

THE EFFECT OF HEATING RATE AND HOLD TIME ON PRIMARY COAL PYROLYSIS PRODUCT DISTRIBUTION

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Introduction

The study of primary pyrolysis reactions in coals is complicated by the number of secondary effects that must be considered. In particular, secondary volatile-cracking reactions are likely to occur with most pyrolysis techniques for low heating rates (eg. Fischer Assay, Gray-King, thermobalance), which use a relatively large coal sample and allow the volatiles to remain in the heated zone for extended periods. A well-dispersed sample of fine coal must, however, be used to achieve high heating rates (eg. as in a fluidised bed or wire-mesh reactor). This has made it impossible to determine whether the increases in volatile yields noted in many fast heating rate studies (probably the best-known of which is the work by Howard and associates at MIT using a wire-mesh apparatus (1)) were due entirely to a reduction in secondary char-forming reactions, or were at least in part an effect of the heating rate itself. The MIT apparatus used a pulse of direct current to heat the sample holder and the lowest heating rate that could be obtained was about 100 K/s; in any case slow heating experiments might also have been affected by secondary reactions, because volatile products were allowed to circulate freely in the same vessel as the hot wire-mesh. Both of these problems have been addressed, though not always together, in subsequent studies (eg. 2,3,4,5,6), but a systematic examination of the effect of time/temperature history under conditions where secondary reactions would be at a minimum appears to be lacking. It was therefore proposed to construct a wire-mesh apparatus which could cover virtually any time/temperature history and provide for rapid removal of volatile products as part of a study on fundamentals of coal pyrolysis and hydropyrolysis funded by the UK Science and Engineering Research Council (GR/D/06582). Although work has concentrated on British coals, the wealth of published data available for US coals made it essential to test some of these for comparison. These trials, with samples from the Argonne Premium Coal (APC) Sample programme, have shown a general increase in volatile yield with heating rate that does not appear to be due to secondary effects. This suggests that more complex interactions occur in pyrolysis than has sometimes been considered.

Sample preparation

To avoid loss of particles through the wire-mesh sample holder all coals were screened to 100-150 microns. The Pittsburgh#8, Illinois#6 and Pocahontas#3 samples were all obtained as -100 mesh and were screened without further treatment. The Wyoming subbituminous sample was originally -20 mesh and was ground gently by hand in air to all pass through a 150 micron sieve. After screening, coals were dried overnight at 105°C in a nitrogen-purged oven and stored under nitrogen until required. A large amount of fines had to be rejected from all the original samples; this would seem to be a general problem for any experiment requiring sieved coal as it may result in selective enrichment with certain petrographic constituents. An agreement to establish standard sub-fractions of sized coal would be welcome.

Apparatus and experimental procedure

principal features of the apparatus, shown in Fig.1, are a sweep gas flow through the wire-mesh sample holder and a feedback temperature control system using alternating current. The sweep gas, helium flowing at 0.1 m/s, gives a mean volatile residence time within the sample holder of less than 2 ms. Five to ten milligrams of coal are spread in a 12 mm diameter circle at the centre of the sample holder, less than monolayer loading. The sample temperature is defined as the average from two chromel/alumel thermocouples, at the centre and approximately 1mm from the edge of the coal sample, formed from wires inserted through the mesh. Typically, temperatures across the sample are within 20 K of the average and the average is less than 10 K (or 20ms in time at high heating rates) from the target control value. Tar can be caught in a pre-weighed sinter trap cooled with liquid nitrogen which is then heated to 50°C for 30 minutes in air and re-weighed. More details of the apparatus will be available elsewhere (7).

Results and discussion

Fig.2 shows variations with peak temperature in total volatile yields from Pittsburgh#8 coal at 1000 K/s and 1 K/s with zero hold time, and at 1000 K/s with 30 seconds hold time. The reactor geometry, gas flow rate etc. are identical for all runs. With zero hold time, volatile yields for the two heating rates follow different trends, and the higher heating rate yield is below that for slow heating up to about 700°C, after which the 1 K/s yield reaches a plateau at about 42% while the 1000 K/s yield continues to rise to about 48% at 950°C. It could thus be concluded that increasing the heating rate would give either lower or higher yields depending on the peak temperature. At 30 seconds' hold, however, the volatile yields for the two heating rates follow similar trends, and the higher heating rate gives greater weight losses at all temperatures above 400°C. This suggests that provided pyrolysis reactions are allowed to run to completion higher heating rates give higher primary volatile yields.

Runs with Pittsburgh#8 at 1,10,100 and 1000 K/s to 700°C with 30 seconds' hold using tar trapping, plotted in Fig.3, confirm the trend of higher volatile yields with faster heating and indicate that the rise in total volatile yields is due mainly to an increase in tar production. Such differences might be caused by more rapid removal of tar by gas entrainment at the higher heating rates, leaving less time for char-forming reactions. Experiments under vacuum at 1 K/s and 1000 K/s to 700°C were therefore made, with the expectation that if evaporation was a limiting step at low heating rates the 1 K/s yield would increase by more than the 1000 K/s yield. In fact the opposite was observed: the 1 K/s volatile yield increased by about 2% while the 1000 K/s yield went up by about 4%. Under vacuum the 1000 K/s samples swelled much less, suggesting that some plasticising/swelling agent was being removed. The 1 K/s samples never swelled, but were fused. It was also considered that slow heating might be allowing time for slight oxidation of the sample by adsorbed gases, or even the trace of oxygen (less than 2 vpm) in the helium gas supply, and that this enhances subsequent tar-precursor polymerisation reactions. Trials on a UK coal indicate, however, that pyrolysis yields at both high and low heating rates are not sensitive to the level of trace oxygen in the sweep gas.

Comparison with published data for Pittsburgh#8 coal (1,4,8), mostly for 1000 K/s and zero hold, showed that while the maximum volatile yields above 800°C were comparable, reported variations in yield with

temperature fell both above and below the zero hold line in Fig.2. Since the cooling rate in these previous experiments varied from about 10^2 to 10^4 K/s its effect was examined but, as Fig.4 shows, at 600°C yields are not sensitive to cooling rate above 100 K/s. Subsequent experiments demonstrated that the hold time at 600°C is an important factor, however, and the results in Fig.5 show that one second suffices for almost complete devolatilisation. This, together with the steepness of the Fig.2 1000 K/s zero hold curve around 600°C , suggests that experimental variations in the time that the coal is held at 600°C or above are more important than the length of time spent at lower temperatures during cooling. Uncertainties in temperature measurement are possible in cases where, to avoid interference from the heating current, the thermocouple had to be electrically isolated from the sample holder (1) or the junction placed away from the surface (4). The local effect of the thermal inertia of the coal sample itself, reported by Freihaut and Seery (8), could also lead to the temperature being overestimated by perhaps as much as 100°C if the loading near the thermocouple was not representative. As far as possible these errors have been minimised in this apparatus since the sample holder is part of the thermocouple circuits and the coal sample is held around the thermocouples. The temperature of the coal is not, and cannot, be measured directly, however, nor can variations in temperature away from the thermocouples be detected, so experimental scatter can still be significant in regions where yield is a sensitive function of temperature. This is not the case for the conditions used to establish the effect of heating rate as Fig.2 shows, and it is therefore unlikely that errors in temperature measurement could be responsible.

Volatile yields from Illinois#6 and Wyoming subbituminous coals were also found to increase with heating rate, but the yield from the Pocahontas#3 sample showed little or no variation. Results for heating rates between 1 and 1000 K/s are shown in Fig.6.

Conclusions

When secondary effects are minimised, an increase in heating rate from 1 to 10^5 K/s will increase pyrolysis yields from a number of coal types provided that sufficient time is allowed at peak temperatures. The extra volatiles are mainly tars, suggesting either a reduction in polymerisation reactions among tar precursors and/or an increase in tar precursor production due to a greater concentration of reactive species within the coal mass. One coal tested showed little or no effect of heating rate, however, and this, together with the absence of more abrupt variations in volatile yields with heating rate for the other coals, probably means that only a portion of the potential volatile-forming pathways in coals are being affected.

References

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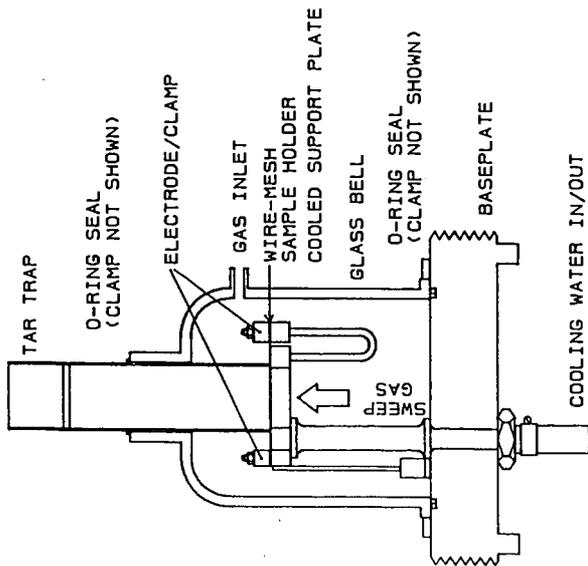


FIG. 1 WIRE-MESH APPARATUS

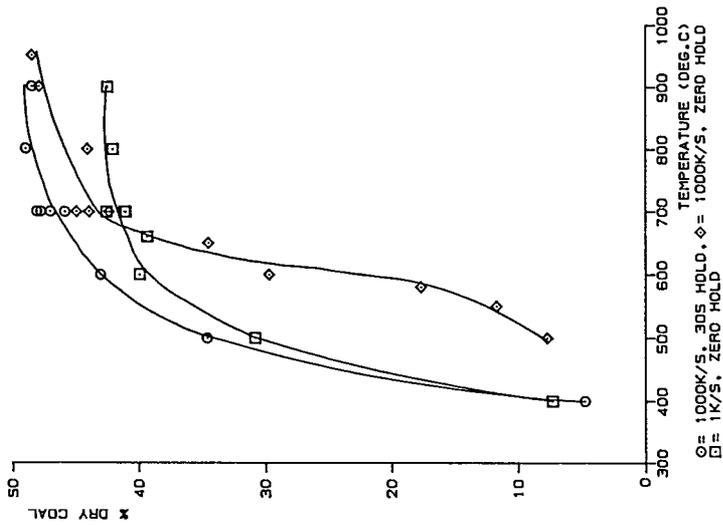


FIG. 2 PYROLYSIS YIELDS FROM PITTSBURGH#8
EFFECT OF TIME/TEMPERATURE HISTORY

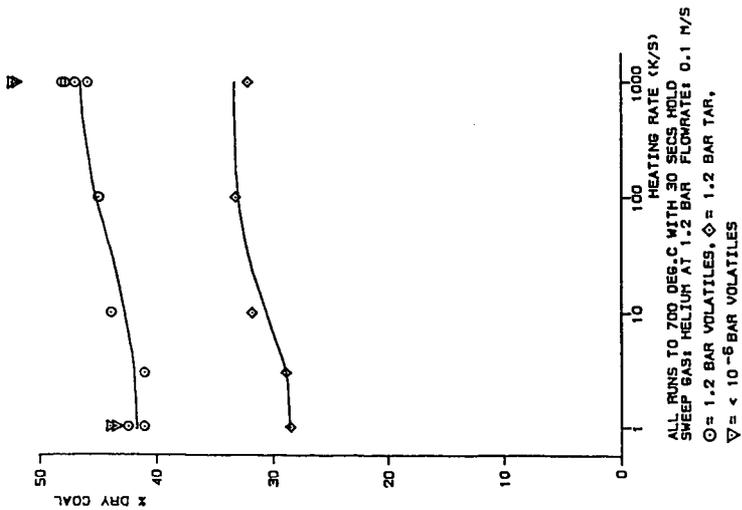


FIG. 3 PYROLYSIS YIELDS FROM PITTSBURGH#8
EFFECT OF HEATING RATE AND PRESSURE

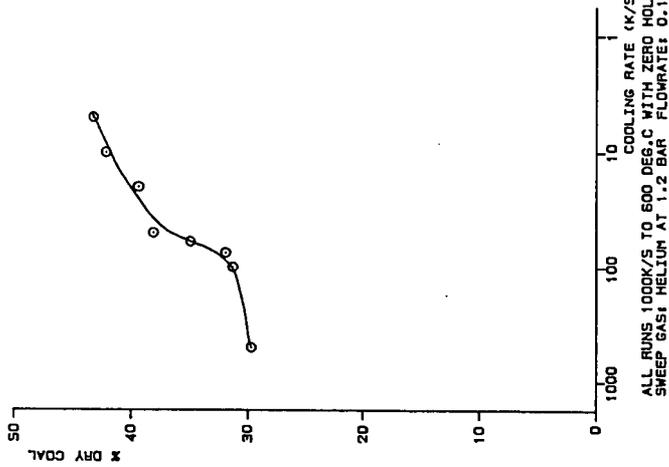
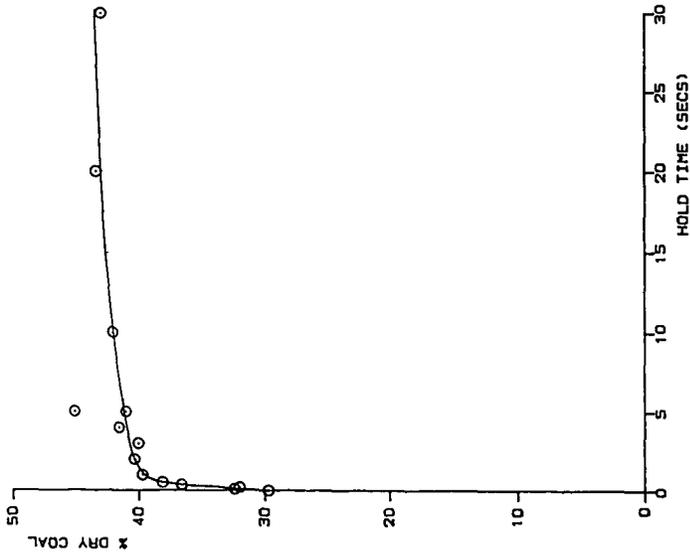
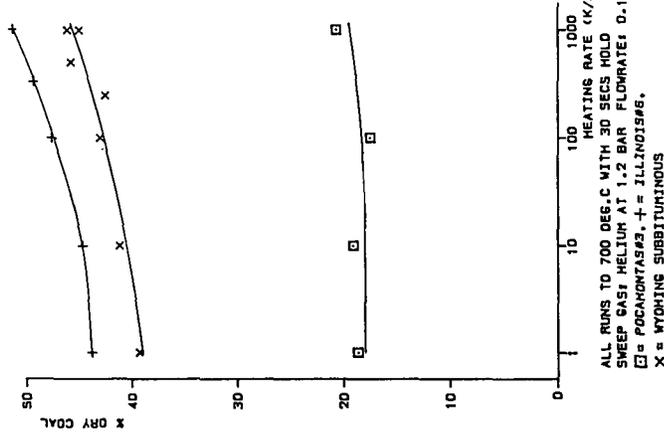


FIG. 4 PYROLYSIS YIELDS FROM PITTSBURGH#8
EFFECT OF COOLING RATE FROM 600 °C



HEATING RATE 1000K/S, COOLING RATE 500K/S APPROX.
 SWEEP GAS: HELIUM AT 1.2 BAR FLOWRATE: 0.1 M³/S
FIG.5 PYROLYSIS YIELDS FROM PITTSBURGH#8
EFFECT OF HOLD TIME AT 600 DEG.C



ALL RUNS TO 700 DEG.C WITH 30 SECS HOLD
 SWEEP GAS: HELIUM AT 1.2 BAR FLOWRATE: 0.1 M³/S
FIG.6 EFFECT OF HEATING RATE ON VOLATILE YIELDS
FROM ARGONNE PREMIUM COAL SAMPLES
 □ = POCAHONTAS#3, + = ILLINOIS#6,
 X = WYOMING SUBBITUMINOUS