

**Fast Analysis of Fluidised-Bed Combustion**

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**Background**

Researchers at Chemical Engineering at Cambridge University were perplexed by some results which appeared to show a transition in the measured order of reaction of coal char with O<sub>2</sub>, when measured in a fluidised bed, from just less than unity to zero. These results were at variance with a number of other sets of results reported in the literature; the researchers believed that the true kinetics of the reaction might be obscured by analyser response – hence, an NDIR500 fast analyser for CO<sub>2</sub> / CO was used to test this theory.

**Introduction**

A fluidised bed of sand has a number of advantages when it comes to the measurement of the oxidation of particles of coal char – the rates of heat and mass transfer to reacting particles are high and are also well characterised. Problems have arisen due to the slow response of the typical CO<sub>2</sub> and CO analysers used in the laboratory, with response-times of ~ 4 s. One further problem is that the mixing of gases within the fluidised bed itself can obscure the observed results. This work miniaturised the fluidised bed and also used the NDIR500 system in order to reduce the total system (analyser + bed) response time from ~ 8 s to ~ 0.3 s (governed entirely by gas mixing in the fluidised bed) and allowed us to finally match the results in fluidised beds with the results in other types of reactor, finally solving a problem which has been under investigation for over ten years.

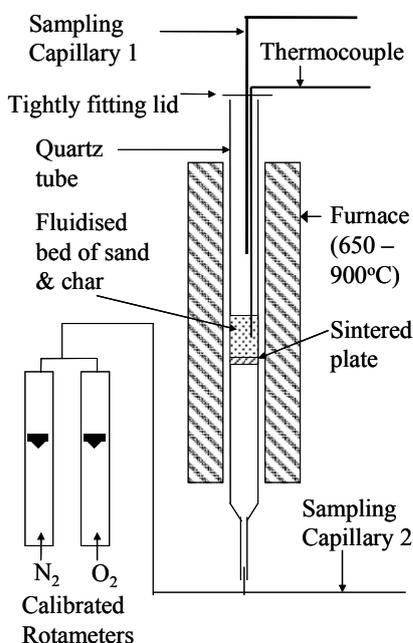


Figure 1 – The experimental setup.

Figure 1 shows the apparatus. A small bed (i.d. 30 mm; unfluidised depth  $\sim 30$  mm) of quartz sand (355 – 425  $\mu\text{m}$ ), supported on a sintered quartz distributor was held in a quartz tube and fluidised by a mixture of  $\text{O}_2$  and  $\text{N}_2$  (flowrate = 83 ml / s N.T.P *i.e.* a vigorously bubbling bed) containing 5 - 100 vol. %  $\text{O}_2$ . The flowrates of  $\text{O}_2$  and  $\text{N}_2$  were measured by calibrated rotameters. A tightly fitting steel lid prevented ingress of laboratory air. The bed was surrounded by a tubular furnace and controlled to a steady temperature (650 – 900°C), as measured by a type K thermocouple. Weighed batches ( $\approx 2$  mg) of coal char (sieved to 75 – 106, 150 – 212 or 300 – 355  $\mu\text{m}$ ) were mixed with a small quantity ( $\sim 0.1$  g) of sand and thrown on to the hot sand from above. The response time of the bed was measured by adding a step of  $\text{CO}_2$  and measuring the response before and after the bed. The rate of burning, as determined by the rate of evolution of  $\text{CO}_2$  and  $\text{CO}$  was measured by the NDIR500, and is shown for three different sizes of chars in Fig. 2.

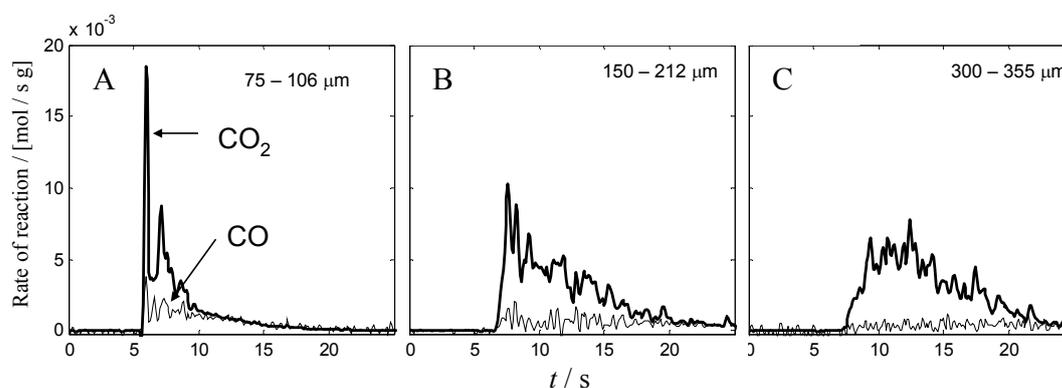


Figure 2. Typical corrected rates of combustion for three different particle sizes (as shown) of Cynheidre char.  $Q_{\text{tot}} = 83$  ml / s,  $X_{\text{O}_2} = 0.2$ ,  $T = 900^\circ\text{C}$ , sand 355 – 425  $\mu\text{m}$ , approx. mass of char 2.0 mg. Measured recovery of carbon as gaseous products: A = 55 %, B = 90 % C = 88 %. Estimated maximum rates of reaction are: A  $7.5 \times 10^{-3}$ , B  $9 \times 10^{-3}$  and C  $6 \times 10^{-3}$  mol / s g.

## Reaction Kinetics.

The measurements in Fig. 2 were the most difficult to make; they are for the three sizes of char shown, and are typical of observations in the hottest bed, with larger mole fractions of  $\text{O}_2$ . The aim was to measure the initial rate of combustion for the batch of char from the maxima in Fig. 3. However, the results for the 75 – 106  $\mu\text{m}$  char show an initial spike of  $\text{CO}_2$ , when the particles were added to the bed. This spike (not seen with larger char particles) took  $\sim 0.3$  s to rise and a further 0.3 s to fall. It is most probably due to newly added particles of char catching alight, whilst falling through the freeboard, although sand was added to the char to inhibit this. Since the problem became more acute at higher temperatures and bigger  $[\text{O}_2]$  in the fluidizing gas, no mole fraction of  $\text{O}_2$  above 20 % was used at 900°C. Likewise,  $[\text{O}_2]$  was limited at other temperatures to ensure that pre-burning of particles in the freeboard was minimized. Next, comparing measurements for the three different sizes of

char shows that the maximum rate of reaction (excluding the short-lived flash) is similar in magnitude for all three particle sizes (with the largest reacting  $\sim 33\%$  more slowly), and that in each case  $\text{CO}_2$  is the major product. The maximum rate of combustion corresponds to conversions of the char of 9%, 5% and 6%, respectively. That the three initial burning rates in Fig. 3 are so similar suggests that all three sizes of char have similar internal surface areas per g, as well as effectiveness factors close to unity, i.e. all of the internal and external surface area of the particles was available for reaction.

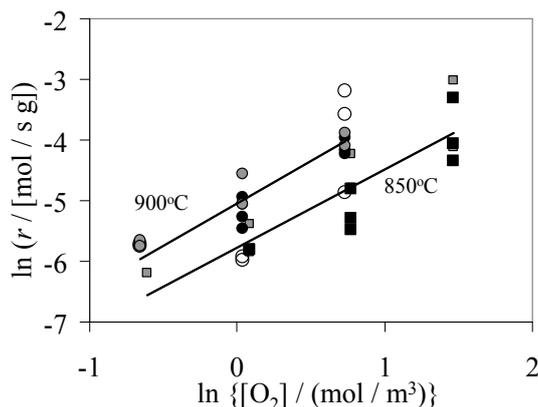


Figure 3. Plot of  $\ln r$  against  $1/T$  to derive the order of reaction. Particle sizes 75 – 106  $\mu\text{m}$ , 900°C  $\circ$ ; 150 – 212  $\mu\text{m}$ , 900°C  $\bullet$ ; 300 – 355  $\mu\text{m}$ , 900°C  $\ominus$ ; 150 – 212  $\mu\text{m}$ , 850°C  $\blacksquare$ ; 300 – 355  $\mu\text{m}$ , 850°C  $\blacklozenge$   $Q_{\text{tot}} = 83 \text{ ml / s}$ , sand 355 – 425  $\mu\text{m}$ .

It can be seen from Fig. 3 that the order of reaction of coal char with oxygen (the gradient of the plots shown) is around unity, in agreement with most previous work, but in disagreement with previous work with slower analysers.

## Conclusions

Some previous measurements of the kinetics of combustion of coal chars suffered because of the slow response of the gas analysers and poor mixing of gases inside the fluidized bed. Here, we reduced both the mixing times of gas and response-time of the analyser. The oxidation of coal-char between 700 and 900°C was found to be first order, in agreement with most of the literature. The measured activation energy of  $145 \pm 25 \text{ kJ / mol}$  now likewise agrees well with earlier literature. This work thus shows that a fluidised bed can be used to measure fast reactions (provided that care is taken to address mixing times), whilst ensuring a constant, well defined particle temperature (in contrast, for example to a thermogravimetric analyser or packed bed). The work also shows the flexibility of the NDIR500 system for use in a laboratory.

The work discussed briefly here was presented as a full paper in the 32<sup>nd</sup> International Symposium on Combustion, 2008: *Proceedings of the Combustion Institute, Volume 32, Issue 2, 2009, Pages 2051-20.*