

AN INVESTIGATION OF HEATING RATE AND PRESSURE EFFECTS IN COAL PYROLYSIS AND HYDROPYROLYSIS

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INTRODUCTION

The high-pressure wire-mesh apparatus (perhaps best known from work by Anthony^{1,2} and Suuberg^{2,3} at MIT) allows a well-dispersed coal sample to be used, which minimises secondary effects and enables a wide range of heating rates to be applied. Generally, however, the heating rates that have been employed in high-pressure wire-mesh experiments have been limited to about 50 K/s and above by the relatively simple one- or two-stage, fixed-level heating systems that have been used, while the absence of any cooling to prevent reactor components overheating has limited maximum run times to about 30 seconds. In this study it has been possible to extend the investigation of the effects of pressure to heating rates as low as 5 K/s in a wire-mesh apparatus with a computerised feedback temperature control system. Water cooling has also been provided for the parts of the apparatus in contact with the heated sample holder, allowing holding times as long as 200 seconds at 600°C. Preliminary data from the apparatus is presented, showing the effect of heating rate on pyrolysis yields under inert gas pressure and the role of heating rate and holding time at temperature in hydroxyolysis reactions.

SAMPLE PREPARATION

The principal coal used in this study is Pittsburgh No. 8 from the Argonne Premium Coal Sample Program. A single 10 gram sample of -20 mesh coal was used for all experiments. All the sample was ground by hand in air, within about 30 minutes, to pass through a 150 micron sieve and then screened to +100 microns. Some supplementary data is also given for a UK bituminous coal, Linby. This was obtained as washed singles (25 mm sized coal) and was first crushed to approximately 6 mm by hand in air and then ground in a small hammer-mill and sieved to 100-150 microns in a glove-box under nitrogen. The sample used was sealed in a screw-top jar in the glove-box and stored for approximately 18 months in a domestic freezer before use; this had no detectable effect on the pyrolysis yields. Both coal samples were dried overnight under nitrogen at 105°C and stored under flowing nitrogen until required. The analysis of the Linby coal is given in Table I.

EXPERIMENTAL APPARATUS AND METHOD

The high pressure wire-mesh apparatus used in this study is shown in Fig. 1. The wire-mesh sample holder (1) is folded to contain the coal sample between two single layers of 65 micron AISI 304 stainless steel mesh. The sample holder, which also serves as an electrical resistance heater, is held between two electrode/clamps (2 and 3), one of which (3) is sprung to keep the sample holder taut when thermal expansion takes place. Beneath the sample holder is a water-cooled brass plate (4) with a 30 mm diameter hole in it below the working section where the coal sample is spread. A layer of amber mica (5), approximately 0.25 mm thick, electrically insulates the sample holder from the brass plate, while still allowing heat conduction. Another layer of mica (6)

is used to isolate the live electrode (2) which is connected to an insulated terminal (7). Cooling water travels through two hollow support pillars (8) connected to longitudinal holes in the brass plate (4) which communicate in turn with the hollow earthed electrode (3) through two 3.5 mm diameter stainless steel tubes (9), which also act as springs. The base of the pressure vessel (10), the top (11) and the clamping collar (12) are made from 316 stainless steel. The apparatus, with the electrode assembly in position, has been hydraulically tested to 300 bars, giving a 50% safety margin at the maximum pressurising gas cylinder pressure of 200 bars. The gas inlet (13) for helium or hydrogen is a compression fitting sealed with a taper thread in the base. A diffuser (14), consisting of approximately twenty layers of wire-mesh in a brass frame, is provided to break up the jet from the small-bore inlet. Other compression fittings are used for the gas outlet (15) at the top and a pressure tapping (16) in the base.

The regulator on the appropriate gas cylinder is used to set the internal gas pressure in the apparatus. This can be held within about ± 1.5 bars of the desired value, over a range of 20 to 170 bars. The gas flow rate is set by a pressure letdown/flow control valve on the outlet line from the reactor and measured, at atmospheric pressure, by a dry gas meter with an opto-electronic shaft encoder added in-house. By counting the encoder's output pulses on a microcomputer the average flow rate is calculated over ten second intervals.

A sample of 100-150 micron coal is placed in a pre-weighed sample holder which is then stretched between the electrodes. A suction nozzle is used to distribute the coal evenly in an approximately 12 mm diameter circle at the centre of the working section; the suction also serves to remove any particles which can pass through the mesh. The sample holder is then re-weighed to determine the sample size. After the sample holder is replaced in the apparatus two thermocouples are formed, at the edge and centre of the sample respectively, by inserting the thermocouple wires through holes in the mesh. This arrangement avoids distortion of the mesh by welding and, since the short length of mesh between the thermocouple wires is itself part of the thermocouple circuit, unambiguously locates the measuring junction on the surface of the sample holder. Before heating, the system is filled to 100 bars with the working gas and then emptied three times to remove air. The apparatus is then pressurised to the desired value and the flow control valve opened to set the required flow rate of 1 litre/min for every bar of internal pressure. After heating is completed the gas supply is shut off and the internal pressure allowed to come to atmospheric. If hydrogen has been used the apparatus is repressurised to 100 bars with helium and emptied again to avoid the risk of ignition when it is opened. Finally, after the thermocouple wires have been withdrawn, the sample holder is removed and weighed to establish the total volatile yield. Further details of the equipment and experimental methods are given elsewhere for this apparatus⁴ and a very similar wire-mesh reactor for atmospheric pressure and vacuum pyrolysis studies^{5,6}.

When the apparatus was conceived it was hoped to provide a forced sweep of gas through the sample holder, a technique that has been demonstrated successfully in this laboratory for atmospheric pressure operation^{5,6}. This would have given positive removal of the volatiles from the hot zone around the sample holder and allowed tars to be collected in an external trap. Unfortunately, even at 20 bars the cooling effect of gas flowing at only a few cm/s through the sample holder was found to be so intense that uniform temperatures could not be maintained and, because very high power inputs therefore had to be applied, even slight deviations in the local cooling effect could cause severe

overheating and melting of the sample holder material. After extensive trials with various gas flow arrangements the best that could be achieved was to provide a diffuse flow of gas upwards from the base of the vessel at a volumetric flow rate (at the internal pressure) of 1 litre/min. This provides some entrainment of the products and also relieves expansion on heating.

In order to observe the flow patterns and to see whether yields differed from other atmospheric pressure results with a forced sweep gas flow, Linby coal was pyrolysed in helium at atmospheric pressure with the diffuse flow. The high-pressure apparatus was used, but with the steel top replaced by a glass top of similar dimensions. As Fig. 2 shows, the absence of the forced sweep caused only a small reduction in total volatile yields and, since tars could be seen to be recirculated back onto the sample holder by natural convection currents, this reduction was probably due more to secondary re-deposition of the volatiles rather than to a significant increase in the surface mass transfer resistance. Some discolouration of the working section of the sample holder was also observed, which tends to confirm this, but when high pressure hydrogen is used no visible deposit is formed on the sample holder. Any tars which touch the surface apparently crack to form lighter volatiles rather than char. As discussed later, however, a direct test of the effect of sweep velocity at pressure would be desirable.

Even with the diffuse flow regime, heat losses by convection from the sample holder are very large: at 70 bars the power input must be increased approximately five-fold compared to atmospheric pressure operation to hold the temperature steady at the same value and the ratio between convective and other heat losses, which is roughly 1:1 at atmospheric pressure, then rises to about 9:1. With convection so dominant, only slight variations in the gas flow are needed to cause significant (up to about ± 50 K) fluctuations in the local temperature of the sample holder. Although the computer feedback control system can usually hold the average of the readings from the two thermocouples within 20 K or less of the desired value, the instantaneous difference between the individual readings is determined solely by the unsteady physical conditions inside the reactor. Similar fluctuations in temperature at high pressures (measured with a single thermocouple) are reported by Anthony¹, despite the use of an insulated baffle below his sample holder to reduce circulation currents. The temperature fluctuations have a time-scale of the order of 0.2 seconds, so to give reasonably representative time-averages for the peak temperature (rather than a possibly misleading instantaneous value) a significantly longer holding period at peak temperature is generally used. The fluctuations do, however, limit the precision with which the effective transition between a slow-heating stage and a rapid-heating stage can be located, since the control system must be set to start rapid heating when the instantaneous control temperature (i.e., the average of the two thermocouple readings) reaches a specified value.

RESULTS AND DISCUSSION

In order to give the effect of hydrogen pressure on primary coal pyrolysis reactions the greatest possible weighting compared to char hydrogasification reactions a peak temperature of 600°C is used in most of the results presented here. Atmospheric-pressure data obtained in this laboratory for Pittsburgh No. 8^{3,6} and Linby⁴ coals suggest that, for holding times in excess of about 5 seconds, this temperature is high enough for the bulk of the thermally-induced primary breakdown reactions to run to completion. A longer hold time,

10 seconds, was chosen to allow for a possible increase in resistance to volatile transport at elevated pressure, and as Fig. 3 for Linby coal shows, even at 100 bars this appears to give an adequate margin for thermally initiated breakdown reactions. As data presented below (Fig. 7) shows, the hydrogasification reactions carry on for a much longer period. With the standard conditions selected, the effect of heating rate on pyrolysis yields for Pittsburgh No. 8 in hydrogen and helium at 70 bars (1000 psig) was investigated. The results (presented in Fig. 4) showed that at 70 bars the yields in helium appear to be unchanged or to decrease slightly, while yields in hydrogen show a very pronounced fall, from about 52% of the daf sample at 5 K/s to around 47% at 1000 K/s.

Although more data over a range of temperatures and pressures, as well as at lower heating rates, is required to allow firm conclusions to be drawn, the level or slight downward trend with increased heating rate in helium at 70 bars is of interest because previous studies in this laboratory^{5,6} have shown an opposite effect of heating rate in helium at atmospheric pressure, with tar being the main product affected. It was suspected at the time (partly because vacuum pyrolysis showed an even greater sensitivity to heating rate) that tar transport was being enhanced due to the greater sample plasticity and more rapid outward flow of volatiles at high heating rates. While observations suggest that plasticity, if anything, increases with pressure, the volume of the volatile products and hence the rapidity of their outward flow must be reduced by the applied pressure, which may account for the observed equality between fast and slow heating at 70 bars in inert gas.

In addition, the helium results can be regarded as a base-line for the hydrolysis data, showing the purely physical effect of the applied gas pressure. The yield at 5 K/s must then reflect a greater degree of chemical interaction between the hydrogen and the coal, but it cannot be deduced from Fig. 4 whether this is due to hydrogen promoting yields during the initial, rapid volatile release stage of pyrolysis or simply more char gasification occurring in the longer time available (ie. during heating, since hold times are identical) at the slower heating rate.

To investigate the temperature range over which hydrogen was enhancing yields at 5 K/s, two-stage heating was used. The sample holder was heated at 5 K/s to the required intermediate temperature and then immediately heated at 1000 K/s to 600°C and held there for 10 seconds. The results, shown in Fig. 5, suggest that varying the heating rate between 5 K/s and 1000 K/s will have no effect below about 500°C. As discussed earlier, precise resolution of the intermediate temperature is difficult, but it appears likely that there is a gradual transition to the higher yield above 500°C. If the effect had been observed at lower temperatures, before significant amounts of volatiles were evolved, it might have been possible to rule out hydrogasification reactions, but Fig. 6 shows that appreciable amounts of devolatilisation will have taken place by 500°C even at 1000 K/s and differentiation between enhanced primary pyrolysis and hydrogasification is therefore not feasible.

To attempt to distinguish between a possible beneficial effect of a lower heating rate in the later stages of the initial, rapid pyrolysis reactions and more extensive char gasification in the extra 20 seconds available between 500°C and 600°C, the total volatile yields as a function of holding time after 5 K/s and 1000 K/s heating were measured. If it was simply that extra time for hydrogasification is available at 5 K/s then presumably this difference would become less significant at longer holding times and the two sets of data would

converge to the same asymptotic value. In fact, as Fig. 7 shows, while the differences do become less significant at longer hold times, even when yields superficially seem to have reached an asymptotic value at 200 seconds there is still an offset of about 2% of the daf sample.

It is tempting to ascribe the additional 2% of material that apparently can be volatilised by reducing the heating rate from 1000 K/s to 5 K/s to increased interaction between hydrogen and the pyrolysing mass; stabilisation of the heavy tar precursors remaining as the melt start to coke could be a feasible mechanism. The magnitude of the difference is, however, well within the likely experimental scatter and a more detailed study would be needed to allow such a definite conclusion. It would also be possible to explain the apparent trends if slower heating produced a more reactive char, unless the extra products could be analysed and shown not to be able to come from char gasification reactions; more detailed product distribution data, including tar/liquid yields, would be needed for this.

Finally, in all the experiments some coked residue from fluid material that had been evolved from the coal particles could be seen. This was much more noticeable for runs in helium, when globules of charred liquid residue covered large areas of the outer faces of the mesh adjacent to the sample. Hydrogen appears to be giving a higher volatile yield as a result of chemical removal of some of this material, probably before charring takes place. While a sweep flow has been shown to be relatively unimportant at atmospheric pressure and flow rates up to 0.3 m/s, the visible availability of un-removed liquid material suggests that a gas sweep, perhaps at a higher flow, might be able to increase volatile yields by promoting evaporation and possibly entrainment.

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TABLE I Linby Coal: Proximate and Ultimate Analyses

----- % dry basis -----							
VM	FC	Ash	C	H	O	N	S
36	60	4.0	77.8	5.1	10.1	1.6	1.4

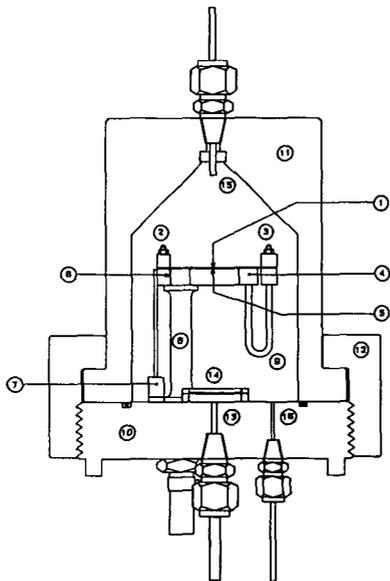


Fig. 1 High pressure wire-mesh apparatus.

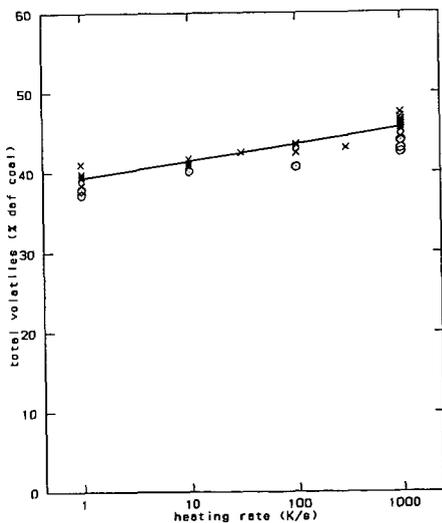


Fig. 2 Effect of 'diffuse flow' regime on total volatile yields from Linby coal heated to 700 deg.C with 30 seconds hold, in helium at 1.2 bars.
x, D.1-0.3 m/s sweep.
o, diffuse flow.

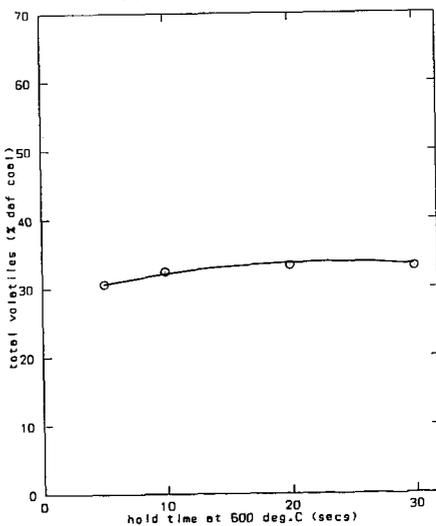


Fig. 3 Effect of hold time at 600 deg.C on volatile yields from Linby coal heated at 625 K/s in helium at 100 bars, diffuse flow.

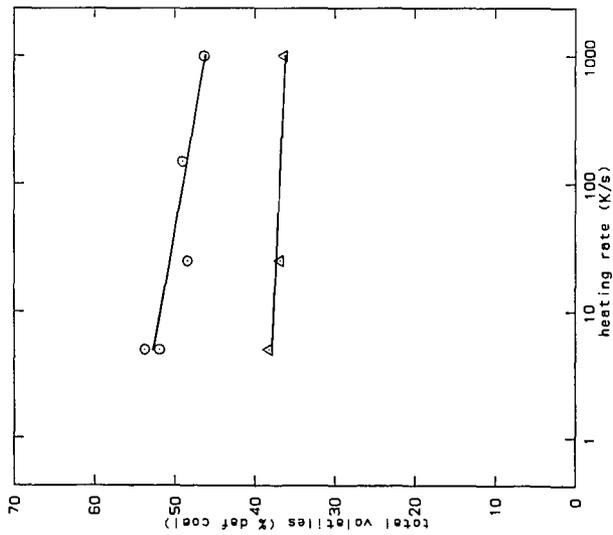


Fig. 4 Effect of heating rate on total volatile yields from Pittsburgh #8 at 70 bars with diffuse flow.
 O, 600 deg.C, 10 s hold, hydrogen.
 Δ, 600 deg.C, 10 s hold, helium.

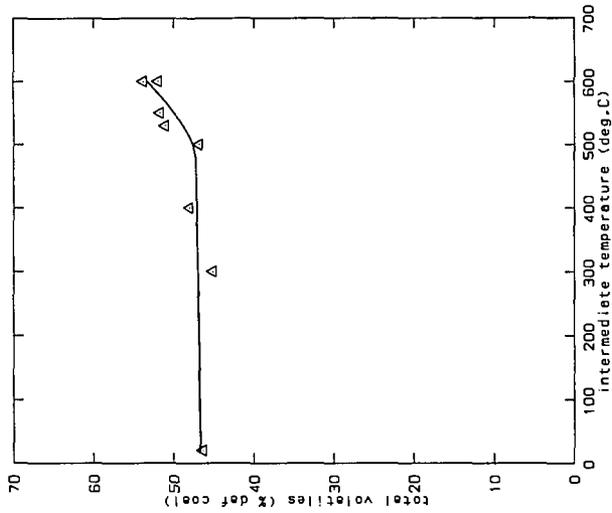


Fig. 5 Effect of intermediate temperature between 5 K/s and 1000 K/s heating on total volatile yields from Pittsburgh #8 in hydrogen at 70 bars.
 Final temperature 600 deg.C, hold time 10 s.

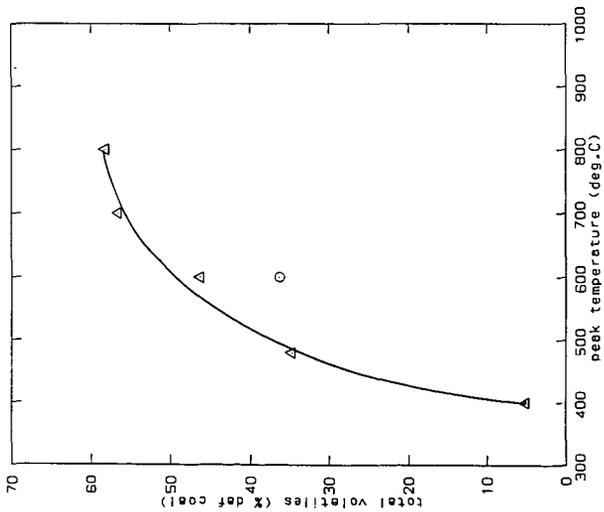


Fig. 5 Effect of peak temperature on total volatile yields from Pittsburgh #8 at 70 bars.
 Δ, 1000 K/s, 10 s hold, hydrogen, diffuse flow.
 O, 1000 K/s, 10 s hold, helium, diffuse flow.

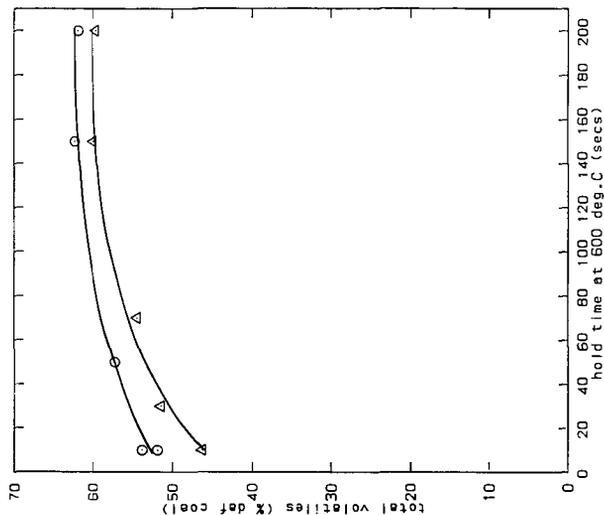


Fig. 7 Effect of hold time at 600 deg.C on total volatile yields from Pittsburgh #8 in hydrogen at 70 bars with diffuse flow.
 Δ, 1000 K/s heating; O, 5 K/s heating.