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Nitrogen Release During Coal Combustion

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Abstract

Experiments in entrained flow reactors at combustion temperatures are performed to resolve the rank dependence of nitrogen release on an elemental basis for a suite of 15 U.S. coals ranging from lignite to low-volatile bituminous. Data were obtained as a function of particle conversion, with overall mass loss up to 99 % on a dry, ash-free basis. Nitrogen release rates are presented relative to both carbon loss and overall mass loss.

During devolatilization, fractional nitrogen release from low-rank coals is much slower than fractional mass release and noticeably slower than fractional carbon release. As coal rank increases, fractional nitrogen release rate relative to that of carbon and mass increases, with fractional nitrogen release rates exceeding fractional mass and fractional carbon release rates during devolatilization for high-rank (low-volatile bituminous) coals. At the onset of combustion, nitrogen release rates increase significantly. For all coals investigated, cumulative fractional nitrogen loss rates relative to those of mass and carbon passes through a maximum during the earliest stages of oxidation. The mechanism for generating this maximum is postulated to involve nascent thermal rupture of nitrogen-containing compounds and possible preferential oxidation of nitrogen sites. During later stages of oxidation, the cumulative fractional loss of nitrogen approaches that of carbon for all coals. Changes in the relative release rates of nitrogen compared to those of both overall mass and carbon during all stages of combustion are attributed to a combination of the chemical structure of coals, temperature histories during combustion, and char chemistry.

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Introduction

Pollutant formation during combustion is a dominant driving force behind combustion research and most modern technology development. The oxides of nitrogen are one of the principal pollutants of concern. Coal combustion produces more NO_x per unit of energy produced than any other major combustion technology, primarily because of the relatively large amounts of fuel nitrogen in coal [Bowman, 1992]. Coal combustion in power plants also represents the single largest point-source of NO_x in the overall nitrogen balance. Fuel-bound nitrogen in coal accounts for over 75%, and sometimes as much as 95%, of the overall NO_x generation in combustion systems [Fiveland and Wessel, 1991; Pershing and Wendt, 1976]. These observations form the motivation for a detailed study of the fate of fuel-bound nitrogen during pulverized coal combustion.

The goal of this investigation is to measure the rates of release of elemental nitrogen during combustion under conditions relevant to pulverized coal-fired boilers. The nitrogen release rates are critical, as they determine the partitioning of fuel nitrogen between the solid phase (coal or char) and the gas/aerosol phase (including suspended soot particles) at each point in the combustion process. The distinction between volatile and char nitrogen is significant as these types of nitrogen are transformed to NO_x by different chemical pathways. Volatile nitrogen has been observed to form HCN, soot-bound nitrogen, and to a lesser extent, NH_3 as intermediate species during the combustion of pyrolysis products [Chen and Niksa, 1992b; Nelson, et al., 1992]. On the other hand, a fraction of char nitrogen may form NO directly [Pohl and Sarofim, 1976a; Pohl and Sarofim, 1976b; Tullin, et al., 1993]. Technologically, the amount of nitrogen released during devolatilization is a particularly important parameter because volatile nitrogen is more amenable to control by modification of combustion zone aerodynamics than is char nitrogen.

Literature Review

The chemistry of coal-bound nitrogen is relatively well understood. Standard texts on coal structure report that coal nitrogen primarily occurs as heteroatoms in aromatic rings or ring clusters [Attar and Hendrickson, 1982; Berkowitz, 1985; van Krevelen, 1981]. Chemical models of coal structures often assume nitrogen is in aromatic rings based on its chemical stability at low temperatures [Shinn, 1984]. More recent and definitive experiments using several techniques establish nitrogen in coal as being either in the pyridinic or pyrrolic structures. Pyridinic structures refer to a large class of compounds containing ring nitrogen with sp^2 hybrid orbitals and one electron in the delocalized aromatic π cloud. The third sp^2 orbital contains a pair of electrons that are active in hydrogen bonding and other extramolecular interactions. Pyrrolic structures do not include unpaired electrons. Rather, two of the nitrogen electrons are involved in the p orbital to form the π cloud aromatic sextet. Both types of ring nitrogen destabilize the aromatic ring by 10 - 14 kcal/mol relative to the comparable homoaromatic ring. Recently, researchers [Nelson, et al., 1992; Wallace, et al., 1989] found that pyrrolic (5-membered ring) structures account for between 50 and 60 % of the total nitrogen in samples ranging in rank from brown to high-volatile bituminous coals. Pyridinic (6-membered ring) structures contribute 15 to 40 percent of the nitrogen. Quaternary nitrogen may contribute some or most of the remainder, with its concentration generally increasing with decreasing rank. Nitrogen contained in pyridinic groups is

found to be more stable than that in pyrrolic groups and to decompose at higher pyrolysis temperatures. Others [Mitra-Kertley, et al., 1993] recently measured a significant fraction of pyridone (i.e., hydroxy pyridine) structures in the low rank coals. Independent investigations [Kelemen, et al., 1993; Mitra-Kertley, et al., 1993] indicate that 6 to 10% of the nitrogen in coals is in the form of aromatic amines (such as aniline, Ar-NH_2). Both of these structures involve resonance-stabilized nitrogen, as opposed to amine functional groups attached to paraffin structures, and are of significantly different chemical character.

Early investigations of the rate of nitrogen evolution during coal combustion [Pohl and Sarofim, 1976a; Pohl and Sarofim, 1976b; Wendt and Pershing, 1977] indicate that 0-20 % of the nitrogen in the coal is released with the early volatiles, primarily in the form of HCN. Several investigators postulate that most of the nitrogen leaves the coal particles during the later stages of devolatilization [Solomon and Colket, 1978; Wendt, 1980; Wendt and Pershing, 1977]. Most of these studies indicate that nitrogen mass loss is proportional to, but different from, overall dry ash-free (daf) mass loss, being smaller by a factor of 1.2 to 1.5 [Blair, et al., 1976; Pohl and Sarofim, 1976a; Pohl and Sarofim, 1976b]. The percentage of nitrogen evolved during pyrolysis was shown to increase significantly with pyrolysis temperature [Blair, et al., 1976; Song, et al., 1982]. Experiments in which particles were heated up to 1000 K indicate tar is the primary means of nitrogen release from coal [Chen and Niksa, 1992a; Chen and Niksa, 1992b]. As particle temperature further increases in an inert environment, fractional nitrogen loss approaches unity while mass loss plateaus at less than unity [Blair, et al., 1976; Pohl and Sarofim, 1976b]. Increases in the heating rate do not significantly increase the nitrogen release when the heating rate exceeds 100 K/s at moderate temperatures of 950 °C [Cai, et al., 1993]. Pressure-dependent nitrogen evolution data indicate coal-dependent behavior [Cai, et al., 1993]. Smoot and coworkers indicate that, to first order, nitrogen evolves at approximately the same rate as overall mass during all stages of combustion and for all ranks of coal [Asay, et al., 1983; Harding, et al., 1982; Smoot and Smith, 1985]. Smoot's conclusions are based on a large number of pulverized coal particle samples from several self-sustained, high-temperature, laboratory combustors burning utility-blend pulverized-coals.

More recent data of Freihaut indicate that nitrogen release during coal devolatilization is less rapid than overall mass release [Freihaut, 1992]. These data are based on samples of intermediate rank coal devolatilized in heated grids. Current work by Solomon and coworkers [Bassilakis, et al., 1993] shows a qualitative correlation of the percentage of nitrogen released during pyrolysis versus the oxygen content of the parent coal (used as a rank indicator). They also measured more NH_3 than HCN in TG-FTIR experiments on the Argonne Premium coals, whereas no NH_3 was measured in corresponding entrained flow reactor experiments at 1100 °C. HCN release is generally associated with secondary pyrolysis of coal tar [Freihaut, et al., 1989]. Others [Chen, et al., 1992; Chen and Niksa, 1992b] find that nitrogen is transported out of the coal matrix in aromatic compounds occurring in tars and oils and subsequently contributes significantly in early soot formation. Models for nitrogen release during devolatilization [Niksa, (submitted 1994); Niksa, 1993] suggest that tar shuttling is the primary mechanism for nitrogen release at particle temperatures up to approximately 1440 K, with HCN production from residual char contributing at higher temperatures or at extended residence times. Additionally, nitrogen release is observed and modeled as a heating-rate-dependent process, with the intraparticle conversion of HCN to NH_3 decreasing with increasing heating rate [R. Bassilakis, 1993].

In this report, we present a unified treatment of nitrogen release data from two facilities at Sandia's Combustion Research Facility, the coal devolatilization laboratory (CDL) and the char combustion laboratory (CCL). Raw data from the CCL and CDL have been presented previously in separate milestone reports [Fletcher and Hardesty, 1992; Mitchell, et al., 1992]. This combined data covers a suite of U.S. coals ranging in rank from lignite to low-volatile bituminous, and spans the complete devolatilization process as well as a large portion of the char combustion process. For each coal, data from the three facilities are combined to yield a single nitrogen release history. The nitrogen release histories are then examined, with particular emphasis on deriving mechanisms that explain the rank dependence and conversion dependence of the results.

Materials and Experimental Methods

Table 1 lists the coals used in this study along with their proximate analyses. All coals examined were size classified. Data from more than one size class have been combined in the following analyses and discussion. Coals were derived for studies conducted for The US Department of Energy (DOE) and the Electric Power Research Institute (EPRI). The DOE-supplied coals are designated by Pennsylvania State Office of Coal (PSOC) numbers and were aerodynamically classified under a nitrogen environment in addition to being size classified. The EPRI-supplied coals were obtained from ABB-Combustion Engineering. They have been subjected to various extents of physical coal cleaning to reduce their mineral content, as represented by the designations RM (run-of-mine), MC (medium cleaned) and DC (deep cleaned). Because these physical cleaning processes should not have major impacts on the organic reactions, data for the three different samples are combined in studying nitrogen release rates.

In all cases, the elemental concentrations of the organic and inorganic components were established by replicate ASTM analyses of the raw coal. Silicon and aluminum were used as tracers to identify the overall rate of mass release from the coal. In the case of the CCL, the ratio of the mass fed to the mass extracted from the combustor was also used to compute the overall mass loss. This procedure could not be used in the CDL, where tar condensation and collection prevent a meaningful measurement. The agreement between the mass balance and tracer results using aluminum and silicon in the CCL is excellent (typically within 5 percent) [Baxter and Mitchell, 1992].

The fractional loss of any element j , from the particle at time t , on either a dry or dry, ash-free basis, is determined from a combination of the overall mass loss and the change in the mass fraction of that element, as follows

$$R_j(t) = \frac{m(t)}{m_o} \frac{x_j(t)}{x_{oj}} \quad (1)$$

where R_j represents the cumulative fraction of the original mass of element j released from the particle up to time t , m is the overall mass of the particle, and x is the mass fraction of element j in the particle. Subscript o represents a value in the raw coal (residence time of 0 ms). All other values are time dependent, as indicated.

Table 1

Size-classified coals used to determine nitrogen release rates and mechanisms.

Coal	PSOC # or other sample designation	Parr Values*			Ash†	Rank
		Fixed Carbon	Volatile Matter	Heating Value		
		mass %	mass %	Btu/lb	mass %	
Pocahontas #3	1508-D	83.8	16.2	15642	7.4	lv Bituminous
Lower Kittanning	1516-D	81.4	18.6	15488	10.3	lv Bituminous
Pittsburgh #8	1451-D	61.2	38.8	14682	13.7	hv A Bituminous
Pittsburgh #8	EPRI-DC	54.9	45.1	13752	8.7	hv B Bituminous
Pittsburgh #8	EPRI-MC	55.2	44.8	13643	11.8	hv B Bituminous
Kentucky #9	EPRI-MC	54.2	45.8	12939	10.3	hv C Bituminous
Pittsburgh #8	EPRI-RM	54.9	45.1	12867	33.7	hv C Bituminous
Illinois #6	1493-D	57.1	42.9	12832	15.2	hv C Bituminous
Hiawatha	1502-D	55.8	44.2	12678	9.0	hv C Bituminous
Kentucky #9	EPRI-RM	54.6	45.4	12286	15.0	hv C Bituminous
Blue #1	1445-D	52.1	47.9	12107	4.6	hv C Bituminous
Dietz	1488-D	56.1	43.9	10000	5.4	Subbituminous B
Smith-Roland	1520-D	38.0	62.0	9177	12.4	Subbituminous C
Lower Wilcox	1443-D	21.8	78.2	8459	21.4	Subbituminous C
Beulah	1507-D	54.3	45.7	7747	12.5	Lignite A

* Fixed carbon and volatile matter are on dry, *mineral*-free (as opposed to ash-free) basis.
Heating value is on a moist, mineral-free basis.

† Ash is on a dry basis.

Results and Discussion

A detailed discussion of the results for one lignite, one high-volatile bituminous coal, and one low-volatile bituminous coal will be presented. The results from the remaining coals will be summarized at the end of the discussion. Cumulative fractional nitrogen and carbon release are illustrated as a function of overall mass release in all cases. These are mathematically represented as $1 - N/N_0$ and $1 - C/C_0$, respectively. When plotted as a function of dry, ash-free mass loss, the trends begin at zero and end at unity. Their deviation from parity (elemental loss equal to overall daf mass loss) is an indication of selective mechanisms of reaction.

The selective removal of nitrogen vs carbon or mass during coal combustion is more easily appreciated when viewed on a differential basis rather than a cumulative basis. The differential changes in nitrogen and carbon composition as a function of overall mass loss are determined by fitting smooth lines through the cumulative data and differentiating the results. These are normalized by the instantaneous nitrogen and carbon concentrations to produce normalized reaction rates dN/N and dC/C . The latter values are plotted as a function of overall daf mass loss to

compare the reactivity of nitrogen and carbon. In general, these functions tend to infinity in the latest stages of burnout. The ratio of the two functions $\frac{dN/N}{dC/C}$ is more well behaved and is a direct indication of the relative reaction rates of carbon and nitrogen. Values greater than unity indicate nitrogen is more reactive than carbon, where *reactive* is understood to mean more prone to devolatilize, oxidize, or otherwise leave the particle. This ratio of rates is a nonnegative function of mass loss, but there are no other bounds on its behavior.

Care has been taken to avoid introducing anomalous behavior when differentiating the data. There is some danger that the data could be overinterpreted. Small features in the differentiated data are not physically meaningful, but large features that persist over significant changes in overall mass loss certainly are.

Representative Results from Three Coals

Cumulative, normalized, nitrogen and carbon release from coal particles is illustrated as a function of dry, ash-free (daf) mass loss in Fig. 1 for the Beulah lignite. Carbon, nitrogen, and mass are all normalized by the initial carbon, nitrogen, and mass of the coal. Also shown is a straight line labeled parity with a slope of unity, which represents elemental loss in direct proportion to dry, ash-free mass loss. The smoothed lines through the data represent smoothed fits of the data and are used to quantify the differential results presented later.

The data in Fig. 1 illustrate how fractional nitrogen loss is significantly less than overall fractional mass loss during the early stages of lignite devolatilization (0-25 % daf mass loss). This difference is attributable to the large amount of light gases released from the lignite during this stage of devolatilization. The light gases contain significant amounts of moisture, derived from hydroxyl functional groups, and carbon dioxide, derived from carboxyl functional groups. Since the dominant form of nitrogen is in heteroaromatic clusters [Attar and Hendrickson, 1982; Nelson, et al., 1992], and since these structures are not released or ruptured to significant extents in the early stages of lignite devolatilization, the nitrogen loss rate is substantially below the overall mass loss rate. On a whole-coal, wet basis, the difference would be larger. During later stages of devolatilization (25-60 % daf mass loss), some aromatic clusters are released intact as tar and others are ruptured to form light gases. This is reflected in the data as an onset of nitrogen loss.

Derivatives of the smooth lines in Fig. 1 are used to quantify the normalized release rates of nitrogen and carbon as function of overall daf mass loss. These reaction rates are defined as the differential mass release rate divided by the residual mass of each element, for example dN/N . Figure 2 presents these relative normalized rates for the Beulah lignite, PSOC-1507D. Both functions tend to large values as fractional daf mass loss tends to unity, but since there is no time information in the data, this is a consequence of data spacing rather than combustion chemistry.

Figure 3 represents nitrogen release relative to both carbon and mass, that is $\frac{dN/N}{dC/C}$ and $\frac{dN/N}{dm/m}$.

This is the most easily interpreted presentation of the data. Values greater than unity indicate more rapid nitrogen loss relative to carbon or overall mass loss, respectively. Values less than unity

Figure 1 Normalized, cumulative nitrogen and carbon loss as a function of normalized, dry ash-free (daf) mass loss for Beulah lignite, PSOC-1507D. The data in Figs. 2 and 3 are based on the smooth lines in this figure.

indicate less rapid nitrogen loss compared with either carbon or mass, respectively. Unlike the functions illustrated in Figs. 1 and 2, these functions are not predisposed to begin or end at fixed values and remain finite over the entire range of daf mass loss.

The data illustrated in Fig. 3 indicate that nitrogen loss rate lags carbon and mass loss rates during the early stages of devolatilization. As devolatilization progresses, there is a large increase in nitrogen loss relative to both carbon and overall mass, with nitrogen loss rates exceeding those of carbon by as much as 60% and exceeding those of overall mass by up to 20%, on normalized bases. This preferential loss of nitrogen relative to carbon persists through the early stages of oxidation, although the ratio of nitrogen to carbon loss decreases from 1.6 to about 1.2.

The major features of the devolatilization portion of Fig. 3 can be related to coal structure and devolatilization mechanisms. Nitrogen loss lags both carbon and mass in the early stages of devolatilization of this lignite because light gases formed from functional groups dominate mass loss. Of the three principal forms of nitrogen in coal (pyrrolic, pyridinic, and quaternary), only

Figure 2 Normalized release rates of nitrogen and carbon as a function of overall mass loss for the Beulah lignite, PSOC-1507D.

quaternary nitrogen in amine forms would be expected to be released during this stage of devolatilization. As indicated earlier, only a small fraction of the total nitrogen is in this form. Carbon, on the other hand, occurs both in aromatic clusters and functional groups.

As tars begin to evolve, normalized rates of nitrogen loss increase relative to carbon and mass loss. Tar-forming constituents of coal are largely aromatic and contain most of the coal nitrogen. The evolution of increasing amounts of tars relative to light gases at this stage of particle reaction effect a notable increase in normalized nitrogen release rates seen during the latter stages of devolatilization. If this were the only mechanism driving nitrogen loss, the normalized reaction rates would become essentially equal. The consistent observation is, however, that normalized nitrogen reaction rates exceed those of either carbon or overall mass during the transition from late stages of devolatilization to early stages of char oxidation.

We postulate that the preferential loss of nitrogen relative to carbon, indicated by values above unity in Fig. 3, is related to the effect of ring nitrogen on ring stability. Nitrogen in an aromatic

Figure 3. Release rates of nitrogen relative to carbon and mass as a function of daf mass loss for Beulah lignite, PSOC-1507D. Normalized nitrogen release rates exceed those of carbon during about half of the combustion lifetime and slightly exceed those of mass for slightly less than half of the combustion lifetime of Beulah lignite.

cluster has the effect of destabilizing the cluster relative to its homoaromatic counterpart. The aromatic stabilization energy of a heteroaromatic cluster is typically about 10-16 kcal/mol less than that of the similar homoaromatic cluster [Morrison and Boyd, 1973]. For example, pyridine has an aromatic resonance energy of about 20 kcal/mole whereas benzene's aromatic resonance energy is 36 kcal/mol. Under conditions of devolatilization sufficiently severe to thermally rupture delocalized aromatic bonds, the less stable heteroaromatic clusters would be expected to rupture first. Others [Wornat, et al., 1988] have studied polyaromatic compounds (PAC) from a bituminous coal, and have observed that nitrogen containing PACs are more quickly transformed to gases and soot than their homoaromatic counterparts. The presence of nitrogen in the ring thus accelerates pyrolytic transformations leading to ring rupture or to ring growth. The ruptured aromatic cluster is less stable than its intact aromatic parent and continues to disintegrate to form smaller, more volatile products. The increase in nitrogen release rate during the late stages of coal devolatilization reflects this volatility of the nitrogen-containing products.

The preferential release of nitrogen continues well into the oxidation stage of combustion. At the beginning of this region, oxygen reacts with the char matrix heterogeneously, with the associated

heat release causing a large and abrupt increase in particle temperature. Particle temperature histories for these coals indicate an abrupt temperature increase of as much as 500 K at the onset of heterogeneous oxidation. *In situ* measurements in the CCL indicate particle temperatures of 1700 - 2000 K in the early phases of char combustion depending on oxygen concentration and coal type. This elevated temperature may accelerate the final phase of devolatilization and nitrogen release. At these temperatures, all nitrogen release cannot be explained by tar production. Song et al. [1982] have observed significant release of nitrogen from an essentially volatile-free char on time scales of 400 msec at 1500 - 1700 K. Evolution of nitrogen-rich volatile matter, accelerated by the elevated particle temperatures, is thus a likely explanation for the preferential release of nitrogen in the early stages of char combustion.

In addition to the thermal mechanism for nitrogen release in the early stages of char combustion, it is also possible that heteroaromatic systems oxidize more readily than their homoaromatic counterparts at high temperature. Char oxidation typically occurs on a relatively small number of active sites, with carbon atoms on the basal planes of large homoaromatic (graphitic) units being quite nonreactive. Potential active sites include the edges of aromatic units, free radicals, heteroatom sites, aliphatic carbon, and sites influenced by inorganic impurities or other potential catalysts. Nitrogen in large aromatic clusters must be located at edge sites based on bonding constraints. Preferential oxidation of heteroaromatic clusters or of edge sites may contribute to the increased rate of nitrogen release observed in the early oxidation stages of combustion, corresponding to the range of 50-70 % overall mass loss in the case of the Beulah lignite. Song et al. [1982], however, present evidence that there is no preferential consumption of nitrogen due to the oxidation process itself. They attribute the observed decreases in N/C ratio as the result of thermally-induced nitrogen liberation occurring at the high temperatures associated with char combustion.

If oxygen preferentially attacks heteroaromatic rings, the preferential nitrogen loss would become self limiting in cases of transport-influenced or transport-limited combustion. For example, under the experimental conditions used to generate the data in Figs. 1-3, the lignite oxidation rate is controlled by mass transfer through the particle boundary layer [Mitchell, et al., 1992]. In this case, as nitrogen became depleted from the thin layer of oxygen-penetrated char surface, the rate of nitrogen loss would decrease as residual carbon in that thin layer must be consumed to expose additional nitrogen sites. This transport effect would reduce the rate of nitrogen release in the intermediate-to-late stages of char combustion. Overall, the results presented here do not identify the relative importance of the thermal and oxidative mechanisms. We will demonstrate, however, that the high relative rate of nitrogen release during the transition from devolatilization to combustion and the modestly higher rate of nitrogen release during combustion is a feature of coal combustion for a large range of coal types.

Rank Dependence

The same coal-structure-based interpretation of the data for Beulah lignite is useful in examining behaviors observed for coals of different rank. The data in Figs. 4 and 5 are derived from an Illinois #6 coal (see Table 1) and illustrate a change in behavior as coal rank changes from lignite to

Figure 4. Normalized, cumulative nitrogen and carbon loss as a function of normalized, dry ash-free (daf) mass loss for Illinois #6, PSOC-11493D. The data in Fig. 5 are based on the smooth lines in this figure.

Figure 5. Release rates of nitrogen relative to carbon and mass as a function of daf mass loss for Illinois #6, PSOC-11493D. General features of nitrogen loss rates relative to carbon and mass resemble those in Fig. 3 for Beulah lignite. The primary difference lies in the initial rates of nitrogen loss.

high-volatile bituminous coal. Compared to Beulah lignite, this coal produces less light gas and more tar during devolatilization [Fletcher and Hardesty, 1992], as has been observed for other bituminous coals [Howard, 1981]. Nitrogen is not expected to be found in the light gases generated by functional group decomposition during the early stages of devolatilization with the possible exception of a small amount of amine nitrogen, but it is expected in the tars and devolatilization products formed from aromatic ring rupture. Because of the higher tar yields of Illinois #6 coal, the nitrogen loss and overall mass loss curves are more similar during the early stages of devolatilization than for the Beulah lignite. Nitrogen loss rates still lag mass and carbon loss rates during early stages of devolatilization, but the difference is less pronounced than was observed for Beulah lignite. During the later stages of devolatilization, when tar dominates the primary devolatilization products, nitrogen release rates increase relative to carbon and mass loss rates. During the early stages of oxidation, temperatures are sufficiently high to cause aromatic clusters to rupture, and nitrogen loss exceeds that of carbon or mass by a significant margin. As in the case of the Beulah lignite, the nitrogen loss rate exceeds that of either overall mass or carbon well into the char oxidation stage of combustion.

Data for a lv bituminous coal, Pocahontas #3, are shown in Figs. 6 and 7. This coal produces the least amount of light gas during devolatilization [Fletcher and Hardesty, 1992] among the coals investigated. Data are also limited to about 50 % mass loss due to the low volatile yield, low reactivity, and limited residence time available in the reactor. During devolatilization and the early stages of oxidation, the data indicate the largest observed enhancement of nitrogen loss relative to the release rates of either carbon or overall mass of any of the coals investigated. Nitrogen loss rates for this coal exceed those for carbon or overall mass during all stages of combustion. This behavior is consistent with the organic structure of this coal and the mechanistic description given above.

Data for Remaining Coals

Data for the remaining coals are compiled in Figs. 8-16. The remaining coals exhibit trends consistent with those seen in Figs. 1-7, although in several cases the data are less complete than for the three coals examined thus far. Consistent trends in these data include: (1) during the early stages of devolatilization, nitrogen release rates are low for lignites and increase with increasing rank, becoming approximately equal to the rates of mass and carbon loss for high-rank (hV A bituminous and higher) coals; (2) during the late stages of devolatilization the rates increase and typically exceed the normalized rates of mass loss and carbon loss; (3) during early stages of oxidation, normalized nitrogen release rates continue to increase, typically exceeding the normalized rates of mass loss by about 40 % and exceeding the normalized rates of carbon loss by 60 %; and (4) during the late stages of oxidation, the normalized rates of nitrogen, carbon and mass loss become comparable. Many of the figures also suggest that nitrogen evolution occurs in two overlapping stages – one during late stages of devolatilization and a second during early stages of oxidation. These types of details in the reaction rate curves are less definitive than the previous four observations, but this two-stage evolution of nitrogen is consistent with previous results and models [R. Bassilakis, 1993].

Figure 6. Normalized, cumulative nitrogen and carbon loss as a function of normalized, dry ash-free (daf) mass loss for Pocahantas #3, PSOC-1508D. The data in Fig. 7 are based on the smooth lines in this figure.

Figure 7. Release rates of nitrogen relative to carbon and mass as a function of daf mass loss for Pocahantas #3, PSOC-1508D. A consistent increase in the rate of nitrogen release relative to either carbon or mass with increasing rank is observed during early stages of devolatilization by comparing Figs. 3, 5, and 7. As with lower-ranked coals, the rates become more similar during later stages of combustion.

Figure 8. Cumulative losses of carbon and nitrogen (top) and release rates of nitrogen relative to carbon and mass (bottom) as a function of daf mass loss for Lower Wilcox lignite, PSOC-1443D. Data are available only for the oxidation portion of coal combustion.

Figure 9. Cumulative losses of carbon and nitrogen (top) and release rates of nitrogen relative to carbon and mass (bottom) as a function of daf mass loss for Smith Roland coal, PSOC-1520D. Data are available only for the oxidation portion of coal combustion.

Figure 10. Cumulative losses of carbon and nitrogen (top) and release rates of nitrogen relative to carbon and mass (bottom) as a function of daf mass loss for Dietz coal, PSOC-1488D. Data are available only for the oxidation portion of coal combustion.

Figure 11. Cumulative losses of carbon and nitrogen (top) and release rates of nitrogen relative to carbon and mass (bottom) as a function of daf mass loss for Blue #1 coal, PSOC-1488D.

Figure 12. Cumulative losses of carbon and nitrogen (top) and release rates of nitrogen relative to carbon and mass (bottom) as a function of daf mass loss for Kentucky #9 coals. Data for the run-of-mine and medium-cleaned versions of the coal are combined.

Figure 13. Cumulative losses of carbon and nitrogen (top) and release rates of nitrogen relative to carbon and mass (bottom) as a function of daf mass loss for Hiawatha coal, PSOC-1502D. Data are available only for the oxidation portion of coal combustion.

Figure 14. Cumulative losses of carbon and nitrogen (top) and release rates of nitrogen relative to carbon and mass (bottom) as a function of daf mass loss for Pittsburgh #8 EPRI coals. Data for the run-of-mine, medium-cleaned, and deep-cleaned versions are combined.

Figure 15. Cumulative losses of carbon and nitrogen (top) and release rates of nitrogen relative to carbon and mass (bottom) as a function of daf mass loss for Lower Kittanning coal, PSOC-1451D.

Figure 16. Cumulative losses of carbon and nitrogen (top) and release rates of nitrogen relative to carbon and mass (bottom) as a function of daf mass loss for Lower Kittanning coal, PSOC-1516D. Data are available only for the oxidation portion of coal combustion.

Observations of differential rates of nitrogen loss relative to carbon or overall mass are most easily made using size-classified particles. Systems using utility-grind coal may result in smaller observed differences since large particle-to-particle variations in the extent of reaction typically exist in any given sample. These data provide information regarding the rates and mechanisms of nitrogen release from coal that is not easily obtainable from practical systems but that is instrumental in developing improved understanding of such practical issues as NO_x formation and burner design.

Conclusions

Rates of nitrogen release during pulverized coal combustion vary with coal type and also change significantly over the course of the combustion process. The relative rates of release of elemental nitrogen and total sample mass show clear and consistent trends with parent coal rank that can be rationalized mechanistically in terms of the mode of occurrence of nitrogen in coal.

For lignites and subbituminous coals in the early phases of devolatilization, fractional nitrogen release rates are much slower than the fractional release of carbon or overall mass. The early volatiles released from lignites and subbituminous coals are dominated by light gases formed from functional groups in the coal containing little, if any, nitrogen. As particle temperatures rise and aromatic clusters are either volatilized or ruptured to form volatile products (tar), nitrogen release is initiated. During tar expulsion, nitrogen is released *preferentially* to carbon or total sample mass, because nitrogen-containing heteroaromatic ring clusters are less stable than their homoaromatic counterparts. The ratio of the normalized release rates is observed to be as high as 1.8.

For the low rank coals, the preferential release of nitrogen continues in the early stages of char combustion. After the disappearance of the visible volatiles flame, a slower evolution of volatiles continues, in which elemental nitrogen, hydrogen and oxygen are released preferentially to carbon. Oxygen also begins to attack the char matrix heterogeneously at this point, causing a large and abrupt increase in particle temperature, which accelerates the final phase of devolatilization. In the young char in the early stages of combustion, nitrogen-containing aromatic structures are less stable thermally, and may also be more susceptible to heterogeneous oxidative attack. Finally, in the intermediate to late stages of char combustion, the release of nitrogen slows and the fractional release rate of nitrogen relative to total mass drops to near one.

For bituminous coals the sequence of events is similar to the one described in the two preceding paragraphs for low-rank coals, with the exception that the bituminous coals do not show the initial release of nitrogen-poor light gases. The initial retention of nitrogen that is pronounced for low rank coals, is barely measurable for the Illinois #6 high-volatile bituminous coal, and does not occur for the high-rank Pocahontas coal. The volatile matter in higher rank bituminous coals is dominated by aromatics, and this results in a preferential loss of nitrogen (in a cumulative sense) throughout the entire devolatilization and char combustion processes.

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