char consumption rate and compensate for the changes in the gaseous atmosphere at the low oxygen concentrations.

In this study a series of laboratory experiments have been conducted in isothermal drop-tube to asses the

char gasification rates with CO_2 and H_2O and include their influence on the total char consumption in commercial CFD code.

2. Experimental setup

2.1. Char combustion facility

The experiments were conducted in the facility, showed in Fig. 1, which main element is an electrically heated, silicon carbide drop–tube with a 38.5 mm inner diameter and 6–meter length. The desired reaction atmosphere composition is formed using mass flow controllers. Pulverized solid fuel is dosed using the precise screw feeder, and pneumatically transported by the cold, primary gas to the reactor through the one of the twelve, sloped ports installed along the reactor height. The particle residence time was varied by changing the position of the feeding probe while the collection point remained stationary.

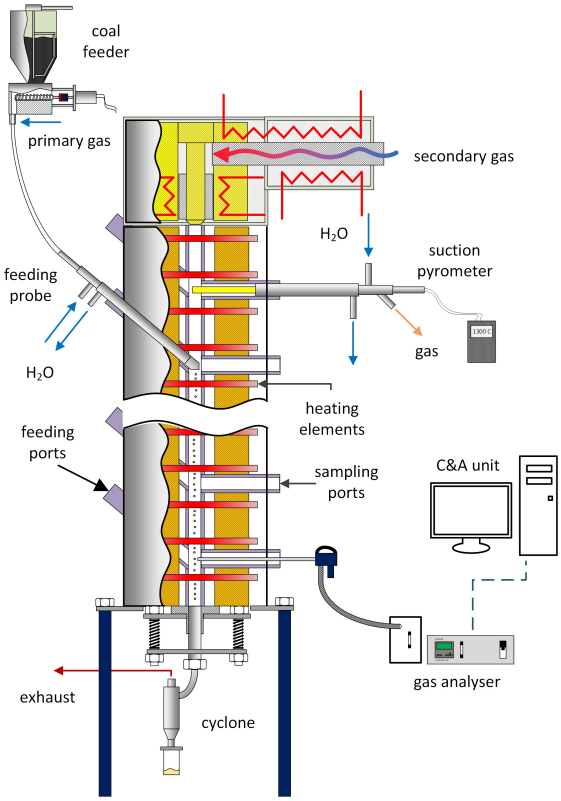


Figure 1: Char combustion facility

2.2. Char properties

Bituminous coal, originating from Poland, was selected for experiments. Before the tests, raw fuel was dried, milled and sieved in order to obtain the desired particle size in a range of 63–80 μm. Then the pulverized fuel was devolatilised at 1300 °C at high heating rate of 10^4 K/s in pure nitrogen. The residence time for devolatilization test was set up to 250 ms ensuring complete devolatilisation. The char and parent fuel properties, on analytic basis, are collected in Tab. 1. Char particle size distribution is presented in Fig. 2.

Table 1: Parent fuel and char properties

quantity	parent coal	char
M, %wt.	5.6	2.6
A, %wt.	10.9	11.5
VM, %wt.	32.5	1.4
C, %wt.	63.90	74.60
H, %wt.	4.08	0.27
N, %wt.	1.11	1.29
S, %wt.	1.25	1.02
O_{diff}, %wt.	13.25	0.18
HCV, kJ/kg	25097	26614
LCV, kJ/kg	26492	24071
$\bar{d}$, μm	-	71

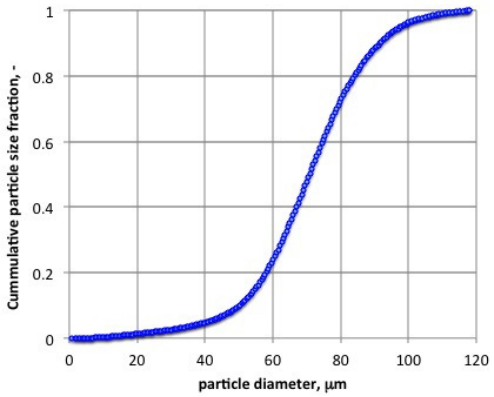


Figure 2: Cumulative char particle size distribution

2.3. Methodology

Experiments were carried out in the following conditions:

- reaction temperatures: 900, 1050 and 1200 °C,
- for gasification with CO_2 : CO_2 mole fraction in N_2: 50%, 70%, 90%,

- for gasification with H_2O : H_2O mole fraction in N_2: 20%, 30%, 40%,
- residence time varying from 0.1 to 1.5 s.

Conversion levels (char burnout) were calculated by the following equation

$$X_C = \frac{f_a - f_{a,0}}{f_a(1 - f_{a,0})} \tag{1}$$

derived on the basis of the ash tracer method [8].

3. Char combustion model

In this study the single-film model [9, 10] has been adopted, since is acceptable model for particle sizes up to 100 μm [11] and is widely used to describe char combustion, especially in CFD. When pulverized char particles are burnt in oxy–fuel conditions, the combustion mechanism, besides oxidation, additionally should take into consideration the gasification with CO_2 and H_2O. The combustion mechanism of char carbon is composed of three surface reactions and defined as follows:

$$C + \tfrac{1}{2}\,O_2 \longrightarrow CO, \tag{R1}$$

$$C + CO_2 \longrightarrow 2\,CO, \tag{R2}$$

$$C + H_2O \longrightarrow CO + H_2. \tag{R3}$$

The total rate of char carbon consumption, r_C, is defined as follows

$$r_C = \sum_{i=1}^{i=3} r_{C,i} \tag{2}$$

where i numbers the i-th surface reaction, and

$$r_{C,i} = A_p\, M_C\, \psi_i\, |\dot{\boldsymbol{n}}_g^{''}| \tag{3}$$

in which $g \in \{O_2, CO_2, H_2O\}$ for $i \in \{1, 2, 3\}$ respectively, $A_p = \pi d_p^2$ is the reaction area expressed as the external particle surface, $\psi_1 = 2$ mol-C/mol-O_2 , $\psi_2 = 1$ mol-C/mol-CO_2 and $\psi_3 = 1$ mol-C/mol-H_2O.

The molar flux of the g-th gas reagent, $\dot{\boldsymbol{n}}_g^{''}$, results from the balance of rates between gas diffusion and the surface reaction, i.e.

$$|\dot{\boldsymbol{n}}_g^{''}| = k_d\, C \ln\left(\frac{y_{g,\infty} + 1}{y_{g,s} + 1}\right) = k_{c,i}\, C_{g,s}^{n_i} \tag{4}$$

where

$$C = \frac{p}{RT_s} \tag{5}$$

is the total molar concentration,

$$k_d = \frac{D}{r_p} \tag{6}$$

is the mass transfer coefficient,

$$k_{c,i} = A_i\, T^{\beta_i} e^{-E_i/(RT_s)} \tag{7}$$

is the rate coefficient of the i-th surface reaction expressed in the form of the modified Arrhenius equation.

In the current study, it is assumed that the reactions (R1), (R2) and (R3) are independent of each other allowing to write the molar flux of the g-th gas reagent as Eq.(4) which mathematically presents the single-film model for char combustion in the current approach.

The effective diffusion coefficient, D, expressed as [9, 12]

$$D(T) = D_0 \left(\frac{T_{f,\infty} + T_p(t)}{2T_0}\right)^{1.75}, \tag{8}$$

has got different values for air and oxy-fuel combustion. Namely, at air combustion, just the oxidation reaction (R1) is considered to be important in the combustion mechanism so that $D_0^{air} = D_{O_2-N_2} = 0.181$ cm^2/s at $T_0 = 273$ K [13]. At oxy-fuel combustion, also reactions (R2) and (R3) are expected to be active but the in the present conditions they are completely kinetically controlled [14], so that

$$r_{C,2} = A_p\, M_C\, \psi_2\, k_{c,2}\, C_{CO_2,\infty} \tag{9}$$

$$r_{C,3} = A_p\, M_C\, \psi_3\, k_{c,3}\, C_{H_2O,\infty} \tag{10}$$

are applied in the current model.

Finally, the governing equations of the char combustion model can be presented. It is assumed that the char particle is treated as a discrete Lagrange particle. It was assumed that the particle volume, $V_p = \frac{\pi}{6} d_p^3$, is constant during combustion, so that the mass conservation law of the char particle is expressed in the following form:

$$V_p \frac{d\rho_p}{dt} = -r_C(t)\,, \quad \rho_p(0) = \rho_{p,0} \tag{11}$$

and the char particle mass is then defined as

$$m_p(t) = m_a + m_C(t) \tag{12}$$

in which

$$m_a = f_{a,0}\, \rho_{p,0}\, V_p \tag{13}$$

is constant mass of ash contained in the char particle. The char particle temperature, $T_p(t)$, is defined by the conservation law of particle energy as follows [15]:

$$m_p(t) c_p \frac{dT_p(t)}{dt} = hA_p(T_{f,\infty} - T_p(t)) + \\ + A_p \varepsilon_p \sigma\,(T_{f,\infty}^4 - T_p^4(t)) + \sum_{i=1}^{i=3} r_{C,i}(t) \Delta H_i \tag{14}$$

with the initial condition

$$T_p(t = 0) = T_{p,0}\,, \tag{15}$$

where the heat transfer coefficient h is defined as

$$h = \frac{k_{f,\infty}}{d_p}\,\mathrm{Nu} \tag{16}$$

in which $\mathrm{Nu} = 2 + 0.6\,\mathrm{Re}_p^{1/2}\mathrm{Pr}^{1/3}$ is the Nusselt number.

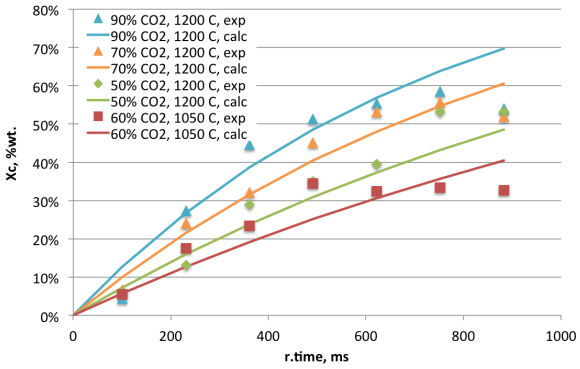
4. Results and discussion

A set of two ordinary differential equations have been determined by the generalized reduced gradient method [16] for which the fourth-order Runge-Kutta method was used to solve the system and thus determine the values of $\mathrm{X_C}^{num}$. More details of the coupling of the Ansys Fluent and Matlab and determining of the kinetic parameters are given elsewhere [17]. Values of the optimal kinetic parameters determined in Matlab are presented in Tab. 2. Fig. 3 shows evolution of char consumption for examined coal char gasified with CO_2 and H_2O. The gasification at low temperature (900 °C) and low mole concentration of H_2O (20, 30 $\%_{mol.}$) was negligible (results not shown here). In present study the gasification reactions begin at higher temperatures (≥1050 °C) and higher concentrations of H_2O (≥40 $\%_{mol.}$). It can also be noted that, in current experimental conditions, the gasification reaction can be responsible up to 60 and 50 $\%_{wt.}$ of the char mass loss in case of gasification with CO_2 and H_2O respectively. Even at reasonably low temperature (1050 °C) the gasification with CO_2 is not negligible, reaching 30$\%_{wt.}$ after 500 ms.

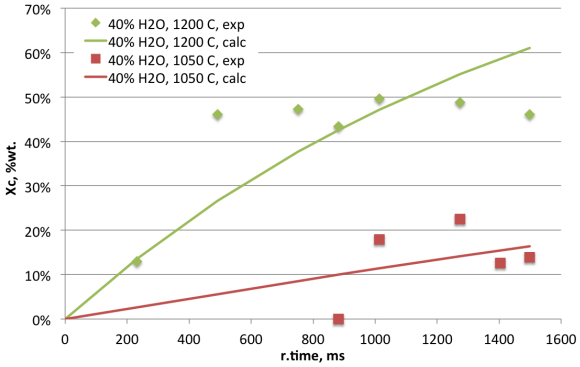
Table 2: Optimal values of the kinetic parameters

reaction	A kg/m^{2}sPa	E kJ/mol
gasification with CO_2	3.867×10^{-6}	46.3
gasification with H_2O	2.140×10^{-1}	179.5

When the two reactions are compared it can be observed that gasification with H_2O begins later than with CO_2, exhibiting higher activation energy, but when the temperature is high enough (1200 °C) then the gasification rate with H_2O is even higher than with CO_2 (see Fig. 4).



(a) Gasification with CO_2



(b) Gasification with H_2O

Figure 3: Coal char gasification with CO_2 and H_2O

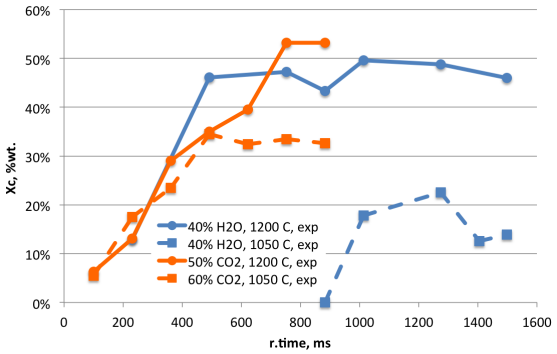


Figure 4: Comparison of the char gasification with CO_2 and H_2O in selected conditions

5. Conclusions

Laboratory experiments of the coal char gasification with CO_2 and H_2O, conducted in conditions comparable to pulverised fuel boilers, have shown that, at no presence of the O_2, the char consumption due to gasification can be up to 60 $\%_{wt.}$, showing that at low oxygen concentrations, the gasification reactions may compensate for lower temperatures in oxy-fuel combustion conditions. On the other hand, it is necessary to include those reactions in combustion modelling, as they may influence the overall combustion rate. Although the mathematical modelling, using combustion model presented in this study, showed reasonably good agreement with the experimental data, it seems that mutual effect of the surface reactions should be also addressed as the total reaction rate isn't most likely the simple sum of the three reactions.

Acknowledgments

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