



A thermogravimetric method for the measurement of CO/CO₂ ratio at the surface of carbon during combustion

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Abstract

This work presents a new method of measuring the CO/CO₂ ratio at the surface of carbon particles during combustion. This thermogravimetric method deduces the ratio of CO to CO₂ by comparing the rate of consumption of carbon with the rate of oxidation of an external reference material with fast oxidation kinetics, in this case Cu. The method is useful when combustion is controlled by external mass transfer, commonly encountered in large-scale processes. The viability of this method has been demonstrated experimentally with graphite and a lignite char. It was found that in an atmosphere of ~ 1% O₂, the graphite produced CO₂ between 700 and 900 °C whilst the lignite char produced a mixture of CO and CO₂ between 700 and 800 °C with the proportion of CO increasing with temperature, and above 850 °C, only CO was produced. It was also found that for this particular lignite char, the ratio of CO/CO₂ increased with decreasing pO₂ in the environment.

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Keywords: CO/CO₂ ratio; Mass transfer; Combustion; Coal char; Thermogravimetry

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1. Introduction

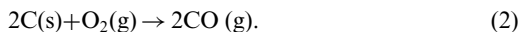
There are many factors affecting the combustion of char particles. In a fluidised bed combustor, the rate of combustion of char can be influenced by

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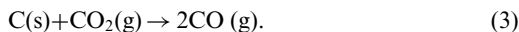
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the intrinsic chemical kinetics, intra-particle mass transfer of the gaseous species or the mass transfer of gases in the boundary layer surrounding the particle [1]. For char particles larger than 2 mm in diameter or so, the combustion is most likely to be controlled by external mass transfer [2,3]. In pulverised coal-fired boilers, where the size of the coal particles is considerably smaller, the burning of the char could also be limited by external mass transfer, owing to the high reaction temperature giving very rapid intrinsic kinetics [4]. In fact, the combustion of large spheres of carbon has often been used to measure the mass transfer in a fluidised bed, as discussed by Scala [5]. However, there are a number of reasons why the measured rate of combustion cannot always be used directly to deduce the rate of mass transfer [6]. One is that, even under the assumption that a char particle consists of carbon only, two possible reactions with oxygen could take place:



If CO_2 is present at the surface of the char particle, gasification is also possible:



Based on simple Fickian diffusion, it is clear that in the mass transfer limit, if a carbon particle burns according to reaction (2), the rate of consumption of carbon, and hence the apparent rate of mass transfer, would be twice as high compared to a carbon particle which combusts to CO_2 exclusively, leading to potentially erroneous determination of the mass transfer coefficient. A more rigorous analysis of this issue was undertaken by Hayhurst [7], in which the effect of non-equimolar counter diffusion was also taken into account, but the deviation from the Fickian approximation was small, especially when the gaseous species were dilute.

The ratio CO/CO_2 at the surface of the char particles during combustion has been the subject of a large number of studies. In the early days of research on the combustion of carbon, it was proposed that gas phase oxygen would be chemisorbed on the surface of the carbon to form some surface complex, C_xO_y , which would subsequently decompose, on heating or in an oxygen-rich environment, to produce CO and CO_2 [8]. Experimental evidence from the same work suggested that the fraction of CO , measured against the total amount of CO and CO_2 being produced, increased with temperature up to at least 600°C and a more complicated trend was observed at higher temperatures, attributed to the onset of secondary reactions such as combustion of CO or reaction (3) [8]. Arthur [9] attempted to isolate the so-called primary CO/CO_2 ratio, *i.e.*

the ratio of these gases produced from the intrinsic chemical reaction of O_2 with solid carbon, by adding POCl_3 in the gas phase to inhibit the oxidation of CO by O_2 , when combusting two types of carbon in a fixed bed. It was found that neither the gas flowrate nor the extent of conversion of the carbon affected the characteristics of the combustion, *e.g.* the CO/CO_2 ratio and the rate of combustion, at moderate temperatures, but these characteristics did change with the gas flowrate at higher temperatures [9]. In hindsight, it is probable that at moderate temperatures, the combustion was controlled by chemical reaction at the surface of the carbon whereas at higher temperatures, mass transfer was the rate-determining factor. The primary CO/CO_2 ratio was correlated with temperature using an expression analogous to the Arrhenius equation, *i.e.*

$$A \exp(-B/RT),$$

where A was a constant independent of temperature and the parameter B , analogous to an activation energy, was rationalised as the difference between the activation energies of reactions (2) and (1), respectively [9]. Over the following decades, many quantitative studies have presented the primary CO/CO_2 ratio as varying with an Arrhenius dependence on temperature [10–16]. Some of these studies have also noted the effect of the partial pressure of O_2 [12,14] and water [14] on the measured CO/CO_2 ratio. The large variation in the absolute values of CO/CO_2 ratio reported indicates that the ratio also depends on the type of carbon used. In particular, Laine *et al.*, argued that the active surface area of the carbon could affect the product ratio [11].

It should be noted that all of the aforementioned studies, [8–16], measured the concentrations of CO and CO_2 downstream of the reactor, and could therefore have been affected by further gas mixing before measurement and possible secondary oxidation of CO by the remaining O_2 in the gas. Recently, in an attempt to minimise the uncertainties associated with such effects, Scala [17] proposed a method of measuring the primary CO/CO_2 ratio by burning a single sphere of carbon in a fluidised bed with a low concentration of O_2 in the gas phase. By using a low concentration of O_2 , the simple case of equimolar counter diffusion can be used to calculate the flux of various gaseous species without introducing large errors arising from the neglect of advective terms. Furthermore, the temperature of the carbon particle would be very close to that of the bed material, and the molecular diffusivity would remain reasonably constant across the boundary layer. The problem of secondary reaction was overcome by using appropriate values for the Sherwood number, determined independently for the reactor under similar conditions, so that knowing the total amount of carbon being combusted would be sufficient to calculate the CO/CO_2 ratio at the surface of the particle. However, a model of

Table 1
Elemental analysis (dry basis, wt%).

	C	H	N	Balance
Lignite coal	39.1	4.8	0.65	55.5
Char	75.2	0.79	0.89	23.1

the fluidised bed was needed to account for further mixing of gases in the reactor.

In this work, a novel thermogravimetric technique was developed for the measurement of the primary CO/CO₂ ratio, minimising some of the uncertainties described above. The new method is applicable when combustion is limited by external mass transfer of oxygen to the surface of the carbon. Thermogravimetric methods have been used to measure the rate of combustion before [15,18], but no link between the rate of combustion and the primary CO/CO₂ ratio has been established from such measurements until now.

2. Experimental

2.1. Materials

A coal char, derived from a German lignite coal (Hambach, kindly provided by RWE Power AG) was investigated in this work. To prepare the char, approximately 1 kg of the air-dried coal in the size fraction 1600–2280 μm was fed continuously to an electrically-heated fluidised bed (i.d. 78 mm) using a screw feeder at a constant feed rate of ~0.2 g/s. The bed material consisted of 500 mL of silica sand in the size fraction 300–425 μm and the bed temperature was maintained at 900 °C. The bed was fluidised by 12 L/min of N₂ (BOC, >99.998%; flowrate measured at 1 atm, 20 °C, same for all flowrates reported hereafter, unless specified otherwise) during the entire preparation. After all the coal had been fed, the temperature of the fluidised bed was maintained for a further 30 min before cooling down in N₂. The resulting char was collected when the bed had reached room temperature and was sieved to 100–180 μm fraction for further studies. The elemental analyses of the char and the parent coal are given in Table 1. In addition, a reference fuel – graphite (Fisher Chemical, pure, powder, part number 10336090) was also studied. The graphite was used as received, without further processing.

Particles (300–425 μm) consisting of 60 wt% copper oxide supported on calcium aluminate were used as the reference material to measure the mass transfer coefficient. This material has been shown to react fast with oxygen and are resistant to sintering. Details of the preparation and characterisation of this material can be found elsewhere [19].

2.2. The combustion of char

The combustion of char was performed in a thermogravimetric analyser (TGA/DSC 1, Mettler Toledo) with a horizontal gas flow configuration. A schematic diagram of the TGA furnace is provided in the Supplementary Information. The TGA furnace was constantly purged with 100 mL/min of Ar (BOC, >99.998%). In addition, a stream of “reactive gas” can be introduced close to the crucible containing the sample. In this work, a mixture of N₂ (BOC, >99.998%) and compressed air (BOC, >99.995%) was used as the reactive gas with a total flow rate between 50–60 mL/min. In a typical experiment, a small amount of sample (4.5–4.8 mg of lignite char, or 4 mg of graphite) was placed in a cylindrical 70 μL alumina crucible (i.d. 4.90 mm, depth 4.00 mm). The crucible was covered with a standard issue alumina lid with a hole (diameter 0.90 mm) at the centre. A lid was used to limit the rate of mass transfer of gaseous species into and out of the crucible so that any reaction being investigated would be limited by mass transfer of gas in the crucible. The sample was held at 50 °C for 5 min in a stream of N₂ with a flowrate of 50 mL/min as the reactive gas. At $t = 5$ min, the temperature set-point was changed to a value between 700 and 900 °C, and the sample heated to this reaction temperature within 2 min. N₂ was continuously passed over the crucible until $t = 20$ min to allow the temperature of the sample to stabilise, before air was mixed into the reactive gas. The char was then combusted isothermally and kept in this atmosphere for at least 40 min. The majority of this work was carried out with a pO_2 of ~0.01 bar (around 1 mol% in the bulk gas mixture) although the pO_2 in the bulk gas was also varied in some experiments to investigate its effect on combustion.

2.3. Calibration experiment

Similar to the approach adopted by Scala [17], an independent measurement of the rate of transfer of oxygen in the crucible was made using the supported CuO particles in place of the char. The particles had been previously reduced with H₂ (5 mol%, balance N₂) in the TGA at 900 °C until the mass of sample had stabilised. The mass loss corresponded to all the CuO being reduced to Cu. The furnace was then cooled to room temperature in the flow of H₂ to recover the particles. In a typical calibration experiment, a monolayer of the reduced particles (approximately 7 mg) was placed in the crucible and covered with the lid. The temperature programme was identical to that described in Section 2.2 and the calibration experiments were performed at 700 °C regularly throughout the experimental campaign to check the reproducibility. The purpose of the calibration experiments was to measure the rate of mass transfer at the reaction temperatures and to estimate

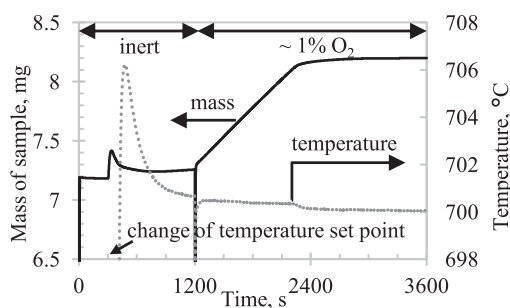


Fig. 1. Typical calibration experiment, the oxidation of Cu by O_2 , at 700 °C. The spikes at $t = 0$ and 1200 s are experimental artefacts due to switching of the reactive gas. Temperature set point: 50 °C for $t < 300$ s and 700 °C for $t \geq 300$ s.

the concentration of oxygen in the atmosphere: details of the calculation are given in Section 3.1, below.

3. Data analysis

3.1. Measuring the rate of mass transfer

The measurement of the rate of mass transfer from outside the crucible to the solid sample is illustrated by a typical calibration experiment shown in Fig. 1. The important feature is that, shortly after the reactive gas was switched to a mixture of air and N_2 at $t = 1200$ s, the rate of oxidation of Cu remained constant for a substantial period of time and an abrupt decline in the rate occurred towards the end of experiment when the oxidation was nearly complete. This apparently zeroth-order reaction profile with the present reaction is a strong indication that it was dominated by the diffusion of O_2 from the top of the crucible to the surface of the Cu particles. The intrinsic oxidation kinetics of Cu have been described by the parabolic rate law where the rate of mass gain is inversely proportional to the mass gain [20]. Had either the intrinsic chemical reaction or the diffusion of O_2 within the Cu particles had significant influence on the observed rate of oxidation, the reaction profile would not have been linear (*i.e.* independent of the conversion of the reacting solids). Thus, the observed rate of oxidation provides a measure of the rate of supply of oxygen. To compare with combustion experiments performed at other temperatures, the estimated diffusion rate was scaled by $(T + 273.15)^{0.75}/(973.15)^{0.75}$ where T is the temperature of the reaction measured in °C, to account for the change of gas diffusivity with temperature.

In addition, it is possible to estimate the partial pressure of O_2 (pO_2) in the bulk gas so that the effect of pO_2 in the bulk on the combustion can be assessed. This was done using a numerical model

based on the Maxwell–Stefan multicomponent diffusion model in 2-D cylindrical geometry, with the diffusivities of gaseous components estimated *via* the Fuller–Schettler–Giddings correlation [21]. The following assumptions were made in order to obtain the numerical solution:

- (i) pO_2 at the base of the crucible was constant and close to zero due to the even distribution of the solids and the fast chemical kinetics of the solid-gas reaction.
- (ii) pO_2 just outside the crucible was constant across the entire top surface of the crucible (and equal to the pO_2 in the bulk).
- (iii) Mass transfer of gaseous species within the crucible was *via* diffusion only.
- (iv) The temperature of the gas within the crucible was uniform and equal to the temperature of the solids.

A detailed description of the numerical model is given in the Supplementary Information.

3.2. Inferring the primary CO/CO₂ ratio

When the diffusing species (O_2 , CO, CO_2) are dilute, the difference in rate between (i) only O_2 diffusing from the top surface of the crucible to the reacting solid, as is the case for the calibration experiments, and (ii) equimolar counter diffusion of O_2 and CO_2 inside the crucible, when the product of the combustion of char is exclusively CO_2 , or even (iii) non-equimolar counter diffusion, where both CO and CO_2 are the products of combustion, would not be significant [7]. Thus the results of the calibration experiment can be compared directly with the corresponding combustion experiments performed in the same atmosphere, without the need for a numerical model for multicomponent diffusion. Under the same atmosphere, one would expect the same rate of supply of oxygen if a sample of char were used instead of the Cu particles, assuming the intrinsic chemical rate of combustion is very rapid. Given that carbon is the major component in the char that can react with O_2 , the char was modelled as pure carbon, for the purpose of measuring the rate of combustion. With this assumption, the expected rate of combustion of char in an identical atmosphere would be at least the same as the rate of oxidation of Cu on a molar basis (only reaction (1)) and at most twice as fast (only reaction (2)). A measured value between the two limits can be used to deduce the CO/ CO_2 ratio in the product.

4. Results

4.1. The combustion of graphite

The combustion profile of graphite samples can be exemplified by the results of two experiments

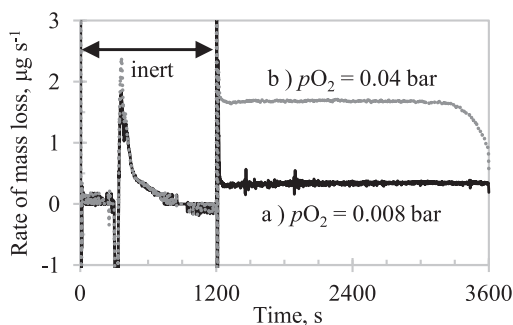


Fig. 2. Rate of loss of mass of graphite (DTG curve) measured at 800 °C in different atmospheres. The spikes at $t = 0$ and 1200 s are experimental artefacts due to switching of the reactive gas. The rapid changes around $t = 300$ s are results of the very fast heating rate of the furnace when the temperature set point was changed. The stated pO_2 values are estimated partial pressures of oxygen in the bulk for each experiment.

performed at 800 °C, shown in Fig. 2, at two different partial pressures of oxygen. The mass change of the graphite as the furnace was rapidly heated up to the reaction temperature in an inert environment ($t = 300$ –800 s) can be attributed to a combination of buoyancy effect of the TGA as well as degassing of the sample, and this change was found to be reproducible. After oxygen was introduced into the system ($t = 1200$ s), the rate of combustion remained constant for a sustained period of time in both cases and the rate only slowed down in b) when the mass of graphite fell below 0.7 mg (from an initial mass of 4.0 mg, as measured just before the combustion stage). This behaviour is typical of the reaction being controlled by external mass transfer of O_2 to the surface of the graphite.

To ascertain further that the combustion was limited by mass transfer of O_2 , the rate of combustion of graphite at different temperatures was compared with the estimated rate of diffusion, calculated from the rate of oxidation of Cu in the same atmosphere at 700 °C and extrapolated to other temperatures (as described in Section 3.1). Based on 4 repeats, the rate of diffusion was calculated to be $0.0275 \mu\text{mol s}^{-1}$ of O_2 , with a standard deviation of $1.7 \times 10^{-4} \mu\text{mol s}^{-1}$. The comparison is shown in Fig. 3 and the measured rates of combustion were found to be slightly lower than the estimated rates of diffusion in the crucible but the differences were less than 5%. This indicates that the combustion of graphite powder was primarily limited by gas phase mass transfer within the TGA crucible and perhaps at lower temperatures (700–800 °C) the chemical kinetics also had a small effect.

4.2. The combustion of lignite char

Similar to the combustion of graphite, the lignite char also exhibited a constant rate of mass

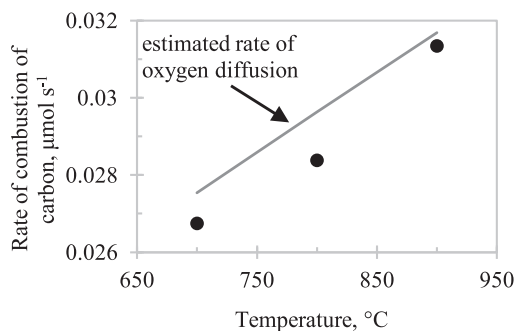


Fig. 3. Comparison between the measured rates of combustion of graphite powder in ~ 1 mol% O_2 and estimated rate of diffusion obtained from the oxidation of Cu under the same gas atmosphere.

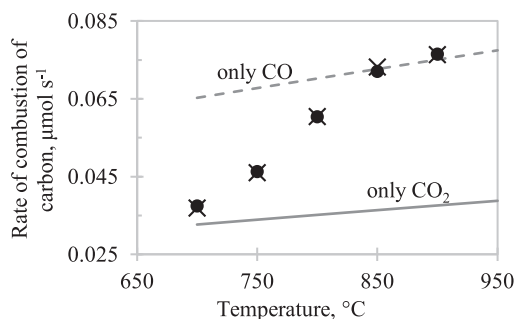


Fig. 4. Comparison between the measured rates of combustion of lignite char in ~ 1 mol% O_2 and estimated rate of diffusion obtained from the oxidation of Cu under the same gas atmosphere (solid line). The dashed line represents twice the rate of diffusion. Two repeats were performed at each temperature (dots and crosses).

loss during 40 min of combustion in an atmosphere with ~ 1 mol% O_2 in the bulk. Depending on the reaction temperature, approximately 30–60 wt% of the char was consumed during this time. Figure 4 compares the rate of combustion of char with the rate of diffusion of O_2 into the crucible (by way of measuring the rate of oxidation of Cu at 700 °C). In contrast with the combustion of graphite, the rate of combustion of the char was slightly higher than the rate of diffusion of O_2 at 700 °C and gradually increased to approximately twice the rate of diffusion at 850 °C and 900 °C. This suggests that for this particular type of char, the main product of combustion at low temperatures is CO_2 , whereas above ~ 850 °C, the product is almost exclusively CO.

Since the lignite char can produce a mixture of CO and CO_2 around 800 °C, the effect of pO_2 on the ratio of combustion products was also investigated at this temperature and the results are shown in Fig. 5. Assuming a power law relationship between CO/ CO_2 ratio and pO_2 , a best fit of the data in Fig. 5 yields an exponent (associated with pO_2)

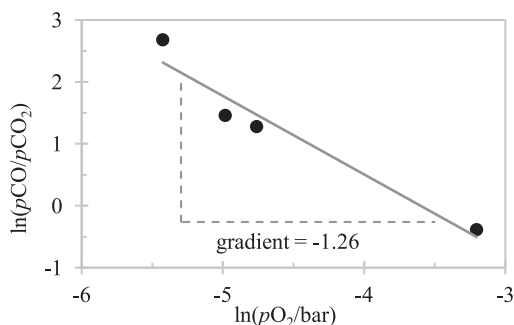


Fig. 5. Dependence of the CO/CO₂ ratio on the partial pressure of oxygen of the bulk gas for the combustion of lignite char at 800 °C.

of -1.26 . For comparison, previous investigations summarised by Tognotti et al. [14] found the exponent to be between -0.18 and -0.27 . The result suggests that increasing pO_2 in the bulk gas favours the production of CO₂ but the effect seems to be more pronounced here compared to previous studies. This difference could be caused by a range of factors, such as the type of carbon used, the flow patterns in different systems, or the different ranges of pO_2 used in various studies.

5. Discussion

It is clear from this work that under external mass transfer limitations, the combustion products of graphite and the German lignite char can be very different depending on reaction temperature and pO_2 in the bulk gas. It is conceivable that the primary CO/CO₂ ratio of a solid fuel would be a unique characteristic of the fuel and must be measured individually and the thermogravimetric method proposed can be a simple way to quantify it.

One subtle point of interest emerging from this work is that the measured rates of combustion were constant over a large range of fuel conversion. This implies that when a mixture of CO and CO₂ was produced, the CO/CO₂ ratio was not affected by the conversion of the char. This is further illustrated in Fig. 6, which shows the reaction rate profile of lignite char combusted in ~ 5 mol% O₂ at 800 °C until completion, along with the measured rate of diffusion of O₂ under the same conditions, obtained from the oxidation of Cu.

It can be seen that the rate of combustion changed very little during the course of reaction and the average rate was about 1.3 times the rate of diffusion of O₂. Assuming that different active sites at the surface of the carbon are responsible for the production of CO and CO₂, respectively, then the density of the active sites at the surface of the car-

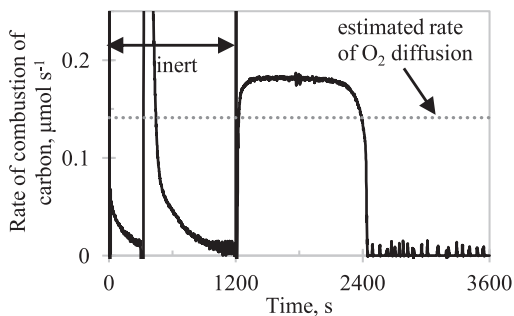


Fig. 6. Rate of combustion of lignite char at 800 °C in ~ 5 mol% O₂ compared with the measured rate of diffusion of O₂ in the same atmosphere (horizontal dotted line). O₂ was introduced at $t = 1200$ s.

bon must remain roughly constant while the morphology of the surface changes during combustion.

An alternative explanation is that molecular oxygen reacts at the carbon surface only to form CO₂ and part of the CO₂ then gasifies the carbon to produce CO before leaving the surface. However, at intermediate temperatures where a mixture of CO and CO₂ is produced, pCO_2 at the surface of the carbon would be sufficient for the gasification reaction not to be limited by external mass transfer. Under such conditions, the rate of gasification should depend on the degree of conversion [22] and therefore the apparent CO/CO₂ ratio being measured should also change with conversion of the solid. Furthermore, assuming that gasification follows a simple power law relationship with respect to pCO_2 at the surface of the carbon, it can be estimated, based on the results from Fig. 4 between 700 and 800 °C, that the activation energy for a first order reaction would be 33.9 kJ/mol. This value is very low compared to typical activation energies for gasification, which are of the order of 100 kJ/mol or more. Based on these observations, it is unlikely that *in situ* gasification is responsible for the changing CO/CO₂ ratio with temperature and pO_2 .

A third possible explanation is that only one type of active site of carbon exists but O₂ can form different carbon-oxygen complexes at the solid surface, *i.e.* one type of surface complex (type A) is formed first, which will generate CO on decomposition. If additional oxygen is available, this surface complex can be further oxidised (type B) to generate CO₂ instead. If this is the case, the proportion of CO and CO₂ in the product will be independent of the conversion of the carbon, but dependent on the availability of O₂. Given a constant pO_2 in the bulk gas, such as in Fig. 4, the flux of O₂ arriving at the solid surface is approximately constant over the range of temperature investigated. However it is likely that such surface complexes become less stable at higher temperatures. As a result, the probability of oxidising a type A surface complex further

before its decomposition decreases with increasing temperature and the proportion of CO in the product increases. Similarly, at a constant temperature, such as in Fig. 5, a higher pO_2 in the bulk would lead to a higher flux of O_2 arriving at the solid surface, increasing the probability of further oxidation of this surface complex and resulting in more CO_2 being formed. If this is the case, then the different behaviours from different fuels would be an indication of the difference in the ability of different surfaces to stabilise these surface complexes – in this case, graphite would appear to be much more capable of stabilising the proposed type A surface complex than Hambach lignite char.

6. Conclusion

In this work, a novel thermogravimetric method for measuring the CO/CO₂ ratio during the combustion of solid carbon was developed. This method minimises the influence of secondary oxidation of CO in the off gas and does not rely on any mass transfer models of the apparatus. Instead, a direct comparison of the mass loss during combustion to the rate of diffusion of oxygen to the surface of the solid sample is used. The latter was measured by oxidising a metal (Cu) under identical reaction conditions. Under low oxygen concentrations and between 700–900 °C, the graphite was found to produce CO₂ exclusively, whereas for Hambach lignite char, the combustion product distribution changed from mainly CO₂ at 700 °C to mainly CO at >850 °C. With increasing pO_2 in the bulk gas, the product distribution shifts towards CO₂ and the influence of pO_2 on the lignite char appears to be stronger compared to other fuels investigated in previous studies.

7. Data access

Data supporting this publication is openly available under an 'Open Data Commons Open Database License'. Additional metadata are available at: <http://dx.doi.org/10.17634/154300-84>. Please contact Newcastle Research Data Service at rdm@ncl.ac.uk for access instructions.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.proci.2018.05.040.

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