

ACTIVATION OF CARBON FIBRES USING CONTROLLED RATE METHODS

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Introduction

Many forms of carbon, including pitch based carbon fibres, can be activated in steam or CO₂ at temperatures in the range 800-1000 °C. This method yields microporous carbons of high surface area (ca 1000 m² g⁻¹) dependant on the extent of burn off or reaction time.

A different approach, using constant rate (CR) methods has shown [1,2] that in addition to the mild oxidising gases above, air or oxygen mixtures at lower reaction temperatures (500-700 °C) can also produce activated carbons with similar properties. Furthermore, the problems of excessive external burn off and thermal runaway can be avoided.

Experimental

The CR method can be used in either of two modes of operation, with a feedback loop between the detector (mass spectrometer), computer and either a temperature programmer or mass flow controllers (fig. 1). In the first mode, (thermal control) the rate of evolution of one of the product gases (CO₂) is monitored and maintained at a pre-set target level by forcing the furnace temperature to rise or fall as necessary while keeping the activating gas (O₂) concentration constant. In the second mode, (gas concentration control) the furnace temperature is constant and the reaction rate is controlled by altering the concentration of the oxidant.

Thermal control is difficult at high reaction rates as the exothermic nature of the oxidation process can cause thermal runaway. In contrast, gas concentration control is inherently better as any tendency to thermal runaway is accompanied by a depletion in the oxygen level. This reinforces rather than opposes the control mechanism. Most of the results reported here were obtained using gas concentration control of the reaction rate.

A further advantage of the software developed for these methods is the ability to integrate continuously the evolved gas peak produced by the mass spectrometer (MS) and terminate any activation at a specified peak area, making the preparation of samples to identical degrees of burn off easier in certain circumstances (see Results and Discussion).

Samples of pitch based carbon fibres (Asbury, AGM 95, 500 mg) were placed in a quartz reaction tube within a water cooled furnace. Initial experiments were carried out in air/N₂ blends, but this made MS analysis of the CO evolution impossible and O₂/argon (20%) was blended with helium in subsequent experiments. A constant split to the MS was achieved by opening the bypass valve to give the same initial reading for the O₂ level at the start of each experiment. Target activation rates chosen were those which produced MS CO₂ signals of 50 mV above the baseline level. Activations were halted when the total area under this curve reached 5000 mV min. At the start of the gas concentration control experiments a 25 min delay was allowed for the sample to reach thermal equilibrium at the reaction temperature before blending was begun. At the end of each experiment the sample was weighed.

Surface areas and pore size distributions were measured on a commercial instrument (Omnisorp 100CX, Beckman Coulter) using N₂ as the adsorbate at -196 °C.

Results and Discussion

Early thermal control experiments indicated a linear relationship between the amount of CO₂ evolved and the % burn off, as determined gravimetrically. However, later work showed that this was only true at constant temperature due to the simultaneous evolution of CO. A typical reaction profile, showing O₂ uptake and CO₂ evolution, for air activation of carbon fibres under thermal control of the rate is in fig. 2. The actual rate of activation in terms of mass/min of carbon burnt off was calculated as follows for thermal control experiments from the total carbon lost and the related CO₂ peak area (see also fig. 2):

$$\text{as } \frac{\text{CO}_2 \text{ area}}{\text{total CO}_2 \text{ area}} = \frac{\text{mass lost}}{\text{total mass lost}}$$

$$\text{hence rate} = \frac{\text{CO}_2 \text{ area} \times \text{total mass lost}}{\text{total CO}_2 \text{ area} \times (t_2 - t_1)} \text{ mg / min}$$

The above method was also used to give an *average* burn off rate in the gas concentration experiments. CO₂ target levels and their equivalent reaction rates are given in table 1. Because the temperature during the constant rate

regime of thermal CR experiments did not vary greatly (ca. 490 °C, fig.2), the relationship between burn off rate and temperature of reaction was not apparent. However, the effect can be clearly seen for the rates under the gas concentration control (see table 1). Despite the constant rate of CO₂ evolution, the average burn off rate reached a maximum at 700 °C, and fell away thereafter.

This effect in the gas concentration experiments was accompanied by some interesting trends in the supplied O₂ and evolved gas (CO and CO₂) profiles (figs. 4-6) at temperatures of 500 - 800 °C, and the associated burn off and surface area figures (table 2).

At 500 °C, there was considerable breakthrough of O₂ (fig. 3) indicating relatively slow oxidation throughout the fibre bed, and rates of CO₂ and CO evolution were similar (figs. 4 and 5), both gases being involved in sample mass loss. It is probable that only CO₂ evolved from the carbon-oxygen surface reaction was responsible for the target CO₂ signal of 50 mV above baseline.

However, at 600 °C, whilst still in slight excess, (fig. 3) the O₂ supplied was also less (fig. 6) indicating that reaction was still required throughout the sample to achieve the target CO₂ level, but as expected, the reaction rate was higher. The CO evolution was raised, (fig. 5) making a greater contribution to the overall burn off.

At 700 °C, there was no breakthrough of O₂ (fig. 3) and furthermore, CO evolution was at its maximum level (fig. 5), indicating maximum mass loss (see table 2). In order to achieve the target rate of CO₂ evolution however, the supplied O₂ was higher than at 600 °C (fig. 6). This could be evidence for the onset of gas phase oxidation of CO (the auto ignition temperature is 605 °C) or secondary activation of the fibres by the evolved CO₂.

At 800 °C the level of CO actually detected was again at a minimum (fig. 5). This was probably due to a major contribution to the CO₂ target level from gas phase oxidation of CO and at this temperature, only part of the CO₂ target area was due to primary oxidation of carbon. This would also account for the observed decline in the carbon mass loss (see table 2).

The relationship between % burn off and the amount of CO evolved is illustrated in fig. 7, showing the decline after 700 °C (the CO₂ amount is constant, but not included).

The evolved gas profiles therefore reflected the complex mix of primary and secondary reactions of this system

and further experiments using CO as the evolved species to control the rate may provide further insight into some of these conflicting trends.

Inspection of the surface area data in table 2 indicated that for a given CO₂ target area (which has now been shown not to be related to % burn off if the temperature is not constant), the optimum activation was at 600 °C under gas concentration control which gave a surface area of 1531 m² g⁻¹ at a burn off of 54 %. The O₂ concentration for this experiment was approximately 9%. The associated isotherms in fig. 8 are typical of microporous solids obtained under more conventional activation regimes, with the 600 °C sample showing evidence of a widening of the micropore size distribution in the broader "knee" of the isotherm. Thermal control of the rate to the same evolved CO₂ peak area (5000 mV min) yielded activated fibres of surface area < 1000 m² g⁻¹.

It is significant that the most successful activation conditions were found to be where the O₂ was in slight excess, i.e. not rate limiting itself, and at a higher temperature than would be practical using thermal control due to thermal runaway.

Conclusions

Using CR techniques it was shown that microporous carbon fibres could be prepared using O₂ as the activating gas and that thermal runaway could be avoided. Higher surface areas could be obtained using reduced O₂ concentrations (compared to air) at higher temperature (600 °C) within a gas concentration regime. The alternative CR method of thermal control with air (i.e. 20 % O₂) and lower temperatures was slightly less effective.

References

1. Dawson EA, Parkes GMBP, Barnes PA, Chinn MJ Norman PR. A study of the activation of carbon using sample controlled thermal analysis. *J Therm Anal Cal* 1999;56:267-73.
2. Dawson EA, Parkes GMBP, Barnes PA, Chinn MJ Norman PR. Comparison of new thermal and reactant gas blending methods for the controlled oxidation of carbon. *Thermochim Acta* 1999;335:141-46.

Table 1. Conversion of CO₂ targets to actual rates of carbon burn off for (a) gas concentration and (b) thermal control

MS target 50 mV	(a) Gas concentration rate (average) / mg min ⁻¹				(b) Thermal rate /mg min ⁻¹
	500 °C	600 °C	700 °C	800 °C	0.9
	0.9	1.6	2.0	1.2	

Table 2. Effect of activation temperature during gas concentration control experiments in O₂/Ar - helium mixtures on % burn off and surface area

Furnace temperature / °C	% burn off	Surface area / m ² g ⁻¹
500	29	1344
600	54	1531
700	68	544
800	39	201

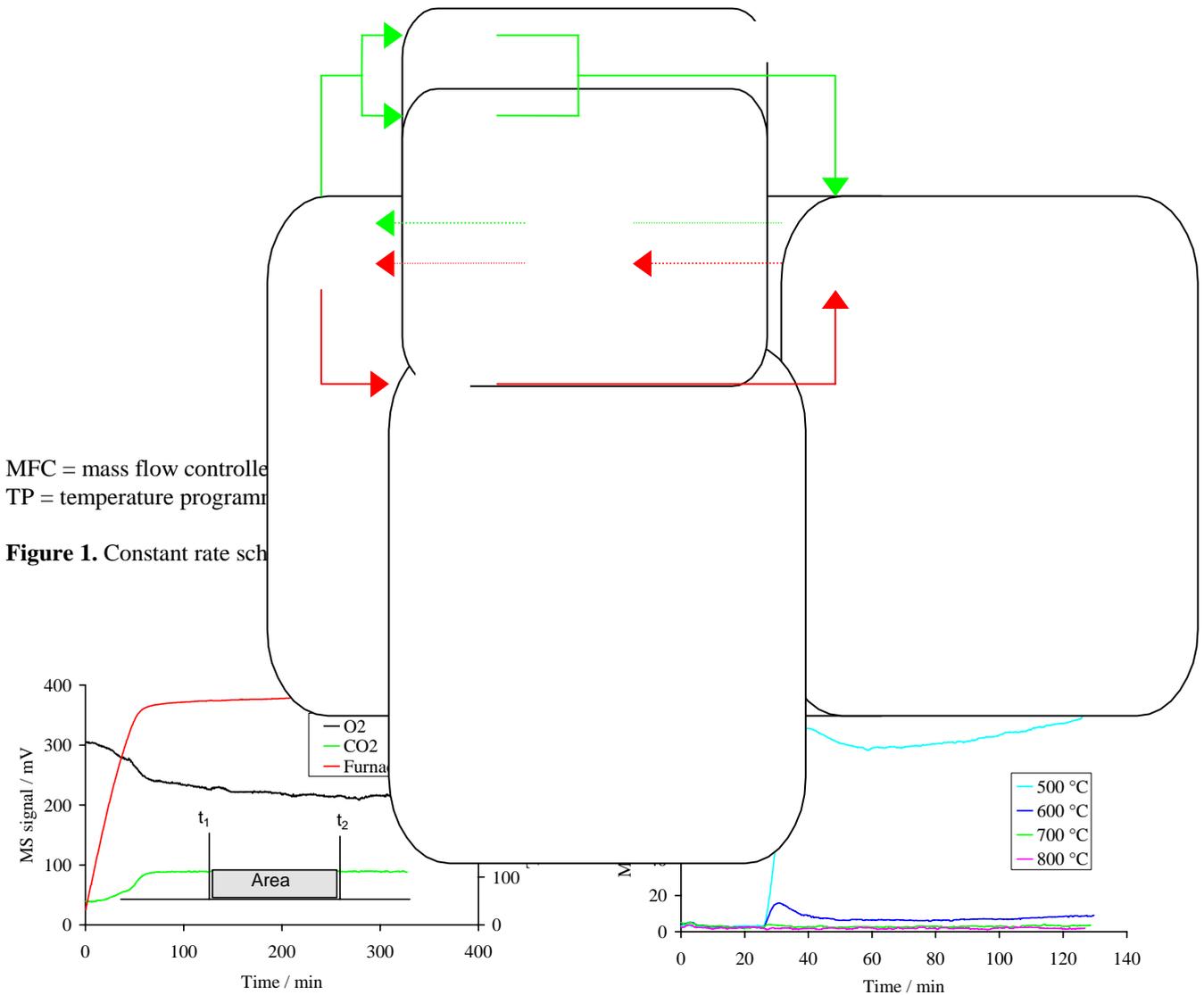


Figure 2. Reaction profile during thermal CR activation of carbon fibres in air: calculation of rate of burn off

Figure 3. O₂ breakthrough plots from gas concentration control experiments in O₂/Ar - helium blends

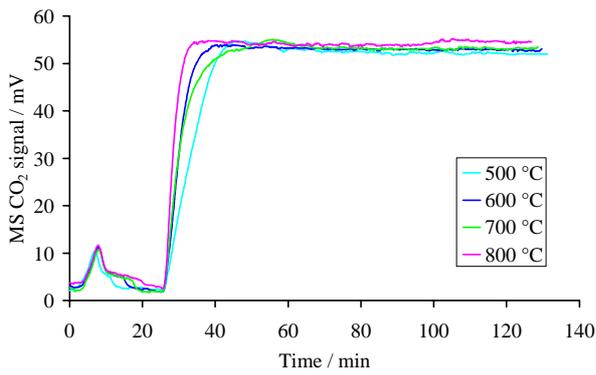


Figure 4. CO₂ evolution plots from gas concentration control experiments in O₂/Ar - helium blends

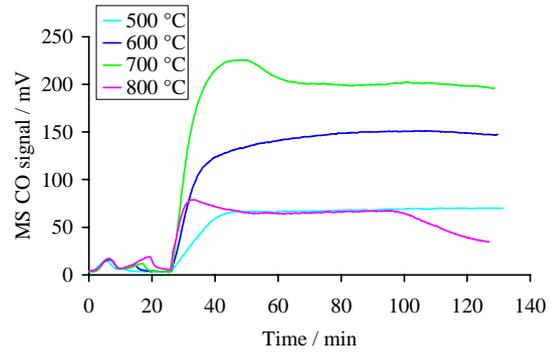


Figure 5. CO evolution plots from gas concentration control experiments in O₂/Ar - helium blends

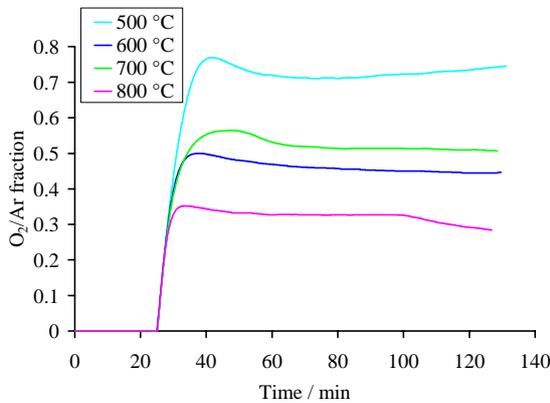


Figure 6. O₂ supply plots from gas concentration control experiments in O₂/Ar - helium blends

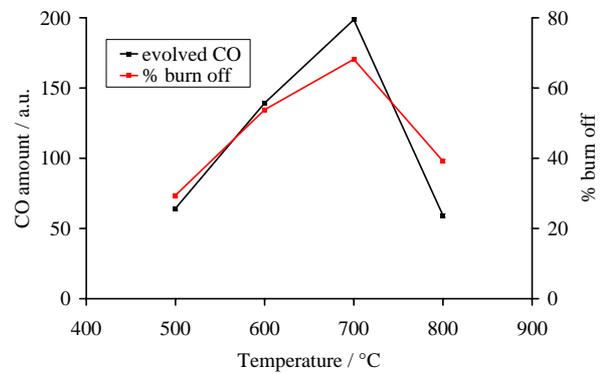


Figure 7. Effect of temperature on CO evolution and associated burn off

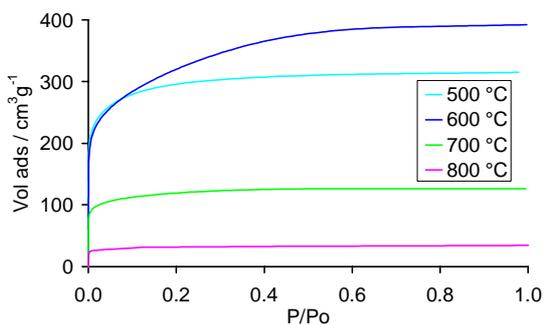


Figure 8. N₂ adsorption isotherms for carbon fibres activated at increasing temperature under gas concentration control CR