

## PORPHYRIN- AND METALLOPORPHYRIN-DERIVED CARBONS AS MODELS FOR COAL CHARs

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### INTRODUCTION

Factors which govern the release of fuel-nitrogen as NO<sub>x</sub> (rather than N<sub>2</sub>) during coal combustion are of interest because of the environmental implications. Coal is a complex material which can be considered to be composed of large polymeric, molecules comprising aliphatic cross-linked polyaromatic structural units which contain many heteroatom types and functionalities. Within this polymeric matrix smaller molecules are dispersed, together with mineral particles, metal salts etc. Model coals derived from carbonisation of organic precursors offer an approach for examining the role of some of these variables (nitrogen-functionality, oxygen content, metal type, environment and content etc.) on NO<sub>x</sub> formation during combustion. In principle, such models are easier to characterise, compared to coal, with regards to their chemical and physical properties.

The nitrogen in coal is virtually exclusively organic and typical nitrogen contents are in the range 0.7-2.1 wt%. The chemical form of the nitrogen is mainly pyrrolic and pyridinic, with smaller amounts of quaternary nitrogen within the aromatic units. Lower rank coals may possess other functional groups such as amines. As a consequence model coals derived from carbazole, acridine, or ammonia-treated carbons etc. have been studied for their combustion behaviour.<sup>1-5</sup>

One source of this nitrogen in coal is derived from porphyrin and other plant protein structures which are degraded via different routes during coal diagenesis. These types of systems have been identified in coals as well as coal extracts.<sup>6,7</sup> Such systems are of interest because of their ability to chelate metals, in particular vanadium and iron. Nitrogen chelates and chelated metal species are expected to have very different nitrogen release behaviour during combustion, compared to free pyrrolic or pyridinic systems because: (i) the nitrogen:carbon ratio is unusually high in the porphyrin chelate; (ii) the nitrogen atoms are in close spatial proximity within the chelate; (iii) there exists intimate contact between the chelated metal and the nitrogen atoms.

In the present study, model coals derived from porphyrin and metalloporphyrin chelates have been characterised for their chemical and physical properties with particular emphasis on their behaviour during pyrolysis and combustion. To the authors' knowledge such types of systems have not been studied previously.

### EXPERIMENTAL

The model carbons were prepared by atmospheric pressure co-carbonisation of a 10:1 by weight acenaphthylene and the porphyrin (or metalloporphyrin) mixture under an argon atmosphere. The heating rate was 1 K/min and initially the carbons were heat-treated at 873 K for 1 h. Carbons treated at higher temperatures were heated again in argon at 4 K/min to the desired temperature and held for 1 h. Surface areas were measured by the BET method using a Quantachrom Quantasorb QS-13 surface area analyser. Pyrolysis studies at 1273 K were performed using a Chemical Data Systems, Inc., 190 Pyroprobe pyrolysis system interfaced to a Perkin-Elmer 8700 capillary GC, with FID and NPD detectors. Combustion studies were performed in a Shimadzu TGA-50H thermogravimetric analyser (15 K/min heating rates) in air, or in 20% O<sub>2</sub>/Ar using a Stanton Redcroft STA 1500 thermogravimetric analyser coupled to a VG Quadrupole mass spectrometer by means of a heated capillary sampling probe. Further details are described elsewhere.<sup>1</sup>

### RESULTS AND DISCUSSION

The elemental analyses of the model coals are given in Table 1, together with surface areas, where available. The surface areas of the carbons were, in general, quite low which may be expected for the anisotropic acenaphthylene derived carbons, due to small pore sizes. The N:V ratio in the carbon prepared from pure tetraphenyl porphine (CTTPV) is much larger than that in the precursor suggesting that much of this metal is no longer chelated, and may be present as the oxide. In contrast, the N:M ratio for the 873K heat-treated Fe- and Co-containing co-carbonised carbons are essentially unchanged compared with the corresponding metalloporphyrin precursors, which may indicate that the chelate is intact, to some extent.

The evolved gas profiles during the temperature programmed combustion (TPC) of the tetraphenyl porphine starting material are given in Figure 1. The main fuel-N product is  $N_2$ , and relatively large amounts of NO, HCN and other cyano species were detected. The cyano species are seen to be evolved during the onset of combustion, while the majority of fuel-N is evolved as  $N_2$  towards the latter stages of combustion. This type of behaviour is often seen for coals and coal chars, where nitrogen is retained in the char until its eventual release at high levels of burnout.

The evolved gas profiles during TPC of the carbonised tetraphenylporphyrin and carbonised vanadyl porphyrin are given in Figures 2 and 3 respectively and Table 2 quantifies the differences in the fuel nitrogen conversions. Comparison of Figures 1 and 2 show that the structural changes which occur during carbonisation have profound effects on the fuel-N released. In particular, the HCN gas evolution profile is quite different, and far more  $N_2$  is evolved after carbonisation. This  $N_2$  is evolved at almost the same temperature as observed during the TPC of the pure tetraphenylporphine precursor, suggesting structural similarities. The evolution of  $N_2$  during combustion may be indicative of N atoms in the carbon structure which are close spatially. Alternatively mobile C(N) surface species may participate. The presence of the metal (Figure 3, and Table 2) also has a marked effect on the fuel-N conversions. This may be the result of a catalytic effect of vanadium on the reduction of NO to  $N_2$ . The catalytic effects of the metal on combustion is illustrated dramatically when comparisons of Figures 2 and 3 are made. Catalysis was seen to occur for the combustion of all the co-carbonised carbons, and a compensation effect on the rates was apparent, as shown in Figure 4.

During pyrolysis of the co-carbonised samples, the major products observed were hydrogen cyanide and acetonitrile. The presence of the metal decreased the amount of both these species which may be indicative of the persistence of M-N interactions in the carbons.

#### CONCLUSIONS

Carbons derived from porphyrin and metalloporphyrin precursors can be used to investigate the influence of such moieties on the conversion of fuel-nitrogen in coals. The presence of metals catalyses the combustion and appears to lower the amount of fuel-N converted to HCN in the volatiles, and increase the fuel-N to  $N_2$  conversions. It is unclear, at the present time, as to whether chelated or unchelated metals are responsible for this.

#### REFERENCES

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TABLE 1: Properties of the model carbons

sample i.d.†	HTT (K) ‡	wt% C	wt% H	wt% N	wt% O*	wt% metal	surface area (m <sup>2</sup> /g)
CTPP-873	873	83.1	2.4	8.8	5.7	-	nm
CTPPV-873	873	52.1	1.4	5.5	13.5	27.5	nm
ACE-TPP-873	873	94.1	2.1	0.5	3.3	-	5
ACE-TPP-V-873	873	93.1	1.7	1.6	0.9	2.7	5
ACE-TPP-Fe-873	873	92.1	1.8	1.6	3.0	1.5	5
ACE-TPP-Co-873	873	89.6	1.7	1.8	5.0	1.9	3
ACE-TPP-Cu-873	873	89.5	1.8	1.6	5.0	2.1	3
ACE-PC-873	873	92.2	2.1	0.8	4.9	-	2
ACE-PC-V-873	873	88.6	1.8	2.8	3.2	3.6	11
ACE-TPP-1073	1073	97.4	0.9	0.6	1.1	-	2
ACE-TPP-V-1073	1073	93.2	1.0	1.5	1.4	2.9	6
ACE-TPP-Fe-1073	1073	96.2	0.3	0.7	1.2	1.6	149
ACE-TPP-Co-1073	1073	94.6	0.3	0.7	2.2	2.2	57
ACE-TPP-Cu-1073	1073	94.5	0.7	1.5	1.2	2.1	3
ACE-TPP-1273	1273	95.9	0.3	0.5	3.3	-	3
ACE-TPP-V-1273	1273	95.2	0.3	1.1	0.5	2.9	2

†ace - acenaphthylene; tpp - tetraphenylporphyrin (free base or chelated to denoted metal); nm: not measured. \*By difference. ‡HTT: Heat treatment temperature.

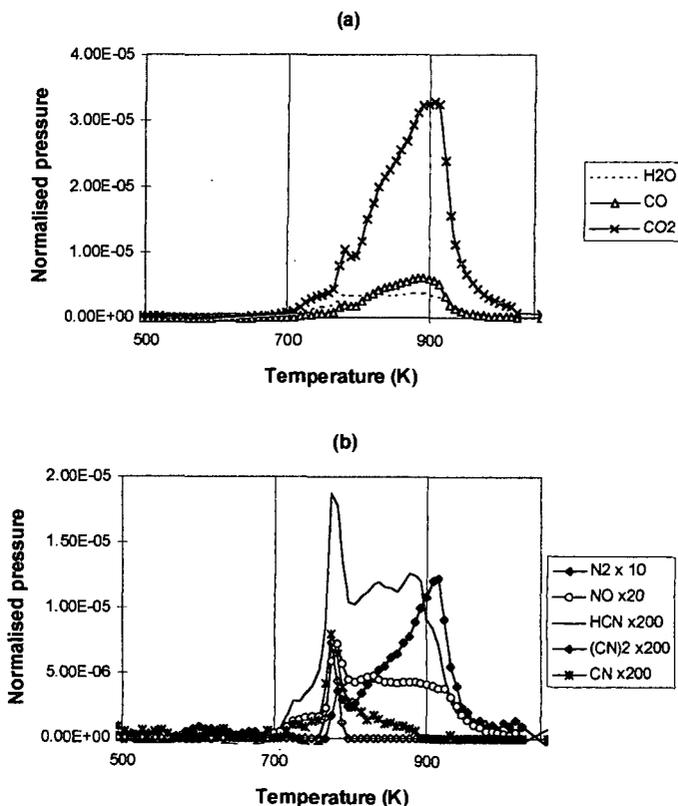
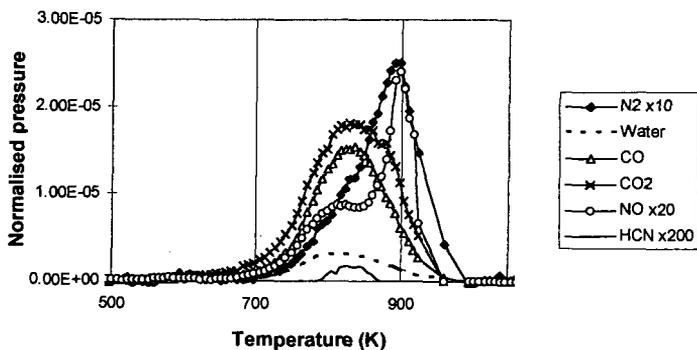


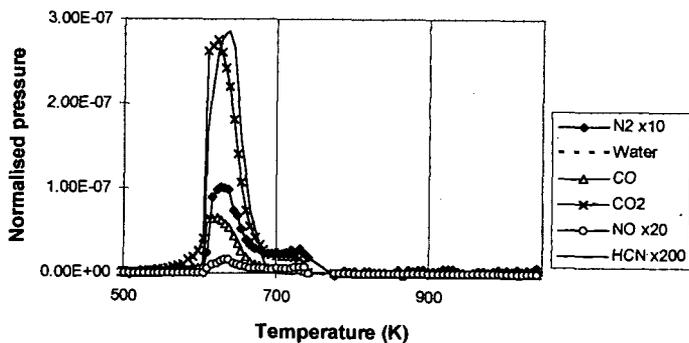
FIGURE 1: Gas evolution profiles during the temperature programmed combustion of tetraphenylporphine in 20% O<sub>2</sub>/Ar (a) major products, (b) fuel nitrogen products.

**TABLE 2: Product distribution ratios during temperature programmed combustion.**

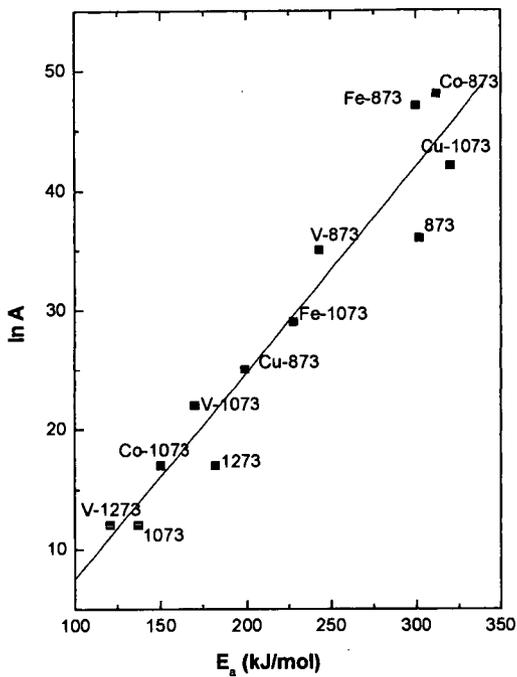
Product Ratio	TPP	CTPP-873	CTPPV-873
CO/CO <sub>2</sub>	0.173	0.713	0.235
NO/N	0.090	0.213	0.033
HCN/N	0.021	0.0005	0.041
N <sub>2</sub> /N	0.452	0.807	0.822
C <sub>2</sub> N <sub>2</sub> /N	0.002	-	-
CN/N	0.004	-	-
<b>Total N/fuel N</b>	<b>0.569</b>	<b>1.0205</b>	<b>0.896</b>



**FIGURE 2: Gas Evolution profiles during the temperature programmed combustion of CTPP-873 in 20% O<sub>2</sub>/Ar**



**FIGURE 3: Gas Evolution profiles during the temperature programmed combustion of CTPPV-873 in 20% O<sub>2</sub>/Ar**



**FIGURE 4:** Compensation effect for metal-free and metal containing carbons. The ACE-TPP prefix has been dropped from the sample designation.