

NO RELEASE FROM THE ISOTHERMAL COMBUSTION OF COAL CHARs.

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Introduction

Coal combustion for power generation has associated environmental problems, in particular, the release of oxides of sulphur and nitrogen which are involved in the formation of acid rain ^{1,2}. The modification and optimization of the combustion process to minimise the NO_x emissions is therefore of considerable interest and importance. The combustion of coal occurs over two stages;

- 1) the rapid devolatilisation followed by combustion/ignition of the volatiles *and*
- 2) slower gasification of the residual char.

The nitrogen present in the coal is partitioned between the volatile matter and the residual char. Char nitrogen has been identified ³ as the main contributor to NO emissions from low NO_x burners. Previous work on the gasification of char nitrogen ⁴⁻⁶ concentrated on temperature programmed conditions and possible mechanisms of the release of nitrogen. Carbons derived from polynuclear heterocyclic aromatic hydrocarbons with well defined initial functionality ⁷⁻¹⁰ and isotopic carbon (¹³C) ^{11,12} were also used as models for char gasification.

In the present investigation, the release of NO during isothermal combustion of a suite of coal chars produced from a rank series of coals in an entrained flow reactor under conditions similar to those in pulverised fuel combustion systems was studied. The relationships between coal and char structural characteristics and NO release were investigated.

Experimental

Coal Samples

Twenty coals were used in the study, covering a wide range of rank from anthracite to high volatile bituminous coal.

Char sample preparation in an Entrained Flow Reactor(EFR)

Pyrolysis of the coal size fraction (38 - 75µm) to produce char samples was achieved by the injection of coal into an entrained-flow reactor at 1273K in a nitrogen atmosphere. The reactor had a zone length of 1.66m and the particles experienced residence times of ~1s. Char samples were collected using a water cooled probe and a cyclone.

Char characterisation data

Carbon, hydrogen and nitrogen contents were determined using a Carlo Erba 1106 elemental analyser. Proximate analyses of the chars were determined by modified thermogravimetric analysis using a Stanton Redcroft ST780 thermogravimetric analyser. Surface area measurements were obtained from CO₂ adsorption measurements at 273K in a McBain spring gravimetric apparatus.

Combustion measurements

A Thermal Sciences STA 1500 thermogravimetric analysis instrument was connected to a VG quadrupole 300 amu mass spectrometer via a 1mm i.d. silica lined stainless steel probe. The probe was placed directly above the sample at a distance of 10mm from the surface of the sample. Isothermal combustion was carried out by heating the sample to the desired temperature (873 - 1323K) in an atmosphere of argon. After thermal equilibrium was reached, the gas was switched to 20% oxygen/argon. A gas flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ was used with ~5mg of char sample with particle size 38-75 μm . The gaseous species evolved and the weight loss profile were recorded with respect to time. Reactivity measurements were determined from isothermal gasification in 20% O_2/Ar at 773K. The reactivities of the chars during combustion were calculated from the rectilinear region of the weight loss-time curve.

Results

Isothermal Gasification measurements

The gasification rates of the coal chars at various temperatures between 773 and 1323K are shown in Figure 1 as a function of isothermal gasification temperature and volatile matter of the parent coal. It is apparent that there are two regions corresponding to the reaction being under chemical control at temperatures typically less than 973K, while above 973K the reaction is under diffusion control. In the chemical control region (below 973K), the gasification rate increases markedly with temperature. In the diffusion controlled region, above 973K, there is a very slow increase in the rate of gasification with temperature. In the region where the reaction is under chemical control, the gasification rate increases quite sharply with decreasing rank. In the region where the reaction is under diffusion control, there is a slight decrease in the gasification rate with coal rank.

Conversion of char nitrogen to NO

Isothermal Combustion profiles

Figure 2 shows the isothermal combustion profiles for a low rank coal char at 873 and 1273K in 20% O_2/Ar . At 873K, the combustion takes place where the reaction is under chemical control while at 1273K, the reaction is under diffusion control. It is evident that the $\text{NO}/(\text{CO} + \text{CO}_2)$ ratio increases with increasing burn-off for combustion at both temperatures. Similar trends were observed for the combustion of the suite of chars under both chemical and diffusion control.

Gas concentration measurements

The release of nitric oxide from the combustion of the E.F.R. coal chars varied with the rank of the parent coal and the isothermal gasification temperature. In regions of low gasification temperature and for high rank coals, the ratio of nitric oxide released normalised to the initial amounts of nitrogen in the char ($\text{NO}/\text{char-N}$), was highest. For low rank coals, the effect of temperature on the $\text{NO}/\text{char-N}$ ratio was not as great. It was also apparent that there was a dependence of the $\text{NO}/\text{char-N}$ ratio on coal rank at any given temperature. There was a marked decrease in the $\text{NO}/\text{char-N}$ ratio with a decrease in coal rank. Again, this was less apparent at the higher combustion temperatures when the reaction was under diffusion control.

The relationships between carbon structural characteristics and the conversion of char nitrogen to NO during combustion are of considerable interest. At low temperatures, gasification rate is governed by chemical control, and therefore the porous and surface structure of the char need to be taken into consideration. Figure 3 shows that there is a correlation between gasification

rate and the evolution of char-N as NO at 873K (chemical control region). At 1273K, when the reaction is under diffusion control, there was no correlation between char gasification rate and NO evolution. The clear correlation of NO/char-N with gasification rate observed for isothermal combustion at 873K was less evident when the rate was normalised by the surface area of the char. This indicates that the porous structure is a factor which influences the gasification of the char under chemical control and also the conversion of char-N to NO during combustion. In diffusion control, the external surface of the char is the important parameter.

Discussion

Char nitrogen conversion to NO

In this study, the gas sampling probe to the mass spectrometer was placed directly above the sample and this has been shown to detect reactive intermediate species before they are converted to equilibrium species (direct sampling) ^{6,10}. When the sampling probe is moved to the exhaust of the TGA, near equilibrium conditions are obtained (exhaust sampling). At this sampling position, the NO/N ratio increases due to small amounts of reactive intermediate species, such as HCN and (CN)₂ produced in the char gasification being converted to NO in the gas phase by reaction with oxygen ¹⁰. NO is the major primary product of char-N gasification. Mass transport effects and reduction of the NO in the carbon bed in the TGA may also modify the conversion of char nitrogen to NO during gasification/combustion. Figure 2 shows that the NO/(CO + CO₂) ratio increases with increasing carbon conversion and similar results were obtained for the combustion of the suite of chars under both chemical and diffusion control conditions. This can be attributed to two reasons; a) the retention of nitrogen in the char and/or b) the lower extent of reduction of the primary char nitrogen oxidation product NO, in the pores or on the surface of the char as the structure changes with carbon conversion.

Tullin *et al* have proposed ¹³ that char nitrogen reacts with either oxygen to form NO or with NO to form N₂O as the char undergoes gasification. The NO and N₂O are reduced by the char to N₂. Since the diameter of the char particles decreases with increasing carbon conversion there is less opportunity for the NO to be reduced. This explains the increase in NO/(CO + CO₂) with increasing carbon conversion. These authors also observed a decrease in N₂O with carbon conversion. They proposed that there was a decrease in NO concentration in the pores, thus causing a reduction in the formation of N₂O. These authors used modelling studies ¹⁴ to support the proposal.

Previous studies of the isothermal combustion of model carbons prepared by the high pressure carbonization of polynuclear aromatic hydrocarbons gave similar results ⁷⁻⁹. In addition, analytical data showed that the N/C ratio increased with increasing carbon conversion thereby supporting the former explanation. Therefore it is possible that both nitrogen retention and lower NO reduction occur with increasing carbon conversion.

Temperature programmed combustion studies of E.F.R. chars have shown ^{3,4} that the conversion of char-N to NO increases with rank up to ~ 1.5% vitrinite reflectance before reaching a plateau. High levels of NO release were also associated with lower reactivity chars and it was proposed that the char reactivity, total surface area, and char surface structure are factors which influence the conversion of char nitrogen to NO during combustion.

Previous studies have suggested that NO is reduced on the carbon surface to form N₂ and/or N₂O ^{4-8, 10, 13,14}. Also the CO reaction with NO may be catalysed by the char

surface ¹⁵. High rank coals have a more ordered structure than the lower rank coals and there are generally fewer active sites available. In addition, the porous structure varies systematically with rank. Coals which develop thermoplasticity give rise to anisotropic chars where there is an increase in the extent of alignment of the carbon lamellae resulting in a low surface area. It is apparent that the coal chars which have the lower surface areas tend to be associated with higher levels of NO release. This indicates that the lower reactivity and available surface area of the high rank coal chars gives rise to higher NO/char-N conversion ratios due to a lower reduction of the primary char oxidation product NO on the surface and/or in the pores of the char. Figure 3 clearly shows that the less reactive chars are associated with high levels of NO release, at low temperatures where the reaction is under chemical control.

Conclusions

The release of nitrogen in the combustion of coal chars derived from a suite of coals covering a wide range of rank has been studied. The NO/(CO + CO₂) ratios increased with increasing burn-off for isothermal combustion in both the chemical and diffusion control temperature regimes. This suggests that the nitrogen is retained preferentially in the char and/or the extent of reduction of NO on the char surface is lower as carbon conversion proceeds. Lower conversions of char nitrogen to NO are observed from low rank coals. Chars with low surface areas and low reactivity have high conversions of char-N to NO. The primary product of char-N combustion, NO, is reduced in the porous structure and/or on the surface of the coal char. The char structure may also catalyse the reaction of CO with NO. The extent of reduction varies with temperature and mass transport limitations as well as the structure of the char.

References

1. Sloss, L.L., *NOx Emissions from Coal Combustion*, IEACR/36, 1991, IEA Coal Research, London.
2. Davidson, R.M. *Nitrogen in Coal*, IEAPER/08, 1994, IEA Coal Research, London.
3. Phong-Anant, D., Wibberley, L.J. and Wall, T.F. *Combust. Flame* **62**, 21 (1985).
4. Wang, W., Brown, S.D., Hindmarsh, C.J. and Thomas, K.M. *Fuel* **73**, 1381 (1994).
5. Brown, S.D. and Thomas, K.M. *Fuel* **72**, 359 (1993).
6. Varey, J.E., Hindmarsh, C.J. and Thomas, K.M. *Fuel* accepted for publication.
7. Wang, W. and Thomas, K.M. *Fuel* **71**, 871 (1992).
8. Wang, W. and Thomas, K.M. *Fuel* **72**, 293 (1993).
9. Spracklin, C.J., Thomas, K.M., Marsh, H. and Edwards, I.A.S. *International Conference on Coal Science Proceedings*, IEA Coal Research, 1991, p. 343.
10. Jones, J.M., Harding, A.W., Brown, S.D. and Thomas, K.M. *Carbon* **33**, 833 (1995).
11. Thomas, K.M., Grant, K. and Tate, K. *Fuel* **72**, 941 (1993).
12. Jones, J.M. and Thomas, K.M. *Carbon* **33**, 1129 (1995).
13. Tullin, C.J., Sarofim, A.F. and Beer, J.M. *J. Inst. Energy* **66**, 207 (1993).
14. Tullin, C.J., Goel, S., Morihara, A., Sarofim, A.F. and Beer, J.M. *Energy and Fuels* **7**, 796 (1993).
15. Goel, S.K., Morihara, A., Tullin, C.J. and Sarofim, A.F., 25th Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh, 1051 (1994).

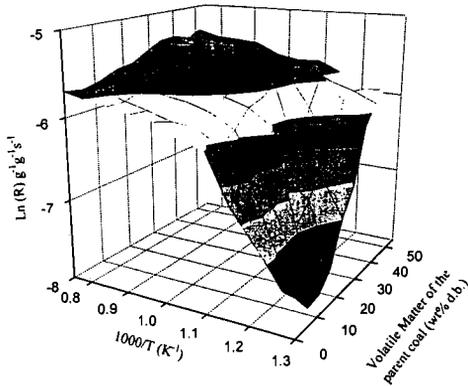


Figure 1. The variation of char reactivity with $1/T$ and volatile matter of the parent coal.

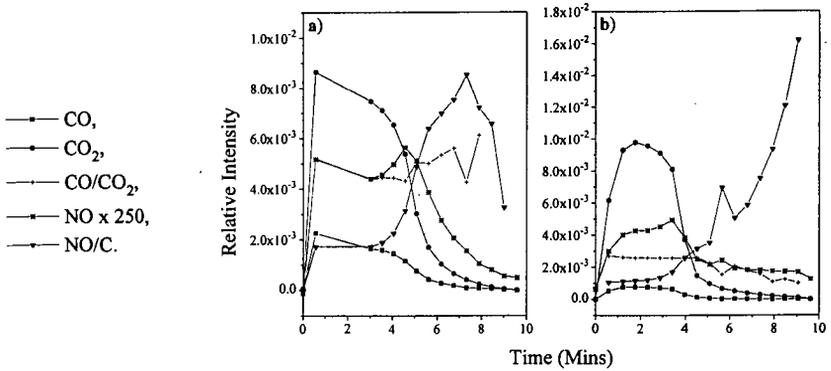


Figure 2. Gas evolution profiles from the isothermal combustion in 20% O_2/Ar of a) char-T at 873K, b) char-T at 1273K.

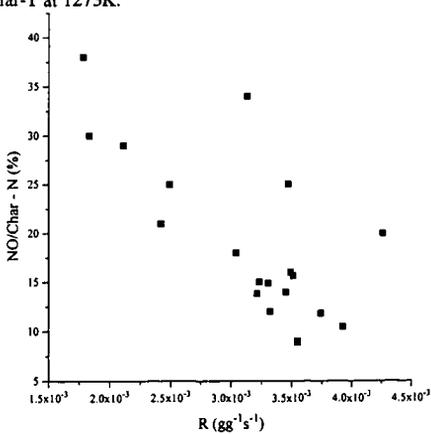


Figure 3. The variation of $NO/char-N$ with gasification rate at 873K.