

## A STUDY ON COAL BLENDING FOR REDUCING NO<sub>x</sub> AND N<sub>2</sub>O LEVELS DURING FLUIDIZED BED COMBUSTION

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The objective of the study was to investigate the effect of blending on the emissions of NO<sub>x</sub> and N<sub>2</sub>O during the fluidized bed combustion of five coals with different levels of nitrogen, volatile matter, and fixed carbon contents, and diverse coal and char petrographic composition.

The devolatilization chars were produced in a fluidized bed combustor. Using the petrographic analyses of the coals, sixteen coal blends were made to carry out the combustion tests.

The combustion of individual coals and the sixteen blends was carried out in an electrically heated atmospheric fluidized bed combustor.

The emissions of NO<sub>x</sub> reached maximum values at a bed temperature around 1173 K and decreased with lower combustion temperatures. The amount of nitrous oxide formed decreased, for all five coals, as the bed temperature increased from 1053 to 1303 K. These trends are consistent with the observed experimental data obtained by other researchers. It was observed that for ratios of 1.3 to 1.6 of fixed carbon to volatile matter, both NO<sub>x</sub> and N<sub>2</sub>O emission levels were minimal and, outside this range, both oxides showed a sharp increase in their formation/emissions. The coal blends were also found to show similar trends with increasing the bed temperatures.

The results serve to establish the relative importance of volatile and fixed carbon reactivity and coal and char petrography, which is believed to significantly contribute to devolatilization mechanisms and char reactivity.

*Keywords:* NO<sub>x</sub>; N<sub>2</sub>O; coal blends; fluidized bed combustion (FBC)

### INTRODUCTION

It is inevitable that permitted levels of emissions concerning the release of the oxides of nitrogen from utility coal-fired boilers will become more stringent with

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time. Simple modifications involving the combustion geometry or mode of firing do not result in reductions that could satisfy the pending legislation in the future. The most common method available to operators that has proved to be effective in this respect is reagent injection, but this also has disadvantages, such as restricted temperature operation, complications like  $\text{NH}_3$  slip, cost, and so on. Although the implementation of primary and secondary measures, such as fuel blending and deep fuel staging (reburn), respectively, cannot individually meet the future levels for emissions. Nevertheless, their combined use could prove to be effective and could satisfy environmental requirements with the advantage of being more suitable with the boiler operation than the reagent injection.

Coal blending is a technique very much utilized in coal boilers using pulverized fuel (pf). The main purpose of its use is primarily to minimize the adverse effects of fouling and slagging observed in the boilers resulting from the behavior of coal ash. In addition, because fouling and slagging are particularly more serious with coals containing high sulfur, the blending of coals in pf systems has the objective of reducing the extent of fouling and slagging with a simultaneous reduction in  $\text{SO}_2$  release. Furthermore, the blending could also improve the ignition characteristics and coal reactivity.

In most cases, the blends of distinct rank coals with those of lower rank did not appear to result in significant improvement in combustion efficiency (Lee and Whaley, 1983; Vleeskens, 1983; Artos and Scaroni, 1993; Rubiera *et al.*, 1999a). Nevertheless, Rubiera *et al.* (1999a) verified that the ignition of high volatile coals might enhance the burning of a higher rank coal.

The pf work undertaken by Rozendal *et al.* (in Maier *et al.*, 1994) and Maier *et al.* (1994) and those of TGA (Thermogravimetric) and DTF (drop tube furnace) by Rubiera *et al.* (1999b) revealed that blending high volatile coals with low volatile coals could reduce  $\text{NO}_x$  emissions, due to the release of higher quantities of volatile species in the flame zone.

Nevertheless, the application of the use of coal blending in FBC systems is very recent and its objective is related more to the control of  $\text{NO}_x$  emissions. As the combustion temperature in FBC is lower than that of pf, the ash behavior is different and the capture of  $\text{SO}_2$  during the combustion in FBC somewhat alters the gas composition of the flue gases. Consequently, the fouling and slagging observed in FBC involve different mechanisms which could also be controlled with coal blending. Presently, most of the coal blending work is still at the R&D phase with very little industrial applications.

The present study aimed at determining the effects of coal blending on the emissions of  $\text{NO}_x$  and  $\text{N}_2\text{O}$  from fluidized bed combustion and correlating them with petrographical characterization of the coal.

## FUEL CHARACTERISTICS

### Analyses of Coals

#### *Proximate and ultimate analyses*

The origin, rank, proximate and ultimate analyses, and also the fuel and N/C ratios of the individual coals are given in Table I.

#### *Petrographic analyses*

Each coal and sample was crushed below 1mm and embedded in resin in order to prepare a classical particulate block, subsequently polished and labeled. The method is in accordance with ISO Standard 7404-2.

The equipment used was a MPVC Leitz microscope with magnifications up to 500 $\times$ , and the MPVGEOR computer program. With the objective of studying the coal composition three analyses were performed:

1. Vitrinite reflectance, in accordance with ISO 7404-5;
2. Maceral group composition, in accordance with ISO 7404-3.

TABLE I Coal characterization: rank, proximate and ultimate analyses

Samples	Puertollano, C1	Sasol, C2	Carbocol, C3	C coal, C4	Ashland, C5
Rank <sup>1</sup>	HVbit.	HVbit.	HVbit.	HVbit.	HVbit.
Origin	Spain	S.Africa	Colombia	S.Africa	USA
Proximate (db <sup>2</sup> , wt%; daf <sup>3</sup> , wt%)					
Ash <sup>2</sup>	46.0	10.2	8.9	16.5	14.0
Volatile matter <sup>3</sup>	47.7	35.9	42.4	27.8	39.3
Fixed Carbon <sup>3</sup>	52.3	64.1	57.7	72.2	60.7
Ultimate (daf <sup>3</sup> , wt%)					
Carbon	76.3	80.5	82.0	79.0	84.9
Hydrogen	5.0	5.0	5.8	4.4	5.1
Nitrogen	2.2	2.1	1.6	1.7	1.5
Sulphur	1.7	0.8	0.9	0.6	1.1
Oxygen <sup>4</sup>	14.8	11.7	9.7	14.2	7.4
Fuel ratio (FC/VM)	1.1	1.8	1.4	2.6	1.6
N/C <sup>5</sup>	2.8	2.6	1.9	2.1	1.8

<sup>1</sup>in accordance with ASTM D 388 and Damberger *et al.* (1984).

<sup>2</sup>db-dry basis

<sup>3</sup>daf-dry ash free

<sup>4</sup>by difference

<sup>5</sup>values were multiplied by a factor of 100 for a better reading.

3. Microlithotypes, carbominerites, and minerite composition, in accordance with ISO 7404-4.

The results of the coal petrographic analyses are presented in Table II.

Puertollano coal has a vitrinite mean random reflectance (Rr) of 0.59%, is vitrinite rich, with a significant amount of inertinite and mineral matter. Liptinite is not abundant but it is nevertheless frequent and dominated by megaspores (Table II).

Sasol coal has an Rr of 0.61%. Due to the large amounts of vitrinite (colotelinite) and inertinite (semifusinite) the microlithotypes vitrite and inertite are the most representative (Table II).

The Carbocol coal is very rich in vitrinite and has an Rr of 0.63%. Inertodetrinite is finely dispersed on vitrinite and causes a large vitrinertite volume (Table II).

C coal has an Rr of 0.73%, however, the vitrinite reflectance measurements revealed a large dispersion of values (ranging between 0.55% and 1.00%, with a standard deviation of 0.10) which is an indicator of a blend. This coal is also inertinite rich.

TABLE II Coal petrography: vitrinite mean random reflectance, maceral group composition, and microlithotypes, carbominerites and minerite composition

Samples	Puertollano, C1	Sasol, C2	Carbocol, C3	C coal, C4	Ashland, C5
Vitrinite reflectance					
Rr % <sup>1</sup>	0.59	0.61	0.63	0.73	0.81
Maceral group composition (% in volume)					
Vitrinite	44	41	83	13	65
Liptinite	5	5	3	5	10
Inertinite	21	51	13	76	21
Mineral matter	30	3	1	6	4
Microlithotypes, carbominerites and minerite composition (% in volume)					
Vitrite	29	24	52	4	29
Liptite	0	0	0	0	0
Inertite	5	26	4	52	3
Clarite	5	2	8	1	12
Durite	4	8	0	15	10
Vitrinertite	13	18	29	12	12
Trimacerite	10	13	7	6	23
Carbominerite	13	7	0	10	7
Minerite	21	2	0	0	4

<sup>1</sup>vitrinite mean random reflectance.

Ashland coal has an Rr of 0.81%. Vitrinite is dominant which contributes to high volumes of vitrite. Trimacerite amounts to 23% due to the large volume of liptinite (10%) (Table II).

### Petrographic Analyses of Chars

Chars were obtained from coal devolatilization in a fluidized bed reactor with 80 mm of internal diameter and 500 mm height. The inert carrier gas used in all tests was N<sub>2</sub>. During the volatile release, CO and CO<sub>2</sub> amounts were measured with nondispersive infrared analyzers and, when the analyzers could no longer detect these gases, the heating was switched off while maintaining the N<sub>2</sub> flow. Chars were produced at four temperatures (973 K, 1073 K, 1173 K, and 1273 K) and at a heating rate of ca. 104 K/s. Fluidized bed systems usually operate over a temperature range of 1073 to 1123 K and coal particles entering the bed, upon heating and depending on their residence times in the bed and their sizes, could attain temperatures varying from 973 to 1273 K which consequently influence the formation of chars (La Nauze, 1985).

TABLE III Char petrography (volume %, devolatilization char produced at 973 K, 1073 K, 1173 K, and 1273 K)

	T(K)	Tsphere <sup>1</sup>	Csphere <sup>2</sup>	Tnetwork <sup>3</sup>	Cnetwork <sup>4</sup>	Mixed	Solid	Fused fragment	Unfused fragment	Group 1 <sup>5</sup>	Group 2 <sup>6</sup>
Puertollano, C1	973	0	0	48	10	25	14	1	2	50	50
Puertollano, C1	1073	2	6	65	8	12	8	0	0	73	27
Puertollano, C1	1173	0	4	74	4	12	7	0	0	78	22
Puertollano, C1	1273	1	10	68	6	10	4	0	0	79	21
Sasol, C2	973	2	6	40	16	20	16	0	0	48	52
Sasol, C2	1073	2	7	40	13	22	15	0	1	50	50
Sasol, C2	1173	3	2	52	8	17	17	0	0	57	43
Sasol, C2	1273	1	4	58	6	19	12	0	0	63	37
Carbocol, C3	973	14	13	44	16	9	4	0	0	71	29
Carbocol, C3	1073	16	15	46	13	6	1	4	1	80	21
Carbocol, C3	1173	18	10	55	8	6	2	0	0	84	16
Carbocol, C3	1273	10	16	64	3	6	1	0	0	90	10
C coal, C4	973	4	5	18	6	33	34	0	0	27	73
C coal, C4	1073	3	2	36	6	30	21	2	0	43	57
C coal, C4	1173	10	4	37	9	29	11	0	0	51	49
C coal, C4	1273	4	4	49	6	29	6	0	1	58	42
Ashland, C5	973	16	15	29	4	2	4	28	2	88	12
Ashland, C5	1073	29	19	31	2	6	5	9	1	87	13
Ashland, C5	1173	24	16	43	10	2	2	4	0	86	14
Ashland, C5	1273	13	14	60	7	2	2	1	2	88	12

<sup>1</sup>Tenuisphere

<sup>2</sup>Crassisphere

<sup>3</sup>Tenuinetwork

<sup>4</sup>Crassinetwork

<sup>5</sup>high porous chars: tenuispheres+crassispheres+tenuinetworks+fused fragments

<sup>6</sup>mean to low porous chars: crassinetworks+mixed+solid+unfused fragments

The petrographic observations were performed in a Leitz microscope with a 25× oil objective, which permits the identification of the particles according to their shape and mosaic texture.

The procedure used for point-counting was as follows: at each location if the crosswire, landed on the carbonaceous material of a char particle, the particle was classified and counted. This procedure ensures that the particles counted represent the total volume of the char material (Álvarez *et al.*, 1997).

The detailed char classification was adopted from Álvarez *et al.* (1997) and the reclassification in Group I and Group II was made in accordance with Bailey (1994) and Diessel (1998) as follows: Group I chars are characterized by high macroporosity (*i.e.*, visible under the microscope), generally in excess of 50%; and Group II chars consist of medium to low porosity chars.

The main results of the char petrography are presented in Table III.

## COMBUSTION TESTS EXPERIMENTS

### Experiment Procedures

Five single coals (Tables I and II) were burned in a fluidized bed reactor. Later, based on the petrological characterization of coals by the University of Porto and the combustion tests results obtained from INETI, fifteen coal blends given below were prepared, in accordance with ISO Standard 1988, at INETI:

Blend 1	Blend 2	Blend 3	Blend 4	Blend 5
80% Ashland + 20% Puertollano	20% Ashland + 80% Sasol	20% Ashland + 80% C	20% Carbocol + 80% Sasol	20% Carbocol + 80% C
50% Ashland + 50% Puertollano	80% Ashland + 20% Sasol	50% Ashland + 50% C	50% Carbocol + 50% Sasol	50% Carbocol + 50% C
20% Ashland + 80% Puertollano	20% Ashland + 80% Sasol	80% Ashland + 80% C	20% Carbocol + 80% Sasol	80% Carbocol + 20% C

Combustion tests of coals and blends were carried out in an electrically heated fluidized bed with 80 mm internal diameter and 500 mm height (Figure 1). The inert bed material was constituted of silica sand with a particle average size of 370 µm.

The operating conditions were:

- Bed weight (g): 400
- Fluidization air pressure (Pa):  $1.013 \cdot 10^5$

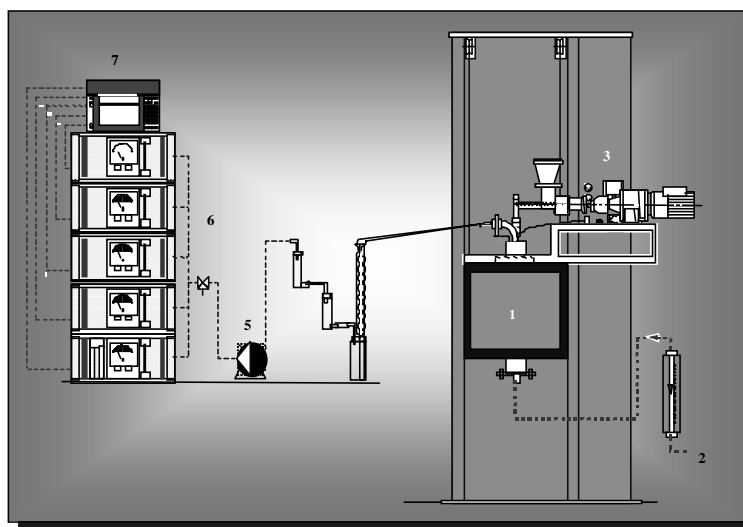


FIGURE 1 Experimental apparatus: 1) reactor electrically heated, 2) combustion air, 3) screw feeder, 4) condenser and filters, 5) pump, 6) analyzers, 7) recorder.

- Fluidization airflow rate ( $\text{dm}^3/\text{min}$ ): 14
- Coal feed rate (g/min): 1.2
- Coal particle sizes ( $\mu\text{m}$ ): 500-1000

The combustion temperature was varied in the range of 1053 to 1323 K, and controlled automatically by a Eurotherm controller. The bed temperature was continuously monitored with a thermocouple type K.

The combustion gases, after being filtered and dried, were continuously analyzed at the exit of the combustor, with specific analyzers, which were previously calibrated. Paramagnetic method was employed for  $\text{O}_2$  measurements and the non-dispersive infrared technique was used for measuring the amounts of CO,  $\text{CO}_2$  and  $\text{N}_2\text{O}$ . The  $\text{NO}_x$  and  $\text{SO}_2$  measurements were carried out with a chemiluminescence and pulsed fluorescent analyzer, respectively.

## Results and Discussion

The results of the emissions of  $\text{NO}_x$  and  $\text{N}_2\text{O}$  from the combustion trials of single coals and blends are presented in Table IV.

### *Combustion of the single coals*

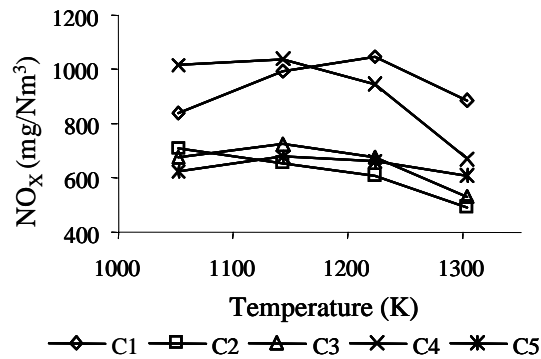
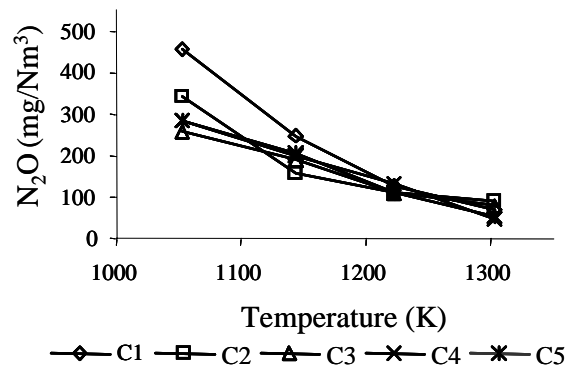
The  $\text{NO}_x$  and  $\text{N}_2\text{O}$  emissions obtained from the combustion of the five single coals are given in Figures 2 and 3.

The  $\text{NO}_x$  emissions were found to increase from 1053 K to 1173 K, with the exception of Sasol coal ( $\text{C}_2$ ). Relatively high emissions of  $\text{NO}_x$  at lower tem-

TABLE IV NO<sub>x</sub> and N<sub>2</sub>O emissions for single coals and blends (values corrected for 6% O<sub>2</sub>, mg/Nm<sup>3</sup>)

T(K)	NO <sub>x</sub> 1053	NO <sub>x</sub> 1143	NO <sub>x</sub> 1223	NO <sub>x</sub> 1303	N <sub>2</sub> O 1053	N <sub>2</sub> O 1143	N <sub>2</sub> O 1223	N <sub>2</sub> O 1303
<b>Blend Ashland+Sasol</b>								
Ashland%								
100	624	681	664	610	283	207	108	53
80	787	815	723	688	229	146	96	48
50	811	885	825	779	294	200	139	66
20	813	897	890	832	307	230	149	66
0	706	656	608	495	339	157	108	88
<b>Blend Ashland+C coal</b>								
Ashland %								
100	624	681	664	610	283	207	108	53
80	806	879	749	741	273	177	95	52
50	860	906	877	758	284	193	111	57
20	960	998	997	861	254	165	90	30
0	1018	1037	948	669	284	198	132	49
<b>Blend Ashland+Puertollano</b>								
Ashland %								
100	624	681	664	610	283	207	108	53
80	798	786	832	698	213	196	88	38
50	854	1003	830	770	200	118	82	37
20	871	1051	845	783	210	106	51	30
0	838	994	1044	882	455	248	126	69
<b>Blend Carbocol+Sasol</b>								
Carbocol %								
100	675	721	680	527	256	191	111	81
80	882	906	821	766	205	128	82	26
50	912	972	893	873	226	140	82	21
35	954	1026	1027	849	245	156	84	26
20	928	1005	939	945	278	190	151	67
0	706	656	608	495	339	157	108	88
<b>Blend Carbocol+C coal</b>								
Carbocol %								
100	675	721	680	527	256	191	111	81
80	925	950	812	776	216	139	138	79
50	927	965	842	839	254	169	147	84
20	967	925	983	947	321	252	150	82
0	1019	1037	948	669	284	198	132	49

peratures (1053 to 1143 K) were observed with C Coal (C4) and Puertollano coal (C1) that produced the highest NO<sub>x</sub> emissions at 1223 K. At 1223 to 1303 K, NO<sub>x</sub> emission decreased in all coals. The high reactivity of C Coal (C4) for NO<sub>x</sub> formation could be attributed to the presence of high inertinite amounts compared with other coals, and considering that it has a fuel-N content about the same as Carbocol (C3) and Ashland (C5) coals which produced one third less NO<sub>x</sub> but are poor in inertinite. It is more difficult to correlate the behavior of Sasol coal (C2)

FIGURE 2 NO<sub>x</sub> emissions versus temperature, for the five single coals.FIGURE 3 N<sub>2</sub>O emissions versus temperature, for the five single coals.

with its petrological composition. It is a coal with high fuel-N content and with about the same amounts of vitrinite and inertinite.

The increase in NO<sub>x</sub> with temperature is already well established (Jonhsson, 1993; Hayhurst and Lawrence, 1996) and could be due to both higher reaction rates of oxidation of fuel-N to NO<sub>x</sub> and thermal destruction of N<sub>2</sub>O, either directly or indirectly by favoring the reactions leading to the formation of NO<sub>x</sub>. Nevertheless, the reduction in NO<sub>x</sub> at higher temperatures could result from the destruction of NO<sub>x</sub> by char becoming very significant, as previous studies showed that the NO<sub>x</sub>-char reaction had relatively high activation energy and the reaction seemed to be favored at temperatures above 1173 K (Abelha *et al.*, 1999). Considering the fact that vitrinite rich coals produced highly porous chars (Table III), the reduction of NO<sub>x</sub> in the interior of particles could become significant, thus giving rise to a decrease in NO<sub>x</sub>. In fact, with Ashland and Carbocol, both rich

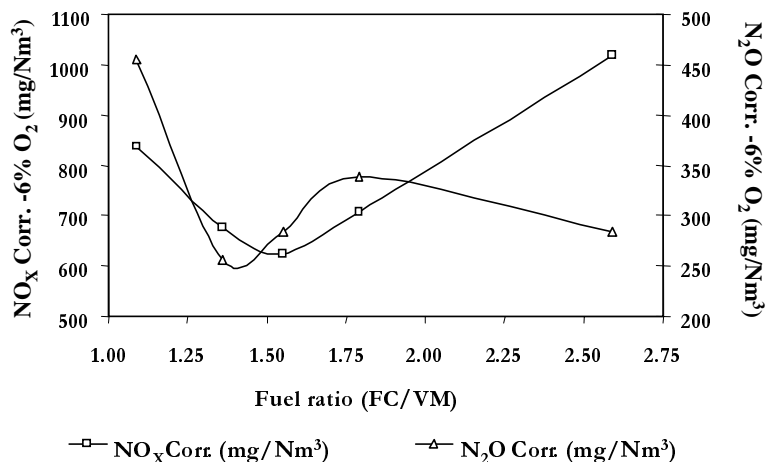


FIGURE 4 NO<sub>x</sub> and N<sub>2</sub>O emissions versus fuel ratio (fixed carbon/volatile matter) for  $T = 1053$  K, for the five single coals.

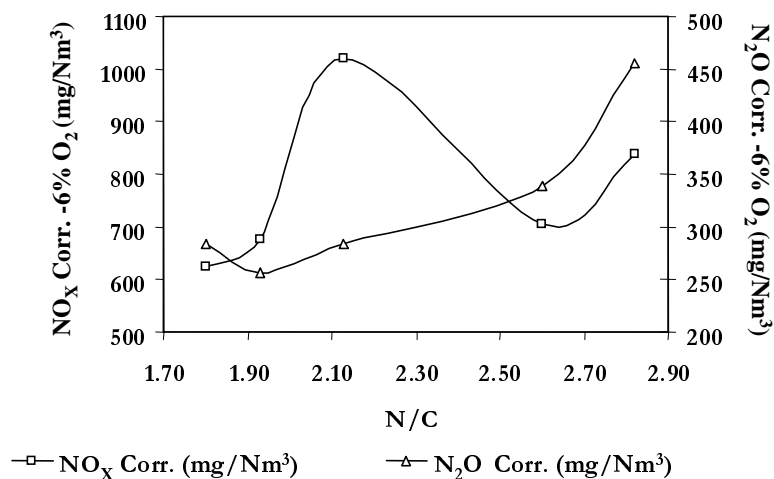


FIGURE 5 NO<sub>x</sub> and N<sub>2</sub>O emissions versus nitrogen/carbon ratio (N/C) for  $T = 1053$  K, for the five single coals.

in vitrinite, the reduction started at about 1143 K. At these high temperatures, the gas phase reaction of NO<sub>x</sub> with CO catalyzed by the relatively porous char is found to become important, thus leading to the reduction in NO<sub>x</sub> emissions.

It was observed that there was a dependency between the amounts of NO<sub>x</sub> and N<sub>2</sub>O released and the fuel ratio (Fixed Carbon/Volatile Matter) and fuel N/C ratio. At 1053 K, as can be seen in Figures 4 and 5, at low fuel ratios, most of fuel-N appeared to be released with volatiles and then was oxidized to form NO<sub>x</sub>. This could be the reason why there was a high amount of NO<sub>x</sub> formed. This was

probably controlled by temperature only. As the fixed carbon content of the fuel increased, the  $\text{NO}_x$  formation appeared to be more controlled by char oxidation and the heterogeneous reactions started to play an important role, and a transition could take place in which the presence of volatile still evolving might have caused an atmosphere not so rich in oxygen close to the char oxidation which could first lead to a decrease in  $\text{NO}_x$  formed (Thomas, 1997). As the fixed carbon content increased, more fuel-N remained in the char, and less volatiles were present, the oxidation of char became dominant and produced higher quantities of  $\text{NO}_x$  and this resulted in an increase in the  $\text{NO}_x$  formation. It was observed that for fuel ratio of 1.55 the lowest amount of  $\text{NO}_x$  formed. A similar behavior was observed for  $\text{N}_2\text{O}$  and it appeared that the volatile-N could contribute, very significantly, to the formation of  $\text{N}_2\text{O}$  as Figure 4 illustrates. At fuel ratios above 1.75, the  $\text{N}_2\text{O}$  started to decrease which suggests that the char reduction of  $\text{N}_2\text{O}$  became important.

For  $\text{N}_2\text{O}$  emissions at 1053 K, the N/C ratio was found to correlate well with the amounts formed as shown in Figure 5. At this temperature, the  $\text{N}_2\text{O}$  emissions were the highest as expected (Davidson, 2000) and the increased fuel-N content, leading to a rise in N/C ratio, strongly favored the formation of  $\text{N}_2\text{O}$ . This may be due to the fact that at higher N/C ratios, more nitrogen was released as volatile-N and was then oxidized in the gas phase to  $\text{N}_2\text{O}$  (Pels *et al.*, 1993; Hämäläinen and Aho, 1995). The  $\text{NO}_x$  amount was first found to increase with N/C ratio up to 2.1, then to start decreasing until N/C = 2.7 and finally beyond this value to increase again. This could be due to the fact the volatile-N oxidation might first favor more the formation of  $\text{N}_2\text{O}$  at the expense of  $\text{NO}_x$ . Only at very

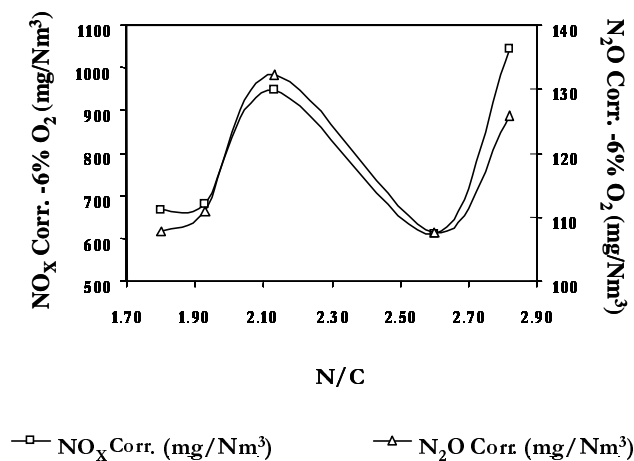


FIGURE 6  $\text{NO}_x$  and  $\text{N}_2\text{O}$  emissions versus nitrogen/carbon ratio (N/C) for  $T = 1223$  K, for the five single coals.

high N/C ratios, the oxidation of volatile-N could result in the formation of further  $\text{NO}_x$ .

At temperatures above 1053 K, a similar pattern of dependency for both  $\text{NO}_x$  and  $\text{N}_2\text{O}$  on the ratios of both fuel and N/C was observed which suggests that the oxidation of fuel-N released in volatiles may dominate the formation and destruction of both oxides of nitrogen, and the precursor responsible for the reaction could be HCN. Nevertheless, some reduction by char most likely occurred (Jonhsson, 1993; Rodriguez-Mirasol *et al.*, 1994; Thomas, 1997). As shown in Figure 6, at 1223 K the  $\text{N}_2\text{O}$  curve had the same shape as that of  $\text{NO}_x$ , possibly because of competing reactions between the destruction of  $\text{N}_2\text{O}$  and those leading to its formation. The influence of inertinite present in C Coal (Table 1) is very clear, as both  $\text{NO}_x$  and  $\text{N}_2\text{O}$  values were high at relatively lower N/C ratio. At very high N/C ratios (above 2.7), the  $\text{N}_2\text{O}$  formed increased which could be due to the fact that the fuel-N concentration was high enough to enhance the formation of  $\text{N}_2\text{O}$  to overcome those factors responsible for its disappearance (Thomas, 1997; Winter *et al.*, 1996).

### Combustion of the blends

All the blends showed similar pattern for the release of  $\text{NO}_x$  as shown in Figures 7 to 10, and presented the same trend as the parent coals. The amounts of  $\text{NO}_x$  formed increased with temperature up to about 1173 K and then started to decrease.

In the case of blends that were made of Ashland + C Coal, and Carboacol + C Coal (Figures 7 and 8), involving one coal rich in inertinite (C Coal) and two others rich in vitrinite (Ashland and Carboacol), at temperatures above 1203 K the blends produced  $\text{NO}_x$  emissions even higher than those obtained individually for

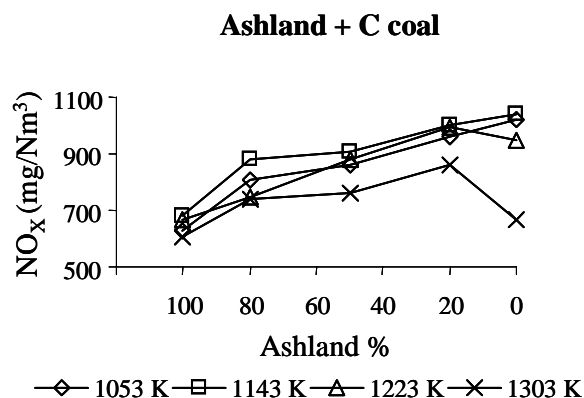
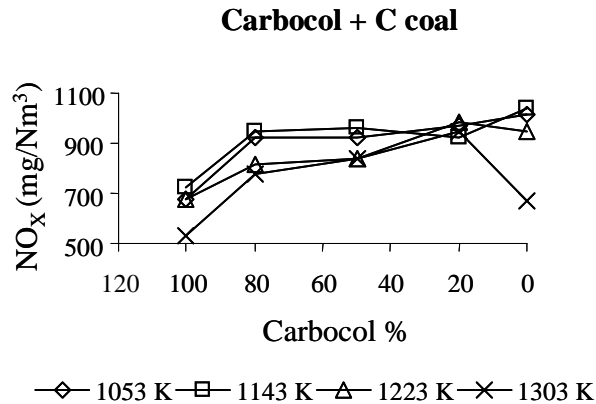
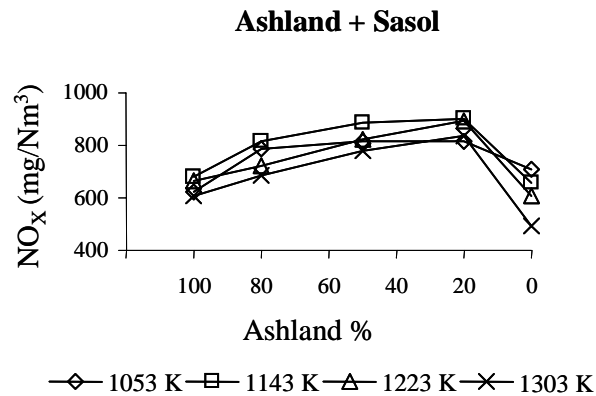
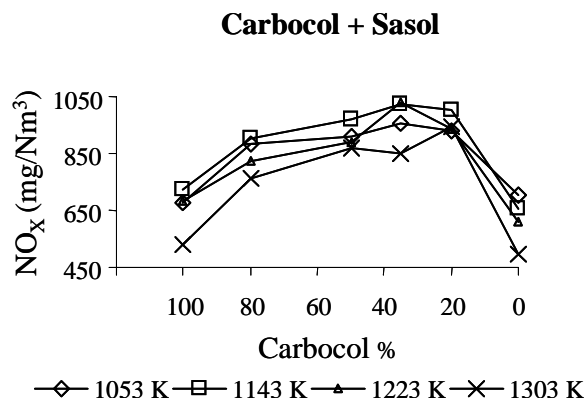
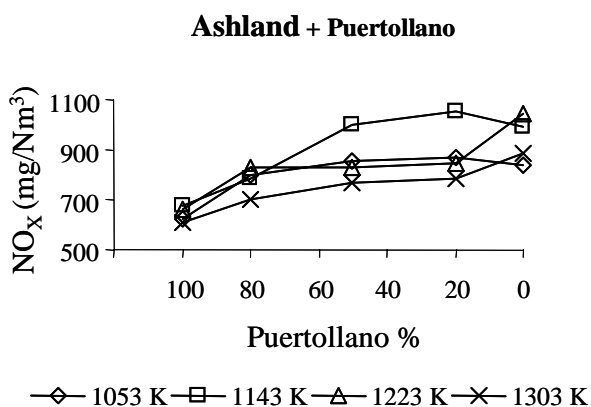


FIGURE 7  $\text{NO}_x$  emissions versus Ashland % for blend Ashland + C coal.

FIGURE 8 NO<sub>x</sub> emissions versus Carbocol % for blend Carbocol + C coal.FIGURE 9 NO<sub>x</sub> emissions versus Ashland % for blend Ashland + Sasol.

the two parent coals. Additionally, NO<sub>x</sub> and N<sub>2</sub>O emissions increased with the percentage of C Coal in the blend.

The blends, which involved Ashland + Sasol, and Carbocol + Sasol (Figures 9 and 10), were found to produce, for all temperatures, greater NO<sub>x</sub> amounts than those obtained during the combustion of each parent coal individually. At higher temperatures, the production of N<sub>2</sub>O was also greater when blends were burned. The Sasol coal has about equal amounts of both inertinite and vitrinite, which means that chars produced from this coal are fairly porous. Considering that this coal was found to produce large quantities of N<sub>2</sub>O when burned alone, this suggests that most of nitrogen groups released were CN groups, as ammonia does not give rise to N<sub>2</sub>O (Jonhsson, 1993; Aho *et al.*, 1993; Goel *et al.*, 2002). During the combustion of blends, it appears that the CN pool was very much enriched originating from both parent coals, thus producing larger NO<sub>x</sub> in all

FIGURE 10 NO<sub>x</sub> emissions versus Carbocol % for blend Ashland + Sasol.FIGURE 11 NO<sub>x</sub> emissions versus Ashland % for blend Ashland + Puertollano.

temperatures, and N<sub>2</sub>O even up to 1223 K. This could be expected because all the coals have high volatile content and tend to produce porous chars that could facilitate the release of volatiles. This rich CN pool could be assumed to result in NO<sub>x</sub> in such manner that the char reduction was not sufficient to bring down the levels of NO<sub>x</sub> formed.

The blend Ashland + Puertollano showed a similar behavior to that of Ashland coal burned alone as NO<sub>x</sub> emissions first increased up to 1143 K and then started to decrease, as shown in Figure 11. Nevertheless, the levels of NO<sub>x</sub> in the temperature range 1053 to 1143 K were higher for blends than for parent coals. Above 1143 K, the amount of NO<sub>x</sub> formed remained between the values obtained during the individual combustion of each coal. The Puertollano coal was found to give rise to very high N<sub>2</sub>O levels when burned alone, producing highest N<sub>2</sub>O

emissions at 1143 K. The rapid decrease of  $N_2O$  with temperature is consistent with other works (Jonhsson, 1993; Davidson, 2000). Nevertheless, the blend Ashland + Puertollano resulted in  $N_2O$  levels, for all temperatures and mixtures, between those of parent coals. This could suggest that the CN groups were somewhat diluted by volatiles released from Ashland coal and the gas phase reactions involving CN groups, particularly at high temperatures, gave rise to the formation of ammonia groups which were subsequently oxidized to  $NO_x$ . Furthermore, at temperatures above 1143 K, the char reduction of both  $NO_x$  and  $N_2O$  may become significant, thus keeping the levels between individual values of each coal in the blend.

## CONCLUSIONS

Combustion results of blends showed that the emission levels of  $NO_x$  observed were, on the whole, higher than expected, based on the linear correlation from the proportional amounts of parent coals in the mixture of the blend.

The blending did not cause reduction in  $NO_x$  values over the temperature range usually used in fluidized beds, that is 1073 to 1123 K. In fact, in most cases,  $NO_x$  increased, possibly due to the enrichment of precursors responsible for  $NO_x$  formation, originating from both coals making up the blend and the char oxidation.

In all series of blends studied for  $N_2O$  emissions the temperature effect was dominant, namely in the reduction of the  $N_2O$  emissions. It was also clear that  $N_2O$  was very much influenced by the nature of nitrogenous groups, as Sasol and Puertollano coals gave rise to very high  $N_2O$  levels at 1053 K, almost reaching 50% of  $NO_x$  formed. Blending, however, did not result in great reductions in  $N_2O$  levels over the usual temperature range of operation in fluidized beds, *i.e.*, 1073 to 1123 K.

Both the nature of nitrogenous groups released with volatiles and char reactivity contribute to both formation and destruction of  $NO_x$  and  $N_2O$ . It is believed that the char reactivity increased with temperature, which could be the main route for the reduction of  $NO_x$  at high temperatures. The char reactivity is dependent on the petrological composition of coal and vitrinite coals provide more porous chars, which could also facilitate the release of volatiles during combustion.

## Acknowledgments

The authors would like to thank the ECSC for financing this project, Contract 7220-ED/068.

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