

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231273238>

Release Of Nitrogen Precursors From Coal And Biomass Residues in a Bubbling Fluidized Bed

ARTICLE *in* ENERGY & FUELS · DECEMBER 2007

Impact Factor: 2.79 · DOI: 10.1021/ef700430t

CITATIONS

27

READS

33

3 AUTHORS, INCLUDING:



Pedro Abelha

Energy Research Centre of the Netherlands

34 PUBLICATIONS 369 CITATIONS

SEE PROFILE



Isabel Cabrita

DGEG - Directorate of Energy and Geology

76 PUBLICATIONS 1,436 CITATIONS

SEE PROFILE

Release Of Nitrogen Precursors From Coal And Biomass Residues in a Bubbling Fluidized Bed

P. Abelha,* I. Gulyurtlu, and I. Cabrita

Edifício J, DEECA-INETI, Instituto Nacional de Engenharia, Tecnologia e Inovação, I.P., Azinhaga dos Lameiros, Estrada Paço do Lumiar 22, 1649-038 Lisboa, Portugal

Received July 23, 2007. Revised Manuscript Received October 11, 2007

This work was undertaken with the aim of quantifying the relative amounts of NH_3 and HCN released from different residues, which included sewage sludge, refuse derived fuel (RDF), and sawdust, during their devolatilization under fluidized bed conditions. The results were compared with data collected for bituminous coals of different origin (USA, South Africa, Colombia, and UK). The relation between amounts of HCN and NH_3 released and the levels of NO_x and N_2O formed during cocombustion was also addressed. The partitioning of nitrogen between volatiles and char was also quantified. The pyrolysis studies were undertaken in a small fluidized bed reactor of 80 mm of ID and 500 mm high using an inert atmosphere (N_2). The HCN and NH_3 were quantified by bubbling the pyrolysis gases in absorbing solutions which were subsequently analyzed with selective electrodes. The combustion studies were carried out on a pilot installation. The fluidized bed combustor is square in cross section with each side being 300 mm long. There is secondary air supply to the freeboard at different heights to deal with high volatile fuels as almost all waste materials are. The temperatures in the bed and in the freeboard and that of the flue gases leaving the reactor were continuously monitored. The results obtained suggest that, while coal releases nitrogen mostly as HCN, residues like RDF and sewage sludge give out fuel-N in greater quantities as NH_3 . Residues at fluidized bed combustion (FBC) temperatures release more than 80% of the fuel-N with the volatiles. The NH_3 evolved during pyrolysis acted as a reducing agent on NO_x emissions. The presence of calcium significantly reduces the emission of N_2O probably by interfering with HCN chemistry. With high amounts of residues in the fuel mixture, the relative importance of char on the nitrogen chemistry substantially decreases. By using cocombustion, it is possible to reduce fuel-N conversion to NO_x and N_2O , by tuning the amounts of coal and residue in the mixture.

1. Introduction

Cofiring of coal mixed with biomass has advantages mostly for reducing anthropogenic CO_2 emission levels, but it could also create positive synergies between the two fuels to reduce the emission of pollutants. It should be pointed out that the ash of biomass may cause problems due to its very different nature compared with that of coal; however, this can be avoided if the operating conditions and blending of the two fuels are correctly applied. The synergy that could be achieved in cofiring is particularly applicable to the formation and eventual destruction of gaseous pollutants. Biomass fuels generally have very low sulfur content, so the formation of SO_2 can be lowered just as a result of the dilution effect. In addition, depending on the nature of the biomass ash, having Ca in relatively sufficient amounts could help in capturing gaseous SO_2 into solid CaSO_4 and, hence, improve the retention of S, particularly in fluidized beds, in which temperatures for sulfur capture are optimized. Furthermore, the possibility of reducing the addition of limestone to retain SO_2 in the fluidized beds could be beneficial because limestone is observed to catalyze the formation of NO_x . Both coal and biomass fuels have fuel-N in comparable amounts; however, the nature of fuel-N in the two fuel types is not the same and hence the precursors originating from these fuels that are responsible for the formation of NO_x are different. Compared with coal, the waste fuels derived from biomass, sewage sludges, or municipal solid wastes (MSW) are commonly referred in

the literature to give higher levels of volatile species, like tars and light gases, and less relative quantities of char.^{1–3} There have been previous studies that show some correlation between the fuel volatile matter content and the relative quantities of nitrogen released during pyrolysis.^{3,4} On the other hand, for the ranges of different coals most commonly used, data for nitrogen composition and its functional groups are available;^{5–11} for wastes and biomass fuels, such data is still scarce,^{7,12,13} and more

- (1) Desroches-Ducarne, E.; Marty, E.; Martin, G.; Delfosse, L. *Fuel* **1998**, *77*, 1311–1315.
- (2) Leppälähti, J. *Fuel* **1995**, *74*, 1363–1368.
- (3) Werther, J.; Saenger, M.; Hartge, E.-U.; Ogata, T.; Siagi, Z. *Prog. Energy Combust. Sci.* **2000**, *26*, 1–27.
- (4) Johnsson, J. E. *Fuel* **1994**, *73*, 1398–1415.
- (5) Kelemen, S. R.; Gorbaty, M. L.; Kwiatek, P. J. *Energy Fuels* **1994**, *8*, 896–906.
- (6) Davidson, R. M. *Nitrogen in coal*; IEAPER/08, IEA Coal Research: London, 1994.
- (7) Glaborg, P.; Jensen, A. D.; Johnsson, J. E. *Prog. Energy Combust. Sci.* **2003**, *29*, 89–113.
- (8) Nelson, P. F.; Kelly, M. D.; Wornat, M. J. *Fuel* **1991**, *70*, 403–407.
- (9) Nelson, P. F.; Buckley, A. N.; Kelly, M. D. Function forms of nitrogen in coals and the release of coal nitrogen as NO_x precursors (HCN and NH_3). *Proceedings of the 24th International Symposium on Combustion*; The Combustion Institute: Pittsburgh, PA, 1992; pp 1259–1267.
- (10) Wójtowicz, M. A.; Pels, J. R.; Moulin, J. A. *Fuel* **1995**, *74*, 507–516.
- (11) Pels, J. R.; Kapteijn, F.; Moulijn, J. A.; Zhu, Q.; Thomas, K. M. *Carbon* **1995**, *33* (11), 1641–1653.
- (12) Tian, F.-J.; Li, B.-Q.; Chen, Y.; Li, C.-Z. *Fuel* **2002**, *81*, 2203–2208.
- (13) Werther, J.; Ogata, T. *Prog. Energy Combust. Sci.* **1999**, *25*, 55–116.

* Corresponding author. E-mail: pedro.abelha@ineti.pt.

fundamental research is needed. Although more recent studies consider that most of the nitrogen in biomass origin materials is bounded in protein structures,¹⁴ it is difficult to find data considering the individual mass fractions of light nitrogen oxides precursors that potentially could be released during pyrolysis of biomass wastes and there is not much data related with the evolution of nitrogen precursors when residues are used in cocombustion with coal.

It is commonly accepted that biomass fuels produce larger ratios of NH_3/HCN than coals. In addition, the main source of NO_x formation from coal is usually the oxidation of char and this occurs in the bed. Fuel-N from biomass is mostly liberated with volatiles which tend to burn in the freeboard of the bubbling bed reactor, thus causing higher temperatures in that zone. The NO_x released from coal, leaving the bed, could react with NH_3 that is present in the freeboard, verifying that the conditions of NCSR (nuncatalytic selective reduction) could be created in the freeboard, to improve the reduction of NO_x , promoted with the presence of volatiles that could enlarge the optimum temperature window to the lower values^{4,15} usually used in fluidized bed systems. Furthermore, with cocombustion using additional fuels with less nitrogen, the amounts of NO_x formed could be reduced. In addition, depending on the nature of nitrogen compounds in the fuel, the formation of NO_x could be brought down, during cocombustion.¹⁶ Limestone is usually used to remove SO_2 from coal combustion; however, this could lead to increased NO_x , so steps are required to avoid this. Cocombustion could provide one way to avoid high NO_x levels due to limestone addition.

The objective of the present work is to verify to what extent NO_x reduction by NH_3 originating from biomass fuels is possible, in order to achieve significant reductions in NO_x , without the use of NH_3 injection. The synergy between coal and biomass fuels could create favorable conditions for NO_x reduction, and the work reported in this paper provides some of the results obtained so far. Complementarily, the intention of this work is to provide data regarding the individual fractions of light nitrogen oxides precursors (NH_3 and HCN) released during pyrolysis of different waste materials, compare it with several bituminous coals, and elucidate the interactions concerning NO_x formation, providing also some evidence of the advantages of adding them as additional fuels to coal, as base fuel, to simultaneously minimize nitrogen oxides, sulfur dioxide, and other gaseous pollutant emissions. Normally in the literature, the studies on pyrolysis tests are reported separately from combustion trials. In this work, those results are analyzed together and some synergies between the different fuels are identified.

2. Experimental Details

2.1. Fuels Characterization. The fuels used in this study include four bituminous coals from different origins and three types of residues that are of most interest for combustion, as sawdust from the pine cutting industry (SD), predried granulated sewage sludges (SS1 and SS2), and municipal solid waste refuse derived fuels (a typical refuse derived fuel (RDF) and a PPR, which is a nonrecyclable mixture of 15% plastic and 85% paper, by weight). The coals were from South Africa (C-SA), USA (C-US), and the UK (C-UK) and two of them were from Colombia (C-CB1 and C-CB2).

(14) Hansson, K.-M.; Samuelsson, J.; Tullin, C.; Åmand, L.-E. *Combust. Flame* **2004**, *137*, 265–277.

(15) Wenli, D.; Dam-Johansen, K.; Ostergaard, K. Widening the temperature range of the thermal DeNO_x process. An experimental investigation. *Proceedings of the 23th International Symposium on Combustion*; The Combustion Institute: Pittsburgh, PA, 1990; pp 297–303.

(16) Abelha, P. Gaseous emissions during the co-combustion of coal with wastes. PhD Thesis, FCT/UNL: Lisbon, Portugal, 2005.

Table 1. Fuel Characterization—Proximate Analysis

fuel	proximate analysis: dry basis (wt%)			LHV (MJ/kg)
	mineral matter	vol. matter	fixed carbon ^a	
C-US	7.5	39.3	53.2	29.7
C-UK	10.7	19.7	69.7	28.3
C-SA	6.2	34.8	58.9	30.4
C-CB1	26.3	22.6	51.1	27.1
C-CB2	8.3	38.5	53.2	29.7
SS1	42.8	49.8	7.4	13.1
SS2	45.6	47.8	6.6	11.6
SD	1.7	80.6	17.7	18.7
PPR	16.7	72.4	10.8	15.5
RDF	22.5	68.2	9.3	16.4

^a Results obtained by difference.

Table 2. Fuel Characterization—Ultimate Analysis

fuel	ultimate analysis: dry basis (wt%)						
	C	H	N	S	Cl	Ca	O ^a
C-US	74.9	5.1	2.0	2.1	0.05	0.20	8.4
C-UK	75.0	3.4	1.3	0.5	0.06	0.23	9.0
C-SA	77.4	6.0	2.2	0.5	0.05	0.36	7.6
C-CB1	58.7	4.5	1.2	0.6	0.04	1.2	8.7
C-CB2	76.7	5.7	1.5	0.6	0.04	0.81	7.2
SS1	34.8	5.0	4.6	0.9	0.27	4.2	11.6
SS2	30.9	3.8	3.7	0.7	0.07	5.3	15.2
SD	52.1	5.9	0.2	0.1	0.02	0.07	40.0
PPR	41.9	6.2	0.8	0.1	0.13	0.10	34.2
RDF	43.8	7.3	0.9	0.2	0.62	4.5	24.6

^a Results obtained by difference considering the mineral matter (db).

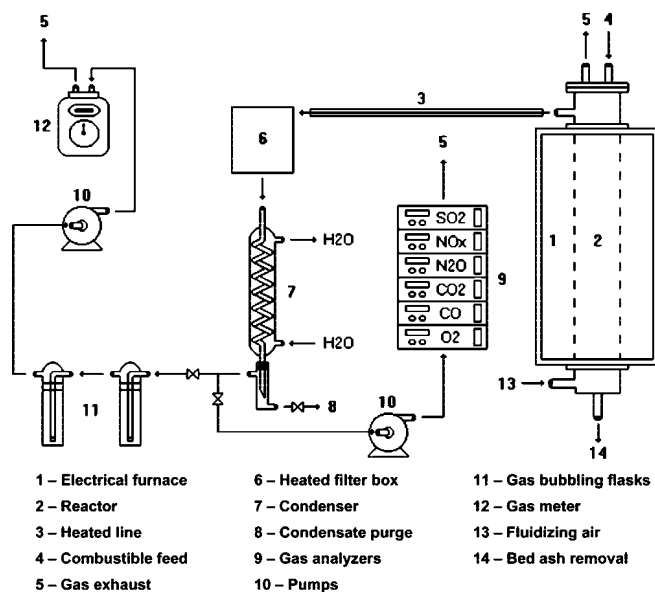


Figure 1. Experimental apparatus for the nitrogen volatile species analysis tests.

Proximate and ultimate analyses were carried out on each fuel, and the results are presented in Tables 1 and 2, respectively. Typically, waste materials have higher volatile matter/fixed carbon ratios than bituminous coals, and these properties are found to influence the temperature profile in the combustor, when adding waste to coal combustion. Mineral matter content in sewage sludge could reach 40–50% on a dry basis due to digestion of the sludge prior to the drying process and that represents 4 to 5 times the mineral matter content of typical bituminous coals (a most used solid fuel in power stations).

The carbon content and the combustible matter are smaller for the residues, in relation to the coals, and consequently, their calorific value is also lower. This has a direct implication in the fuel feed rate that has to be increased to achieve the same thermal input when adding the waste to coal combustion.

Table 3. Operating Conditions during Pilot Fluidized Bed Combustion Tests

fuels and mixtures	fuel feed rate (kg/h)	energy input (MJ/h)	fluidizing velocity (m/s)	excess air (%)	secondary air (%)	static bed height (m)
100(C-CB1)	9.1	269	1.1	50	19	0.18
70(C-CB1) + 30(RDF)	10.8	247	1.0	60	22	0.15
100(RDF)	13.4	225	0.9	61	24	0.19
100(C-US)	9.4	293	1.1	48	28	0.19
65(C-US) + 35(SS1)	10.6	258	1.0	55	24	0.19
100(SS1)	12.5	151	0.7	56	27	0.21
100(C-UK)	7.0	199	0.9	57	23	0.18
60(C-UK) + 40(SD)	9.56	224	1.0	54	24	0.17
100(SD)	9.11	146	0.6	55	26	0.13

2.2. Fuel Handling Prior to Feeding. The coals were dried, to a moisture content below 10% wt, crushed, and sieved, before collecting the size fraction between 0.5 and 4.0 mm.

The sewage sludges, SS1 and SS2, consist of a predried granulated material and were used as received, since their moisture content was about 5% wt and about 95% of their mass was between 0.5 and 4.5 mm.

The waste SD was sieved, and the fraction below 0.2 mm was rejected. It was observed that 90% of its mass was below 4.0 mm.

The PPR was shredded using in the outlet a sieve with a size of 8.0 mm. The dust generated was then separated and rejected using a 0.2 mm sieve. The bulk density of this material was quite low, being about 78 kg/m³, and the PPR was subsequently densified to 320 kg/m³, in a form of weakly bounded pellets (4 × 10 mm).

The RDF was processed from the MSW from the city of Lisbon, removing the inert materials, like glass and metals. The waste was then shredded and pelletized in cylindrical particles of 13 × 8 mm. Its composition in mass was 35% paper, 35% organics, 15% plastics, 5% textiles, and 10% dust material.

2.3. Bed Material and Limestone. The bed material was composed of washed silica sand (99.4% wt) extracted from a river. The average particle diameter, given by geometric mean calculation based on sieve retention, was 0.36 mm, and the particle density was of 2650 kg/m³. The static bed bulk density was about 1580 kg/m³.

Limestone was used in some combustion runs. The limestone was supplied by a Portuguese extracting industry and consisted of CaCO₃ of 99.5% wt purity, with particle diameters between 125 and 500 μm and a bulk density of 1540 kg/m³. The limestone was fed continuously above the bed and was previously mixed with the fuel at the desired Ca/S molar ratio.

2.4. Pyrolysis Tests. The quantification of the amounts of HCN and NH₃ released from the coals and residues was performed in the experimental apparatus represented in Figure 1. The fuels were pyrolyzed in the temperature range of 700–900 °C using an electrically heated cylindrical laboratory-scale fluidized bed with a 0.08 m i.d. and 0.5 m height. The fuels were continuously fed to the top of the bed by means of a precalibrated screw feeder and were introduced inside the reactor through a water cooled probe to prevent any volatile release inside the feeding system. The fuel feeding was fixed at a rate of 1.0 g/min. Nitrogen was used to fluidize the bed, assuring an inert atmosphere, at a flow rate of 15–20 dm³/min. After 7 min of feeding, once the pyrolysis was observed to reach stabilization, the sampling was initiated, first for HCN and then for NH₃. The volatile gases were filtered at a temperature between 140 and 180 °C and then cooled, before bubbling in the two trap solution flasks, cooled in an ice bath. The second trap solution flask was used just to ensure that all the HCN or NH₃ was collected in the first one. To collect the HCN, a 2 × 200 mL solution of NaOH 0.01 M was used, and for NH₃, a 2 × 200 mL solution of H₂SO₄ 0.01 M was utilized in an independent run. The bubbling flow rate was about 1–2 dm³/min, and the samples were collected during a period of 10–20 min. The liquid samples, including the condensates, were then analyzed using CN[−] and NH₃ Orion selective electrodes connected to an Orion 920A pH/ISE meter. The NH₃ and HCN were analyzed by trapping solution flasks (one set of two for NH₃ and another for HCN) and then using the ion selective electrodes. An alternative to wet

chemistry analysis is to use online Fourier transform infrared (FTIR) that allows studying one other nitrogen containing gas species, normally present in lower amounts at FBC temperatures, which is HNCO.¹⁴ However, an FTIR apparatus was not available for this work. One drawback of the method used in this work, concerning NH₃ determination, is that HNCO in acidic solutions can be hydrolyze to NH₃¹⁷ and the measurement will probably represent the sum of the yield of NH₃ and HNCO.

2.5. Combustion Tests. The combustion studies were carried out using the same INETI pilot installation as used in previous works that was fully described elsewhere.¹⁸ The fluidized bed combustor is square in cross section with each side being 300 mm long with a height of 5000 mm. Secondary air was supplied to the freeboard at a height of 1 100 mm from air distributor. The temperatures in the bed and in the freeboard and that of the flue gases leaving the reactor were continuously monitored. The gases were sampled through a ceramic filter and a poly(tetrafluoroethylene) (PTFE) line, both heated at 120 °C, and were analyzed for CO, CO₂, NO_x, N₂O, SO₂, and O₂ with Horiba analyzers. The methods used for gas analyses were nondispersive infrared absorption (NDIR) for all gases except for O₂ for which the paramagnetic method was used.

The fuel feeding system consists of a hopper, which has a variable screw feeder at the bottom end that discharges the fuel at the desired rate to the top of the bed.

Predefined mixtures between coal and the alternative fuels were made. The C-US, a coal with high volatile matter and sulfur content, was blended with SS1. To compensate for the lower volatile matter of the coal C-UK, it was blended with SD (the higher volatile content fuel) to maintain a mixture volatile content similar to the other blend mixtures. One other different origin coal C-CB2, with much less sulfur, was also mixed with sludge (SS2) in order to verify if similar behavior during cocombustion would take place. RDF was mixed with C-CB1, a common coal in Portuguese power stations, and a similar waste (PPR) was blended with a different origin coal C-SA, which is also habitually used in national power stations, in order to find potential synergies between coal and this type of waste. Operating conditions of the pilot-scale fluidized bed combustor are given in Table 3 for the combustion of mixtures of C-US + SS1, C-UK + SD and C-CB1 + RDF.

3. Results and Discussion

3.1. Pyrolysis Tests. Results of the pyrolysis of the coals and the wastes are summarized in Figures 2–4. Details on the individual fuels are given in Figures 5–9. The pyrolysis tests showed that there was, more or less, a linear increase of the release of gaseous nitrogen species from the fuel with the higher amounts of volatile matter entered. In fact, considering the difference in the volatile matter contents (daf) between the coals and the wastes used, it was observed that there were two distinct groups completely separated, as shown in Figure 2. This result was ever more pronounced by raising the temperature, in the

(17) Ledesma, E.; Li, C.-Z.; Nelson, P.; Mackie, J. *Energy Fuels* **1998**, *12*, 536–541.

(18) Gulyurtlu, I.; Boavida, D.; Abelha, P.; Lopes, M. H.; Cabrita, I. *Fuel* **2005**, *84*, 2137–2148.

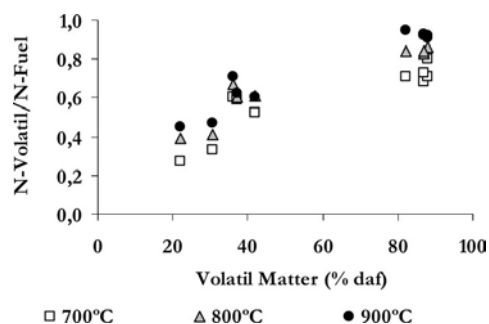


Figure 2. Influence of volatile matter in the fuel-N split to the volatile phase during pyrolysis.

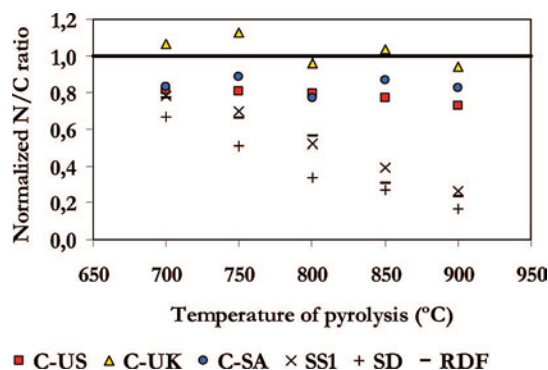


Figure 3. Nitrogen char enrichment during pyrolysis of coals and residues.

range of 700–900 °C. It is also clear that, depending on temperature, more than 80% of the fuel-N of the wastes was found in the gas phase.

One other difference, that was quite distinct, was that the chars from coals could generally maintain the original N/C ratio, as can be seen in Figure 3, while the chars from wastes tend to lose nitrogen faster than carbon giving lower normalized N/C ratios, as the temperature was increased. Values of normalized N/C ratio lower than 1 are only possible if light nitrogen rich species, like NH_3 and HCN, are released. This fact could be explained by the stronger connection of the nitrogen in the coal solid matrix, in pyrrol and pyridine rings of 5 and 6 structure members, respectively,^{8–10,19,20} whereas in wastes the nitrogen is more weakly attached, in relatively fragile structures like amines, and in protein structures,¹⁴ and in the specific case of SS, ammonium ions could also be present.¹³

Such divergences, in the nature of nitrogen functional groups and its different bindings to the solid structure of the fuel, could also explain the very different results obtained when measurement of the light nitrogen species were undertaken during pyrolysis tests. This way, it could be observed in Figure 4 that the coals released less than 5% of the fuel-N as NH_3 . However, the yield of HCN could represent about 40% of the fuel-N, as in the case of coal C-US. On the other hand, the waste derived fuel, like RDF, or wastes like SS revealed much higher NH_3 yields during pyrolysis. Values between 15 and 30% were obtained (Figure 4). Furthermore, depending on devolatilisation temperature, that value could even be higher than 30%. With the waste SD, with very low nitrogen content, there was a high uncertainty in the results obtained for NH_3 and HCN levels. However, it seems that it followed the path of coals releasing

light nitrogen species mainly as HCN, although the extremely low specific amounts released (Figure 4) must be considered. Contrary to SD, SS was found to have very high levels of nitrogen. As a result, the release of high levels of light nitrogen species were measured (Figure 4) that can act as precursors for nitrogen oxide emissions.

Pyrolysis of Coal C-US and the Waste SS1. The quantities of N-volatile released during the pyrolysis of coal C-US and the waste SS1 increased with the temperature over the temperature interval studied (700–900 °C). As it can be seen in Figure 5, the nitrogen fraction released by the coal as HCN is about 40%, being superior to the fraction liberated by the SS1, in the entire temperature range. On the other hand, the NH_3 released by the coal corresponded to less than 3% of the fuel-N, while about 30% of the fuel-N comes out as NH_3 in the sludge pyrolysis, decreasing however to 15% at 900 °C.

In an opposite trend of what happens with US coal pyrolysis, the temperature has an important role in the NH_3 /HCN ratio released by the sludge SS1, since the level of NH_3 decreased and the level of HCN increased with the temperature. However, the total quantities of N-volatile were greater, while the quantities of $(\text{NH}_3 + \text{HCN})\text{-N}$ diminished. Possibly, the presence of high amounts of iron oxides in the sludge, representing about 2% wt, catalyzes the decomposition of NH_3 to N_2 and H_2O at higher temperatures.²¹ Over the temperature range studied, SS1 had the tendency to release higher quantities of HCN than NH_3 , and for this reason, attention should be paid to N_2O formation during sewage sludge combustion, since HCN is a precursor for the formation of N_2O .

Pyrolysis of Coal C-CB2 and the Waste SS2. The total volatile-N released, from the pyrolysis of these fuels, was greater with temperature increase, in the range studied. Although both fuels are completely different in nature, the fuel-N fraction pyrolyzed as HCN was almost the same, as well as its variation with the temperature (Figure 6). However, with respect to NH_3 release, the behavior of the two fuels is completely different. The SS2 was found to liberate about 35% of the fuel-N as NH_3 at 700 °C, decreasing to 20% at 900 °C, for the same reasons pointed out before for the SS1 (the iron content of the sludge). On the other hand, the coal C-CC2 released only trace amounts of NH_3 .

Pyrolysis of Coal C-UK and the Waste SD. During coal C-UK and waste SD pyrolysis, runs the volatile-N fraction was observed to increase with the temperature, in the whole range studied. At lower temperatures of about 700 °C, the volatile-N released (about 30% of the fuel-N for C-UK and about 70% of the fuel-N for SD) should be mostly composed by tars-N and N_2 , since only about 5% of the fuel-N was released as NH_3 and HCN from both fuels, as can be seen in Figure 7. A strange observation is that the fuel-N fraction released as NH_3 is very low for the waste SD. However, the extremely low N content of the SD should be taken into consideration. For the coal UK, the NH_3 released was found to be not more than 5% of the fuel-N, and this value was not influenced by temperature change, while the HCN increased from 5 to 15% of the fuel-N when the temperature was raised from 700 to 900 °C.

Pyrolysis of Coal C-CB1 and the Waste RDF. The volatile-N fraction of these two fuels increased with the temperature rise. Furthermore, with higher temperatures, it appears that more nitrogen was released as N_2 , because the difference in the quantities of $\text{NH}_3 + \text{HCN}$ measured and the total volatile-N released was greater. During coal C-CB1 pyrolysis, upon raising

(19) Kelemen, S. R.; Gorbaty, M. L.; Kwiatek, P. J.; Fletcher, T. H.; Watt, M.; Solum, M. S.; Pugmire, R. J. *Energy Fuels* **1998**, *12*, 159–173.

(20) Kambara, S.; Takarada, T.; Yamamoto, Y.; Kato, K. *Energy Fuels* **1993**, *7*, 1013–1020.

(21) Li, C.-Z.; Nelson, P. F. *Fuel* **1996**, *75*, 525–526.

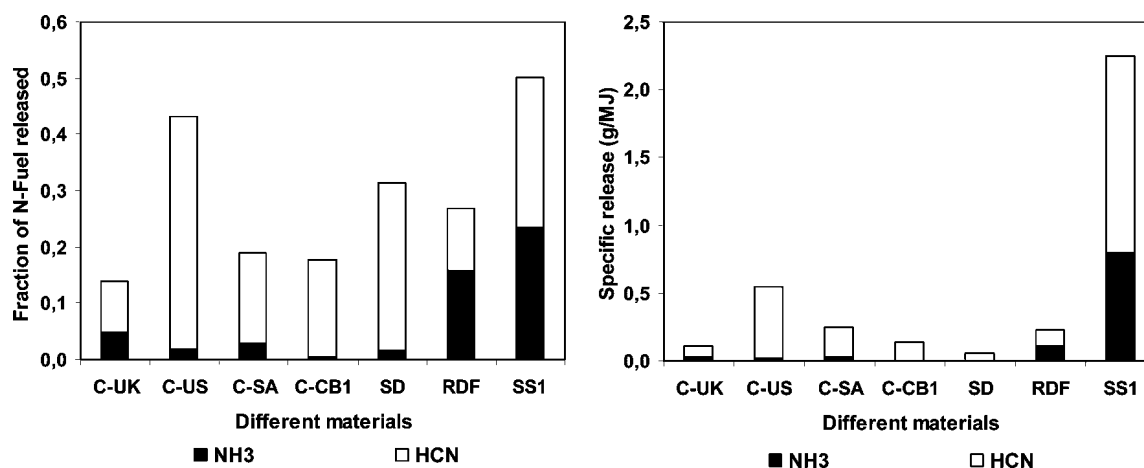


Figure 4. Nitrogen release yields as NH_3 and HCN during pyrolysis of coals and residues at 800 °C.

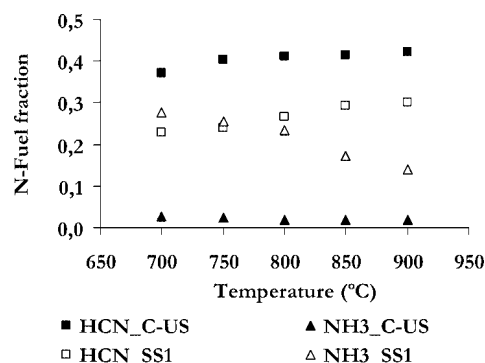


Figure 5. Nitrogen release yields as NH_3 and HCN during the pyrolysis of coal C-US and waste SS1, as functions of temperature.

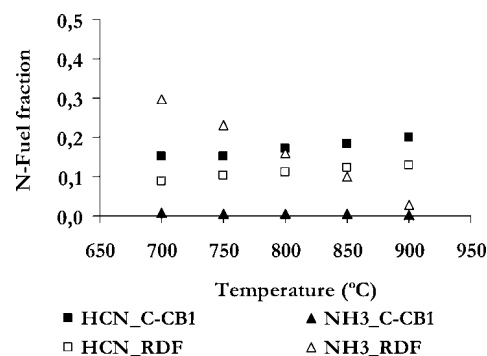


Figure 8. Nitrogen release yields as NH_3 and HCN during the pyrolysis of coal C-CB1 and waste RDF, as functions of temperature.

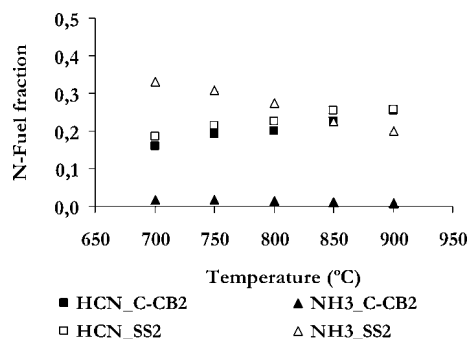


Figure 6. Nitrogen release yields as NH_3 and HCN during the pyrolysis of coal C-CB2 and waste SS2, as functions of temperature.

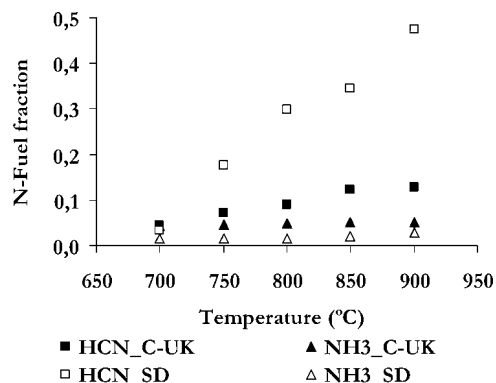


Figure 7. Nitrogen release yields as NH_3 and HCN during the pyrolysis of coal C-UK and waste SD, as functions of temperature.

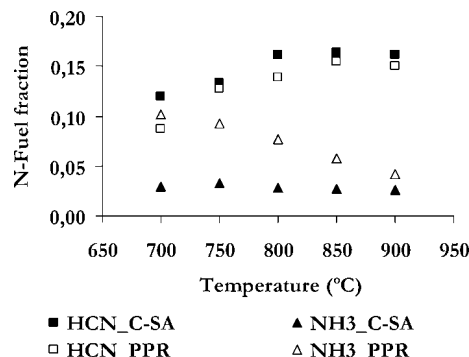


Figure 9. Nitrogen release yields as NH_3 and HCN during the pyrolysis of coal C-SA and waste PPR, as functions of temperature.

The RDF presented lower conversions of fuel-N to HCN, compared to coal, although its amount tended to get higher, from 9 to 13%, when the temperature was increased from 700 to 900 °C. On the other hand, the fuel-N conversion to NH_3 was reduced by a factor of 10, from 30 to 3%, for the same temperature increase. This could be due to some catalytic decomposition of the NH_3 , promoted by the ash or the furnace stainless steel walls, at higher temperatures.

Pyrolysis of Coal C-SA and the Waste PPR. The quantity of NH_3 released during the coal C-SA pyrolysis was under 3% of fuel-N conversion, and it was not influenced by the temperature change in the interval studied, as can be seen in Figure 9. When compared to coal, the PPR pyrolysis was found to lead to higher fuel-N conversions to NH_3 , from 10 to 5%, respectively, for the temperature range of 700 to 900 °C. The decreasing conversion with temperature was probably due to the some artifact referred to above for the RDF waste.

the temperature from 700 to 900 °C, the quantity of HCN released slightly increased from 15 to 20% of fuel-N and only trace amounts of NH_3 (<1%) were observed (Figure 8).

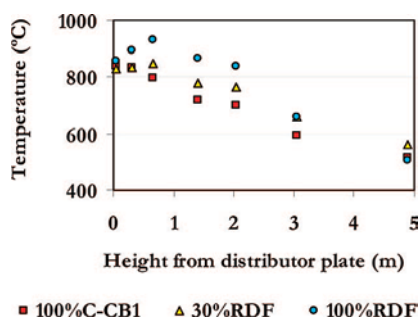


Figure 10. Influence of adding high volatile fuel to coal combustion on the temperature profile.

The fraction of HCN evolved from the pyrolysis of both fuels was quite similar, increasing from 10 to 15% in the same temperature range.

3.2. Combustion Tests. The addition of high volatile fuels to coal, during combustion, significantly alters the combustion profile, as was reported earlier in other works.^{22–24} The implications of this addition are a higher combustion rate of the volatile fuel fraction, in the freeboard of the bubbling fluidized bed reactor, increasing the temperature levels in that zone, as can be observed in Figure 10, for the cocombustion of coal C-CB1 and the RDF waste. On the other hand, the bed zone operates with less fuel. Consequently, a higher air staging ratio and a more intense mixing between the fuel and air in freeboard are required for complete combustion.

The combustion gases were analyzed for NO_x and N_2O contents, at three different heights of the combustor (0.5, 1.6, and 4.9 m from distributor plate), for establishing a concentration profile, during the cocombustion tests of the different mixtures tested. These results are presented and discussed below for each mixture studied. In order to make it easy to follow the reaction path of nitrogen oxides formation, during combustion, a simplified mechanism diagram is provided in Figure 11.

Cocombustion of C-US + SS1. Considering that the nitrogen content of the waste SS1 is twice that of the coal C-US, a significant increase in the NO_x emission would be expected, when sludge was added to coal combustion. However, during the combustion of coal, the NO_x concentration at the exit of the combustor was slightly higher than that obtained during both cocombustion with the addition of 35% wt of SS1 and the monocombustion of the SS1, as can be observed in Figure 12. This was due to the noticeable reduction of NO_x between 0.5 and 1.6 m of the freeboard height, during SS1 combustion, that could be attributed to the reaction between the NO_x formed and the NH_3 released during pyrolysis of SS1. Furthermore, in that zone of the reactor, the temperature was higher and more volatile material was present when adding SS1; this could enhance the DeNO_x mechanism.^{4,15,25–27} In fact, the conversion of fuel-N to NO_x is extremely low during SS1 combustion, as can be seen in Figure 12 (left figure at height = 4.9 m), increasing as the fraction of coal in the fuel increased.

It is also interesting to note that, during coal combustion alone, a reduction in the NO_x concentration was also recorded,

along the freeboard, although coal did not release significant levels of NH_3 . In this case, the reduction could be related to a higher concentration of carbon rich char particles, elutriated from the bed, and heterogeneous reduction of NO most likely played a significant role.

The concentration of N_2O at the reactor exit (at 4.9 m from the distributor plate) increased with the increment of SS1 fraction in the fuel, as can be observed in Figure 13. It appears that, during the combustion of SS1 alone, the formation of N_2O only occurred above the height of 0.5 m from the distributor. On an energy basis, the SS1 waste releases 3 to 4 times more HCN than coal C-US, and therefore, the homogeneous formation of N_2O is favored during sludge combustion. However, from a closer analysis of Figure 13, it appears that the fuel-N conversion to N_2O seems to be enhanced with a higher coal fraction in the fuel. Possibly, the HCN released during the pyrolysis of SS1 seems to be partially reduced to N_2 or NH_3 by catalytic action of the higher Ca content of the sludge (see Table 2), as the CaO formed catalyzes the reduction of HCN with H_2 and H_2O (Figure 11), via H and OH radicals, present in higher quantities when sludge is added to combustion, given that volatile matter, H/C, and O/C ratios are also greater. Furthermore, the CaO also catalyzes the oxidation reaction of HCN to NO as well as its reduction to N_2 (Figure 11), leaving less HCN available for the oxidation to N_2O .

To confirm the influence of calcium in the conversion of fuel-N to N_2O , some tests were done with limestone addition. The results are presented in Figure 14 for the cocombustion of coal C-US with 35% wt of the SS1 waste. It could be observed that the influence is very significant. With the fraction of the added Ca/S molar ratio in the fuel, ranging from 0 to 2.5, the conversion of fuel-N to N_2O diminished by about 30%.

The analysis of the data obtained during the cocombustion of the mixture C-CB2 + SS2 was found to give similar results independently of the differences between the two coals.

Cocombustion of C-UK + SD. The concentration of NO_x and N_2O , obtained during combustion and cocombustion of the coal C-UK and the waste SD, can be observed in Figures 15 and 16, respectively. Higher levels of NO_x and N_2O were achieved, as expected when increasing the share of C-UK fraction in the fuel, since the coal has about 6–7 times higher nitrogen content than the SD (Table 2). It can also be observed that there is a decrease in the global NO_x formation, along the reactor, while the N_2O concentration had an opposite trend. However, this behavior is much more pronounced with higher coal fractions in the fuel. This fact could partially be explained by the relatively higher specific quantities of NH_3 and HCN released during coal pyrolysis when compared with SD (Figure 4), since the NH_3 could react with NO_x reducing it to N_2 and the HCN is known to be the principal precursor of the N_2O in the gas phase (Figure 11). However, the quantity of NH_3 released by the coal, apparently, is not enough to explain the observed reduction of NO_x along the reactor. For this reason, it is believed that NO_x heterogeneous reduction, by elutriated char particles from coal resulting from attrition in the bed zone, plays a fundamental role in fluidized bed combustion. It should be remembered that the concentration of char in the bed is higher during coal combustion. In fact, a significant decrease in the fuel-N conversion was recorded, between 0.5 and 1.6 m from the distributor plate, during combustion of 100% coal C-UK (Figure 15). The presence of the coal char could explain the reason why the conversion of fuel-N to NO_x was lower in the combustion of the mixture of 60% C-UK, when compared to that obtained during the combustion of the SD alone.

(22) Gulyurtlu, I.; Abelha, P.; Gregório, A.; García-García, A.; Boavida, D.; Crujeira, T.; Cabrita, I. *Energy Fuels* **1991**, *18*, 604–610.

(23) Gulyurtlu, I.; Crujeira, T.; Lopes, M. H.; Abelha, P.; Boavida, D.; Seabra, J.; Gonçalves, R.; Sargação, C.; Cabrita, I. *J. Energy Resour. Technol.* **2006**, *128*, 123–128.

(24) Gulyurtlu, I.; Boavida, D.; Abelha, P.; Lopes, M. H.; Cabrita, I. *Fuel* **2005**, *84*, 2137–2148.

(25) Lyon, R. K. *Environ. Sci. Technol.* **1987**, *21*, 231–236.

(26) Miller, J. A.; Bowman, C. T. *Prog. Energy Combust. Sci.* **1989**, *15*, 287–338.

(27) Miller, J. A.; Glaborg, P. *Int. J. Chem. Kinet.* **1999**, *31*, 757–765.

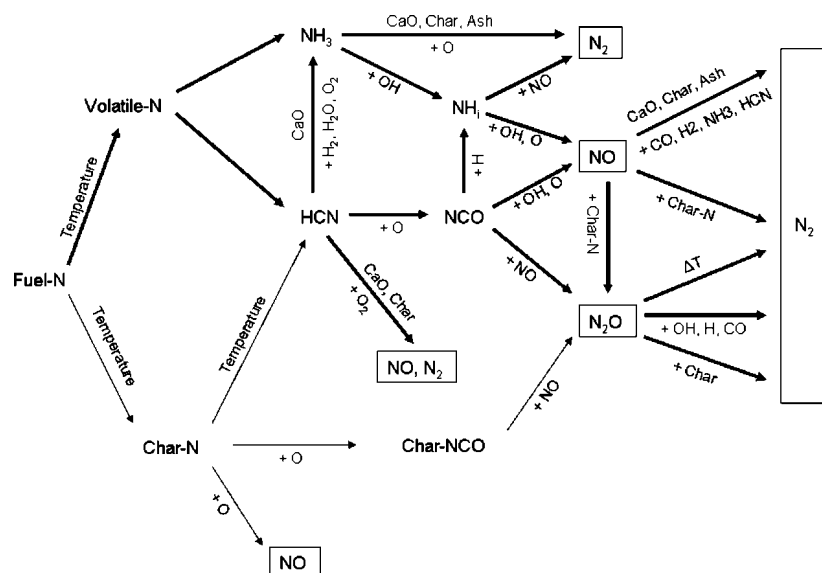


Figure 11. Simplified mechanism of the nitrogen oxides (NO and N₂O) formation. The bold arrows represent the privileged paths for high volatile biomass wastes that produce very low char-N contents, relative to coals. Adapted from ref 16.

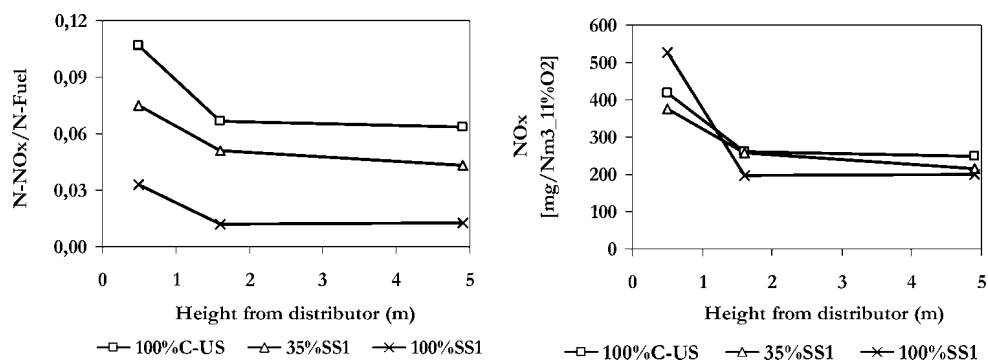


Figure 12. Conversion of fuel-N to NO_x and concentration profile of NO_x during the cocombustion of coal C-US and SS1 waste.

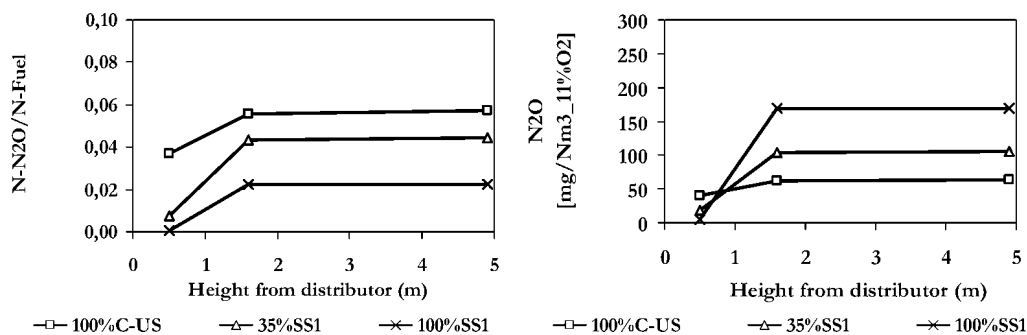


Figure 13. Conversion of fuel-N to N₂O and concentration profile of N₂O during the cocombustion of coal C-US and SS1 waste.

The fuel-N conversion to N₂O was found to increase during the combustion of SD when compared to coal C-UK combustion, as can be seen in Figure 16. This could be due to the higher fraction of fuel-N released as HCN from waste SD pyrolysis (see Figures 4 and 7), when compared to that of coal, and the lack of char promoting heterogeneous reduction of N₂O to N₂. The net conversion of fuel-N to N₂O could even be higher during the SD combustion, if the temperature would not have increased so much due to the burning of volatiles in the freeboard, as happened during cocombustion of RDF (see Figure 10). It can also be observed in Figure 15 that the different behavior of the two fuels discussed above resulted in a positive synergy between the fuels using the mixture of 40% wt of SD, since the total fuel-N conversion to N₂O obtained with the mixture, at the reactor exit, is lower than when the two fuels were burned alone.

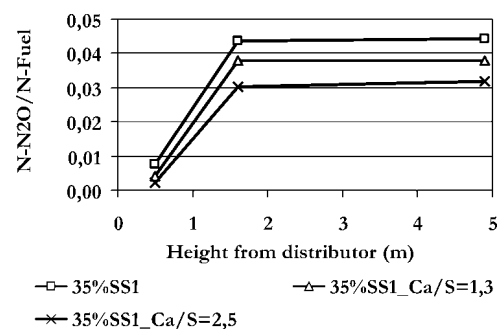


Figure 14. Influence of calcium on the conversion of fuel-N to N₂O during the cocombustion of coal C-US with 35% wt of the SS1 waste.

Cocombustion of C-CBI + RDF. The results of NO_x concentration, obtained along the combustor, are presented in

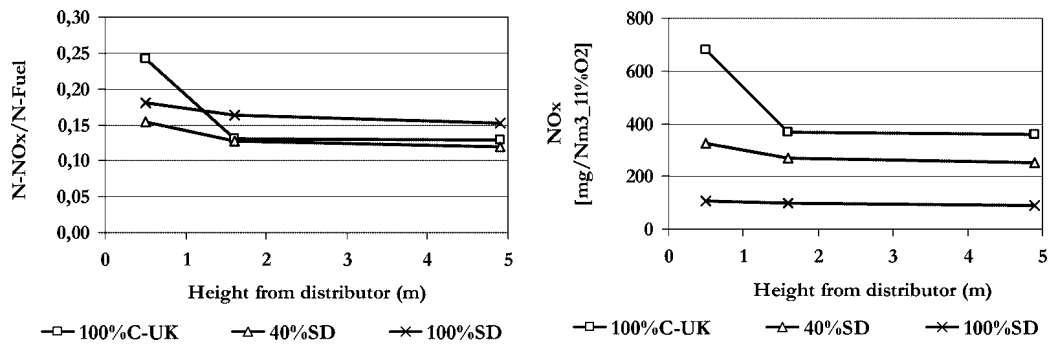


Figure 15. Conversion of fuel-N to NO_x and concentration profile of NO_x during the cocombustion of coal C-UK and SD waste.

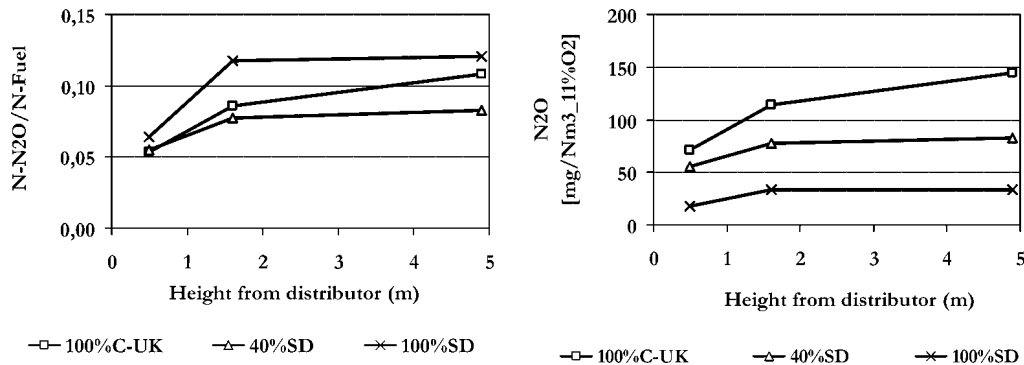


Figure 16. Conversion of fuel-N to N_2O and concentration profile of N_2O during the cocombustion of coal C-UK and SD waste.

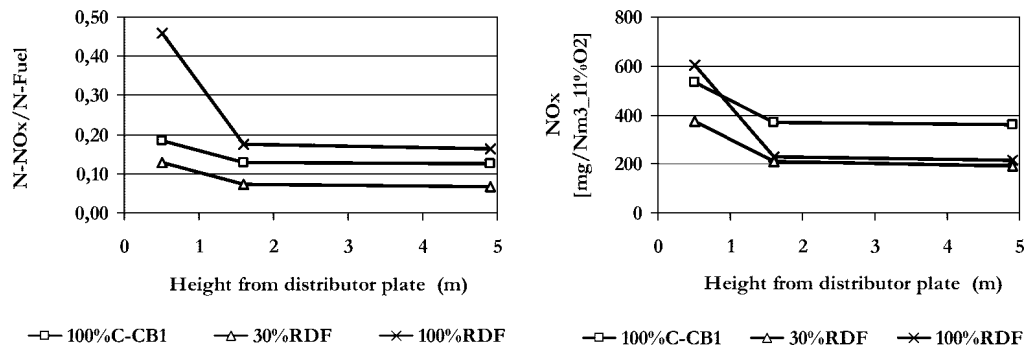


Figure 17. Conversion of fuel-N to NO_x and concentration profile of NO_x during the cocombustion of coal C-CB1 and RDF waste.

Figure 17, for the combustion and cocombustion of coal C-CB1 and RDF. It was verified that, along the combustor, there was a net reduction of the NO_x for both of the fuels, this reduction being more significant lower than 1.5 m above the air distributor, above which it was stable. It was also observed that the formation of NO_x was lowered significantly when adding of 30% wt of RDF to the coal combustion. However, during the combustion of the RDF alone, the formation of NO_x was observed to be higher than that resulting from coal combustion at a height of 0.5 m from the distributor, above which it was drastically decreased to levels similar to those obtained for the cocombustion of 30% wt RDF. In the same figure, the results for the fuel-N conversion to NO_x are also presented and it could be verified that a decrease in the levels of conversion was observed, along the entire freeboard zone, when about 30% wt of RDF was added to coal combustion. However, the conversion increased dramatically at 0.5 m above distributor, during the combustion of RDF alone, in relation to the two other cases. This phenomenon could be explained considering the differences between the char amounts and the yields of NH_3 released, observed with the two different fuels. The combustion of RDF gave rise to insignificant amounts of char, compared with coal combustion that has a 5 times greater fixed carbon content (Table 1). Furthermore, about 15–20% of the nitrogen present

in the fuel could be released as NH_3 at 800–850 °C during RDF pyrolysis (Figure 8), while coal released insignificant amounts of NH_3 . In this way, during cocombustion of coal with 30% wt of RDF, the gas phase reduction reaction between NO_x and NH_3 could be catalyzed by coal char (Figure 11), occurring in parallel to the heterogeneous reduction by coal char of the NO_x formed in the bed zone, creating a synergy to diminish NO_x formation.

During the combustion of 100% of RDF, the bed char concentration is very low and the conversion of fuel-N to NO_x was observed to increase substantially, as recorded at the top of the bed (0.5 m) in Figure 17.

The phenomenon as described above, occurring during the RDF combustion and cocombustion of RDF with coal, was not observed so clearly in the cocombustion with sewage sludges. This may be due to the higher quantities of NH_3 released during its pyrolysis that probably maximized the gas phase reduction of NO_x , resulting in a relatively smaller contribution of the reduction by char.

During the combustion of coal C-CB1 and the cocombustion with 30% wt RDF, it was observed that the reactions leading to the formation of N_2O prevailed over the reduction ones, along all the combustor freeboard. However, there was no significant production of N_2O during monocombustion of RDF, as can be seen in Figure 18. This could be explained similarly as before for

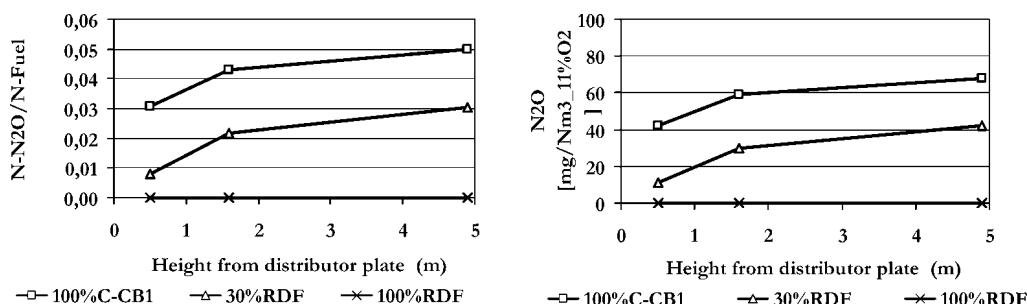


Figure 18. Conversion of fuel-N to N_2O and concentration profile of N_2O during the cocombustion of coal C-CB1 and RDF waste.

the sewage sludges, with the higher calcium content of the RDF, which is about 4 times higher than that of the coal as can be seen in Table 2. In this way, the catalysis of the reduction reaction of HCN to NH_3 , or to N_2 (Figure 11), was favored with higher fractions of RDF in the fuel. On the other hand, in spite of the higher volatile matter content of the RDF, compared to coal, the quantity of HCN released was lower. One other relevant parameter was the freeboard temperature, which increased with the share of the RDF in the fuel (see Figure 10), and the higher temperatures reached promoted the production of NO_x instead N_2O and also enhanced the N_2O thermal decomposition, which can be catalyzed by various solids, especially by calcium and char.²⁸ Furthermore, in the case of using high volatile fuels with very low fixed carbon content and very low nitrogen retention in the char, the formation of N_2O seems to occur mainly in the freeboard, through gas phase reactions. Moreover, the RDF contains a plastic fraction that during combustion could produce a high radical concentration flame contributing to N_2O destruction in a similar mechanism as the afterburning reported by Gustavsson et al.²⁹ In this way, the progressive introduction of RDF to the coal combustion could promote a gradual decrease in the fuel-N conversion to N_2O until the complete destruction of N_2O at 100% RDF combustion (Figure 18).

4. Conclusions

The wastes tested in this work produced less char, during pyrolysis, although they were more reactive, when compared with coal chars. For these two reasons, the quantity of char present in the bed inventory decreased for the combustion of blends with higher fractions of waste.

The fate of the fuel-N depends strongly on the volatile matter (VM) content of the fuel. A higher VM content favors the release of light nitrogen species, and the chars formed retain very low nitrogen contents. Residue fuels devolatilized at FBC temperatures could release more than 80% of the fuel-N with the volatiles. In this way, these wastes preferentially release the nitrogen in the freeboard, when fed above the bed. In an opposite trend, the coals retain more nitrogen in the bed with higher levels of char, promoting the heterogeneous mechanism of nitrogen oxides formation during the oxidation of the char. The fact that the nitrogen was bound in more stable structures, of 5 and 6 member rings, in the coal may explain that behavior.

Fundamental differences in the type of nitrogen species evolved were also observed for coals and wastes. The sewage sludges and the waste derived fuels (RDF and PPR) released significantly higher NH_3 /HCN ratios than coals. The different coals were observed to release less than 5% of the fuel-N as NH_3 , while the wastes could release yields up to 30%. Coal releases nitrogen oxide precursors mostly as HCN.

The addition of wastes like RDF and PPR to coal combustion could contribute to the reduction of nitrogen oxides emission, resulting in a positive synergy effect of cocombustion of high volatile residue fuels to coal as base fuel. The higher quantities of NH_3 , the higher volatile matter released, and the higher freeboard temperatures, promoted by waste combustion, altogether contributed to an improved NO_x reduction in relation to the case of coal alone. Furthermore, on one hand, less HCN was released decreasing the levels of potential precursors more likely to form N_2O ; on the other hand, greater calcium content was introduced with the fuel, leading to catalytic reduction of HCN and the catalyzing of the oxidation reactions of HCN to NO, as well as its reduction to N_2 , leaving less HCN available for the oxidation to N_2O .

The cocombustion of sewage sludges with coal appears to be a good option, since the NO_x emissions do not increase, although the nitrogen content in sludge is at least twice that of the coal. The higher quantities of NH_3 released during its pyrolysis was found to be responsible for the strong reduction of the NO_x formed, a reduction that mainly takes place along the freeboard of the reactor. On the other hand, due to the much higher quantities of the HCN released by the sludges, the N_2O emissions could increase with a higher share of sludge in the fuel feed. For this reason, special attention should be paid to keeping relatively high freeboard temperatures if significant N_2O emissions are to be avoided. These considerations should be kept in mind regardless of which kind of bituminous coal that is used as base fuel together with sludge as additional fuel.

The SD waste had very low nitrogen content, releasing small amounts of NH_3 and HCN during pyrolysis, and the emissions of NO_x and N_2O were easily brought down during cocombustion with coal C-UK. The C-UK coal has a relatively low volatile content, and it is a less reactive coal, compared to the two other coals used in this study. C-UK was found to give some combustion problems (low combustible conversion efficiency), and the addition of SD successfully increased the combustion efficiency, resulting in an additional positive synergy between coal and biomass wastes.

With cocombustion, it is possible to reduce fuel-N conversion to NO_x and N_2O by blending correctly the mixture of coal and residue, maintaining an adequate fuel/air mixture and a correct temperature. Since the Ca/S ratio content is normally higher for wastes than for coal, the cocombustion of both could result in lower SO_2 emissions without raising the NO_x , an advantage compared to the usual NO_x increase when limestone is used.

Acknowledgment. During the course of this work, the grant of P.A. was financed by the Fundação para a Ciência e a Tecnologia, through the Praxis XXI programme, and the authors would like to recognize the importance of this support.

EF700430T

(28) Bonn, B.; Pelz, G.; Baumann, H. *Fuel* **1995**, *74*, 165–171.

(29) Gustavsson, L.; Glarborg, P.; Leckner, B. *Combust. Flame* **1996**, *106*, 345–358.