

The influence of mass transfer in DTG combustion tests

B. Stanmore¹, P. Gilot* and G. Prado

*Laboratoire Gestion des Risques et Environnement, Université de Haute Alsace,
25 Rue Chemnitz, 68200 Mulhouse, France*

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Abstract

The effects of oxygen transfer on carbon burning rates measured in particle beds with a DTG are considered. Transfer both to the surface of the particulate bed and within the bed is analysed under typical conditions. Oxygen supply to the bed surface is depleted generally under those conditions (high bed Thiele modulus) when there are oxygen transfer limitations within the bed. The value of the bed Thiele modulus also determines whether combustion takes place throughout the bed or in a surface layer.

INTRODUCTION

The use of differential thermogravimetry (DTG) for the measurement of the combustion kinetics of carbons has been characterised by a lack of agreement between different workers using different forms of the instrument in different modes. The confusion is compounded by the lack of comparative studies on identical carbonaceous materials.

Recently, it has been shown [1] that under suitable conditions DTG can give results similar to those obtained by other means. With proper precautions and suitable equipment, it should be possible to obtain fundamental data from DTG tests.

There are at least three conditions which will produce invalid kinetic data, resulting respectively from the type of material burned, the configuration of the DTG and the method of operation. These are in addition to the need to establish such fundamental kinetic information as the primary gas product, the combustion regime, the order of reaction, etc.

(i) Type of material. High volatile content materials such as coals experience a range of parallel oxidation reactions, both homo- and heterogeneous. Allocating kinetic values to any particular phase is difficult. At the moment, only low volatile content carbons can be successfully analysed in a DTG.

¹ Current address: Department of Chemical Engineering, University of Queensland, Qld 4072, Australia.

* Corresponding author.

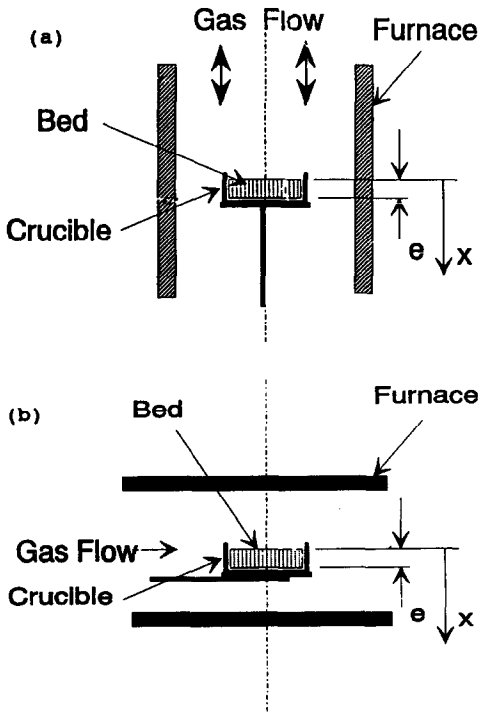


Fig. 1. Arrangement of carbon beds in a DTG apparatus. a. Vertical gas flow. b. Horizontal gas flow.

(ii) Configuration of the DTG apparatus. Poor temperature sensing applies to some types of DTG, where the sample thermocouple is not in direct metal contact with the sample but merely in the gas space adjacent to it. The indicated temperature then lags behind the sample temperature, being influenced by the furnace/gas temperatures as well as the sample temperature.

(iii) Method of operation. For a bed of burning particulate material to be under kinetic control, the mass transfer rates of oxygen from the bulk gas phase to the bed and into the bed must be much greater than the combustion kinetic rates.

This note is concerned with the last of these effects, i.e. the mass transfer of gas to and through the bed.

A kinetic test in a DTG instrument involves placing mg size samples into a small crucible mounted on a metal pan, see Figs. 1a and b. When the gas containing the oxidant is supplied from above or below, it will flow around the crucible, sweeping radially across the top of the sample (Fig. 1a). Alternatively, in some instruments the flow will be horizontal, moving transversely across the lip of the crucible (Fig. 1b).

Consider the mass transfer associated with a homogeneous bed of particulates as depicted in Figs. 1a and b, with the coordinate system as shown.

The bulk oxygen concentration remote from the bed surface is maintained constant at y_0 and the bed is isothermal. Gilot et al. [2] have shown that the concentration of oxygen in the gas phase in terms of bed depth x (expressed as a mole fraction y) is given by

$$\frac{d^2y}{dx^2} - \frac{K}{D_e}y = 0 \quad (1)$$

where K is the gas phase kinetic rate for oxygen consumption (s^{-1}), and is taken as first order. D_e is the effective oxygen diffusion coefficient within the bed. Equation (1) is subject to the boundary condition at the bed surface

$$h_m(y_0 - y_{x=0}) = -D_e \left(\frac{dy}{dx} \right)_{x=0}; \quad x = 0$$

For the other boundary condition

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

where e is the thickness of the bed.

The solution is [2]

$$y = A \exp\left(\sqrt{\frac{K}{D_e}} x\right) + B \exp\left(-\sqrt{\frac{K}{D_e}} x\right) \quad (2)$$

where

$$A = \frac{y_0 \exp(-2\theta)}{Da[1 - \exp(-2\theta)] + [1 + \exp(-2\theta)]}$$

and

$$B = \frac{y_0}{Da[1 - \exp(-2\theta)] + [1 + \exp(-2\theta)]}$$

The term θ is a form of the bed Thiele modulus and Da is a form of the Damköhler number

$$\theta = \sqrt{\frac{K}{D_e}} e; \quad Da = \frac{\sqrt{KD_e}}{h_m}$$

The oxygen concentration ratio at the bed surface ($x = 0$) is

$$\frac{y_s}{y_0} = \frac{1 + \exp(-2\theta)}{Da[1 - \exp(-2\theta)] + [1 + \exp(-2\theta)]} \quad (3)$$

The oxygen concentration ratio at the bottom of the crucible, $x = e$, is

$$\frac{y_e}{y_0} = \frac{2 \exp(-\theta)}{Da[1 - \exp(-2\theta)] + [1 + \exp(-2\theta)]} \quad (4)$$

The total oxygen flux across the bed surface is then

$$\begin{aligned}\omega &= -D_c \rho_g \left. \frac{dy}{dx} \right|_{x=0} = \rho_g \sqrt{KD_c} (B - A) \\ &= y_0 \rho_g \sqrt{KD_c} \left[\frac{1 - \exp(-2\theta)}{Da \{1 - \exp(-2\theta)\} + \{1 + \exp(-2\theta)\}} \right] \text{ mol cm}^{-2} \text{ s}^{-1} \quad (5)\end{aligned}$$

where ρ_g is the molar gas density.

The solution depends on the relative values of the Thiele and Damköhler numbers, which indicate whether mass transfer is exerting limitations on reaction either within or to the bed. When both numbers are small, mass transfer is not significant in any respect. When the Thiele modulus is large, there will be an oxygen gradient within the bed; and when the Damköhler number is large, the surface concentration will be less than in the bulk.

It is preferable that the rate of mass transfer should be high enough to maintain the oxygen concentration at the surface of the bed at the bulk level, which is then used for calculation of the results. Obviously a downward flow is desirable and the lip of the crucible should be as short as possible.

An estimate of the conditions under which external mass transport will be important can be derived by considering the relative rates of transport and reaction. The driving force for mass transfer Δy should be a small fraction of the bulk concentration y_0 . Taking $\Delta y/y_0$ as δ , the external oxygen transport flux is

$$\omega = \rho_g h_m \Delta y = \rho_g h_m \delta y_0 \quad \text{mol cm}^{-2} \text{ s}^{-1}$$

where h_m is the overall mass transfer coefficient (cm s^{-1}). This can be equated to the consumption rate within the bed (eqn. (5)), which rearranges to

$$h_m \frac{\delta}{1 - \delta} = \sqrt{KD_c} \left[\frac{1 - \exp(-2\theta)}{1 + \exp(-2\theta)} \right] \quad \text{cm s}^{-1} \quad (6)$$

The expression can be non-dimensionalised to give

$$\frac{\delta}{1 - \delta} = \theta \frac{D_c}{h_m e} \left[\frac{1 - \exp(-2\theta)}{1 + \exp(-2\theta)} \right] \quad (7)$$

In order to maintain δ at a low value, say 0.02, the value of the mass transfer coefficient must be large in relation to the group $\theta(D_c/e)$ $[(1 - \exp(-2\theta))/(1 + \exp(-2\theta))]$. For a given geometry, this implies a low value of the Thiele modulus.

It can be concluded from this analysis that the relative magnitudes of the bed Thiele and Damköhler numbers describe the oxygen transfer situation during carbon combustion in a DTG apparatus.

The oxygen concentration at the bed surface depends on both parameters, and in general it is not possible to separate their effects because they contain common variables (K , D_c). If θ is very small ($< 5 \times 10^{-3}$), there will

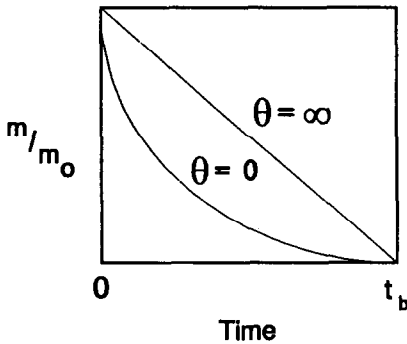


Fig. 2. Relative rate of mass loss during combustion as a function of bed Thiele modulus.

be no depletion whatever the value of Da . This is unrealistic as it probably implies negligible reaction; thus the external flow conditions will always play a role.

The fall in oxygen concentration within the bed, i.e. y_o/y_s , depends on θ only. If θ is large there will be a significant fall in concentration due to reaction, but if θ is less than 0.2, the fall can be neglected.

Because of the range of possible conditions which may exist, the application of the analysis will be demonstrated for two practical situations in which θ has different magnitudes. In practice its difficult to evaluate the mass transfer coefficient so that the magnitude of Da is often uncertain.

The Thiele modulus is small ($\theta < 0.2$)

This will be the case for a thin bed with comparatively low reaction activity which implies a low temperature. When θ tends to zero, the oxygen concentration is y_s throughout the bed, i.e. remains uniform through the bed at the surface value.

A plot of sample mass against time in an isothermal test will take the form of a power law decline as shown for $\theta = 0$ in Fig. 2. If the individual particles experience burning in the interior pores, the power law exponent will be less than 3, see the Appendix. In the shrinking core mode with no internal burning, the decay is cubic.

A practical technique which is carried out in this regime is the traditional burning profile test originally developed by Wagoner and Winegartner [3], but used extensively by others, e.g. refs. 4–6. Combustion occurs at low temperatures because the temperature is taken from ambient and increased continuously at a rate of $15^\circ\text{C min}^{-1}$. The particles are comparatively large, lying in the pulverised fuel range.

To illustrate this, some burning profile tests on petroleum coke burned in air [1] can be considered. These involved beds of about 18 mg of $140\ \mu\text{m}$ diameter particles which burned in the range $500\text{--}650^\circ\text{C}$. For such large

particles, the diffusion coefficient will be that of the bulk gas. The bed thickness in the 7 mm diameter crucible was about 0.4 mm which means that there were only a few layers of particles present.

The oxygen reaction rate K can be evaluated from the global carbon reaction rate R_c ($\text{g cm}^{-2} \text{s}^{-1}$) by

$$K = R_c S_v / 12 \rho_g \quad \text{s}^{-1} \quad (8)$$

where S_v is the surface area of solid per unit bed volume.

At 600°C which is typical of the burning profile test, K was 11 s^{-1} [1] and D_e is $1.28 \text{ cm}^2 \text{ s}^{-1}$ [7], giving a value of θ of 0.114. Combining eqns. (3) and (4) gives

$$\frac{y_e}{y_s} = \frac{2 \exp(-\theta)}{1 + \exp(-2\theta)} \quad (9)$$

from which the value of y at the bottom of the crucible is $0.994 y_s$, effectively the same as that at the surface. The assumption of complete oxygen penetration made in analysing the result was therefore justified.

This analysis will be applicable for θ less than 0.2, which gives a value of y_e/y_s at the bottom of the crucible of 0.98. It should apply to all burning profile tests provided that the particle size is large (of the order of $100 \mu\text{m}$) and the bed size is small.

The arrangement of the crucible was as shown in Fig. 1a, with the gas in upflow. Evaluation of the mass transfer coefficient in such a geometry requires a mathematical simulation of some complexity, such as a computational fluid dynamics package.

However, a reasonable indication of mass transfer to the surface of the bed will be found by considering it as the upstream (or downstream) side of a bluff body. Inserting typical values for a DTG furnace of diameter 20 mm with a crucible diameter of 7 mm, with a gas flow (generally air) or 100 ml min^{-1} at 600°C , the Reynolds number is very low, around 0.35. In this flow regime, the upstream and downstream flow patterns should be identical for a symmetrical bluff body.

Because there is little literature on mass transfer to such geometry, the analogy between momentum and mass transfer as outlined by Bird et al. [9] is utilised. For a circular disc normal to the flow, Midoux [10] reports

$$C_d = \frac{64}{\pi Re_p}$$

for the Stokes regime. Application of the mass transfer analogy gives an overall mass transfer coefficient for oxygen of 19 cm s^{-1} . This value is probably too high for the particular application as the bed surface was facing downstream and there was a lip on the crucible.

Taking a value of 40% of that calculated, i.e. 8 cm s^{-1} , the Damköhler number is 0.47 and the surface concentration calculated from eqn. (3) is

0.95 of the bulk. There would thus be an error of 5% in the evaluation of combustion kinetics due to external mass transfer limitations. It is of interest to note that the mass transfer coefficient for molecular diffusion processes alone to a sphere of 7 mm diameter is 3.9 cm s^{-1} , so the above value appears to be reasonable. If the transfer coefficient is 3.9 cm s^{-1} , the error becomes 10%.

Two conditions should be noted in relation to this result. The reaction rate used was a maximum and would have been operative for only a small part of the burnout process. At lower combustion rates, the value of Da would be less and the error therefore diminished.

There will also be a natural convection effect as the burning bed will be slightly hotter than the gas stream flowing past it. An energy balance over the bed which assumes that the heat of reaction is being lost uniformly over the surface of the total bed surface will give the temperature difference between the bed and the gas. Taking CO_2 as the primary product, the combustion rate as that for petcoke at 600°C and a heat transfer coefficient from the analogy used above, the difference is found to be of the order of 15°C . This will superimpose a natural convection mass transfer onto the forced convection.

The nett result for a burning profile test should be virtually no oxygen depletion at the bed surface. This has been confirmed in practice by varying the flowrate of the oxidant gas [4].

The Thiele modulus is large ($\theta > 8$)

When the Thiele modulus is very large, the solution to eqn. (1) tends to the simplified solution

$$y = \frac{y_0}{1 + Da} \exp\left[-\sqrt{\frac{K}{D_e}} x\right] \quad (10)$$

The oxygen concentrations become

$$\frac{y_s}{y_0} = \frac{1}{1 + Da}; \quad \frac{y_e}{y_0} = 0$$

The total oxygen consumption is

$$\omega = \frac{y_0}{1 + Da} \rho_g \sqrt{KD_e} \quad \text{mol cm}^{-2} \text{ s}^{-1} \quad (11)$$

Because oxygen consumption is rapid, the value of the oxygen concentration will fall to zero within the bed. Combustion is then taking place only in a surface layer which gradually works its way down the bed as the carbon in it is consumed.

The thickness of the layer x_p can be approximated as the point where the oxygen concentration falls to say, one fiftieth of the surface value, i.e. when $y_x/y_s = 0.02$, which from eqn. (14) is equivalent to

TABLE 1

Thickness of carbon black beds

Bed mass/mg	5	10	20	40
Bed thickness e /mm	0.29	0.58	1.15	2.31

$$x_p = 3.9 \sqrt{\frac{D_c}{K}} \text{ cm} \quad (12)$$

Thus when θ is greater than 3.9, the penetration thickness equals the bed thickness and the concentration of oxygen at the bottom of the bed has fallen effectively to zero. In a typical situation, when the initial value of θ is greater than 8, constant rate burning will be present for at least the initial half of the burnout process.

In such a case, a plot of sample mass against time in an isothermal test will exhibit a linear decline as shown for $\theta = \text{infinity}$ in Fig. 2.

The value of θ will be large at high temperatures with small particles, such as experienced when burning carbon black. Carbon black forms porous aggregates of about 200 nm diameter, consisting of smaller (40 nm) particles. The small aggregate size limits diffusion because it lies in the Knudsen regime.

The effect can be illustrated from the work of Gilot et al. [2] where beds of carbon black of various masses were burned isothermally in a DTG apparatus over a temperature range from 600 to 900°C. A uniform rate of removal of carbon is demonstrated by the straight line thermogram in Fig. 2 of ref. 2, indicating that combustion in that case (40 mg) is taking place only in a surface layer. This is confirmed by their Fig. 4, where the overall combustion rate (mg s^{-1}) is effectively constant for beds larger than 20 mg at 600°C and larger than 10 mg at 900°C (see also Table 2).

The thicknesses of the carbon black beds used can be calculated, given the crucible size and the bulk solid density, Table 1.

TABLE 2

Summary of external mass transfer variables

Temperature/°C	600	650	700	800	900
K/s^{-1}	15	29	65	77	101
$D_c/\text{cm}^2 \text{ s}^{-1}$	0.0298	0.0304	0.0312	0.0331	0.0346
$h_m/\text{cm s}^{-1}$	0.635	0.686	0.738	0.847	0.959
Da	1.05	1.37	1.93	1.88	1.95
δ	0.51	0.58	0.66	0.65	0.66
x_p/mm	1.75	1.25	0.85	0.80	0.72

For 20 and 40 mg beds, the thickness of the active oxidation layer can be estimated from eqn. (12). For Knudsen diffusion, the diffusion coefficient can be found from [8]

$$D_e = 0.485 \frac{\varepsilon^2 \sqrt{T}}{\tau S_v} \text{ cm}^2 \text{ s}^{-1} \quad (13)$$

where τ is the tortuosity factor and S_v the surface area per unit volume.

At 650°C, the diffusion coefficient in a bed of 200 nm particles of porosity $\varepsilon = 0.5$ and with a tortuosity factor of 4 is $3.1 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$. Because K is 29 s^{-1} [2], the penetration thickness was about 1.25 mm.

By comparison, the thickness of the 20 mg bed is 1.15 mm which is consistent with the penetration calculated. The oxidation layer will be somewhat thinner at higher temperatures, as the calculated value of the kinetic rate K increases slightly even though D_e does not change much, see Table 2.

The external mass transfer coefficients for the bed estimated from the boundary layer theory of Gilot (which are probably too low) can be used to analyse the external transfer situation. The calculated Damköhler numbers range from 1.05 to 1.95 as listed in Table 2. The calculated penetration thicknesses and values of δ derived from eqn. (6) are also shown. The values of δ are very dependent on the magnitude of h_m . Because δ ranges from 0.52 to 0.66, significant surface depletion of oxygen has taken place in this situation.

The bulk of the oxygen consumption will take place close to the surface. From a point flux calculation at depth x

$$\omega_x = \frac{y_0}{1 + Da} \rho_g \sqrt{KD_e} \exp\left[-\sqrt{\frac{K}{D_e}} x\right] \text{ mol cm}^{-2} \text{ s}^{-1}$$

and

$$\frac{\omega_x}{\omega} = \frac{y_x}{y_s} = \exp\left[-\sqrt{\frac{K}{D_e}} x\right] \quad (14)$$

At 600°C, 90% of the surface oxygen flux will be consumed within a depth of 1.0 mm, which is close to the 20 mg bed thickness. At 900°C, the depth for 90% removal is reduced to 0.43 mm, i.e. less than for the 10 mg bed thickness.

It is interesting to note that application of eqn. (11) at different temperatures predicts the slight differences in combustion rate for the same bed mass at different temperatures depicted in Fig. 4 of Gilot et al.'s paper [2].

Once values of h_m have been established, they will apply for all tests in the same equipment under similar operating conditions. It should be possible to determine experimental values of h_m by applying eqn. (5) to a suitable set of experimental data in which θ is small. This would involve combustion of beds of carbon whose kinetics are known, e.g. petroleum

coke, at various temperatures with all other variables held constant. The Damköhler number will then be the only unknown in eqn. (5). The value of h_m would be given over the range of temperatures.

A second set of tests with the crucible filled to various depths would indicate the effect of the height of the crucible lip on mass transfer to the bed surface.

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APPENDIX

When oxygen completely penetrates the bed, the relative mass change of the bed is identical to that of the individual particles. For spherical particles of initial diameter d_{p0} and density ρ_0 , which reduce in diameter according to

$$d_p = d_{p0}(1 - u)^\alpha$$

the rate of mass loss at constant temperature is

$$-\frac{dm}{dt} = R_c \pi d_p^2$$

which gives

$$\frac{du}{dt} = \frac{6R_c(1 - u)^{2\alpha}}{\rho_0 d_{p0}}$$

Integrating

$$\frac{m}{m_0} = 1 - u = \left[1 - \frac{6(1 - 2\alpha)R_c t}{\rho_0 d_{p0}} \right]^{1/(1 - 2\alpha)}$$

Noting that the burnout time t_b is given by

$$t_b = \frac{\rho_0 d_{p0}}{6(1 - 2\alpha)R_c}$$

this is equivalent to

$$\frac{m}{m_0} = \left(1 - \frac{t}{t_b}\right)^{1/(1 - 2\alpha)}$$

The value of α , which lies between 0 and 1/3, is a function of the material [11] and the temperature of combustion [12]. For the shrinking core situation, it is 1/3 and the mass loss expression becomes

$$\frac{m}{m_0} = \left(1 - \frac{t}{t_b}\right)^3$$