

HIGH TEMPERATURE DEACTIVATION OF COAL CHARs

T. J. Beeley, J. R. Gibbins, R. Hurt*, C. K. Man, K. J. Pendlebury
& J. Williamson*

Department of Mechanical Engineering,

*Department of Materials, Imperial College, London SW7 2BX

†Sandia National Laboratory, Livermore, CA 94551-0969

Keywords: coal char combustion, reactivity

INTRODUCTION

High levels of char burnout, typically to less than 5% by weight of residual carbon in the fly ash, are desirable in large, multi-burner utility boilers fired with pulverised coal in order to optimise plant efficiency and allow the ash to be incorporated in building materials. Achieving high levels of char burnout can be a particular problem with air-staged low-NO_x combustors, where air/fuel ratios (and flame temperatures) have to be constrained to give satisfactory emission levels. Switching to imported low-sulphur coals can also be associated with a need to at least assess the potential for burnout problems.

In general the levels of carbon in ash required represent very high overall fuel conversion. For example, a coal with 10%w/w ash dry basis giving 5% carbon in ash will still achieve 99.4% conversion. The difference between satisfactory and unsatisfactory burnout thus depends on whether a very small fraction of the coal does or does not burn. Due to the heterogeneous nature of pulverised coal the properties of this 'least likely to burn' (LLB) fraction could well differ from the bulk properties of the whole coal. Consideration of heat and mass transfer would suggest that larger particles make up the bulk of the LLB fraction, and particularly those larger particles which form less reactive chars. In contrast to this material, which might be classed as being unlikely to burn because it is inherently 'bad', there is also a strong likelihood that some coal particles do not burn because they are 'unlucky'. Particles which enter through burners which, because of poor fuel distribution, have a lower than average air/fuel ratio fall into this latter category, especially if they also enter in an upper row of burners or adjacent to a wall.

Previous work by one of the authors has confirmed the heterogeneous nature of pulverised coals by showing that combusting coal particles exhibit a range of reactivities, and that average reactivities decrease with increasing conversion¹. A band of reactivities has also been observed in chars collected from utility boiler fly ash, with a general trend for char reactivity to reduce with increasing particle size². Even at relatively high levels of conversion (~ 50%) chars produced in a laboratory entrained flow reactor (EFR) still had significantly higher reactivity than utility fly ash chars from the same coal³.

The deactivation of coal chars obviously has considerable implications for interpreting char burnout behaviour in itself, but why it occurs is not clear. One explanation is that, with a heterogeneous coal and hence char, the components which are inherently more reactive are burnt preferentially leaving a residue of less-reactive material. Another mechanism, which may either dominate or operate in parallel, is that even at the short particle residence times occurring in utility boilers (~2 seconds) thermally-induced heteroatom loss and/or structural reordering in the chars have occurred, with a consequent reduction in the number of active sites. High resolution transmission electron microscopy in fringe image mode has confirmed that chars from utility boilers are indeed more ordered than chars from the EFR³, but this may reflect either heterogeneity in the parent coal plus differences in degree of conversion, or differences in peak particle temperature and residence time (>1800°C vs. ~1570°C, ~1s vs. ~100 ms respectively).

In order to promote an understanding of the relative importance of the two mechanisms, this study examines the effect of time/temperature history on char reactivity. A recently-developed wire mesh (WM) apparatus was used to achieve char temperatures up to 1800°C with, unlike entrained flow apparatus, essentially no constraint on particle heating times. Since heating takes place under inert gas (helium) any effects due to selective oxidation are avoided. The work formed a preliminary stage in a larger project which will also examine the effect of coal heterogeneity in more detail.

EXPERIMENTAL METHODS

Fly ash samples containing char for analysis were obtained from plant trials. Pulverised coal samples were either sampled on plant or prepared from corresponding lump coal. All coal samples were dry sieved to give a 125-150µm size cut for WM analysis. This was dried overnight in a nitrogen-purged oven at 105°C and stored under nitrogen until required. Char samples were obtained from fly ash either by sieving to give a carbon-enriched size cut >150µm, or by particle density segregation in a sub-fluidised bed.

Coal samples were charred using a high-temperature WM reactor developed at Imperial College. The sample (~10mg) is held between layers of folded molybdenum wire mesh which also act as an electrical resistance heater. Heating currents of up to 2000 A are provided under computer control from a 24 V DC source, with a two-colour pyrometer for temperature measurements. A helium gas sweep flows across the mesh (at atmospheric pressure) to remove volatile products. A more detailed description of the apparatus will be published elsewhere⁴. Char samples for two of the coals were also prepared in an entrained flow reactor at Sandia National Laboratory in 12% oxygen at a gas temperature of 1327°C, peak particle temperatures of 1570°C, and residence times from 47 to 234 ms.

Char reactivities were compared using thermogravimetric analysis (TGA). Samples were heated in a PL Thermal Sciences TG760 series TGA to 900°C at 15 K/min in 7% oxygen in nitrogen. This reduced oxygen concentration eliminates 'ignition peaks' (uncontrolled autothermal combustion within the char sample) that can occur if the sample is heated in air. Char samples were ground to <10µm to eliminate any effects due to particle size. Although this technique utilises standard commercial equipment some development work was required to achieve consistent, repeatable results with small samples (2-3mg).

TGA data logging and analysis were carried out using in-house software. The instantaneous sample mass was monitored as the sample was heated. Sample temperature was measured using a thermocouple positioned 0.7 mm under the crucible. Results were expressed as burning profiles (rate of weight loss versus sample temperature), or as Arrhenius plots (logarithmic reaction rate against inverse temperature). This non-isothermal characterisation technique has several advantages over isothermal methods (e.g. time for 50% burnoff). In isothermal char reactivity tests the char must be first heated to the desired temperature in inert gas, before switching to the desired oxygen concentration. Data for the intermediate oxygen levels during switchover periods, which can represent a considerable portion of the total burnoff at elevated temperatures, cannot then be used. Analysis times will also vary significantly at a given temperature with the range of char reactivities encountered in char combustion studies (e.g. low reactivity chars may require a number of hours for 50% conversion at 500°C in 7% O₂). Errors in sample temperature measurements may, however, be worse in non-isothermal analysis due to differential heating, particularly if (as in this case) the thermocouple is not placed in direct contact with the sample.

RESULTS AND DISCUSSION

The variation in reactivity for chars prepared from Illinois #6 coal by different methods is shown as an Arrhenius plot in Fig. 1. As noted already, chars from the EFR have significantly higher chemical reactivities than the utility boiler fly ash chars. Chars obtained after heating in the WM reactor at 1600°C are also significantly more reactive. The reactivity of the WM chars decreases with increased hold time at peak temperature, but even at 10 s hold the 1600°C WM char is more reactive than the fly ash char. The Arrhenius plot line for a WM char obtained with a peak temperature of 1800°C and a residence time of 2 s, however, intersects the Arrhenius plot line for the utility char, being apparently less reactive at low conversions in the TGA but more reactive at higher conversions. Similar trends for the WM chars as compared with the fly ash chars were also observed for a South American coal (Fig. 2) and US Daltex coal (Fig. 3), although this last coal appears to be particularly susceptible to thermal deactivation.

An interesting feature of Figs 1 to 3 is the difference between apparent activation energies for WM and fly ash chars. Both exhibit reasonably straight lines on the Arrhenius plots over the range 5% to 95% conversion (signal/noise ratio makes interpretation difficult at higher conversions), suggesting modelling by a familiar first order reaction rate expression for loss of sample weight, W , of the form:

$$dW/dt = -a.W.e^{-E/RT}$$

For the WM chars, increased heating severity changes the pre-exponential factor, a , but not the activation energy, E , suggesting that the number, but not the type, of active sites is being affected. The lower apparent activation energy for the fly ash chars might then be taken as an indication of the presence of a significantly different type of char, perhaps due to selective oxidation.

If, however, the WM and fly ash chars are in fact different types, it might be considered an unusual coincidence that overall reactivities are still comparable for the similar peak temperatures. This observation is explored in more detail in Fig. 4, which shows the TGA burning profile that would be obtained for a hypothetical heterogeneous char with a single activation energy, but a normal distribution of pre-exponential factors (the WM char data show that this could, for example, be obtained by subjecting a batch of coal particles to a range of different time/temperature histories during devolatilisation). The Arrhenius plot line for 5% to 95% conversion for the modelled TGA burning profile is still extremely linear (correlation coefficient of 0.997), but the heterogeneity has the effect of reducing the apparent activation energy from an assumed 175 kJ/kmole to 145 kJ/kmole.

Since particles in a utility boiler will have experienced a range of time/temperature histories it appears plausible that this, at least partly, accounts for the apparently lower activation energies for fly ash chars shown in Figs 1 to 3. If temperature alone is responsible, then it can further be concluded that the fly ash chars have experienced temperatures both above and below 1800°C. This scenario corresponds with the LLB fraction being made up of particles that are simply 'unlucky'.

The very low reactivities of fly ash chars at higher conversion levels in the TGA compared to 1800°C WM chars suggest, however, that extremely high particle temperatures would have to have occurred to account for all of the differences observed. Some additional char heterogeneity due to differences between the parent coal particles therefore seems likely. This pulverised coal heterogeneity may be in the organic fraction or in the catalytic properties of the mineral matter for graphitisation and/or oxidation. In either case, the LLB fraction would then consist, at least in part, of particles that were inherently 'bad'.

It is also worth considering to what extent the original WM coal samples are themselves heterogeneous in this way. In this case even the higher apparent activation energies observed for the WM chars could still be an underestimate, with considerable implications for extrapolating low-temperature TGA data to boiler combustion temperatures.

CONCLUSIONS

Char oxidation reactivity reduces progressively with increased temperature and hold time under conditions encountered in pulverised coal combustion. At elevated temperatures (1800°C) char reactivities obtained by heating alone approach fly ash residual char reactivities.

Fly ash residual char from utility boilers is probably heterogeneous in its reactivity. If some of the char particles have experienced temperatures well in excess of 1800°C then temperature alone could explain this heterogeneity, otherwise heterogeneity in the original coal plus loss of more reactive material, or catalysis of oxidation or char graphitisation by mineral matter, must also be occurring.

Char reactivities measured by non-isothermal TGA methods are likely to give correct relative trends, but apparent activation energies may not be reliable due to char heterogeneity (and possibly also temperature offsets).

ACKNOWLEDGEMENTS

The authors would like to acknowledge financial support for this work from the UK Science and Engineering Research Council, the British Coal Utilisation Research Association, the UK Department of Trade and Industry through ETSU, National Power PLC, and the US Department of Energy.

REFERENCES

1. Hurt, R.H., *Energy & Fuels* 7, 1993, 721-733.
2. Gibbins, J.R. & Williamson, J., Proc. 7th ICCS, Banff, Sep. 1993, paper PS1.9.
3. Hurt, R.H., Yang, N.Y.C., Headley, T.J. & Gibbins, J.R., Proc. 7th ICCS, Banff, Sep. 1993, paper OS12.2.
4. Pendlebury, K.J., Man, C.K. & Gibbins, J.R., *Rev. Sci. Instrum.*, (in preparation).

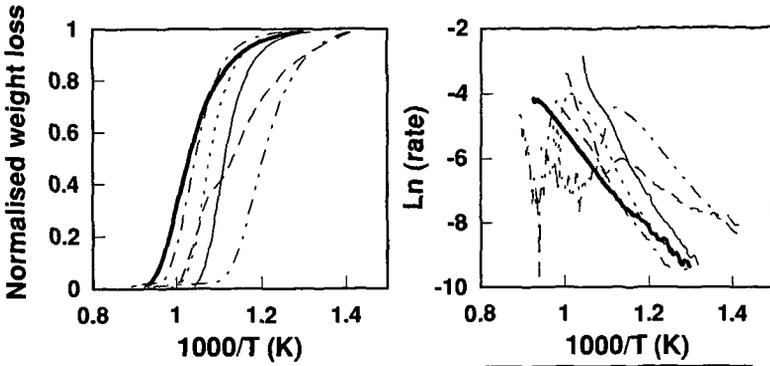


Figure 1 TGA sample weight and reaction rate as a function of inverse temperature for Illinois #6 chars

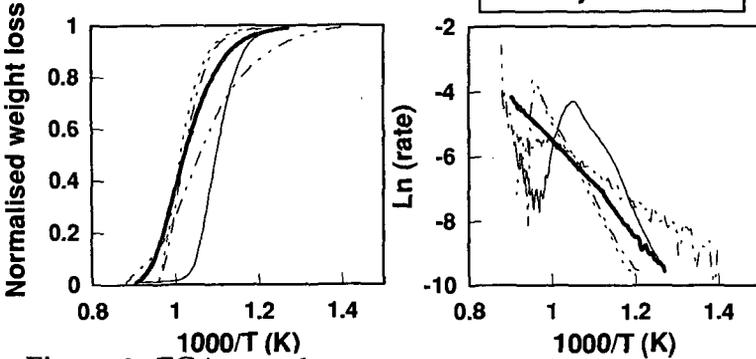
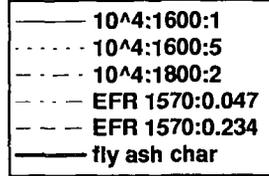


Figure 2 TGA sample weight and reaction rate as a function of inverse temperature for South American coal chars

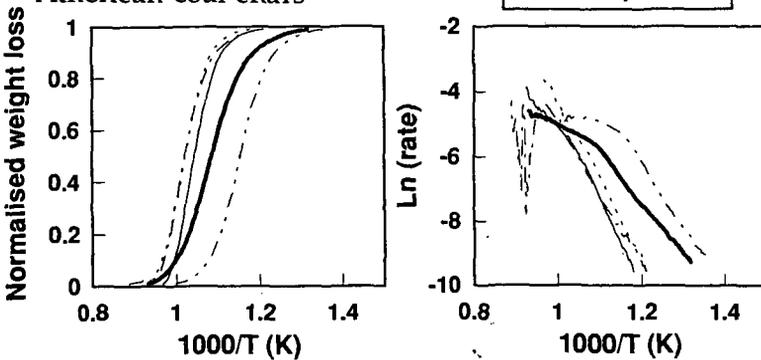
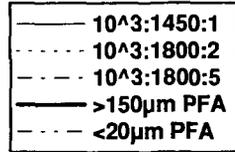
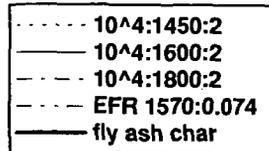


Figure 3 TGA sample weight and reaction rate as a function of inverse temperature for Daltex chars



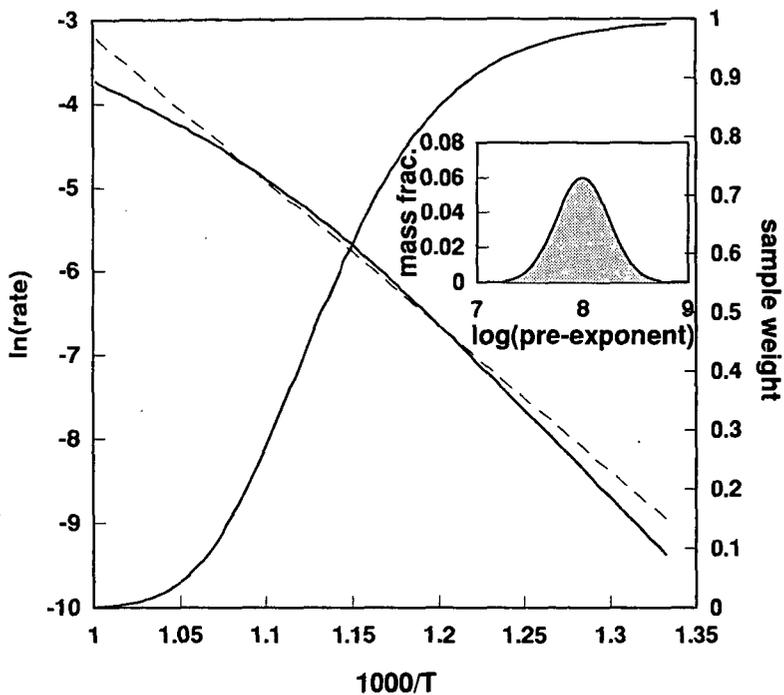


Figure 4 Effect of char heterogeneity on apparent activation energy