

## EFFECT OF COAL PARTICLE SIZE ON VOLATILE YIELDS DURING RAPID HEATING

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### INTRODUCTION

Typically a wide range of particle sizes, with mean diameters between about 10 and 300  $\mu\text{m}$ , are present in feed coal streams to entrained flow combustion and gasification processes. The magnitude of any variation in volatile yield with particle size over this range is therefore relevant for computer modelling of such processes, and possibly specification of an optimum feed particle size distribution. The result will also affect the validity of coal characterisation measurements, made on a sample with a limited size range, for predicting the behaviour of a real coal feed.

Mass transport effects should result in a monotonic increase in volatile yields during rapid heating with decreasing particle size, due to the progressive reduction in retrograde char-forming reactions as the residence time of the nascent volatiles within the particles is reduced. In practice, however, the magnitude of such mass transfer effects may be difficult to measure in isolation. One possible source of interference is the differences in heating rate which will also occur between different-sized particles in tests in entrained flow reactors, another is the difficulty in obtaining different size cuts of a coal with identical mineral and maceral composition. The basic tendency will be for finer fractions to become enriched with the more friable constituents of the coal. Less uniform effects may result, however, from the behaviour of intrinsically-homogenous sub-components of a coal (e.g. fossil spores<sup>1</sup>). These may be released virtually intact from the coal matrix by grinding, but are then resistant to further comminution.

Since a captive-sample wire-mesh reactor was used in the present study, differences in heating rate between different size cuts were not considered to be a problem. Under the test conditions used (1000 K/s heating to 950°C) all of the samples softened in the early stages of heating, ensuring good heat transfer between the mesh and the sample. The temperature of the mesh in the area where the sample was distributed was computer-controlled to give typically better than  $\pm 20$  K compliance with the desired value.

To allow for the effect of compositional differences between size cuts a number of approaches were used in the present study.

- (a) The ash content of size fractions was measured and data reported on a daf basis to avoid interference from mineral enrichment.
- (b) Maceral analyses were performed to identify whether or not maceral enrichment had occurred during grinding.
- (c) A second grinding step, using the top size fraction tested as the starting material instead of the raw coal, was used to give more homogenous samples (see below for more details).
- (d) A vitrain sample with essentially homogenous (>90% vitrinite) starting composition, and thus largely immune to maceral enrichment effects, was also tested.

## EXPERIMENTAL

### Coal preparation

Samples of two U.K. bituminous coals (Daw Mill, type 802, and Kellingley, type 602) and one hand-picked Shirebrook Blackshale vitrain sample (>90% vitrinite) were obtained in lump form from British Coal's Technical Services and Research Executive (TSRE) at Bretby. The Pittsburgh No. 8 sample from the Argonne Premium Coal Sample programme<sup>2</sup> was also used.

The lump coal samples were ground to all <150µm using a Fritsch Pulverisette II motorised grinder with frequent sieving to remove undersize material. The Pittsburgh No. 8 was ground by hand. The ground coal was screened to produce the following size fractions: <38 µm, 38-53 µm, 53-75 µm, 75-106 µm and 106-150 µm. The mass distributions from this first grinding process are shown in Table 1.

For the coals (which showed significant maceral enrichment effects) a second grinding stage was also used. The 150-106µm size fraction was divided into four equal sub-samples, using a Microscal spinning riffler. Three of these sub-samples were subsequently reground to all pass through 53, 75 and 106 µm respectively, and then screened to give 38-53µm, 53-75 µm and 75-106 µm size cuts.

All samples were dried overnight in a nitrogen-purged oven at 105 °C and then stored under nitrogen until required.

### Sample analysis

Small samples of each of the coal fractions (approx. 0.5g) were mounted in a fast-setting 'Buehler Epo-thin' low viscosity resin. After polishing, maceral compositions were observed by examination under a light microscope. To obtain quantitative maceral data, 500 point counts were made on each sample.

Because of the limited amounts of sample available, a thermogravimetric analyser (TGA - Stanton Redcroft Model TG-780) was used to measure ash contents. Approx. 10 mg samples were heated at 30 °C min<sup>-1</sup> to 900 °C in N<sub>2</sub>/air.

### Wire-mesh apparatus

A version of the wire-mesh reactor previously developed at Imperial College<sup>3,4</sup> was used for devolatilization experiments. This incorporates a computer-based temperature control system, with a two-colour pyrometer for temperature measurements. All experiments were undertaken with a flowing helium sweep gas at atmospheric pressure and using a heating rate of 1000 K/s to 950°C, with 10 s hold at peak temperature. Previous work<sup>5</sup> has shown that volatile yields are insensitive to experimental variations in heating rate, temperature or hold time under these conditions.

The sample holder was made from folded AISI 304 stainless steel mesh (25 µm wires x 32 µm aperture). A 5-10 mg coal sample was spread within a 15 mm diameter circle at the centre of the sample holder, and total volatile yields were measured by direct weighing before and after experiments.

## RESULTS AND DISCUSSION

Total volatile yields and ash, vitrinite, liptinite and inertinite contents for the sized fractions of the coals from the first and second grinding stages and the vitrain are shown in Figs 1-4. Data points are included for the daf volatiles values to indicate the experimental scatter in the data, with lines drawn through the average values. Points are also shown for other quantities if only limited information is available.

Considering first the volatile yields on a dry basis for the 'first grind' size fractions of the coals, it is interesting to note that there appears to be relatively little effect of particle size. Thus, although differences in the grinding methods used make definitive general conclusions impossible, the results in Figs 1-3 do suggest that overall volatile release per unit mass from the different size fractions may be roughly constant under actual plant conditions (before any heating rate effects are taken into account).

Inspection of the ash contents for the coal size fractions shows, however, that this apparent invariance in dry volatile yields is the result of two opposing trends rather than of an underlying uniformity in coal behaviour! In line with previous findings<sup>6</sup> the ash contents of the size fractions generally increase with decreasing size. This then tends to counteract the general trend for an increase in volatile release from the organic constituents of the coal with decreasing size, as shown in the daf yields for the first grind size fractions.

Volatile yields on a daf basis from the first grind size fractions were not observed to increase monotonically, however, suggesting that a simple reduction in mass transfer resistance was not the only factor involved. This supposition is confirmed by the variation in maceral analysis between size fractions, although some allowance must be made for scatter in the maceral data (particularly at the smaller particle sizes when edge effects become more common with the point counting techniques used). No clear general trends for maceral enrichment emerge from the (somewhat limited) data presented, however, beyond a probable decrease in liptinite content for the smaller size fractions.

The significance of changes in maceral composition can be inferred from the results of previous work on maceral concentrates<sup>7</sup>. For similar UK coals and under similar experimental conditions, it was estimated that volatile yields from 'pure' vitrinite, liptinite and inertinite were of the order of 40%, 80% and 30% daf respectively. It was also found that in maceral mixtures (including whole coals and different maceral concentrates obtained by density separation), the contribution of individual maceral components to overall yields were simply additive.

In an attempt to allow the effect of mass transfer to be examined with less interference from maceral enrichment effects, a similar set of size fractions was prepared using the 106-150  $\mu\text{m}$  fraction from the first grind, instead of the raw coal, as the starting material. This method was at least partly successful. For the UK coals, ash levels in the samples are relatively constant and, particularly for the Kellingley samples, the overall trend in maceral levels is roughly level. Significant differences still exist in maceral contents for the Daw Mill coal, although the changes are now monotonic. The latter trends perhaps reflect more homogeneity within the individual maceral groups than occurred in the original coal, coupled with grindability differences. The limited data for the Pittsburgh No. 8 sample showed little effect of maceral enrichment in the second grind, but a much more pronounced, monotonic increase in ash content with decreasing particle size. Overall the second grinding strategy can probably be regarded as at least partly successful, in that monotonic changes in daf volatile yields with changing particle size were observed for these samples.

The effect of mass transfer is still not easy to resolve, however, from the second grind daf volatile data. For the Kellingley and Pittsburgh samples volatile yields increased with decreasing particle size, in line with expectations. For the Daw Mill samples no increase was observed, despite maceral changes that suggest that an increase in volatile yield should result even in the absence of any mass transfer effects.

Data from the vitrain samples, shown in Fig. 4, supports the existence of a small mass transfer effect. Two sets of samples were used, obtained by sieving after grinding to all pass 150  $\mu\text{m}$  and 300  $\mu\text{m}$  respectively. Because of the high vitrinite concentration in the original vitrain it was expected that maceral enrichment would not occur during grinding, although there is some evidence for slight enrichment in the limited data obtained. Interestingly, even with the small ash content of the original sample, high levels of ash enrichment occurred in the smaller size fractions from the -300  $\mu\text{m}$  grind. Nonetheless, daf volatile yields from the two sets of samples agreed closely in the overlapping region, despite the significantly different preparation procedures used, suggesting that maceral enrichment was not a major problem.

#### CONCLUSIONS

When interference from mineral and maceral enrichment effects was minimised, small increases in daf volatile yields for rapid heating have been observed with decreasing particle size. This is likely to result from reduced resistance to volatiles mass transfer within the smaller particles. Volatile yield increases varied from nearly zero to 8 percentage points between the 100-150  $\mu\text{m}$  and 38-53  $\mu\text{m}$  size fractions.

In practice, selective mineral and maceral enrichment of different size fractions is very difficult to prevent. Without special preparation procedures these enrichment effects can swamp any effect of changing mass transfer resistance.

In ground samples prepared from whole coals selective enrichment effects probably tend to offset mass transfer effects. Because of this, the simplifying assumption of invariant volatile yields with particle size, often made in combustion and gasification models, appears to be reasonably valid.

The unavoidability of maceral enrichment effects imposes a limit on the accuracy with which a characteristic rapid-heating volatile yield for a whole coal can be measured if, as is often the case, the test method used (e.g. wire-mesh, entrained flow reactor) requires a sample with a restricted size range. The present study indicates a potential uncertainty of about  $\pm 3$  percentage points in indicated daf values. More representative measurements are likely to be obtained if the test sample is prepared by grinding all of the original coal to pass the top size required, instead of screening the test sample out of a grind with some wider size distribution.

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Table 1 Mass distributions from first grinding process

Coal	Size fraction, $\mu\text{m}$ (wt.%)				
	150-106	106-75	75-53	53-38	<38
Daw Mill	18.8	19.2	18.2	11.8	32.0
Kellingley	15.8	60.2	19.2	4.8	n/a
Pittsburgh #8	12.6	17.0	16.1	10.3	44.0
SB vitrain	26.2	22.0	17.1	22.5	12.2

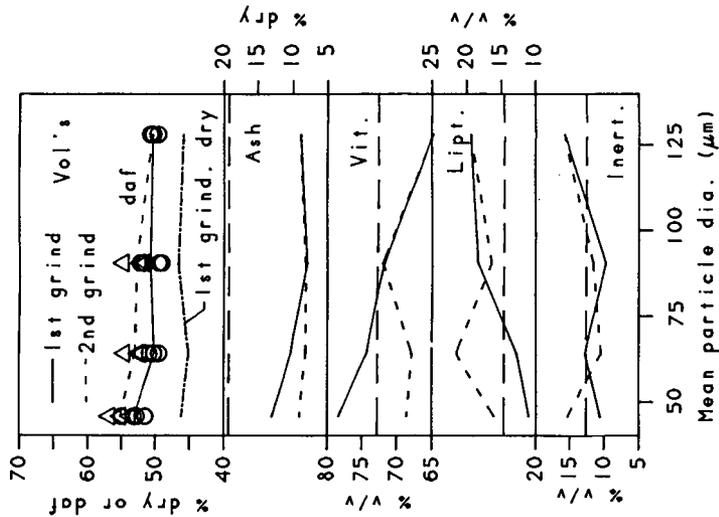


Fig. 1 Daw Mill coal - variation in volatile yields and mineral and maceral enrichment with size fraction.

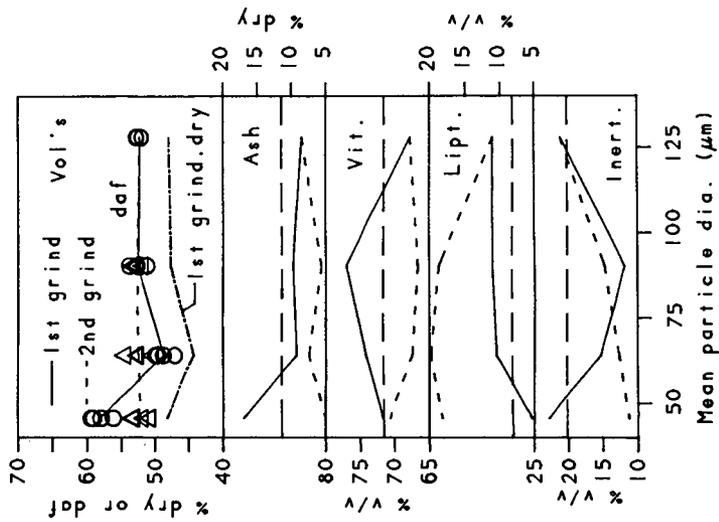


Fig. 2 Kellingley coal - variation in volatile yields and mineral and maceral enrichment with size fraction.

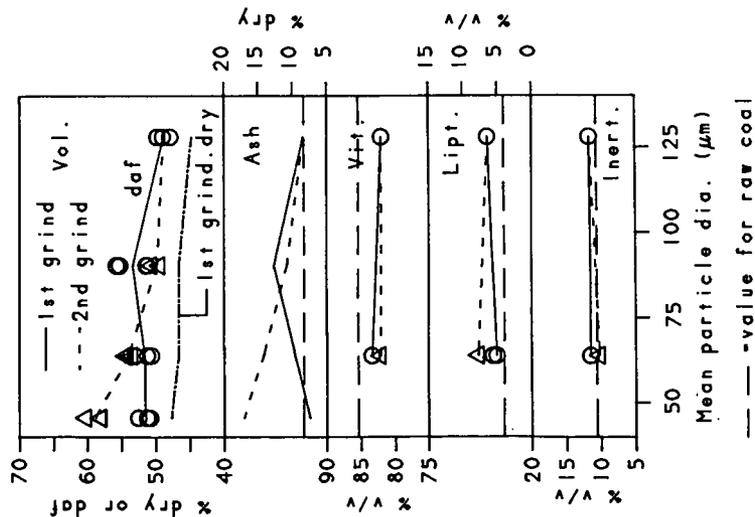


Fig. 3 Pittsburgh No. 8 coal - variation in volatile yields and maceral enrichment with size fraction.

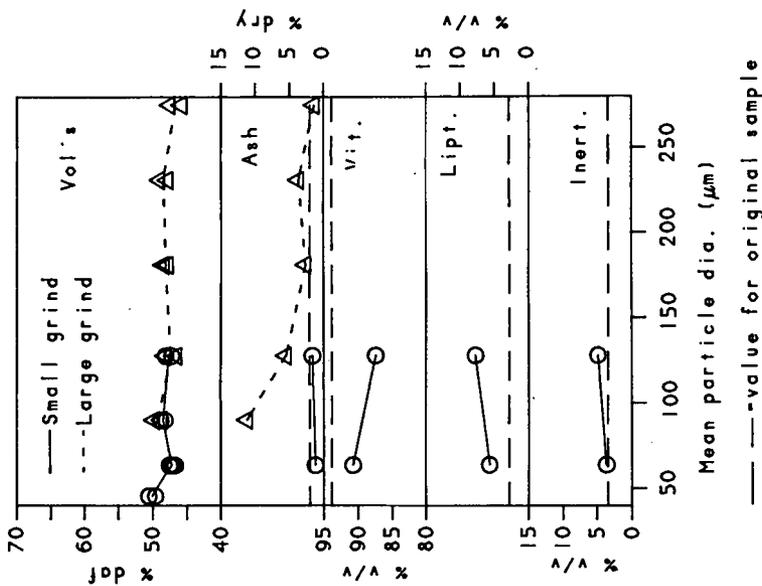


Fig. 4 Shirebrook Blackstone vitrain - variation in volatile yields and maceral enrichment with size fraction.