The influence of sample containment on the thermogravimetric measurement of carbon black reactivity

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Abstract

During the thermogravimetric measurement of carbon oxidation reactivity, the sample is contained in a crucible, and oxygen has access only through the top surface of the particle bed. Condensed carbons such as soot and carbon black have such large surface areas that oxygen mass transfer limitations control their combustion in such situations. A technique to describe the mass transfer processes has been developed, in which the gas phase and in-bed transfer processes have been decoupled. The gas phase is modelled by the CFD package FLUENT and diffusion within the bed is described by a mono-dimensional model. The procedure has been used to examine the accessibility of oxygen to samples contained in deep and shallow crucibles, and also the orientation of the flow with regard to the crucible mouth. In all cases, the transport of oxygen to the bed surface was dominated by molecular diffusion. Some existing experimental data for carbon black combustion were re-analysed to extract the true reactivities.

Keywords: Carbon black oxidation reactivity; Sample containment; Thermogravimetric measurement

List of symbols

D_e	effective oxygen diffusion coefficient in the bed/$(m^2 s^{-1})$
D_{O_2}	oxygen diffusion coefficient in the gas phase/$(m^2 s^{-1})$
e	bed thickness/m

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G	total gas mass flux density/(kg m^{-2} s^{-1})
h_m	oxygen mass transfer coefficient/(m s^{-1})
K	reaction rate constant/s^{-1}
L	crucible depth/m
R	universal gas constant/(J mol^{-1} K^{-1})
R_{O_2}	oxygen consumption rate/(kg s^{-1})
T	temperature/K
x	vertical ordinate/m
y	oxygen mass fraction

Greek symbols

ρ_g	gas density/(kg m^{-3})
θ	Thiele modulus
ω	oxygen mass flux density/(kg m^{-2} s^{-1})

Subscripts

b	in the bulk gas phase
m	mean value at the crucible mouth
o	at the furnace outlet
s	mean value at the bed surface

1. Introduction

The thermogravimetric analyser (DTA) has become a popular instrument for measuring the rates of reaction which involve a mass change in a solid. Small masses of sample can be processed, conveniently contained in a crucible. DTA offers a number of advantages over competitive techniques, but in particular gives good control of temperature and sensitive determination of progressive mass loss. Examples of its use include the rates of devolatilisation of organic materials and the decomposition of solids such as carbonates [1,2].

Combustion reactions involving carbon have also been studied extensively by thermogravimetry, particularly with respect to coal chars [3,4]. With a heterogeneous reaction, the oxygen reactant can enter the particle bed only through the top surface. Mass transfer effects above and within the sample are largely absent in these applications, because of the shallow bed and large particle sizes conventionally used. In contrast, when applied to the combustion of condensed products with large surface areas, such as soot and carbon black, burning rates are found to be significantly influenced by oxygen diffusion [5,6].

Very little attention has been paid to how gas diffusion in such very porous media affects measured reaction rates. It has been found necessary to construct a model of external and internal mass transfer in order to extract true values for the reaction rates from measured data [5-8]. Some of the models have been crude, even though the flow

geometry for the oxidant gas around the sample container was complex. For example, the mass transfer model used to investigate the combustion of a bed of carbon black contained in a small crucible within a DTA furnace was the classical case of a developing boundary layer over a flat plate [5].

In this paper, a more sophisticated approach is developed, based on an analytical solution to oxygen diffusion within the bed and a numerical solution to the flow system above the bed. The latter is based on the CFD code FLUENT, which is used to evaluate a mean mass transfer coefficient for each particular condition. The approach is used to compare the influence of different sample mounting and sample containment arrangements on the measurement of the oxygen reactivity of carbon black. Practical application of the refined technique is illustrated by a re-examination of the experimental data from Ref. [5].

2. Experimental

The Mettler thermobalance and details of the two crucibles used have been described elsewhere [5]. Crucible A was 16 mm in diameter and 15 mm deep, while crucible B, which fitted into the mouth of A, was 14 mm in diameter and only 3 mm deep. The crucibles were mounted inside a vertical ceramic furnace tube of 45 mm inside diameter as detailed in Fig. 1 (which is drawn horizontally for convenience). Very small masses of carbon black, ranging from 4.5 to 40 mg, were used, forming bed depths in the crucibles of less than 1 mm.

The combustion tests were carried out isothermally at temperatures in the 600–900°C range, with a combustion gas comprising 10 mol% oxygen in nitrogen. The gas flow was vertically upwards, away from the open mouth of the crucible. The furnace was brought to operating temperature under nitrogen, and then oxidant was introduced.

Analysis of the product gases showed a fairly constant CO_2/CO ratio of 0.85 at all temperatures, which fixes the mass consumption rate of oxygen at 1.964 times that of carbon consumption.
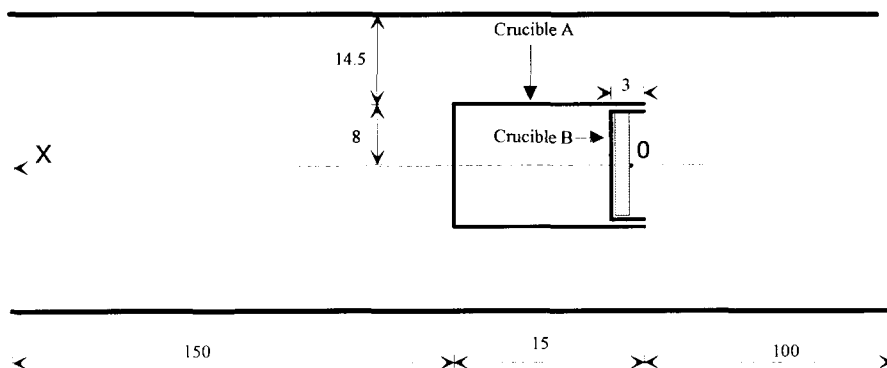

Fig. 1. Model geometry for FLUENT computations. Dimensions are in mm.

3. Modelling

The modelling approach which follows decouples the mass transfer of oxygen in the gas phase from that in the bed. This is possible because a rate of mass loss, which represents carbon consumption, is known from experiment. The rates are nearly constant with time because burning is restricted to a very thin top layer which moves downwards as carbon is removed [6].

This rate is converted to oxygen consumption and used in FLUENT to solve for the mean oxygen concentration at the bed surface y_s. The value of y_s then becomes a boundary condition for the mono-dimensional mass transfer model of diffusion inside the bed. In practice, it has been found that there is little variation in oxygen concentration across the bed surface so that a mean value is appropriate.

3.1. Gas phase mass transfer

The following assumptions have been invoked for the application of FLUENT to the bulk gas phase.

1. The gas flow is constant and in isothermal laminar flow.

2. The DTA furnace tube is cylindrical with a suitable flow entry length provided (150 mm in the case presented here).

3. The burning process can be regarded as steady state (see above).

4. Combustion takes place as a surface reaction and the rest of the bed volume is inert. The reaction rate is specified as a surface rate ω (kg m^{-2} s^{-1}) as in Ref. [6].

5. Only O_2, N_2 and CO_2 are considered as the diffusing species (CO is neglected).

6. The conversion of CO into CO_2 in the gas phase above 700°C is neglected.

7. Convergence of the solution routine is assumed when the oxygen mass fraction at the outlet y_o has reached the theoretical value given by an oxygen mass balance

$$y_o = y_b - \frac{R_{O_2}}{G} \tag{1}$$

where G is the total mass flow rate. For the present case, y_b is 0.1127 and G is 2×10^{-3} g s^{-1}.

The inlet file of the FLUENT package was set up to match the geometry shown in Fig. 1, with either crucible A or B containing the reactive bed surface. The experimental results which are modelled are listed in Table 1. They are the same data which were used in the analysis described in the previous paper [5]. The other necessary data, including physical constants, inlet flow velocities and the values of the surface reaction rate ω, are summarised in Table 2.

3.2. Gas phase results

A typical FLUENT output, in the form of velocity vector arrows, is shown in Fig. 2 for 10 mg of carbon black in crucible A at 600°C. As the system is symmetrical, only half the flow field is presented. There appears to be no flow inside the crucible, so that oxygen must move by diffusion through this stagnant volume to reach the bed surface.

Table 1
Experimental results for thermogravimetric analysis of carbon black reactivity

Temperature/°C	Crucible	Initial sample mass/mg	Specific carbon consumption rate/(mg min^{-1} mg^{-1})	Oxygen consumption rate R_{O_2}/(kg s^{-1})
600	A	10.0	0.017	5.51×10^{-9}
600	B	4.9	0.040	6.36×10^{-9}
600	B	10.3	0.029	9.69×10^{-9}
600	B	20.2	0.019	1.24×10^{-8}
600	B	40.2	0.010	1.30×10^{-8}
700	B	5.1	0.093	1.54×10^{-8}
800	B	4.5	0.104	1.52×10^{-8}
900	B	4.5	0.116	1.69×10^{-8}

Table 2
Input data for computation of the hydrodynamic flow and the oxygen mass fraction field. Computed values of the mean oxygen mass fraction at the soot surface and the mean oxygen mass transfer coefficient

Temperature/°C	Initial mass of sample/(mg)	Crucible	ω/(kg m^{-2} s^{-1})	Inlet gas velocity (m s^{-1})	y_s	h_m/(cm s^{-1})
600	10.0	A	2.74×10^{-5}	3.3×10^{-3}	9.99×10^{-2}	0.71
600	10.0	A[a]	2.74×10^{-5}	3.3×10^{-3}	1.00×10^{-1}	
600	4.9	B	4.13×10^{-5}	3.3×10^{-3}	1.05×10^{-1}	2.38
600	10.3	B	6.29×10^{-5}	3.3×10^{-3}	1.01×10^{-1}	2.37
600	20.2	B	8.09×10^{-5}	3.3×10^{-3}	9.76×10^{-2}	2.34
600	40.2	B	8.47×10^{-5}	3.3×10^{-3}	9.69×10^{-2}	2.34
600	4.9	B[a]	4.13×10^{-5}	3.3×10^{-3}	1.05×10^{-2}	
700	5.1	B	1.00×10^{-4}	3.6×10^{-3}	9.48×10^{-2}	2.84
800	4.5	B	9.86×10^{-5}	4.0×10^{-3}	9.55×10^{-2}	3.39
900	4.5	B	1.10×10^{-4}	4.4×10^{-3}	9.46×10^{-2}	3.90

[a] Crucible in a reverse position.

Fig. 3 depicts the same flow field as Fig. 2, in the form of x velocity profiles in the vicinity of the crucible. The profile which has developed downstream of the crucible is perturbed and the flow is accelerated past its mouth. Nevertheless, the x velocity at the mouth is effectively zero as concluded above.

The contours of oxygen mass fraction for the same conditions are depicted in Fig. 4. As oxygen is being consumed by the bed, a zone of depletion forms around the mouth of the crucible, even spreading upstream against the flow. This is possible because of the low flow rates used; transfer by diffusion is of the same order of magnitude as by convection.

Inside the crucible the contours are parallel and evenly spaced over most of its depth, indicating a constant mass flux across the radius. The oxygen mass fraction at the soot surface y_s is 0.1000 and y_m, the value on the axis of symmetry at the mouth, is 0.1073. These values can be used to estimate the oxygen concentration gradient by diffusion
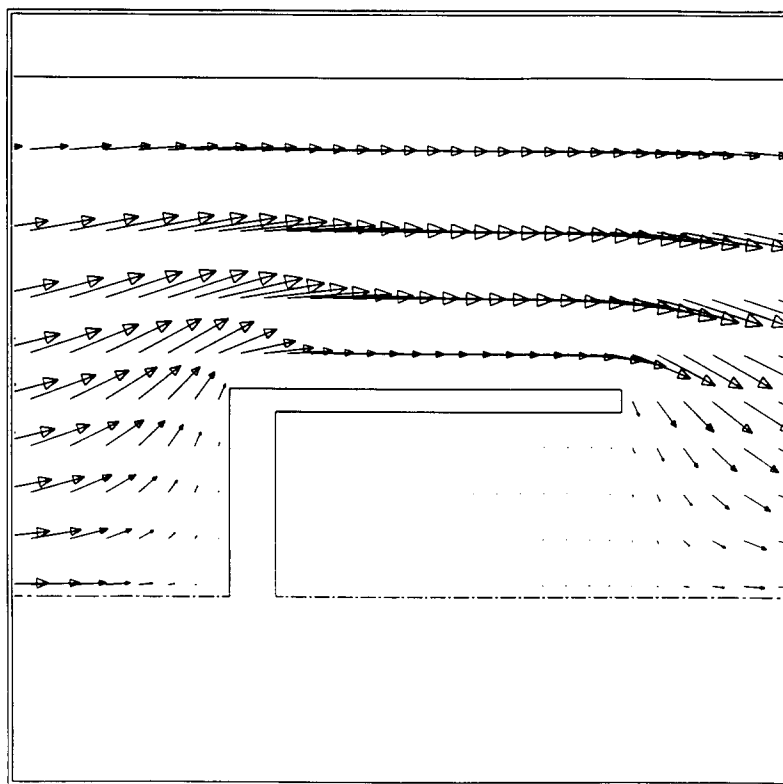
Fig. 2. Velocity vectors computed by FLUENT at 600°C for an initial soot mass of 10 mg, using crucible A: maximum velocity, 5.74×10^{-3} ms^{-1}; ·—·—·, symmetry axis.

down the crucible from

$$-\frac{dy}{dx} = \frac{y_m - y_s}{L} = \frac{\omega}{D_{O_2} \rho_g}$$ (2)

where D_{O_2} is the gas phase diffusion coefficient and L is the depth of the crucible. The value of $\omega/(D_{O_2} \rho_g)$ calculated with D_{O_2} taken from Field et al. [9] was 0.56 m^{-1}, which compares with 0.51 m^{-1} given by $(y_m - y_s)/L$. The small difference of 10% confirms the conclusion that molecular (Fickian) diffusion is the dominant mechanism of mass transfer within the crucible.

The diffusion path in crucible A was large compared to that of crucible B which was only 3 mm deep, so that convective penetration of the latter is more likely. In Fig. 5 the velocity vectors around crucible B containing 4.9 mg of carbon black at 600°C are presented. Flow does not enter far into the crucible and diffusion over a significant distance is once again necessary for mass transfer to occur. The concentration gradient in this case is larger so that under comparable conditions higher mass transfer rates ω are achieved, see Table 2.
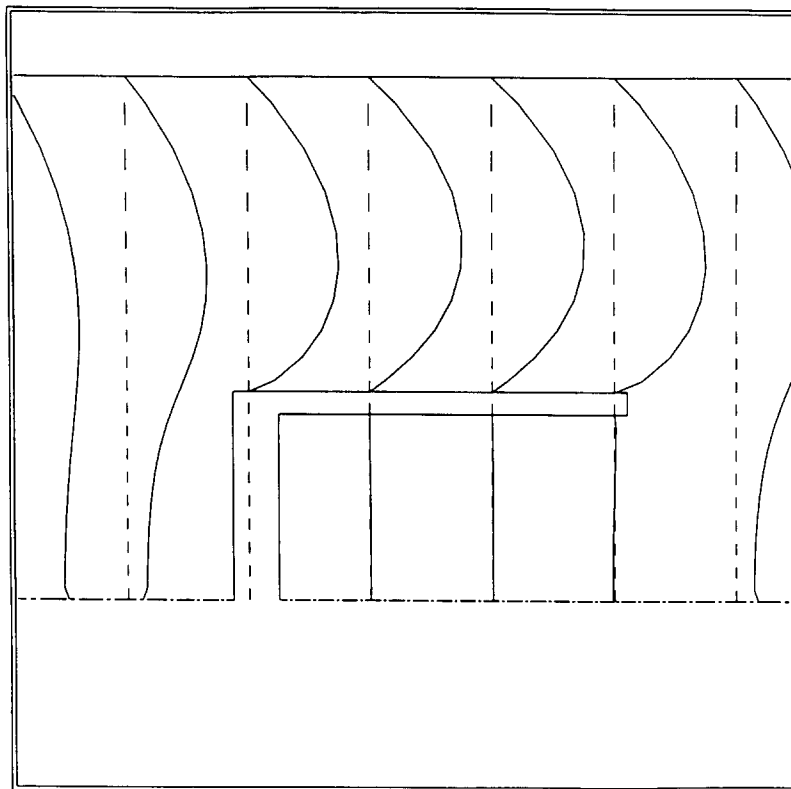
Fig. 3. Profiles of the y component of the velocity vectors computed by FLUENT at 600°C for an initial soot mass of 10 mg, using crucible A: maximum value of this component, 6.48×10^{-3} m s^{-1}; · —·— ·, symmetry axis.

The oxygen mass fraction contours for the above case are shown in Fig. 6. They are not parallel to the bed surface and y_s varies from 0.1046 to 0.1053. The variation is not great and it is possible to take a mean value for calculation of the mass transfer coefficient. The value for $\omega/(D_{O_2}\rho_g)$ calculated from Eq. (2) is 0.81 m^{-1} which is 60% higher than the value of $(y_m - y_s)/L$. This indicates that some convection is present as suggested by the oxygen contours in Fig. 6.

3.3. Evaluation of a mass transfer coefficient

In both cases examined, oxygen must diffuse down the crucible, and the process is close to one-dimensional. Oxygen is brought to the mouth of the crucible by convection as the flow sweeps across it. This permits the application of an overall mass transfer coefficient, which will be defined in terms of the oxygen concentration at the bed surface and remote from the bed at the furnace exit
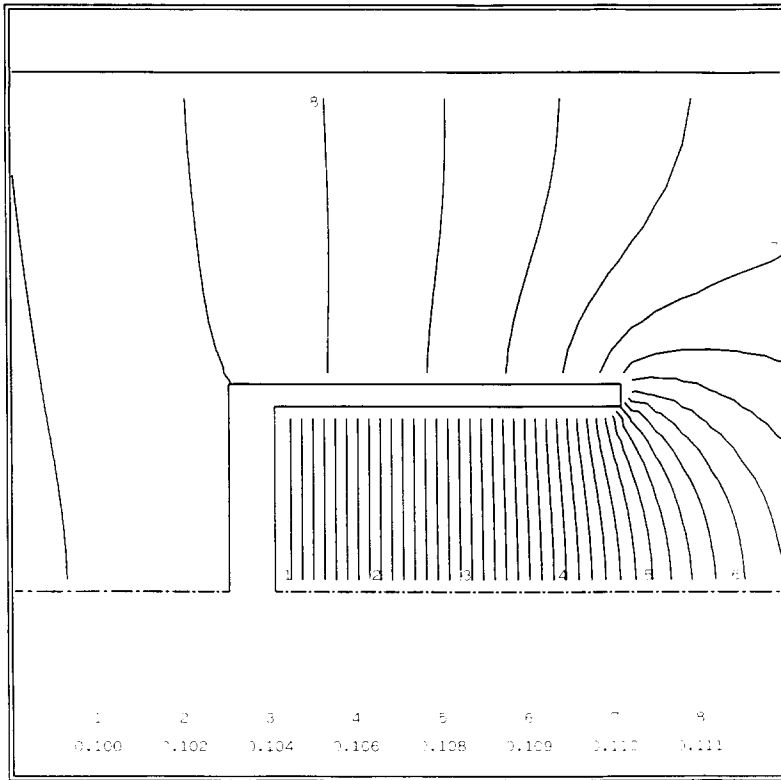
$$h_m = \frac{\omega}{\rho_g(y_o - y_s)} \tag{3}$$

Fig. 4. Contours of oxygen mass fraction computed by FLUENT at 600°C for an initial soot mass of 10 mg, using crucible A: · — · — ·, symmetry axis.

The coefficients calculated from Eq. (3) are listed in Table 2 for all cases. A number of results should be noted.

Firstly, as anticipated the value for the deep crucible A is much less than that for the shallower crucible B under the same conditions. Secondly, the value for crucible B is independent of bed depth (mass) at the same temperature (600°C). This means that h_m is independent of oxygen consumption rate and is characteristic of the crucible geometry and gas flow conditions. The computed values are about 4 times higher than those calculated from boundary layer theory for a flat plate [5].

Finally, as the temperature rises the mass transfer coefficient increases due to the change in gas properties. The density will decrease and the diffusivity increase and when a conventional laminar flow correlation is applied, an overall increase in h_m of 51% is predicted between 600 and 900°C. This compares with a 67% increase calculated from Eq. (3) as h_m rises from 2.34 to 3.90 cm s^{-1}. The increase in diffusion coefficent alone is 61% over the same temperature range.
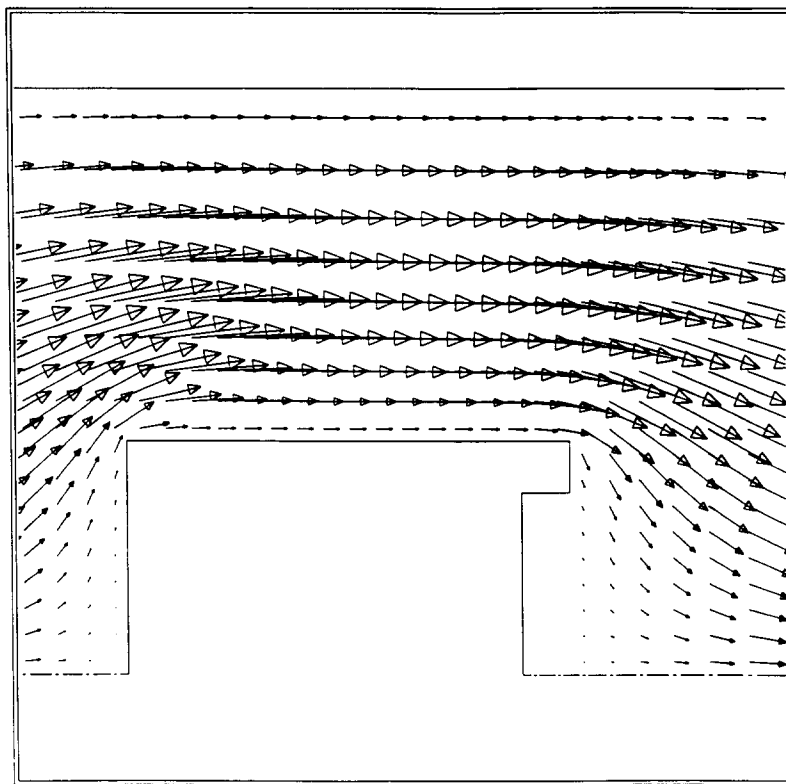
Fig. 5. Velocity vectors computed by FLUENT at 600°C for an initial soot mass of 4.9 mg, using crucible B: maximum velocity, 5.74×10^{-3} m s^{-1}; · — · —·, symmetry axis.

3.4. Reverse flow configuration

The FLUENT package was applied to the same configuration of crucible and furnace as above, but with the flow approaching the open mouth of the crucible. The situation is fictitious and no experimental results are available. The case of crucible A containing 10 mg of carbon black at 600°C was considered as a trial, with the carbon consumption rate unchanged.

The velocity vectors for this case are depicted in Fig. 7, where it can be seen that the flow does not significantly penetrate the crucible, even in this favourable configuration. The flows in Figs. 2 and 7 are very similar; for example the maximum velocities are 5.748×10^{-3} m s^{-1} in Fig. 2 and 5.742×10^{-3} m s^{-1} in Fig. 7. It can be concluded that the flow regime across the mouth of the crucible is similar in each case.

The oxygen concentration contours for this situation as seen in Fig. 8 lead to the same conclusion. The mass fraction at the surface of the bed y_s is 0.1000, compared to 0.0999 for the bottom flow case. The respective values for crucible B under the same conditions are 0.1050 and 0.1049. For the DTA/crucible arrangements in question, we
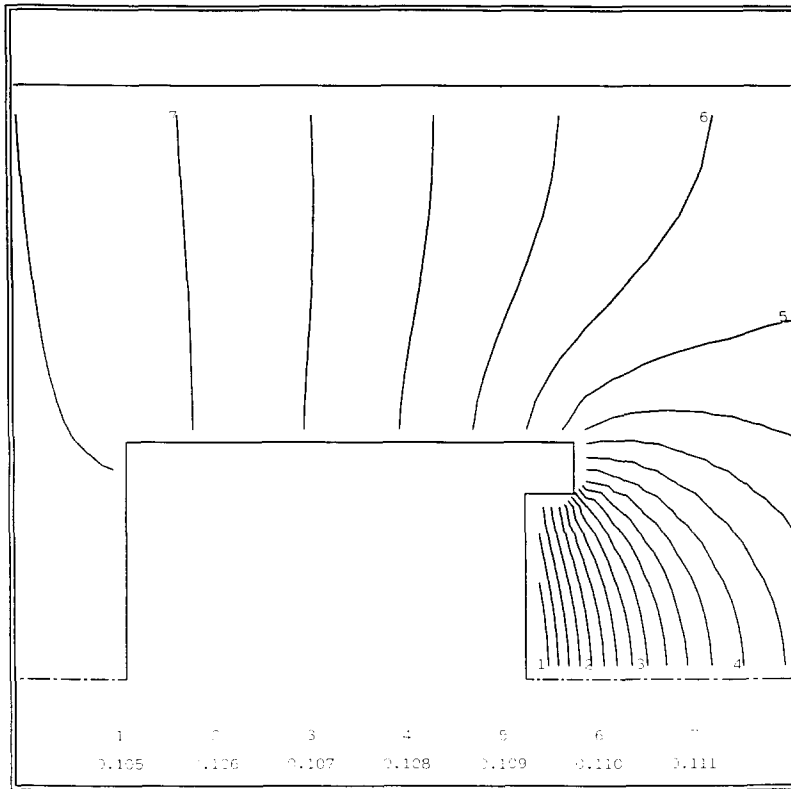
Fig. 6. Contours of oxygen mass fraction computed by FLUENT at 600°C for an initial soot mass of 4.9 mg, using crucible B: · — · — ·, symmetry axis.

can anticipate that the carbon consumption rate will be independent of the orientation of the crucible.

3.5. Diffusion within the porous solid bed

The value of y_s calculated from the gas phase model can now be used to examine the situation within the porous bed of particles. The conditions for oxygen diffusion within the bed have been discussed in a previous paper [6] where it was shown that the concentration at any depth x is given by

$$y = A \exp\left(\sqrt{\frac{K}{D_e}}\,x\right) + B \exp\left(-\sqrt{\frac{K}{D_e}}\,x\right) \tag{4}$$

The boundary conditions are

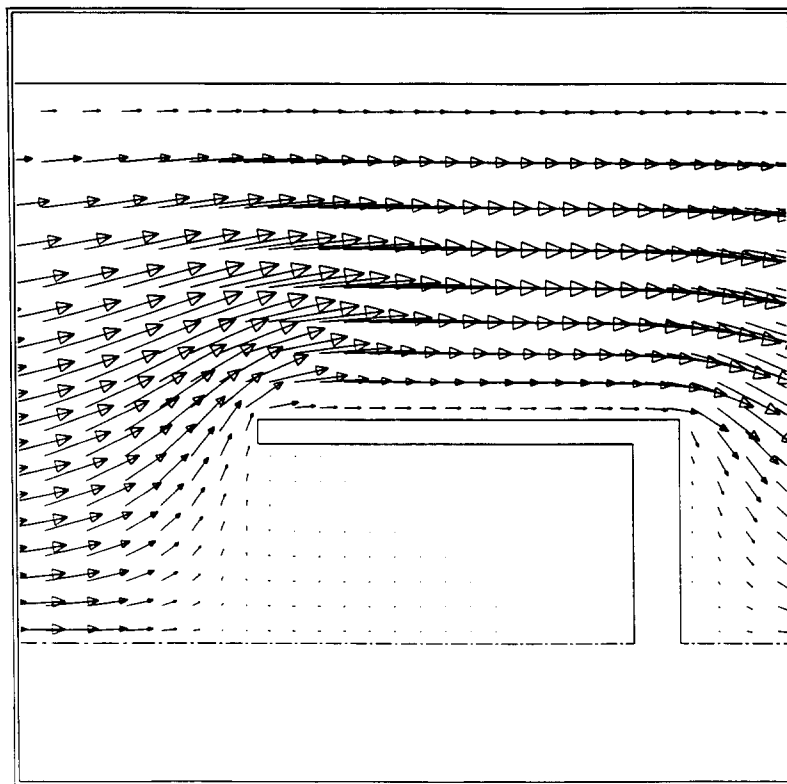$$y = y_s; \quad x = 0$$
$$dy/dx = 0; \quad x = e$$

Fig. 7. Velocity vectors computed by FLUENT at 600°C for an initial soot mass of 10 mg, using crucible A in the reverse position: maximum velocity, 5.75×10^{-3} m s^{-1}; $-\cdot-\cdot-$, symmetry axis.

which lead to

$$y = \frac{y_s}{1 + \exp(-2\theta)} \left[\exp(-2\theta) \exp\left(\sqrt{\frac{K}{D_e}} x \right) + \exp\left(-\sqrt{\frac{K}{D_e}} x \right) \right]$$ (5)

with the bed Thiele modulus

$$\theta = \sqrt{\frac{K}{D_e}} e$$ (6)

The oxygen consumption rate per unit surface area is given by

$$\omega = K\rho_g \int_0^e y \, dx$$ (7)

leading to

$$\frac{\omega}{\rho_g y_s} = \sqrt{KD_e} \left[\frac{1 - \exp(-2\theta)}{1 + \exp(-2\theta)} \right]$$ (8)
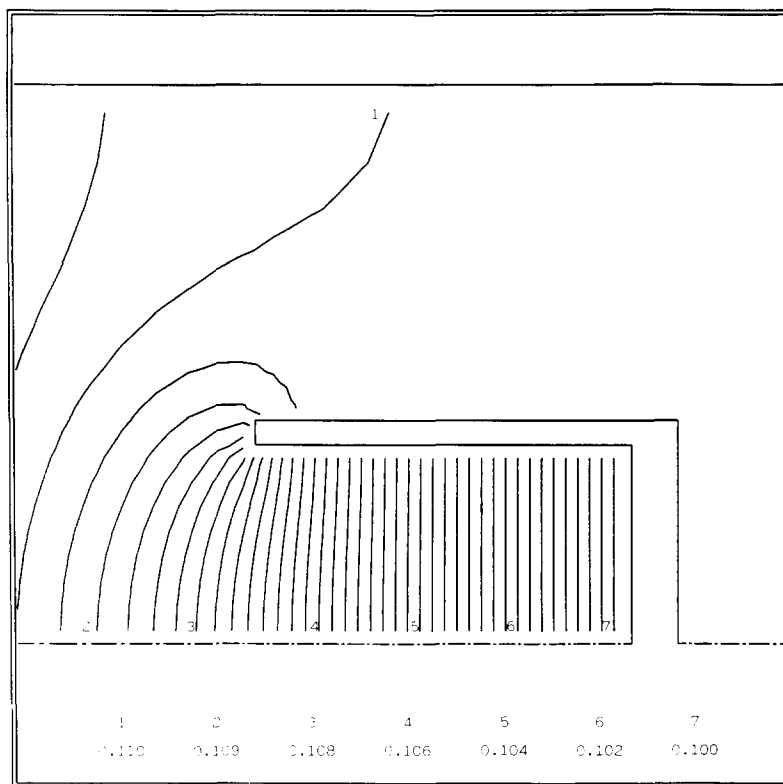
Fig. 8. Contours of oxygen mass fraction computed by FLUENT at 600°C for an initial soot mass of 10 mg, using crucible A in the reverse position; · — · — ·, symmetry axis.

Table 3
Comparison between the kinetic constants obtained before and after the improvement of the oxygen external mass transfer modelling

Temperature/(°C)	600	650	700	800	900
Kinetic constant (new value)/s^{-1}	15		44	54	67
Kinetic constant (previous value [5])/s^{-1}	15	29	65	77	101

New values of K are computed from this equation (see Table 3). They are plotted in Arrhenius form in Fig. 9, together with the previous values from Ref. [5]. It is clear that the allowance for mass transfer made in the previous model was inadequate as the new values for all temperatures other than 600°C are about 50% higher than before. The
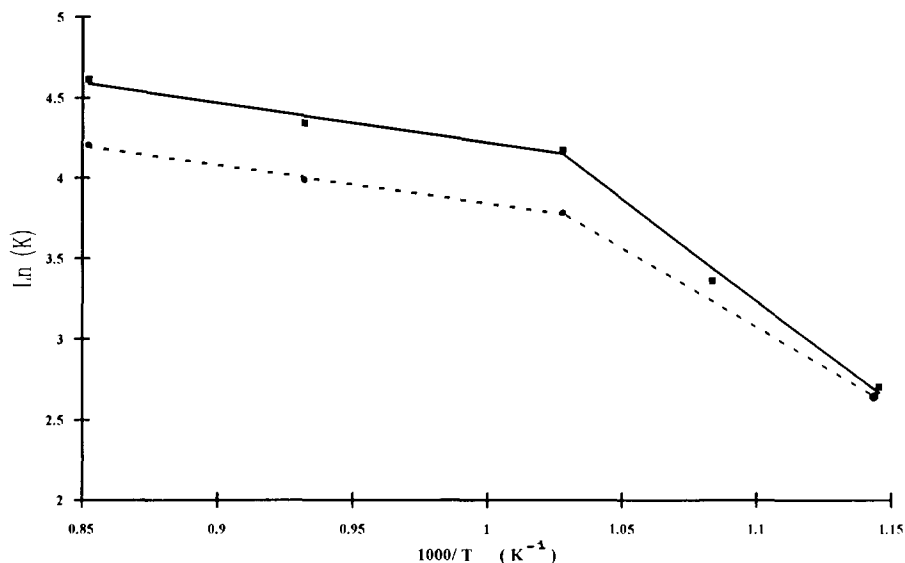
Fig. 9. Arrhenius plot of carbon black reactivity. Previous results [3] (■) and new results (●).

major source of uncertainty in the determination of reactivity in such systems is now estimation of the effective diffusion coefficient D_e.

The activation energy below 700°C is found to be 78 kJ mol^{-1} rather than 103 kJ mol^{-1}. The fall in activation energy above 700°C which was noted previously is confirmed. Above 700°C the value is approximately 20 kJ mol^{-1}. In the temperature range 600–700°C,

$$K = 6.47 \times 10^5 \exp(-77.700/RT)/s^{-1}.$$

4. Conclusions

A model of mass transfer is essential for the correct interpretation of combustion rates in a DTA. With measured rates available, it is possible to decouple the oxygen mass transfer processes which occur above and within a bed of carbon black. The mean surface concentration of oxygen can be calculated from a CFD model such as FLUENT, and the value thus calculated can be used in a mono-dimensional bed model to give true solid reactivity.

Under typical test conditions, mass transfer inside the sample crucible occurs predominantly by molecular diffusion. Deeper crucibles, therefore, offer greater resistance to oxygen transport than shallow ones. Because diffusion dominates, the orientation of the crucible will have a negligible influence on burning rate.

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