

THE EVOLUTION OF FUEL NITROGEN DURING RAPID COAL DEVOLATILIZATION

C. K. Man, K. J. Pendlebury and J. R. Gibbins,
Mechanical Engineering Department, Imperial College, London SW7 2BX

INTRODUCTION

Significant reductions in emissions of NO_x from pulverised fuel (PF) combustion have been achieved by low- NO_x burners employing air staging to ensure that coal volatiles are burnt under fuel-rich, reducing conditions. Almost complete suppression of NO_x formation from volatile nitrogen has been reported¹ for air-staged low- NO_x burners. Air-staging alone cannot, however, reduce the formation of oxides of nitrogen contained in the char residue during its subsequent heterogeneous combustion. The char will typically contain around 50% of the nitrogen in the coal and 10-30% of this may be converted to NO_x ^{1,2}. Techniques to reduce overall emissions of NO_x beyond this limit are available (e.g. fuel staging/reburning, SCR and SNCR) but these will incur additional installation and operating costs².

Because of its relevance for the performance of air-staged low- NO_x burners the pattern of nitrogen release from coals, and in particular the volatile/char nitrogen split, has received considerable attention. It is now well-known that conventional proximate analysis tests based on relatively slow heating of a bulk coal sample in a crucible do not give either accurate total volatile yields or nitrogen release data for devolatilization in PF combustion, where well-dispersed coal is heated rapidly (approx. 10^5 K/s) to high temperatures (approx. 1500°C).

To obtain better nitrogen release data for PF combustion, bench-scale tests based on rapid heating of coal entrained in a laminar (e.g.³) or turbulent (e.g.¹) stream of gas have been widely used. Entrained-flow tests have the advantage that heating rates and peak temperatures similar to those encountered in PF combustion can be attained, although residence times are generally limited to 1 s or less by the length of the reactors. Total volatile yields, however, usually have to be estimated using ash-tracer methods. This can introduce some uncertainty into the estimation of the total volatile yield, and hence also nitrogen release, particularly for coals with a low ash content. Entrained flow reactor studies (i.e. at high heating rates and short residence times) have generally indicated that the fraction of the coal nitrogen in the volatiles is close to the total volatile yield fraction for a wide range of final temperatures (e.g. ^{1,3,4,5}).

Wire-mesh reactors, in which the sample is held between two layers of woven wire mesh that act as an electrical resistance heater, have also been used to study the evolution of nitrogen during rapid heating. Typically samples of 5 mg or greater can be handled, sufficient for direct weighing measurement of the total volatile yield and 'conventional' micro elemental analysis of the chars. In general, heating rates (typically 10^3 - 10^4 K/s) and, more seriously, peak temperatures (usually $<1100^\circ\text{C}$) have been below values for PF combustion. Extended isothermal hold times can be used, however, with suitable reactor design. Maximum temperatures are limited mainly by the decreasing mechanical strength of the mesh material as it approaches its melting point. For the stainless steel meshes used in virtually all studies to date this limit is reached in the region of 1100°C , although workers at United Technologies Research Centre⁶ have demonstrated that higher temperatures (up to 1800°C) can be achieved with molybdenum or tungsten meshes. In the UTRC study Freihaut and Seery observed that, for a constant total run time of 10 s and a heating rate of 500-1000 K/s, at temperatures up to 1100°C the fraction of coal nitrogen volatilized was roughly equal to the total volatiles fraction but at higher temperatures there was 'a substantial increase in nitrogen evolution as HCN' with little accompanying weight loss. Nitrogen retention at high temperatures was found to be a function of rank, with higher rank coal chars retaining more.

Comparison of experimental measurements for nitrogen release in the entrained flow

and wire-mesh reactors thus suggests (in agreement with a theoretical analysis of earlier data⁷) that at temperatures of interest for PF combustion the hold time has a significant effect, while at lower temperatures the amounts evolved are insensitive to holding time. As a preliminary stage in an investigation of high-intensity coal devolatilization it was therefore decided to employ a recently-developed wire-mesh reactor with computerised temperature control, and capable of using molybdenum mesh for high-temperature experiments, to obtain more detailed measurements of the effect of holding time (and other key parameters) on nitrogen release. This information might also indicate whether or not any significant reduction in char N content (and hence subsequent char NO_x production) could be obtained from further devolatilization at elevated temperatures over timescales not achievable in present furnaces (i.e. >1 s) but perhaps feasible for specially designed systems.

EXPERIMENTAL

A rank series of two UK and a US bituminous coal was used, from low to high rank: Daw Mill (UK type 802), Kellingley (UK type 602) and Pittsburgh No. 8 (UK type 402, US HVB). The particle size range for all experiments, 150-180 μ m, was determined by the molybdenum mesh available. The Daw Mill (N 1.4% daf - analysis for prepared sample) and Kellingley (N 1.8% daf) were obtained as lump coal and ground to size in air in a motorised pestle and mortar with frequent sieving to remove undersize material. The Pittsburgh No. 8 (N 1.7% daf), from the Argonne Premium Coal Sample bank, was ground by hand. All samples were dried at 105°C overnight in a nitrogen-purged oven and stored under flowing nitrogen until used.

A modified version of the wire-mesh reactor previously developed at Imperial College⁹ was used for devolatilization experiments. The main changes in the design were the addition of a two-colour pyrometer for high-temperature measurement and a higher-current (400 A) AC power supply system. A diagram of the apparatus is shown in Fig. 1. All experiments were conducted in flowing helium at atmospheric pressure. Stainless steel mesh (AISI 304, 36 μ m wires x 63 μ m aperture) was used for runs up to 1000°C, molybdenum mesh (71 μ m wires x 140 μ m aperture) for runs at higher temperatures. Comparisons of results at 1000°C showed no significant differences between the two meshes. Total volatile yields were measured by direct weighing of the wire-mesh sample holder before and after experiments. The coal loading was 8-10 mg, spread within a 15 mm diameter circle at the centre of the sample holder.

Nitrogen contents of coals and chars were measured using a Carlo Erba elemental analyzer. Sample masses used for analysis were 0.5-0.9 mg, allowing duplicate runs in most cases on the char residue from a single wire-mesh experiment. Typically pairs of measurements (subsequently averaged) agreed within ± 0.05 percentage points. Volatile nitrogen yields were calculated by difference, from the char yields and coal and char nitrogen contents.

RESULTS AND DISCUSSION

The effect of peak temperature on total volatile and volatile nitrogen yields for heating rates of 10 K/s and 1000 K/s is shown in Fig. 2 (Daw Mill), Fig. 3 (Kellingley) and Fig. 4 (Pittsburgh No. 8, to 1000°C only). As expected, for 1000 K/s heating with zero hold time the total volatiles and volatile nitrogen values followed similar trends with temperature across the range 400°C to 1400°C.

At 10 K/s (approximately the same heating rate as the proximate VM test) total volatile yields were slightly reduced compared to the 1000 K/s data (in line with previous studies⁹) but volatile nitrogen yields were proportionally lower for both of the UK coals while for the Pittsburgh No.8 they appeared to be slightly higher. To investigate the effect of heating rate in more detail yields were measured over the range 10-4000 K/s to a final temperature of 1000°C (Figs 5-7) with a hold time of 10 s to ensure that the primary pyrolysis reactions had time to run to completion⁹. This confirmed a progressive reduction in evolved nitrogen with

decreasing heating rate for the two UK coals, but no clear trends emerged for the Pittsburgh No. 8, with any changes in yields being within experimental scatter. Overall, the effect of heating rate on nitrogen evolution appeared to decrease with increasing coal rank.

The effect of heating rate on nitrogen yields is tentatively attributed to differences in tar release, since it is well-known that the bulk of nitrogen evolved in the primary volatiles is contained in the tars⁶ and it has also been shown that it is mainly the tar yield that is affected by changes in heating rate⁹. The apparent variation with rank may then reflect the relatively lower thermal stability of (nitrogen-containing) low-rank tar precursors, which have a greater opportunity to undergo retrograde char-forming reactions during the longer periods between formation and subsequent evolution from the pyrolysing coal as tar that occur at the lower heating rate. The results confirm the inadequacy of the proximate volatile test for characterising nitrogen release under rapid-heating conditions.

Also shown in Figs 2 and 3 are total volatile and nitrogen yields for 1000 K/s heating to 1000-1400°C with 10 s hold time at peak temperature. For both coals, at 1000°C and 1200°C the total volatiles and volatile nitrogen yields with 10 s hold were virtually identical to the zero hold values. At 1400°C with 10 s hold, however, although the total volatiles were observed to increase only slightly there was a marked increase in the evolved nitrogen, in agreement with the previous observations by Freihaut and Seery⁶. The sensitivity to hold time at 1400°C is demonstrated in more detail by Figs 8 and 9, with total volatile yields unaffected by hold times up to 10 s, but nitrogen evolution progressively increasing.

The effect on the total volatiles/volatile nitrogen ratio of this enhanced loss of nitrogen at elevated temperatures is shown in Figs 10 and 11. The transition from the zero hold through intermediate holds to the 10 s values parallels differences between zero and extended hold time results from earlier studies, but obtained using a range of reactor types (e.g. ^{1,3,5,6,7}). Since the same reactor was used for all conditions in this study, however, the differences observed can be attributed entirely to the effect of hold time.

The demonstrated effects of heating rate and hold time at realistic PF combustion temperatures on nitrogen release point to the need to match the conditions in the combustor more closely for char/volatile nitrogen distribution measurements than, for example, for total volatile yield measurements. The relatively rapid initial decline in char nitrogen at 1400°C shown in Fig. 9 also suggests that a reduction in char nitrogen, and hence char NO_x formation, might be feasible with appropriate combustor design.

CONCLUSIONS

The sensitivity of coal nitrogen evolution to heating rate, final temperature and isothermal hold time during devolatilization has been investigated using a computer-controlled wire-mesh apparatus which allows these parameters to be varied independently without the need to change reactor type. The main conclusions, which agree with trends expected on the basis of previous studies are:

- (a) with zero hold time at peak temperature the fraction of coal nitrogen volatilized during rapid (1000 K/s) heating was directly proportional to total volatile yields for all temperatures up to 1400°C
- (b) with extended hold times (10s, up to 100s at 1000°C) at peak temperature the same correspondence was observed at up to 1200°C, but at 1400°C a progressive increase in nitrogen evolution occurred with longer hold times
- (c) volatile nitrogen yields from two lower-rank bituminous coals were also observed to decrease as the heating rate was reduced from 4000 K/s to 10 K/s,

but there was no significant effect of heating rate on yields from a higher-rank bituminous coal.

(d) volatile nitrogen yields exhibit greater sensitivity to experimental conditions than total volatile yields.

ACKNOWLEDGEMENTS

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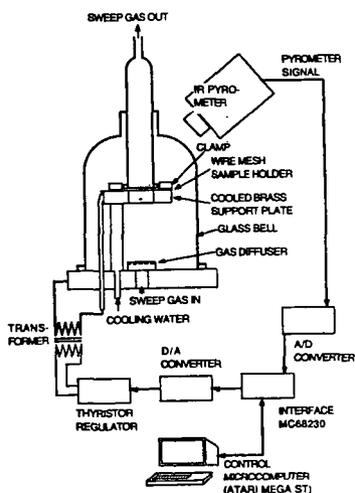


Fig. 1 Wire mesh apparatus

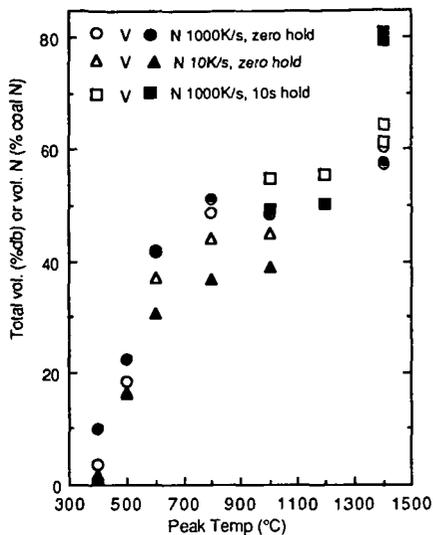


Fig. 2 Effect of peak temperature on yields from Daw Mill coal

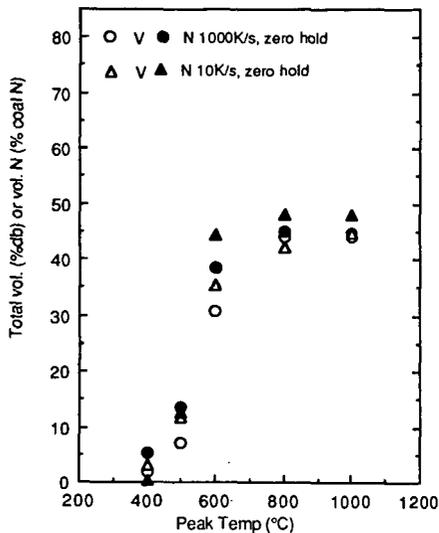


Fig. 4 Effect of peak temperature on yields from Pittsburgh No. 8 coal

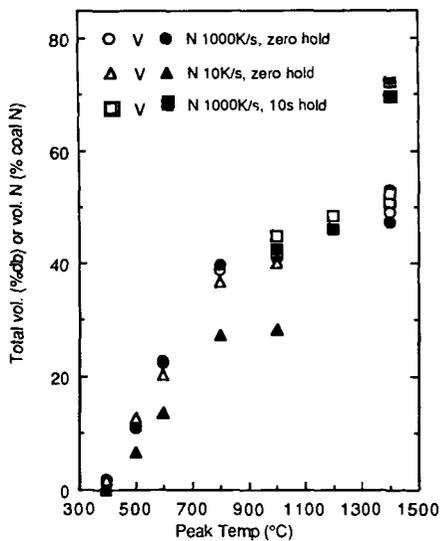


Fig. 3 Effect of peak temperature on yields from Kellingley coal

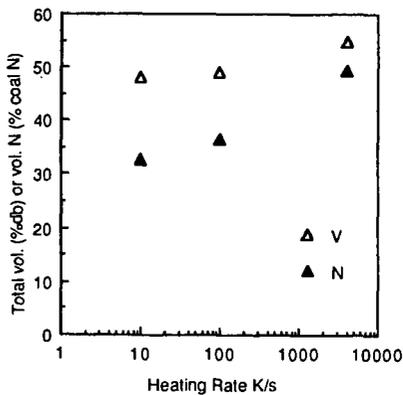


Fig. 5 Effect of heating rate on yields from Daw Mill coal

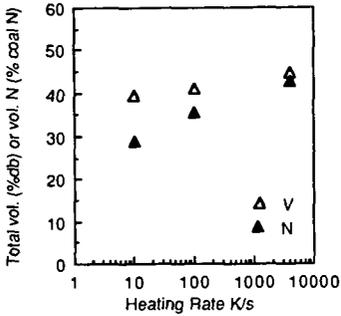


Fig. 6 Effect of heating rate on yields from Kellingley coal

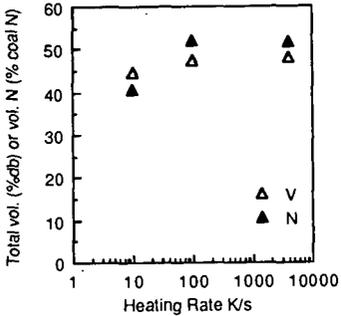


Fig. 7 Effect of heating rate on yields from Pittsburgh No.8 coal

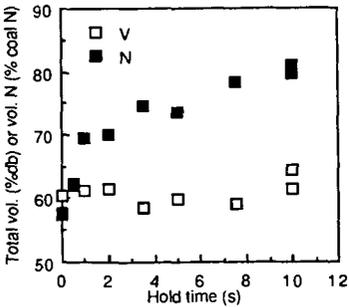


Fig. 8 Effect of hold time at 1400°C for Daw Mill coal

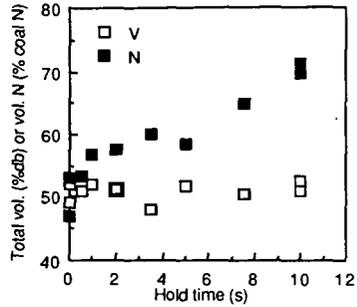


Fig. 9 Effect of hold time at 1400°C for Kellingley coal

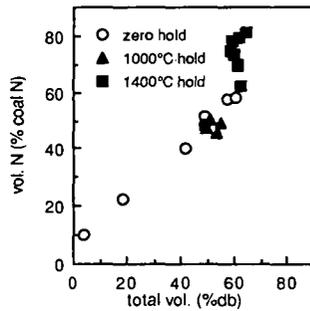


Fig. 10. Volatile N vs. total volatiles for Daw Mill coal

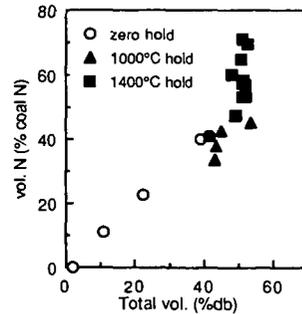


Fig. 11. Volatile N vs. total volatiles for Kellingley coal