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Comparison of new thermal and reactant gas blending methods for the controlled oxidation of carbon

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Abstract

Two approaches to sample controlled thermal analysis (SCTA) used preparatively were contrasted using the air activation of a nutshell derived carbon. The rate of reaction, corresponding to the level of evolved carbon dioxide, was monitored using a quadrupole mass spectrometer and controlled via software using a feedback loop. In the first approach, control of the rate was achieved via temperature under a constant concentration of oxygen in nitrogen, while in the second the reactant gas concentration (oxygen/nitrogen ratio) was changed while the furnace was held isothermally. Due to the exothermic nature of the carbon–oxygen reaction, temperature control of the activation process at high reaction rates was difficult and produced oscillatory behaviour, while good control of the process could be achieved using the gas concentration method at higher reaction rates. By using oxygen rather than the more usual CO_2 or H_2O activation at 800–1000°C, the reaction takes place at 200–300°C with a consequent significant saving in energy costs. Published by Elsevier Science B.V.

Keywords: Carbon activation; Gasification; SCTA

1. Introduction

1.1. *Activation of carbon*

Activated carbons find many uses in fluid filtration due to their highly developed pore structure and large surface area, properties which make them good physical adsorbents. The surface area is developed after the carbonaceous precursor (nutshells, woodpulp, cellulose etc.) has been charred in an inert atmosphere to give a low surface area product. The carbon char is then activated at temperatures of 800–1000°C [1] in a mild oxidising atmosphere, usually steam or carbon dioxide (Equations (1) and (2)), where some of the carbon is slowly burnt off to give a porous material. Carbon gasification in air itself is not usually used [2] due to the exothermic nature of the reaction (Equations (3) and (4)) which can lead to thermal runaway and excessive burn off. The reactions with CO_2 and steam are endothermic [3] and are, therefore, generally considered much easier to perform despite the requirement to heat to a much higher temperature to drive the reaction.

$$C + CO_2 \rightarrow 2CO \quad \Delta H = +173\,\mathrm{kJ\,mol^{-1}} \qquad (1)$$

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = +132\,\mathrm{kJ\,mol^{-1}} \qquad (2)$$

$$C + \tfrac{1}{2}O_2 \rightarrow CO \quad \Delta H = -111\,\mathrm{kJ\,mol^{-1}} \qquad (3)$$

$$C + O_2 \rightarrow CO_2 \quad \Delta H = -395\,\mathrm{kJ\,mol^{-1}} \qquad (4)$$

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In addition to the preparation of activated carbon, there are other situations where it is necessary to consider carbon gasification reactions, including the regeneration of carbon adsorbent beds [4].

1.2. Sample controlled thermal analysis (SCTA)

Sample Controlled Thermal Analysis (SCTA) is the generic name given to a family of techniques where the heating rate is not pre-determined, but rather governed by some function of the measured reaction rate of the process being studied. One of the most important SCTA techniques is Constant Rate Thermal Analysis (CRTA) where the reaction is forced to proceed at a constant (and usually low) reaction rate. Adopting this approach has been demonstrated to improve resolution and provide enhanced kinetic information [5]. Normally control of the reaction rate is achieved by appropriate control of the temperature, but we have demonstrated that, for certain systems, controlling the concentration of a reactant gas (by blending with an inert carrier gas) under isothermal conditions can produce similar results [6]. We have developed these techniques for the preparation of materials by calcination, oxidation and reduction [7,8]. In this paper we adopt the term Constant Rate Gas Blending (CRGB) for experiments involving reactant gas concentration control to distinguish them from techniques which use temperature control.

Recently, we have demonstrated that CRTA can be used to control the activation of carbon in air, without thermal runaway, with the extent of carbon burn-off being selectable prior to the experiment [9]. In this paper, we compare and contrast the degree of control obtained with CRTA and CRGB for the air activation of a nutshell char performed at a range of rates of carbon burn off.

1.3. Control considerations in constant rate thermal analysis

In CRTA, maintaining a constant rate of reaction is achieved by suitable alterations of either the sample temperature or, for CRGB, the concentration of a reactant gas. This requires a *feedback loop* between the detector monitoring the reaction rate and either the furnace where the sample is situated, or the mass flow controllers regulating the blend of carrier and reactant gases. In our SCTA system, this feedback loop is implemented in software using a 3-term, PID control algorithm [10] which uses three terms, Proportional, Integral and Derivative, from which its name is derived. It takes as its input the difference (or *error*) between the *measured* value for a process and the *desired* value (called the setpoint). For a CRTA experiment this corresponds to the difference between the measured reaction rate and the pre-set target reaction rate. The output of the PID algorithm is continuously fed into the equipment which controls the measured value which, in the case of a CRTA experiment, would be the furnace temperature or for CRRGB the concentration of a reactant gas.

The output of the algorithm is given by the following equation:

$$\text{Output} = Pe_n + I\sum_{n=iw}^{n=0} e_n + D\frac{(e_n - e_{n-1}).}{(t_n - t_{n-1}).}$$

where e_n is the error for sample n, P is the proportional gain factor, I is the integral gain factor, D is the derivative gain factor, iw is the integral window and t is the time.

The proportional term is the most important and gives a value directly dependent on how close the measured value is to the desired value. The integral term sums the error over a given time period (set by the integral window) and is used to limit any continuing small 'undershoot' of the measured value which may occur. The value produced by the derivative term is dependent on the rate at which the measured value is approaching, or moving away from, the desired value and is used to limit any 'overshoot' caused if the measured value is approaching the desired value too rapidly.

Setting suitable values for the three gain factors can be difficult, as inappropriate values give rise to loss of control. However, in situations where the process is in near equilibrium and changes only very slowly, as is typically the case for most CRTA experiments, the situation is less critical and the proportional term becomes the most significant.

One assumption underlying the PID approach to control is that the process and the means by which it is controlled do not interact. For instance, in the case of a furnace controller the 'process' is the temperature and the means of control is the electrical power supplied to the furnace windings. For such a system no change in the furnace temperature, of itself, causes a further temperature change. However, this is not the case when controlling the rate of a reaction using temperature because the energetics of the process in question have to be considered. If a sample undergoes an exothermic process then increasing the reaction rate causes a corresponding rise in the sample temperature which in turn increases the reaction rate, potentially leading to thermal runaway. Such a system is inherently unstable and so difficult to control via alterations in an external temperature source such as a furnace. Normally, CRTA is used with low reaction rates and small sample masses and so the effects of enthalpy changes can be assumed to be minimal. However, once larger masses and/or faster reaction rates are used especially with highly exothermic reactions, this assumption may no longer be valid.

The alternative approach of controlling a process via the concentration of a reactant gas does not suffer from this drawback as it is self-limiting. For example, in the case of the thermal decomposition of calcium carbonate, any increase in reaction rate will give a corresponding rise in the partial pressure of the product gas, CO_2, which will tend to inhibit the reaction. In the case of oxidation processes a higher reaction rate will consume more of the reactant gas, so reducing its concentration and giving a stabilising negative feedback.

2. Experimental

2.1. Apparatus

We have previously described an apparatus, a modified form of which was developed for this study, for performing a variety of SCTA techniques using evolved gas analysis to monitor the rate of reaction [11]. The apparatus, the operation of which is shown schematically in Fig. 1, comprises a water-cooled tube furnace (model 761, Stanton Redcroft) in which is situated in a 6 mm diameter silica tube containing the sample. Nitrogen and air flows are set and controlled by two mass flow controllers (Brooks). Evolved gases from the sample are passed, via a heated capillary and bypass interface, to a quadrupole mass spectrometer (model HPR20, Hiden Analytical) set to monitor the desired mass/charge fragments. These values are transferred to an IBM compatible 166 MHz pentium PC (Viglen) running SCTA software developed by the authors. The data is processed and, for CRTA experiments, the furnace temperature altered as necessary during the thermal control experiments via a tempera-

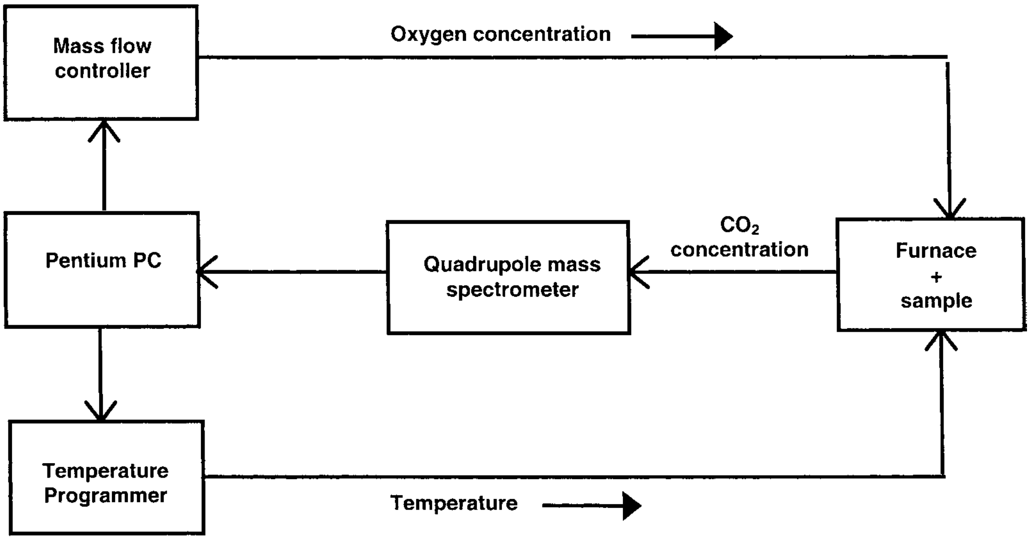

Fig. 1. Schematic diagram of the reaction rate control apparatus.

ture programmer (818P, Eurotherm) interfaced to the computer by an RS232C serial connection. The oxygen concentration is altered during the gas concentration experiments using the nitrogen and air mass flow controllers interfaced to the computer via a 2-channel, 12 bit, 5 V DAC.

Samples (500 mg) were heated in a U-shaped silica sample cell using a fixed total gas flow rate of 35.0 cm^3 min^{-1}. To ensure the mass spectrometer sampled exactly the same proportion of the effluent gas, the capillary inlet valve was adjusted so the reading for N_2 ($m/z = 28$) was the same at the start of each experiment. The sample was weighed at the end of the experiment and, to avoid complications due to diminishing sample size, the extent of burn off was limited to under 20%.

2.2. Materials

An unactivated nutshell char was sieved to obtain the 500–1000 μm fraction and stored in a desiccator. The gases used were nitrogen (O_2 free, BOC) and air (BOC).

2.3. Calibration of the mass spectrometer

A series of calibration experiments was performed by heating char samples isothermally in air and noting the relationship between the area of the CO_2 peak produced ($m/z = 44$) and the mass lost by the char. From this data a calibration graph was obtained, relating reaction rate (mg min^{-1} carbon burnt off) and mass spectrometer target CO_2 signal, as measured in mV above the baseline value. The plot was linear over the range of rates chosen, and had a correlation coefficient of 0.991, enabling reaction rates of the thermal and gas concentration experiments to be compared directly.

2.4. Constant rate thermal analysis experiments

A series of CRTA experiments was performed using a range of rates of CO_2 evolution corresponding to carbon burn-off rates of 0.15, 0.40, 0.75 and 1.05 mg min^{-1}. Adjustment was made to the capillary and bypass valve to the mass spectrometer with nitrogen flowing (see Section 2.1) to calibrate the response. The gas blend was then set to 100% air. Heating rates were allowed to vary between +10°C min^{-1} to −10°C % min^{-1} to achieve the desired reaction rate.

2.5. Constant rate gas blending experiments

A corresponding series of CRGB experiments was performed using a range of rates of CO_2 evolution corresponding to similar carbon burn-off rates (0.15, 0.35, 0.58, 0.81 and 1.05 mg min^{-1}). These experiments were performed at an isothermal temperature of 400°C, reached using a heating rate of 40°C min^{-1} from ambient, under 100% nitrogen. After a period of 20 min to allow thermal equilibrium to be reached, the oxygen concentration was altered to achieve the desired reaction rate by suitable blending of the air and nitrogen while maintaining a total flow rate of 35 cm^3 min^{-1}. The rate of blending was constrained between +4% min^{-1} to −4% min^{-1} of air in nitrogen.

3. Results and discussion

3.1. Constant rate thermal analysis experiments

It can be seen in Fig. 2 that thermal control of carbon gasification in air is possible in the lower reaction rate (0.15 and 0.4 mg min^{-1}) experiments, which achieved and maintained constant rates of CO_2 evolution. At the higher rate of 0.75 mg min^{-1} an initial oscillation in the rate was observed, which tended to die away with time. However, this oscillation was much greater at the maximum rate of 1.05 mg min^{-1} and it persisted throughout the experi-

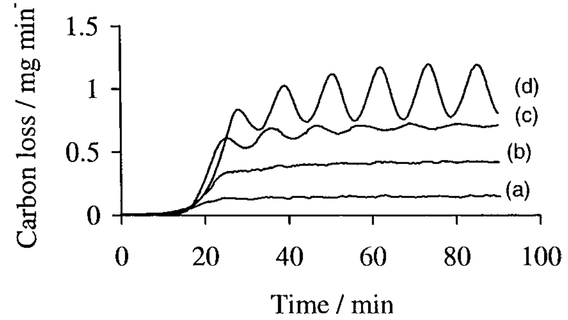

Fig. 2. Variation in the carbon burn off rate during the CRTA experiments at target rates of (a) 0.15, (b) 0.40, (c) 0.75, (d) 1.05 mg min^{-1}.

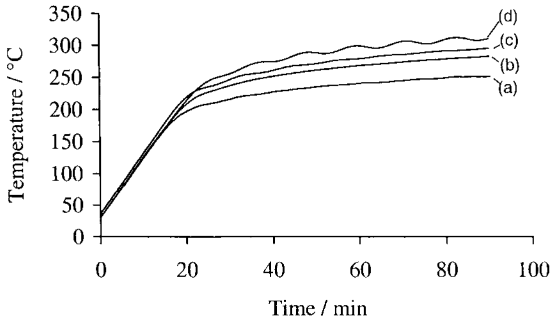

Fig. 3. Reaction temperatures during the CRTA experiments for increasing rates of carbon burn off (a) 0.15, (b) 0.40, (c) 0.75, (d) 1.05 mg min^{-1}.

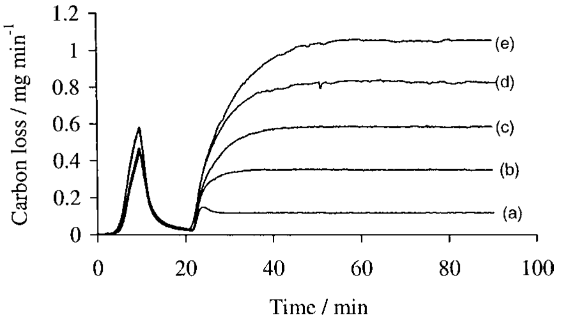

Fig. 4. Variation in the carbon burn off rate during the CRGB experiments at target rates of (a) 0.15, (b) 0.35, (c) 0.58, (d) 0.81, (e)1.05 mg min^{-1}.

ment, showing the difficulty of thermal control at higher reaction rates.

The corresponding temperature/time profiles for these experiments are shown in Fig. 3. Again, the highest rate profile shows a marked oscillation. This phenomenon is probably due to the exothermicity of the carbon–oxygen reaction, which at low rates does not cause a very significant temperature rise, so the furnace temperature does not have to fall in order to maintain the constant rate of CO_2 evolution. However, at higher rates, the temperature rise of the sample is greater and a thermal runaway effect begins. Now the furnace has to cool slightly to prevent an overshoot of the CO_2 target level. The thermal lag, which arises from the heat capacity of the system results in the CO_2 level falling below the target value causing the furnace temperature to rise again, thus setting up an oscillation in the temperature and rate profiles.

The slow net rise in temperature during all the experiments may be due to a combination of factors. The most active sites appear to react at about 200°C, but the temperature must rise continuously to enable the progressively less reactive sites to produce CO_2. Although burn off was restricted to <20%, loss of reactant may also be a factor. However, this must be set against the increase in carbon surface area as activation proceeds.

Although it may be possible to reduce or eliminate the observed oscillations by careful tuning of the PID parameters, this would require several repeated experiments to achieve and would only be applicable for a single rate of oxidation. This is because a different rate of oxidation would release more or less energy (in the form of heat) per unit time which, of itself, would affect the rate of the process thus requiring corresponding alterations in the control parameters. At very high reaction rates the process would release enough heat to cause thermal runaway (i.e. the carbon would ignite) and control via the temperature of an external furnace would become impossible.

3.2. *Constant rate gas blending experiments*

The CO_2 evolution profiles are shown in Fig. 4. The initial peak results from the thermal desorption of CO_2 as the sample is rapidly heated to 400°C under flowing nitrogen. This is not apparent in the thermal control experiments where it forms part of the CO_2 target level when heating is commenced under flowing air. The mean area of the peak is equivalent to 2.5 mg carbon and probably arises from the loss of carbon surface oxygen groups which are usually present in manufactured carbons stored in ambient conditions [12,13]. After ca. 20 min the rate of carbon loss begins to rise to the target CO_2 level as air is gradually blended into the gas stream. It can clearly be seen that even at the highest rate, control is good. The slight overshoot at the lowest rate may be due to the effect of dead volume in the system.

The concentration of O_2 supplied to the sample is shown in Fig. 5. This is the analogous plot to the temperature/time plot in Fig. 3. There is evidence of a slight fall in O_2 demand as the reaction proceeds at all but the lowest rate. Given that the reaction rate is also controlled by the number of active carbon sites avail-

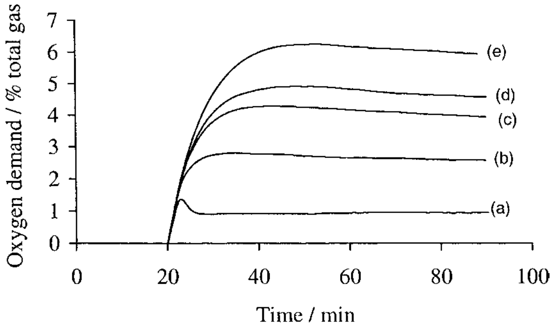

Fig. 5. Oxygen demand during the CRGB experiments for increasing rates of carbon burn off (a) 0.15, (b) 0.35, (c) 0.58, (d) 0.81, (e) 1.05 mg min^{-1}.

able, it could be that the increasing surface area during activation increases the number of sites for reaction, leading to more efficient utilisation of the oxygen.

4. Conclusions

In comparing the two types of control at similar rates of carbon burn off, it is apparent that it is easier to achieve a stable reaction rate by controlling the concentration of oxygen at a fixed higher temperature of 400°C, than controlling the temperature in the lower range of 200 to 300°C in a fixed higher concentration of oxygen (air).

In the case of the carbon–oxygen reaction, gas concentration control was effective at rates of carbon loss greater than 1 mg min^{-1} whereas thermal control was only achieved at rates of less than 0.4 mg min^{-1}. This demonstrates the inherent problems of attempting to control an exothermic process via the temperature of an external furnace, and the benefits of the reactant gas blending approach.

Regeneration of carbon adsorbent beds [4] could possibly be carried out in air at lower temperatures than the conventional methods and therefore, if the reactions can be adequately controlled, the benefits of a lower temperature would be seen in reduced energy costs and longer adsorbent life.

The experiments described here used relatively small samples of low thermal mass which were heated in a fast responding water-cooled furnace. If the process were to be scaled up (i.e. for carbon bed regeneration) both the increased mass of the material and that of the furnace would become limiting factors and sufficiently rapid heating or cooling to maintain controlled oxidation would be extremely difficult. In addition, the risk of thermal runaway would increase with the mass of the bed.

Scaling-up of the process would be simpler with the reactant gas blending approach. Here the effect of thermal mass would be of limited importance, and the response time of the furnace is irrelevant as the oxidation is carried out isothermally. Factors such as gas diffusion would need to be considered, but the risk of thermal runaway would be eliminated partly because of the self limiting effects of the reaction and partly due to the greater speed with which the gas concentration (rather than the furnace temperature) can be changed.

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