Limitation of thermogravimetry for oxy-combustion analysis of coal chars

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Abstract A kinetic study of the oxy-combustion of chars obtained from two Polish steam coals was conducted. A comparative study was focused on the data analysis concerning oxy-combustion of coal chars collected from two thermobalances, which differed in construction, design of crucibles, sample size and gas flow direction. The influence of individual factors such as temperature, O₂ concentration, the dimensions of the crucibles and the dimensions of the char bed on the reaction rate was analysed. On the basis of these results, a global kinetic model was elaborated showing the influence of all factors, particularly mass transfer conditions, on reaction rates. The developed model can be extended to other mass transfer conditions or fluidised bed conditions and can be applied to other fast reactions to ensure they occur in the chemical reaction kinetics control regime during TG tests. It was concluded that the gas–solid fuel contact characteristics are crucial for the measured reaction rate and for the interpretation of kinetic data.

Keywords Diffusion effects · Kinetics · Oxy-combustion · Char combustion

Abbreviations

APTGA Atmospheric pressure thermogravimetric analyser
HPTGA High-pressure thermogravimetric analyser

List of symbols

A	Surface/m ²
A_0	Pre-exponential factor/s ⁻¹
AC	Ash content/mass%
C	Concentration of gas/mol m ⁻³
d	Diameter/m
D	Diffusion coefficient/m ² s ⁻¹
E_a	Activation energy/kJ mol ⁻¹
h	Height/m
k_D	Mass transfer coefficient/m s ⁻¹
l	Length/m
LHV	Lower heating value/J g ⁻¹
m	Mass/mg
M	Moisture content/mass%
N	Molar flow rate of gas/mol s ⁻¹
P	Pressure
r	Reaction/diffusion rate/mol s ⁻¹
R	Universal gas constant/kJ mol ⁻¹ K ⁻¹
R_p	Pore radius/m
Re	Reynolds number/–
S	Specific surface area/m ² g ⁻¹
Sh	Sherwood number/–
Sc	Schmidt number/–
T	Temperature/K
t	Time/s
u	Velocity of gas/m s ⁻¹
V	Volatile matter content/mass%
X	Conversion degree of solid/–
y	Molar fraction/–
β	Heating rate/K min ⁻¹
μ	Viscosity/Pa s
ρ	Density/kg m ⁻³
τ_p	Tortuosity of the pores/–
ε_0	Porosity of the particle/–

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Subscripts

ash	Relates to mineral matter
b	Refers to bed
BET	Brunner–Emmett–Teller
CO ₂	Related to carbon dioxide
con	Refers to convection
D	Refers to diffusion/mass transport
D–A	Dubinin–Astachow
eff	Effective
ext	Refers to external
g	Refers to gas
int	Refers to internal
K	Refers to Knudsen diffusion
N	Refers to crucible
me	Refers to mesopores
mi	Refers to micropores
O ₂	Related to oxygen
obs	Observed
R	Refers to reaction
t	Total
0	Refers to initial state

Superscripts

ar	As-received basis
ad	Air-dried basis
d	Dry basis
daf	Dry and ash-free basis

Introduction

Recently, great attention has been focused on carbon dioxide emissions from the power sector due to the significant impact of the greenhouse effect. To reduce the emissions of greenhouse gases from fossil fuel-fired power generation, the oxy-combustion of coal seems to be a promising future technology combined with retrofitting of existing boilers to allow an O₂-enriched atmosphere for combustion [1, 2].

In the process of oxy-combustion of fossil fuels, a high purity of oxygen (above 95%) and a stream of recycled CO₂ from the flue gas are used to control the combustion temperature. The process product is a gas consisting mostly of CO₂ and water vapour. The considerable concentration of CO₂ in the gas enables direct referral to sequestration, which is followed by condensation of water vapour [3, 4].

The oxy-combustion process comprises several consecutive processes and reactions. When a coal particle is introduced into the combustion chamber of a fluidised bed, it is heated with a high heating rate (up to 1000 K s^{−1}). This step involves drying and pyrolysis of the coal particle, and the evolution of volatile matter consisting of combustible gases, while char is produced. The volatiles burn

in homogenous reactions, and the char reacts with oxygen (heterogeneous reaction). The reaction of carbon from char with O₂ is the slowest step of the whole process [5–7]. Therefore, the present work focuses on the coal char oxy-combustion, because its reaction rate is crucial for boiler design. Since the oxy-combustion of coal char is a heterogeneous reaction, it can proceed under three different reaction-controlling regimes: chemical kinetics, mixed internal diffusion–chemical kinetics and external diffusion [8, 9]. Oxy-combustion in a fluidised bed boiler occurs at a temperature of 1073–1173 K where diffusion limitations exist [3, 4, 10]. The scaling-up of this process requires an extensive computational analysis, which is critical for proper boiler design. Herein, a kinetic analysis is fundamental for oxy-combustion process modelling, where the kinetic equations are implemented using modelling software.

On the other hand, thermogravimetric analysis is a commonly used technique to investigate the kinetics of fast heterogeneous reactions such as the combustion of solid fuels, the oxidation of oxygen carriers [5, 6, 11–19]. It is well known that kinetic parameters should be obtained under a chemical reaction-controlling regime [5, 6, 13, 14, 17–19], which is important for the study of oxy-combustion kinetics.

Some researchers have proposed specific approaches to finding the transport limitations in TGs during combustion or gasification of fuels [11, 12, 20]. They have found a number of parameters which are crucial for shifting the regime from chemical kinetics to diffusion, especially crucibles and their dimensions, fuel bed mass and gas flow direction. The interpretation of these results involves a numerical analysis which is difficult to apply to other cases.

The aim of the paper is the identification of diffusional limitations for the crucibles used in thermobalances, which influence the kinetic analysis of fast reactions, such as, for example, oxy-combustion. As a result of the study, suitable and generalised models for oxygen transport to the coal char particles in TG crucibles were developed. Moreover, the models can be extended for application in fluidised bed processes.

Experimental

Sample properties

Two char samples obtained from Polish lignite (Turów) and hard coal (Janina), which are extensively used for combustion in Polish power plants, were investigated. The chars were prepared using a laboratory stand for the pyrolysis of solid fuels. First, ca 150 g of coal sample of

size 1–3.15 mm was placed in a cylindrical batch reactor. The reactor was heated up to 1273 K at a heating rate of 5 K min⁻¹ under nitrogen. Subsequently, the reactor was flushed with N₂ to cool the sample to room temperature. The coal sample and obtained char samples were crushed and sieved to a particle size smaller than 200 µm and were further analysed.

The proximate analyses of the coal and char samples were performed by a gravimetric method using a LECO TGA701 analyser. The ultimate analysis that followed sulphur analysis was conducted using CHN TruSpec LECO and LECO SC632 apparatus. Pore structure was analysed by nitrogen adsorption at 77 K and CO₂ adsorption at 273 K, using Micromeritics 3Flex apparatus. A Malvern Instruments Mastersizer 2000 particle analyser with a dispersion Hydro 2000G mouthpiece was used for analysing the particle size distribution of coal chars.

The tested samples were significantly different in terms of metamorphism degree, as indicated by the volatile content, elemental composition of coals and particularly the oxygen content (Table 1). The pyrolysis of coal led to an increase in elemental C content to approx. 80% and to the reduction of the hydrogen, oxygen, sulphur and nitrogen contents. The analysis results obtained from the coal chars indicate that the chemical compositions of the chars are similar, even though they come from coals with a different degree of metamorphism. The pyrolysis resulted mainly in the removal of moisture from the coal samples, and in a separation of the volatile components, producing lignite char with zero content, and approximately 0.5% for hard coal char. In other words, the pyrolysis of the coal has increased the degree of metamorphism of the parent coals and conformed them chemically to one another. Although the technical and chemical analyses show that the properties of chars are similar, there are some significant differences in their structure. This has the greatest impact on the char particles' reactivity. For example, the pore structure of the char has a greater impact than its chemical composition. A smaller specific surface area (determined by the BET method), of the order of few m² g⁻¹, is shown by the sample of hard coal char and a significantly larger surface area by the lignite char. The surface area of the micropores, determined by adsorption of CO₂ at 273 K, confirmed the greater surface area of the lignite char micropores (Table 2).

Thermogravimetric analysis

Oxy-combustion tests were conducted in two thermobalances, namely an atmospheric pressure Netzsch STA 409 PG Luxx (APTGA) thermobalance, and a TA Instrument pressurised thermobalance TG-HP150 s with Rubotherm magnetic suspension balance (HPTGA). The dimensions of the TGA's furnace and crucibles, and also the experimental

Table 1 Proximate and ultimate analyses of coal

	Lignite	Hard coal
Proximate analysis		
$M^{\text{ar}}/\%$	44.20	21.30
$M^{\text{a}}/\%$	3.90	12.40
AC/%	7.80	10.40
$V^{\text{daf}}/\%$	59.14	39.56
LHV ^a /MJ kg ⁻¹	24.72	22.84
Ultimate analysis		
$C^{\text{a}}/\%$	62.30	60.40
$H^{\text{a}}/\%$	5.48	3.46
$N^{\text{a}}/\%$	0.61	0.94
$S^{\text{a}}/\%$	1.02	1.22
$O^{\text{a}}/\%$	18.89	11.18

Table 2 Proximate and ultimate analyses of coal chars

	Lignite char	Hard coal char
Proximate analysis		
$M^{\text{a}}/\%$	0.20	0.70
$A^{\text{a}}/\%$	12.32	15.19
$V^{\text{daf}}/\%$	0.00	0.54
Ultimate analysis		
$C^{\text{a}}/\%$	82.50	81.40
$H^{\text{a}}/\%$	0.34	0.35
$N^{\text{a}}/\%$	1.06	0.99
$S^{\text{a}}/\%$	0.93	0.65
$O^{\text{a}}/\%$	2.85	1.42
N ₂ adsorption at 77 K		
$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	17.3	3.8
$V_{\text{t}}/\text{cm}^3 \text{ g}^{-1}$	0.0154	0.0448
$V_{\text{mi}}/\text{cm}^3 \text{ g}^{-1}$	0.0091	0.0011
$V_{\text{me}}/\text{cm}^3 \text{ g}^{-1}$	0.0063	0.0438
CO ₂ adsorption at 273 K		
$S_{\text{D-A}}/\text{m}^2 \text{ g}^{-1}$	719.31	312.9
$V_{\text{t}}/\text{cm}^3 \text{ g}^{-1}$	0.2055	0.0322

conditions, differ in these two thermobalances. The differences are presented in Tables 3 and 4.

The reaction furnaces of the two TGAs in which the crucibles are placed are of the tubular type. For each of the thermobalances, a specific method of crucible mounting is applied. In the APTGA, the crucible is placed on a long rod which is a carrier for the crucible and is connected to the mass measuring system placed below the reaction furnace. On the other hand, HPTGA has a completely different type of crucible mounting. In this case, the crucible is suspended

Table 3 Properties of the crucibles

	Thermobalance Netzsch 409 PG Luxx	Pressurised thermobalance TA TG-HP150 s
Furnace diameter, d_R /mm	22.0	23.0
Cross-sectional area of the reactor, A_N /mm ²	380.1	415.5
Crucible diameter, d_N /mm	5.9	10.0
Cross-sectional area of the crucible (area of the char layer), A_N /mm ²	27.3	78.5
Height of the crucible, h_h /mm	3.9	25.0
Sample mass, m_0 /mg	5.0	10.0
Total gas flow rate, $\dot{V}$ /cm ³ min ⁻¹	125	1000
Flow rate of O ₂ , $\dot{V}$ /cm ³ min ⁻¹	20	200

Table 4 Properties of the sample bed

	Lignite char APTGA	Hard coal char APTGA	Lignite char HPTGA	Hard coal char HPTGA
Height of the char layer, h_b /mm	257.6	215.2	179.3	149.8
Mean char particle diameter, d_p /mm	225.2	172.5	225.2	172.5
Ratio of char bed height to particle diameter, h_b/d_p	1.14	1.25	0.80	0.87

on a weighing hook which is connected to the permanent magnet (magnetic roller) of the upper part of the reactor. The permanent magnet is maintained by a magnetic field from an electromagnet, which is a part of the electronic measuring system of the balance. Gas entering the APTGA is introduced at the bottom of the furnace and flows upwards washing the crucible. Therefore, the gas cannot interfere with the stationary gas layer in the crucible in any way. In the case of the HPTGA, the gas is introduced into the upper part of the furnace and it flows vertically downwards. Therefore, the gas could influence the gas layer in the crucible. In Tables 3 and 4, the dimensions of the individual furnaces of the thermobalances are shown together with dimensions of the crucibles used. The gas flow values and the properties of the char beds are also included.

The experiments were conducted at isothermal conditions by applying the temperature of 450 (only for the lignite char), 500, 550, 600, 700, 800, 900 and 1000 °C. In

the APTGA an alumina crucible was used, and in the HPTGA a quartz crucible with porous bottom was used. Reaction gases with defined composition and specific volume flow were fed into the reaction furnace. The gaseous mixtures with a suitable molar fraction of oxygen y_{O_2} in CO₂ equal to 0.2 were introduced into both TGAs. Moreover, a protecting gas of ca 25 N cm³ min⁻¹ of Ar was dosed into the APTGA. For APTGA the char sample mass was $m_0 = 5$ mg, while for HPTGA it was 10 mg. Comparison of the flow conditions showed that the flow rate of the gas through the furnace was approximately eight times higher for HPTGA than it was for APTGA. All these parameters could have a significant effect on the results obtained from the thermogravimetric analysis.

Analysing the presented data, it can be concluded that the height of the char bed in both cases is comparable to the diameter of the particles. Therefore, considering the properties of the char bed it can be assumed that it is a monolayer of particles, almost evenly distributed at the bottom of the crucible. In addition, the ratio of the char bed diameter to its height is very large: for the lignite char and hard coal char for the APTGA crucible, it amounts to 22.9 and 27.4, respectively. The corresponding values for the HPTGA case are 55.8 and 66.8. For this reason, it can be assumed that the char bed is a single char tablet with height h_b . The crucible diameter is designated d_N , and the cross-sectional area (footprint) is A_N . This assumption is used to describe the reaction rate in crucibles for both thermobalances.

Results and discussion

Model development

After the initial coal pyrolysis stage, the combustion of coal chars proceeds in several consecutive and parallel processes. Inside a real industrial boiler, a single particle is raised in the reacting gases flowing upwards and is surrounded by a laminar gas layer, as shown in Fig. 1a. Oxygen from the bulk gas enters the laminar layer surrounding the char particle by convection, and then the O₂ transport occurs by diffusion. Therefore, the process can be divided into several stages as follows:

- O₂ transport to the particle and within the particle, which consists of:
 - O₂ convection to the gas film surrounding the char particle,
 - O₂ diffusion in the laminar gas layer surrounding the particle,
 - O₂ diffusion in the pores of the char particle.

Fig. 1 Model approach of O_2 transport: **a** fluidised bed, **b** APTGA, **c** HPTGA

- A chemical reaction on the internal surface of the char particle.

In the TGA, char particles are not carried in the gas but they form a fixed bed of thickness h_b at the bottom of the crucible. The mass transfer differs from that in the fluidised bed, which may affect the oxy-combustion reaction rate. Figure 1 shows schematically the flow patterns in the fluidised bed and in the crucibles used in TGA.

The overall oxy-combustion reaction rate is a result of all existing resistances, and it can be shown as Eq. (1):

$$\frac{1}{r_{\text{obs}}} = \frac{1}{r_R} + \frac{1}{r_D} \quad (1)$$

where r_{obs} is the observed overall reaction rate, r_R is the chemical reaction rate, and r_D is the O_2 transport rate.

In the chemical kinetic regime, the chemical reaction is the slowest step of global reaction, and the main rate-determining step is a chemical reaction rate. Thus, the condition $r_{\text{obs}} = r_R$ is valid, and the reaction can be described using n th-order kinetics as in Eq. (2):

$$r_{\text{obs}} = r_R = k_R \cdot f(X) \cdot C_{O_2}^n \quad (2)$$

where k_R is a chemical reaction constant, C_{O_2} is the O_2 concentration on the surface of the char particle (in the kinetic regime on both the inner and outer surface of particle), n is the reaction order with respect to O_2 concentration, and $f(X)$ represents the reaction model.

The reaction rate in this analysis is represented as the rate of C element loss from the char in moles, in a specified time interval, i.e. dN_C/dt as calculated from Eq. (3):

$$r = \frac{dN_C}{dt} = \frac{dm}{dt} \frac{1}{M_C}, \text{ mol s}^{-1} \quad (3)$$

where dm/dt is the reaction rate from DTG and M_C is the molar mass of carbon (12 g mol^{-1}).

The mean value of the reaction rate from a conversion range of 0.2–0.8 was used in this paper, and only one concentration of oxygen was applied. Therefore, the reaction model $f(X)$ and the O_2 concentration are both included in the reaction rate constant which is equal to the reaction rate ($r_R = k_R$). The Arrhenius equation is shown in Eq. (4):

$$\ln(r_R) = \frac{-E_a}{R \cdot T} + \ln(A_0) \quad (4)$$

where E_a is the activation energy and A_0 is a pre-exponential factor.

With increasing temperature, the main resistance to the reaction may be O_2 transport to the char particle surface (diffusion regime). In these conditions, when the temperature is increased, the reaction rate is not significantly increased, because of the small increase in O_2 transport rate. Therefore, the overall reaction rate may be equal to the rate of O_2 transport, or in other words $r_{\text{obs}} = r_D$. Therefore, specific O_2 transport models can be applied for different apparatus and for different types of solid–gas contact.

The transport model of O_2 in the APTGA crucible

In the APTGA crucible, the gas flows vertically upwards and it flows around the crucible. Subsequently, it joins the uniform gas flow which takes place over the crucible. Figure 2 shows a schematic representation of the APTGA crucible, with the directions of reactant transportation and their local concentrations indicated (Fig. 2a). The potential distribution of the O_2 concentration as a function of crucible height is shown in Fig. 2b.

At the top of the crucible, the O_2 concentration is the same as in the bulk gas and is equal to the initial concentration of O_2 directed to the furnace, $C_{O_2,1}$. In the crucible

Fig. 2 Model approach of O₂ transport in the crucible of the APTGA thermobalance: **a** schematic with selected concentrations and the molar fraction of O₂, with dimensions and directions of flow of the reactants, **b** distribution of O₂ concentration as a function of crucible height

above the bed of char considered as a tablet, there is a stationary layer of gas with height h_D equal to the height of the crucible h_N minus the thickness of the char layer h_b . When oxy-combustion of the char takes place, the concentration of O₂ on the surface of the char bed, $C_{O_2,2}$, decreases as a result of the reaction. Combustion of one mole of O₂ results in the formation of one mole of CO₂. Therefore, for each mole of O₂ flowing towards the particle there is one mole of CO₂ which diffuses in the opposite direction, as described by Eq. (5):

$$\dot{N}_{O_2} = \dot{N}_{CO_2}, \text{ mol s}^{-1} \quad (5)$$

Fick's first law defines the equimolar countercurrent diffusion rate, which is proportional to the concentration gradients of the components and inversely proportional to the length of the diffusion path which is the height of stationary gas layer. As a consequence, for O₂ diffusion, it can be mathematically expressed as in Eq. (6) [18]:

$$\dot{N}_{O_2} = D_{O_2} \frac{dC_{O_2}}{dh_D}, \text{ mol m}^{-2} \text{ s}^{-1} \quad (6)$$

where dC_{O_2} is the O₂ concentration gradient between two points along the length of the diffusion path dh_D and D_{O_2} is the molecular diffusion coefficient of CO₂ in O₂.

After separation of variables, integration and taking into consideration the surface of the char bed (the crucible area), this is modified as follows:

$$\dot{N}_{O_2} = \frac{D_{O_2}}{h_D} A_N (C_{O_2,1} - C_{O_2,2}), \text{ mol s}^{-1} \quad (7)$$

where A_N is the surface of the char bed in the crucible calculated according to the equation $A_N = \pi \cdot d_N^2/4$.

The molecular diffusion coefficient is dependent on both the temperature and the pressure value, and it can be calculated from the Fuller-Schettler-Giddings equation shown as Eq. (8) [18]:

$$D_{O_2} = \frac{9.86 \times 10^{-5}}{\left(\frac{1}{v_{O_2}^{1/3}} + \frac{1}{v_{CO_2}^{1/3}}\right)} \sqrt{\left(\frac{1}{M_{O_2}} + \frac{1}{M_{CO_2}}\right)} \cdot \frac{T^{1.75}}{P_t}, \text{ m}^2 \text{ s}^{-1} \quad (8)$$

where v_{O_2} and v_{CO_2} are the molar volumes of both gas components, (i.e. O₂ and CO₂), M_{O_2} and M_{CO_2} are the molar masses of O₂ and CO₂, P_t is the total pressure, and T is the temperature.

There are also other mathematical relations enabling calculation of the molecular diffusion coefficient, and these are widely shown elsewhere [21]. The molecular diffusion coefficient is a parameter which is characteristic for the set of two gases, and it is independent of the components' concentrations. As can be seen, the diffusion coefficient is proportional to the temperature to the power of 1.75 and inversely proportional to the total pressure. As a result, it can be concluded that the reaction steps of oxy-combustion in the reported TGA system are:

- O₂ diffusion in a stationary gas layer in accordance with Fick's first law (from the inlet of the crucible to the surface of the char bed).
- Chemical reaction on the surface of char particles.

The slower of the two above stages will be the rate-limiting step. In the extreme case where the global rate of the reaction is determined by the rate of O₂ diffusion in the crucible, the concentration of O₂ on the surface of the char bed will be $C_{O_2,2} = 0$. This means that the diffusion resistance of O₂ between the inlet of the measuring crucible and the surface of the char bed is the largest. Each oxygen molecule diffusing to the bed surface will immediately react when it makes contact with the nearest carbon atom. Therefore, the model of diffusion in the crucible can be simplified to Eq. (9):

$$\dot{N}_{O_2} = \frac{D_{O_2}}{h_D} A_N C_{O_2,1}, \text{ mol s}^{-1} \quad (9)$$

Oxygen transportation model in the HPTGA crucible

The gas flow in the pressurised thermogravimetric analyser (HPTGA) is directed downwards, resulting in interference with the gas layer in the crucible (Fig. 1c). Furthermore, the crucible has a porous semipermeable bottom, which might result in some partial gas flow throughout the crucible.

In Fig. 3 the schematic of the crucible from the HPTGA is shown. The directions of reactant transportation and their local concentrations, together with the potential distribution of the O_2 concentration as a function of the height of the crucible, are shown for the established convection–diffusion model.

There are two gas layers in the crucible: convection (turbulent gas layer) and diffusion (stationary gas layer). In the upper layer with height h_{con} , the gas flowing into the crucible can cause turbulence and hence transport of oxygen by convection. In the bottom part of the crucible, there is a gas diffusion layer at the char bed surface with height h_D , where the transport of O_2 takes place by equimolar countercurrent diffusion, in accordance with Fick's first law [21]. Therefore, the steps of the oxy-combustion reaction in the analysed HPTGA system are:

- Transport of O_2 to the mouth of the crucible.
- Convection of O_2 to the surface of the diffusion layer.
- Diffusion of O_2 through a stationary gas layer in accordance with Fick's first law.
- Chemical reaction on the surface of the char.

Assuming that the transport of O_2 in the convection zone is carried out over the height of h_{con} to the planar surface of A_N , the transport rate of O_2 is represented by Eq. (10) [21]:

$$\dot{N}_{O_2} = k_{D,O_2} A_N (C_{O_2,1} - C_{O_2,2}), \text{ mol s}^{-1} \quad (10)$$

where k_{D,O_2} is the O_2 transfer coefficient.

The term k_{D,O_2} , which is a mass transfer coefficient for the flat surface, may be defined by Eq. (11), [18]:

$$k_{D,O_2} = \frac{D_{O_2} Sh}{L} = \frac{D_{O_2} Sh}{d_N} \quad (11)$$

where L is the length of the surface on which the penetration of mass is followed (in this work the model presented is the diameter of the crucible d_N), Sh is the Sherwood number, Re is the Reynolds number, and Sc is the Schmidt number.

Sherwood's number for O_2 transport to the flat surface is calculated from Eq. (12) [18]:

$$Sh = 0.664 Re^{1/2} Sc^{1/3} \quad (12)$$

while the Reynolds number is calculated from Eq. (13):

Fig. 3 Model approach of O_2 transport in the crucible of the HPTGA: **a** schematic with selected concentrations and molar fractions of O_2 , with dimensions and directions of flow of the reactants, **b** distribution of O_2 concentration as a function of crucible height

$$Re = \frac{d_N u_g \rho_g}{\mu_g} \quad (13)$$

where u_g is the rate of gas entering the crucible, μ_g is the viscosity of the gas, and ρ_g is the gas density.

The Schmidt number is calculated from Eq. (14):

$$Sc = \frac{\mu_g}{\rho_g D_{O_2}} \quad (14)$$

Above the surface of the char bed is a layer of stationary gas with height h_D , where the transport of O_2 occurs by equimolecular countercurrent diffusion, in accordance with Fick's first law. This is expressed by the relation described in Eq. (15):

$$\dot{N}_{O_2} = \frac{D_{O_2}}{h_D} A_N (C_{O_2,2} - C_{O_2,3}), \text{ mol s}^{-1} \quad (15)$$

Since the oxy-combustion reaction is faster than the transport rate of O_2 , on the surface of the char bed, the concentration of O_2 ($C_{O_2,3}$) is close to zero and is therefore negligible with respect to further calculations. As a consequence, Eq. (15) can be simplified to Eq. (16):

$$\dot{N}_{O_2} = \frac{D_{O_2}}{h_D} A_N C_{O_2,2}, \text{ mol s}^{-1} \quad (16)$$

Calculating the flow rate of O_2 in the HPTGA crucible is problematic because there are some unknown factors, such as the heights of the convection and diffusion layers from Eq. (8) and Eq. (14), respectively. The concentration of O_2 at the interface between the two layers $C_{O_2,2}$ is also unknown. Assuming that conditions are stationary, the transport rate of O_2 in the convective layer must be equal to the diffusion rate of O_2 in the stationary gas layer. Therefore, Eq. (10) and Eq. (16) are related by Eq. (17):

$$\dot{N}_{O_2} = k_{D,O_2} A_N (C_{O_2,1} - C_{O_2,2}) = \frac{D_{O_2}}{h_D} A_N C_{O_2,2} \quad (17)$$

After simplifying and substituting for k_{D,O_2} from Eq. (16), Eq. (18) is obtained:

$$\dot{N}_{O_2} = \frac{D_{O_2} Sh}{d_N} (C_{O_2,1} - C_{O_2,2}) = \frac{D_{O_2}}{h_D} C_{O_2,2} \quad (18)$$

However, the concentration of O_2 at the interface between these two gas layers is still not known. Hence, a further assumption is made, i.e. that O_2 transport resistance in the convection layer and O_2 diffusion in the stationary gas layer are equal. This means that the differences in concentrations in both layers are equal, and this condition can be written in the form of Eq. (19):

$$C_{O_2,1} - C_{O_2,2} = C_{O_2,2} = \frac{C_{O_2,1}}{2} \quad (19)$$

Simplifying Eq. (18) and substituting it into Eq. (17) lead to Eq. (20):

$$h_D = \frac{d_N}{Sh} \quad (20)$$

Furthermore, substituting Eq. (19) and Eq. (20) into Eq. (16), the equation for transport rate of O_2 through the whole crucible in HPTGA is obtained:

$$\dot{N}_{O_2} = \frac{Sh \cdot D_{O_2}}{d_N} A_N \frac{C_{O_2,1}}{2}, \text{ mol s}^{-1} \quad (21)$$

This association allows the calculation of the O_2 stream in the HPTGA crucible, and it also indirectly enables calculation of the thickness of the diffusion convection layers.

Analysis of experimental data

The developed O_2 transport models in the crucibles have been applied to the analysis of the experimental data from oxy-combustion of coal char using both TGAs. The aim of this study was to demonstrate that the differences in the obtained results can be explained by the difference in the effective rate of O_2 transport to the surface of the char bed. Figures 4 and 5 show the reaction rate curves $r = dN_C/dt$ as a function of conversion for the oxy-combustion

Fig. 4 Reaction rate versus X for oxy-combustion of: **a** lignite char and **b** hard coal char, obtained in the APTGA

Fig. 5 Reaction rate versus X for oxy-combustion of: **a** lignite char and **b** hard coal char, obtained in the HPTGA

experiments from the APTGA and HPTGA thermobalances respectively.

The presented data indicate a significant increase in the reaction rate up to a temperature of approximately 600 °C, after which the reaction rate progression is less significant. Comparing the oxy-combustion of the investigated two chars, it can be concluded that the reaction proceeds at a higher rate for lignite char which has the higher BET surface area ($17.3 \text{ m}^2 \text{ g}^{-1}$) compared to hard coal char with lower surface area ($3.8 \text{ m}^2 \text{ g}^{-1}$). Another aspect of this analysis is also extremely important, i.e. the clear difference between the reaction rates obtained depending upon the measuring apparatus used. Higher reaction rates are achieved in HPTGA than are obtained in APTGA.

For the calculation of the reaction rates, the mean value of the reaction rates with a conversion ratio of 0.2–0.8 was used. This range is indicated as a blue field in Figs. 4 and 5. The range of conversion degree is characterised by the smallest changes in the reaction rate, and it can be considered as representative for further analysis.

Figure 6 presents a comparison of the experimental data with the results of the model analysis for both TGs. Analysing the data, it can be seen that in the low-temperature range (up to 550 °C for lignite char and up to 600 °C for

Fig. 6 Arrhenius plots for the oxy-combustion of: **a** lignite char and **b** hard coal char: black colour—APTGA; red colour—HPTGA; dashed line, chemical reaction rate; long dashed line, O_2 transport rate in the crucible; solid line, the overall reaction rate; filled circle, APTGA experimental value; filled triangle, HPTGA experimental value

hard coal char) the reaction rate increases significantly, followed by a slowdown of the reaction rate above these temperatures. Under low-temperature experimental conditions, the chemical reaction kinetics is the rate-limiting step which determines the overall reaction rate. With increasing temperature (greater than 550 °C for lignite char and greater than 600 °C for hard coal char), the diffusion rate of O_2 in the crucibles becomes the main resistance, and O_2 transport is the rate-limiting step. To confirm this thesis, the results of the model analysis and the experimental results are compared, as shown for both TGs in Fig. 6a, b.

In Fig. 6 the model data for the oxy-combustion chemical reaction are shown extrapolated up to a temperature of 1000 °C. The extrapolation of the results was based on data obtained from the estimation of kinetic parameters using Eq. 4. Data from the 450–550 °C range for the lignite char and from the 500–600 °C range for hard coal char were used to estimate the kinetic parameters of chemical reactions in the kinetic regime, i.e. the activation

energy E_a and the exponential coefficient A_0 . These parameters were used to calculate the rate of oxy-combustion chemical reaction up to 1000 °C where the rate-determining step above approximately 600 °C is the extrapolated value. The results of the kinetic parameter estimates are presented in Table 5.

As can be seen, the results from both thermobalances correlate with each other at a very high level, with correlation coefficients above 0.99. As a result, the following values were obtained for lignite and hard coal chars, respectively:

$$\begin{aligned} E_a &= 145 \text{ kJ mol}^{-1} \text{ with } \ln(A_0) \\ &= 6.87 \ln(\text{mol s}^{-1}), \text{ and } E_a \\ &= 134 \text{ kJ mol}^{-1}, \text{ with } \ln(A_0) = 4.38 \ln(\text{mol s}^{-1}). \end{aligned}$$

Figure 6 presents the results of the O_2 transport rate models in the crucible in accordance with Fick's first law for APTGA and a mixed convection–diffusion model for HPTGA. The overall observed reaction rate for oxy-combustion in the crucible from TGA is the sum of the chemical reaction resistance and the O_2 transport resistance in the crucible, and it can be represented by the previously shown Eq. (1).

The presented model analysis indicates the very significant impact of the crucibles and the type of balance used on the reaction rate for coal chars. Among other things, this includes the type of crucible and its dimensions, and the direction of the reaction gas flow which is crucial for the type of gas–solid fuel contact. The results of the analysis are essential for the correct interpretation of the results obtained from oxy-combustion experiments using TG. They allow for clear distinction between the impact of the coal char properties on the reaction rate from the influence of the crucible and the apparatus conditions in which the measurement is performed. At temperatures higher than 600 °C, the oxy-combustion reaction rate is mainly influenced by the measuring apparatus, and also the shape and dimensions of the experimental crucible. The latter factor is responsible for the shifting of oxy-combustion to the diffusion regime. This conclusion gives rise to the comparison of the results obtained from the two TG instruments.

The analysis evidently shows that in the kinetic regime the differences between TGAs are negligible. The obtained reaction rates do not significantly differ, and therefore, the results of the experimental studies in the two different apparatuses are comparable with each other. This means that if adequate working TGA conditions are maintained for the reaction in the kinetic regime, the experimental results should lead to similar reaction rates. However, in the mass transfer-limiting regime the experimental results primarily depend on the apparatus in which they were obtained. Hence, in this regime the apparatus and its specification mainly determine the reaction rate.

In the thermogravimetric analysis, char particles are deposited as a bed in the TG's crucible. Therefore, there is no way for gas to wash each particle separately as it does in a fluidised bed, which has key implications for the kinetic analysis of oxy-combustion. In a boiler, char particles formed after the pyrolysis of coal are carried in the gas stream. Therefore, there are no limitations on the type and depth of the measuring vessel (crucible) affecting the O_2 transport rate. Under such conditions, the model of char oxy-combustion, and in particular the oxygen transport rate model, must be modified. The transport rate of O_2 to the surface of the char particle, assuming that on the particle surface the $C_{O_2,2}$ concentration is zero, is expressed by Eq. (22):

$$r_{D,O_2} = \dot{N}_{O_2} = k_{D,O_2} A_p C_{O_2,1}, \text{ mol s}^{-1} \quad (22)$$

where k_{D,O_2} is the O_2 transport rate constant over the surface of the char particle.

For particles raised in a gas stream, the O_2 transport rate coefficient is calculated from Froessling's equation [5, 6, 9, 18, 19, 21, 22]. For particles with a spherical geometry, this is expressed as follows:

$$Sh = \frac{k_{ext,O_2} d_p}{D_{O_2}} = 2.0 + 0.6 Re_p^{1/2} Sc^{1/3} \quad (23)$$

where d_p is the char particle diameter.

The existence of internal diffusion causes a consequent resistance of both internal and external diffusion which is different from the external resistance itself. A resultant resistance can be calculated from Eq. (24):

Table 5 Estimation of kinetic parameters for chemical kinetic controlling regime

	Lignite char Data set: 450–550 °C			Hard coal char Data set: 500–600 °C		
	APTGA	HPTGA	Mean value	APTGA	HPTGA	Mean value
$E_a/\text{kJ mol}^{-1}$	143	147	145	136	142	139
$\ln(A_0)/\ln(\text{mol s}^{-1})$	6.57	7.23	6.88	4.66	5.83	5.23
R^2	1.00	0.99	–	0.99	0.99	–

$$k_{D,O_2} = \left(\frac{1}{k_{int,O_2}} + \frac{1}{k_{ext,O_2}} \right)^{-1} \quad (24)$$

where the internal diffusion rate constant is determined using Eq. (25):

$$k_{int,O_2} = \frac{D_{eff,int}}{2 \cdot R_p} \quad (25)$$

where $D_{eff,int}$ is the effective diffusion coefficient for O_2 in the char particle pores and R_p is the pore radius.

The diffusion coefficient in the pores refers to single pores; therefore, for the purpose of generalisation to the whole porous particle, the following relationship is used:

$$D_{eff,int} = \frac{D_{int}\varepsilon_0}{\tau_p} \quad (26)$$

where τ_p is the tortuosity of the pores and ε_0 is the porosity of the particle.

Generally, it can be assumed that the pore diffusion rate is in the transition area and is dependent on Knudsen diffusion as well as on molecular diffusion [5–9, 21–23]. Therefore, the diffusion coefficient in the pores is calculated from Eq. (27):

$$\frac{1}{D_{int}} = \frac{1}{D_{O_2}} + \frac{1}{D_K} \quad (27)$$

where D_K is the Knudsen diffusion coefficient and D_{int} is the diffusion coefficient in the pores.

The internal rate of diffusion constant indirectly determines the effect of particle size on the chemical reaction rate, and essentially, it replaces the efficiency factor which is determined by the Thiele modulus. This relationship allows the calculation of internal diffusion resistance independently of the kinetics of the chemical reaction, as is the case for Thiele modulus calculations. Table 6 presents

the specific values of the gas diffusion parameters in pores and dimensionless numbers for both chars.

Hard coal char has a lower diffusional limit because of the lower porosity and specific surface area which results in higher Knudsen diffusion coefficient values and finally higher diffusion coefficients in the pores. Reynolds numbers are higher for the lignite char particles because of the higher particle diameter, resulting in a higher Sherwood number.

The results of the model analysis which show the comparison of the conditions of HPTGA with a fluidised bed boiler are presented in Fig. 7.

For fluidised or raised particles in the gas stream, O_2 transport to the external surface of the particle is several times higher than for a char bed placed in the crucible in the thermogravimetric analyser. For the char used in the study, the diffusion regime could not appear at temperatures below 800 °C. Therefore, the results of the experiments in the temperature range above 600–700 °C, i.e. where the O_2 transport rate in the crucible is a key process for determining the oxy-combustion reaction rate, do not reflect the boiler conditions. On the other hand, the O_2 transport rate in the thermogravimetric crucible indicates the magnitude of this influence during the analysis itself. Figure 7 also shows the results of studies presented in the literature, which were performed in research devices other than the thermobalance. Figure 7 shows results from following papers:

- Saastamoinen et al. [22] who investigated the combustion of coal dust (obtained from Polish coal) using an $O_2/CO_2/N_2$ mixture in a flow reactor.
- Fennel et al. [23] who investigated coal char combustion in a laboratory fluidised bed reactor.
- Lasek et al. [4] who examined the oxy-combustion of various coal types in a fluidised bed reactor with 0.5 kg h⁻¹ capacity.

Table 6 Specific values of char diffusion parameters and dimensionless numbers for both chars

T/°C	Lignite char						Hard coal char				
	$D_{O_2}/m^2\ s^{-1}$	Sc	$D_K/m^2\ s^{-1}$	$D_p/m^2\ s^{-1}$	Re_p	Sh	$D_K/m^2\ s^{-1}$	$D_p/m^2\ s^{-1}$	Re_p	Sh	
450	1.04×10^4	0.617	4.30×10^{-6}	4.17×10^{-6}	29.1	4.76	6.49×10^{-6}	6.21×10^{-6}	17.0	4.11	
500	1.16×10^4	0.617	4.40×10^{-6}	4.28×10^{-6}	26.0	4.61	6.64×10^{-6}	6.37×10^{-6}	15.2	3.99	
550	1.30×10^4	0.616	4.50×10^{-6}	4.38×10^{-6}	23.3	4.46	6.79×10^{-6}	6.53×10^{-6}	13.6	3.88	
600	1.44×10^4	0.615	4.59×10^{-6}	4.48×10^{-6}	21.1	4.34	6.94×10^{-6}	6.69×10^{-6}	12.3	3.79	
700	1.74×10^4	0.611	4.78×10^{-6}	4.68×10^{-6}	17.5	4.13	7.22×10^{-6}	6.98×10^{-6}	10.2	3.63	
800	2.07×10^4	0.608	4.96×10^{-6}	4.86×10^{-6}	14.9	3.96	7.50×10^{-6}	7.27×10^{-6}	8.7	3.50	
900	2.41×10^4	0.603	5.14×10^{-6}	5.04×10^{-6}	12.8	3.82	7.76×10^{-6}	7.54×10^{-6}	7.5	3.39	
1000	2.79×10^4	0.599	5.31×10^{-6}	5.22×10^{-6}	11.1	3.69	8.02×10^{-6}	7.81×10^{-6}	6.5	3.29	

Fig. 7 Comparison of the reaction rate as a function of inverse temperature for coal char oxy-combustion (20% O₂/CO₂, 0.1 MPa, particle size 172 μm)

A comparison of results both from this study and from the literature indicates that in thermogravimeter the mass transport rate is much lower than in a fluidised bed which is resulting from the type and dimensions of the TG's crucible. The kinetic parameters of oxy-combustion such as an activation energy, a pre-exponential factor and a reaction rate with respect to the oxygen concentration should be determined in the low-temperature range. Usually, it should be below approximately 600 °C for oxy-combustion, while the reaction rate at temperatures above 800 °C should be determined by extrapolation based on the Arrhenius equation. The practical result of the work, which is crucial for its scientific interpretation, is that diffusion effects are essential for the rate-determining step the combustion reaction under standard laboratory conditions where TG is used. Furthermore, they are also important in real devices for coal combustion such as fluidised bed boilers. It should be pointed out that the diffusion limitation in TGA is not the same as that observed in the raised particles in a fluidised bed and in industrial boilers.

In the kinetic analysis for the application of TG, one must be extremely careful during interpretation of the obtained raw results from TG. Summarizing, the TG analysis is very useful for the development of a global model. The reaction rate in the chemical kinetics regime is independent of the apparatus in which the measurement is carried out. However, each type of laboratory equipment, such as a thermobalance, has its construction limitations and differences in reaction rates are observed. Any differences in the reaction rates depending on the apparatus used are due to the presence of reactant gases transportation and the type of gas–solid contact during the analysis.

The proposed oxy-combustion reaction models in TGAs were described in this paper by Eq. (9) for APTGA and by Eq. (21) for HPTGA. They allow estimation of the impact of O₂ transportation on the reaction rate which is observed in the apparatus. Furthermore, knowledge of this impact allows both selections of the particular temperature range where the influence of O₂ transport is significantly reduced and also the range where it is possible to determine the kinetic parameters for the given chemical reaction. Therefore, as a result, reaction rates for industrial boilers can be determined by extrapolating the kinetic data using the Arrhenius equation.

Conclusions

Two different arrangements of gas–solid contact in TGA were investigated for the development of a global reaction rate model of coal char oxy-combustion which explains the differences in testing methods. The reason is that the observed effect is related to the gas–solid phase contact, which is associated with crucible dimensions and the direction of the gas flow. The TGA testing device significantly influences the experimental results presented in this paper.

The proposed model combines chemical reactions and mass transfer kinetics of reagents to the reactive surface of the particle and allows different data to be explained. The kinetics of the chemical reaction is independent of the apparatus, which gives the same model of chemical reaction kinetics based on the Arrhenius equation for all the global models. However, different devices have their own transport limitations which result in specific mass transport

models, e.g. Eq. (9) for APTGA, Eq. (21) for HPTGA and Eq. (22) for a fluidised bed.

The developed model can be used for oxy-combustion process scaling-up purposes, by applying the global model with chemical kinetics and the mass transfer model for a fluidised bed boiler.

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