Homogeneous Nitrous Oxide Formation and Destruction under Combustion Conditions

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N_2O decomposition and formation during the oxidation of NH_3 and HCN were studied in a quartz flow reactor in the presence of CO, NO and other gases. The emphasis is on the influence of CO and NO. In addition, the homogeneous nitrogen chemistry of fluidized bed combustion and the selective noncatalytic reduction of NO (SNR) are discussed. The rate of N_2O decomposition in N_2 agrees with a first-order rate expression. The presence of CO or H_2 increases the decomposition rate regardless of the additional presence of O_2.

For the formation of N_2O, HCN oxidation is more efficient than NH_3 oxidation. The presence of NO increases the amount of N_2O formed during the oxidation of HCN or NH_3. CO moves the N_2O formation toward lower temperatures. H_2O increases the reaction rate where few components are present, whereas H_2O has little influence in the presence of large amounts of a combustible component such as CO. There are indications that NO is a necessary intermediate for any significant formation of N_2O during the oxidation of NH_3 and HCN. NO reduction is obtained when NO is initially present during oxidation of both NH_3 and HCN. These results are comparable to the respective SNR results with reductant ammonia and urea.

Introduction

Nitrous oxide (N_2O) is considered to be a pollutant due to its possible impact on the greenhouse effect (IPCC, 1990) and on the depletion of stratospheric ozone (Proffitt, 1989; EPA, 1989). N_2O is formed by biological processes in soil and water and by combustion processes, in which the stationary combustion sources contribute currently to 3-10% of the total anthropogenic N_2O flux to the atmosphere (Hulgaard, 1991). The N_2O emissions from combustion of natural gas, oil, or pulverized coal are usually low (<5 ppm), whereas N_2O emissions from fluidized bed combustion (FBC) vary within the 0-250 ppm range (Hulgaard, 1991; Åmand and Andersson, 1989; Johansen et al., 1992). The N_2O emissions from FBC depend on the fuel type, and a ranking sequence of decreasing N_2O forming potential may be: petroleum coke, coal, lignite/peat, wood (Hulgaard, 1991; Åmand and Leckner, 1991a). The emissions from FBC usually increase with decreasing reactor temperature and with increasing excess air levels (Åmand and Leckner, 1991a). In-bed measurements by Åmand et al. (1991), Hulgaard and Dam-Johansen (1992), and Moritomi et al. (1991) from different circulating fluid-bed combustors (CFBCs) have shown that N_2O concentrations measured increase through the riser.

N_2O is also formed during certain deNO$_x$ processes. The most important case is the selective noncatalytic reduction (SNR) with urea as reductant where the N content in the N_2O formed may exceed 50% of the NO reduced (Jødal et al., 1990; Zellinger and Tauschitz, 1989). According to a study by Jødal et al., only a small amount of N_2O (5-10 ppm) is formed when ammonia (NH_3) is used as reductant in the SNR process. When additives such as natural gas or ethanol are injected together with ammonia, N_2O emissions may be somewhat higher, though significantly lower than with urea (Hulgaard and Dam-Johansen, 1992).

The nature of mechanisms of N_2O formation and decomposition in fluidized-bed combustors (FBCs) is uncertain. It is in dispute whether the N_2O formation is caused by, for example, oxidation of the volatile N, oxidation of the char N, or reduction of NO by homogeneous or heterogeneous reactions. In the SNR process with urea as reductant, there is also some uncertainty as to the underlying mechanism of N_2O for-

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mation, which probably involves NCO (isocyanate) or HNCO (isocyanic acid) as intermediates (Miller and Bowman, 1989).

The decomposition of HCN probably also proceeds via NCO (Miller and Bowman, 1989). For this reason, HCN may be used as a model component for urea in laboratory experiments. Furthermore, HCN and NH_3 are formed during the pyrolysis of fuels in FBC (Baumann and Möller, 1991). The mechanisms of oxidation of HCN and NH_3 are thus essential for the understanding of the N_2O formation in FBCs and the SNR process.

The objective of this study is to establish an experimental basis for an understanding of the oxidation of NH_3 and HCN in combustion. Since N_2O decomposition readily takes place at combustion temperatures, a thorough study of this reaction has been included. The results are, in addition, intended to be the experimental basis for a verification of kinetic models.

Experimental Setup

A quartz flow reactor designed for obtaining plug flow was used (Figure 1). The reactor is identical to the one used previously by Duo et al. (1990) and Dam-Johansen et al. (1993). The reactor was placed vertically in an electrically heated oven with three separately controllable heating zones securing a uniform temperature profile within ±5 K throughout the reactor. After preheating, the reactant gases were mixed at the inlet point of the flow reactor tube (5.1 mm inner diameter, 14 cm long, surface/volume = 2.5 cm^{-1}). The product gases exited through a narrow air cooled tube. The temperature was measured by a thermocouple placed in a quartz tube with no access for the reactant gases. The flow rate of each gas was controlled by mass-flow controllers. The uncertainty of the listed inlet mole fractions of each component is estimated to be ±4% due to the accumulated uncertainties of gas mixing, analysis, and calibration gases. Fluctuations in the inlet mole fractions during the experiments were insignificant. Water was added by saturating an N_2 stream in a specially designed thermostatic bath. The water content was known within ±2% of the listed value.

Analysis was performed by continuous monitors, except for NH_3 and HCN. HCN was analyzed on-line by gas chromatography (GC) with a thermal conductivity detector. NH_3 was analyzed by sampling in water and the content of NH_3 by flow injection analysis. O_2 was analyzed by a paramagnetic analyzer, NO by a nondispersive ultraviolet analyzer, CO and CO_2 by nondispersive infrared analyzers and N_2O by an infrared analyzer, the performance of which has been reported elsewhere (Hulgaard, 1991; Hulgaard and Dam-Johansen, 1992). Since the N_2O analyzer suffers from interference from NH_3 and H_2O, measures were taken to eliminate these influences. NH_3 was removed by bubbling through a 0.05 M solution of H_2SO_4, and H_2O was either kept constant by running the sample through an ice bath (NH_3 oxidation experiments) or removed by condensation in a dry ice bath. During the HCN oxidation experiments, water was removed by running the sample through a tube maintained at 0°C and containing 1 cm^3 of 0.2 M H_2SO_4 and then dry ice. This treatment had insignificant effect on the HCN content of the gas.

The accuracy of the measured mole fractions in the figures presented is affected by fluctuations in the flows (±1%) and analysis and sampling accuracies, which depend on the component. For O_2 this accuracy is estimated as ±1% (all % readings are of the value measured), for NO ±1% and not less than ±2 ppm, for CO and CO_2 ±2% and not less than ±3 ppm, for N_2O ±1% and not less than ±2 ppm, for NH_3 ±6% and not less than ±5 ppm, and for HCN ±15% and not less than ±20 ppm.

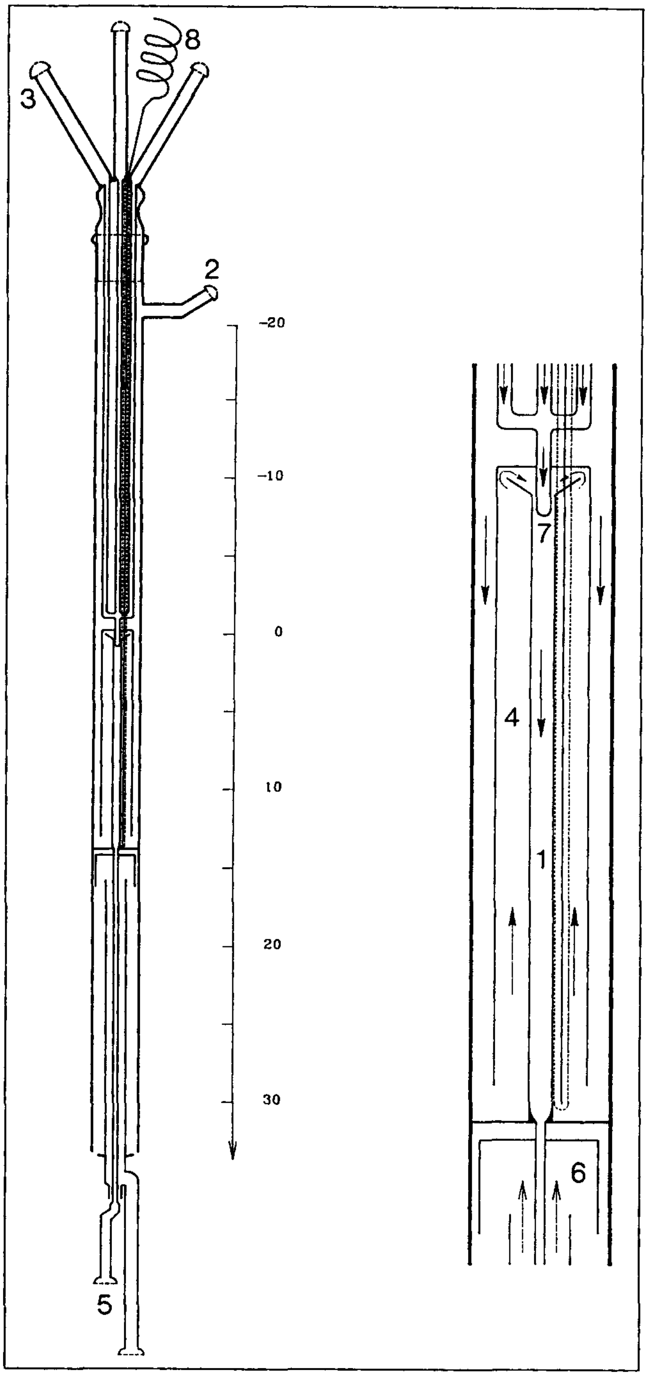

Figure 1. The reactor.

(1) flow reactor tube; (2) main stream inlet; (3) four injectors; (4) preheating zone; (5) outlet tube for reacted gases; (6) cooling zone; (7) extension with small holes to provide good mixing and turbulence; (8) thermocouple in a separated tube. Measurements are in cm.

Most experiments were performed by maintaining a constant mass-flow rate and varying the reactor temperature within the range of 920-1,350 K. Thus, the gas residence time in the reactor depended on the temperature. [The residence time is usually listed as M/T, where M is constant in each experiment and T is the temperature in Kelvin.] At 1,250 K the residence time was about 60 ms in the experiments reported. In a number of experiments, the gases were premixed and fed into the main stream of the reactor (the location indicated by the number 2 in Figure 1) with a residence time of about 2 s at 1,250 K. In these cases, the flow should not be considered as plug flow, and the reactor was not isothermal, since the gases were heated slowly to the listed temperature and cooled rapidly through the narrow exit tube.

Selection of Experimental Conditions

Three series of experiments were conducted: one with N_2O decomposition and one each with oxidation of NH_3 and HCN in the presence or absence of N_2O, CO, or NO. In the N_2O decomposition experiments, the inlet mole fraction of N_2O was maintained at about 200 ppm. This level was chosen since it is in the same order of magnitude as may be seen from FBCs (for example, Åmand et al., 1991). The influence of the simultaneous presence of other components (H_2, CO, NH_3, and O_2) was studied.

In the NH_3 oxidation experiments, the inlet NH_3 mole fraction was maintained at 750–800 ppm, O_2 at 2.4-2.6%, H_2O at 0 or 1.0%, and NO at 0 or about 600 ppm. This simulated the conditions prevailing in the SNR-process (Jødal et al., 1990). The NH_3 level is also in the same order of magnitude as was measured in a CFBC (up to 300 ppm) by Åmand et al. (1991).

In the HCN oxidation experiments, the HCN mole fraction was maintained at 300–330 ppm, O_2 at 2.3-2.5%, H_2O at 0 or about 2.8%, NO at 0 or about 440 ppm, and CO at 0 or about 1,620 ppm. The mole fraction of HCN was chosen in order to simulate urea oxidation in the SNR-process, assuming NCO to be a major oxidation product of each of urea and HCN. Considering CFBC conditions, the HCN level used was somewhat higher than the mole fractions (up to 40 ppm) measured in the bed (Åmand et al., 1991).

When no water was added, trace amounts of H_2O (below 100 ppm) may have been present as an impurity. The reactor pressure was about 5 kPa higher than atmospheric pressure which varied between 98.0 and 102.5 kPa.

Results and Discussion

N_2O decomposition

In Figure 2 the thermal decomposition of N_2O in N_2 can be seen to be very much dependent on the temperature. Below 1,150 K almost no decomposition was observed with the low residence time of about 60 ms which was used in the experiments. At 1,370 K a decomposition of more than 50% of the N_2O occurred of which only a minor part was converted into NO. Also shown in Figure 2 is a reproduction of the experiment. Almost no deviations between the results were observed. Experiments carried out with longer residence times showed a significant decomposition also below 1,200 K.

In a study of Hulgaard (1991) and a later study of Johnsson et al. (1992), the experimental results of Figure 2 were used to establish a pseudo first-order rate constant for thermal N_2O decomposition. Also Iisa et al. (1991) calculated an estimate of such a constant using data obtained in a reactor actually constructed for the study of heterogeneous reactions.

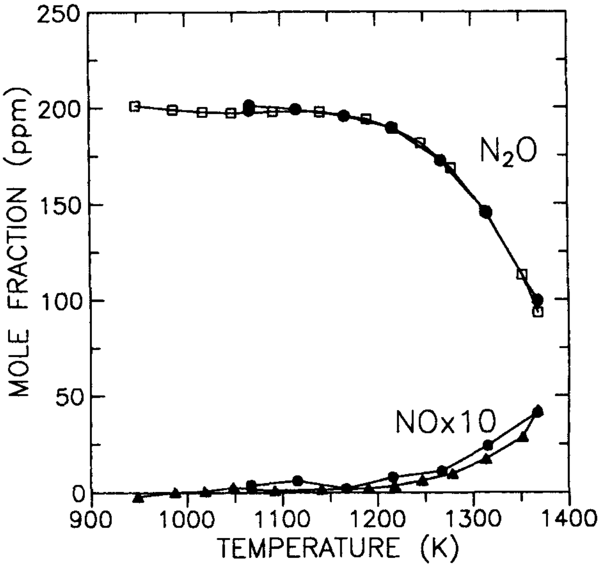

Figure 2. Decomposition of N_2O in N_2.

Inlet mole fractions: 201 ppm N_2O; residence time, $\tau = 71/T$ s, where T is the temperature in Kelvin; symbols: first experiment: N_2O (□), NO (▲); reproduction: N_2O and NO (●).

The pseudo first-order rate constant is defined through $r = -k \cdot [N_2O]$, where $[N_2O]$ is the molar concentration of N_2O, and k is assumed to follow an Arrhenius expression, $k = A \cdot \exp[-E/(RT)]$, in which A is the preexponential factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

Hulgaard (1991) showed that neither axial dispersion nor surface effects in the reactor significantly influence the results, but the presence of trace amounts of water may influence the observed rate through the potential formation of OH radicals:

$$N_2O + OH \rightarrow N_2 + HO_2 \qquad (1)$$

The thermal decomposition of N_2O proceeds via reaction 2, where M symbolizes a so-called "third body," the nature of which affects the observed rate.

$$N_2O + M \rightarrow N_2 + O + M \qquad (2)$$

N_2 is the third body in this study, whereas in the study of Iisa et al., He was used, which by Johnsson et al. was shown to have a third body efficiency at 1,200 K of a factor 2.3 compared to N_2.

In Figure 3 an Arrhenius plot of the data from Figure 2 is compared to literature data assuming plug flow. The error bars were determined on the basis of an experimental accuracy of ±2 ppm for N_2O, resulting in a variation of the determined observed temperature coefficient (E_{obs}/R) of between $26.9 \cdot 10^3$ and $31.3 \cdot 10^3$ K. It should be noted that this temperature coefficient actually comprises the temperature variation of the third body concentration, and for this reason it is not directly comparable to the elementary second-order reaction 2 given by Miller and Bowman (1989) (25,970 K) and by Westley et al. (1989) (28,450 K). For further discussion, please see Johnsson et al. (1992).

A variety of different components which influence N_2O de-

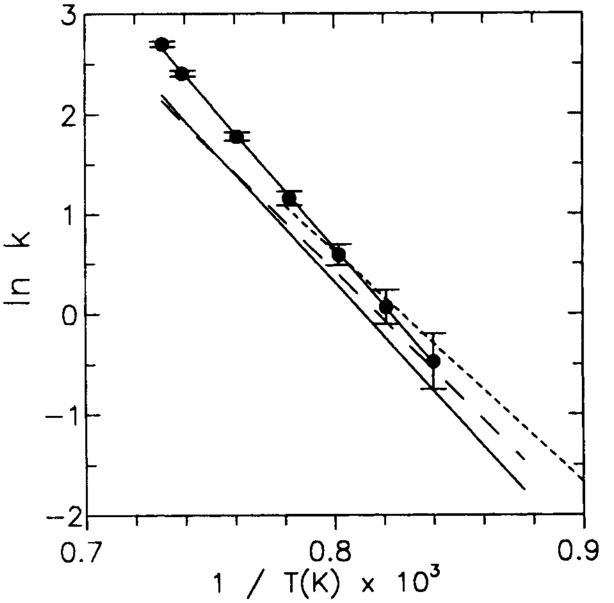

Figure 3. Arrhenius plot of the data in Figure 2, assuming a pseudo-first-order reaction for N_2O decomposition and comparing with literature data. The unit of k is s^{-1}.

-•-•-: data with error bars, see text; ----: observed rate constant obtained by Iisa et al. (1991) using He as carrier gas; — — —: rate constant for reaction 2 with $M = N_2$ using the data of Miller and Bowman (1989) and the temperature-dependent N_2 concentration; ——: rate constant for reaction 2 with $M = N_2$ using the data from the database of Westley et al. (1989) and the temperature-dependent N_2 concentration.

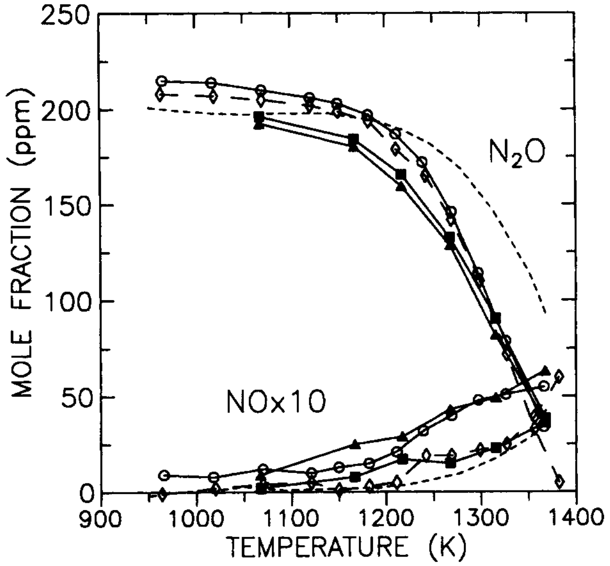

Figure 4. Comparison of the decomposition of 200 ppm N_2O in five systems, including combustible components.

Symbols used, inlet mole fractions, and residence times (N_2 carrier gas): (----) 201 ppm N_2O; $\tau = 71/T$ s (as Figure 2); (■) 198 ppm N_2O, 1,800 ppm CO; $\tau = 70/T$ s; (▲) 193 ppm N_2O; 1,760 ppm CO; 2.5% O_2; $\tau = 68/T$ s; (◇) 208 ppm N_2O; 400 ppm H_2; $\tau = 66/T$ s; (○) 215 ppm N_2O; 400 ppm H_2; 4.0% O_2; $\tau = 65/T$ s.

composition are present in combustion gases. This study covers the influence of O_2, CO, H_2 and NH_3.

The presence of O_2 together with N_2O and N_2 did not influence N_2O decomposition significantly. Injection of combustible components, that is, CO or H_2, together with N_2O resulted in N_2O decomposition at lower temperatures. The N_2O decomposition and the resulting NO formation in five reaction systems are compared in Figure 4: $N_2O + N_2$, $N_2O + CO + N_2$, $N_2O + CO + O_2 + N_2$, $N_2O + H_2 + N_2$, and $N_2O + H_2 + O_2 + N_2$.

The presence of combustible and thereby radical producing components moved the decomposition of N_2O towards lower temperatures. The presence of O_2 did not influence this shift, but it increased the production of NO. An increased NO production was also observed in the presence of NH_3—especially under oxidizing conditions. Figure 5 compares the outlet N_2O and NO mole fractions for three reaction systems: $N_2O + N_2$, $N_2O + NH_3 + N_2$, and $N_2O + NH_3 + O_2 + N_2$.

Most of the NO formed in the presence of NH_3 probably originated from NH_3 oxidation, and a remarkable O_2 influence was observed. Without O_2, the N_2O probably decomposed through $N_2O + H \rightarrow N_2 + OH$, in which the H originated from decomposition of NH_3. With O_2 present, N_2O decomposition competed with N_2O formation through oxidation of NH_3, that is, at 1,360 K there was a difference of more than 50 ppm between the N_2O content in the presence/absence of O_2.

Oxidation of NH_3

To verify to what extent NH_3 decomposed rather than oxidized, a study was made of the thermal decomposition of NH_3. Less than 18% of NH_3 was decomposed at 1,200 K and 54 ms (Hulgaard, 1991). A minor part of this may have been oxidized by an impurity of O_2 (<30 ppm) present in the N_2 carrier gas stream. In any case, however, less than 6 ppm NO and no N_2O were measured.

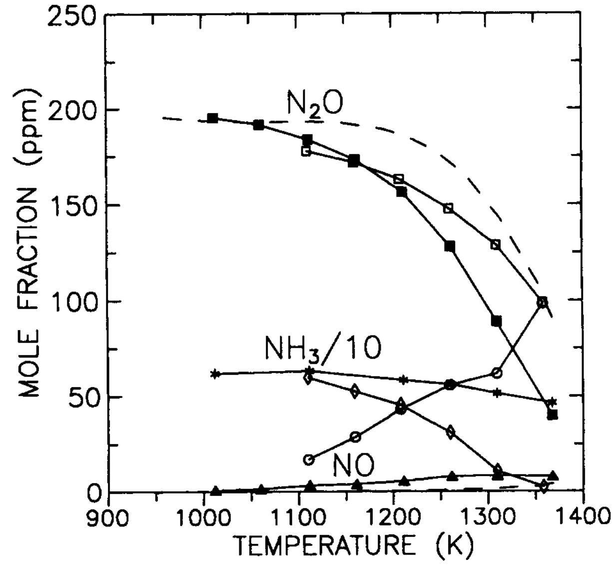

Figure 5. Decomposition of N_2O in the presence of NH_3 or $NH_3 + O_2$.

Symbols used (N_2O, NO, NH_3), inlet mole fractions, and residence times (N_2 carrier gas): (----) 201 ppm N_2O; $\tau = 71/T$ s (as Figure 2); (■, ▲, *) 196 ppm N_2O; 620 ppm NH_3, 70/T s; (□, ○, ◇) 184 ppm N_2O; 610 ppm NH_3; 2.4% O_2, 68/T s; the N_2O data are corrected for interference from NH_3 but not H_2O (< 3 ppm error).

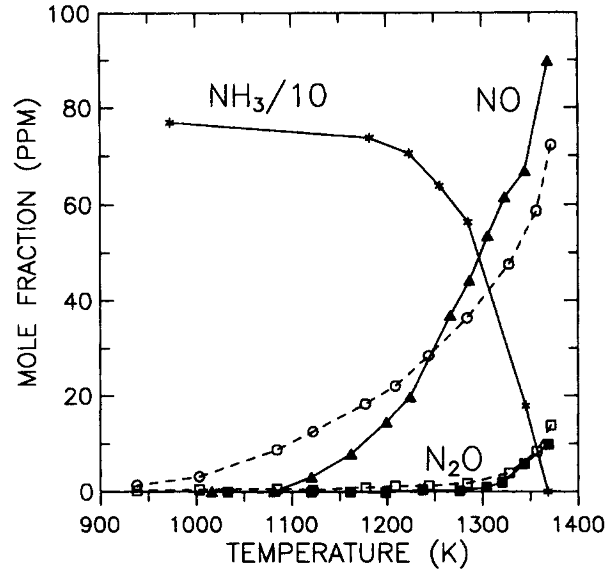

Figure 6. Oxidation of NH_3 without and with N_2O.

Symbols used (N_2O, NO, NH_3), inlet mole fractions and residence times (dry N_2 carrier gas): (■, ▲, *); 800 ppm NH_3; 2.5% O_2; 73/*T* s; (□, ○, –) 760 ppm NH_3; 2.6% O_2; 1.0% H_2O; 71/*T* s.

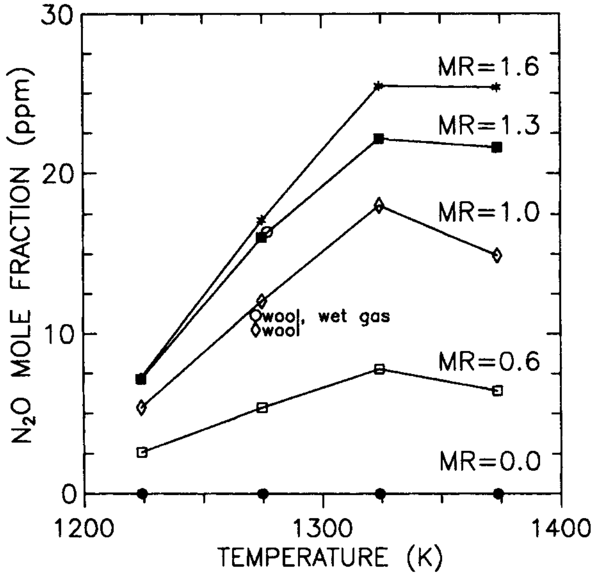

Figure 8. Net formation of N_2O in oxidation of NH_3 with NO and H_2O present.

Residence time constant at 55 ms; inlet mole fractions: about 600 ppm NO; 2.4% O_2; 1.0% H_2O; varying mole fraction of NH_3; single points with quartz wool in the reactor are included (marked wool); symbols used and NH_3/NO molar ratios (MR): (●) MR = 0.0; (□) MR = 0.6; (◇) MR = 1.0; (■) MR = 1.3; (*) MR = 1.6; (○) MR = 2.4.

In the oxidation of NH_3 it is remarkable that NO was produced at temperatures above 950 K, whereas N_2O was not formed in any detectable amounts below 1,250 K (Figure 6). (The words "produced" and "formed" are used for the sake of simplicity, denoting net formation, that is, accumulated formation minus accumulated decomposition.) Less than 4% of the N in the NH_3 was transformed into N_2O between 1,250 K and 1,360 K with a residence time of about 50 ms. At higher temperatures than shown in Figure 6, the N_2O profile would probably drop below 10 ppm, since N_2O decomposes rapidly at high temperatures. The influence of H_2O on the N_2O profile was very small (< 2 ppm); a small difference in NO formation was seen at low temperatures.

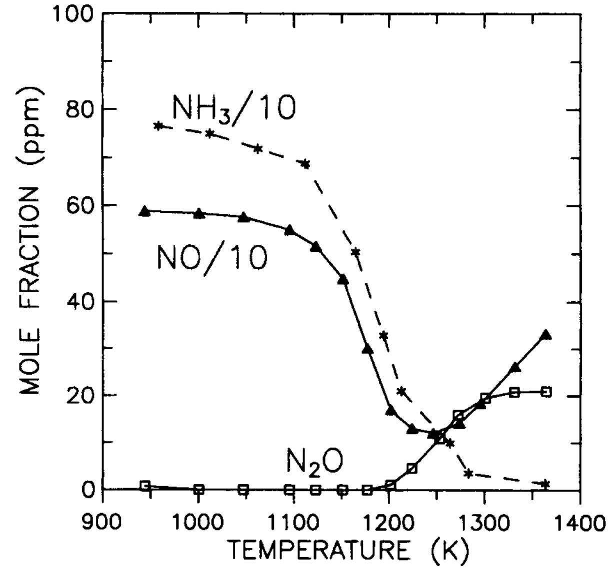

Figure 7. Oxidation of NH_3 with NO present.

Symbols used: N_2O (□); NO (▲); NH_3 (*); inlet mole fractions (N_2 carrier gas): 796 ppm NH_3; 588 ppm NO; 2.5% O_2; $\tau = 73/T$ s.

The results in Figure 6 indicate that NO must be present for N_2O formation to take place. This is in agreement with the reaction $NH + NO \rightarrow N_2O + H$ being important for N_2O formation from NH_3, as suggested by Miller and Bowman (1989), and it is further supported by the results in Figure 7, which clearly show an increased N_2O formation in the presence of NO.

The highest obtained N_2O formation was 22 ppm at 1,370 K in the $NH_3 + NO + O_2$ system (Figure 7). This corresponds to less than 7% of the N content in the NH_3 injected. Relating instead the N_2O formation to the NO reduction yields a relative N_2O production ($-2 \cdot \Delta N_2O / \Delta NO$) of about 4% at the temperature for maximum NO reduction (1,240-1,250 K). The relative N_2O production increased at higher temperatures to about 15% at 1,360 K.

In good agreement with Lyon and Hardy (1986) and Duo et al. (1990), the NO-profile in Figure 7 clearly shows the temperature window of the selective noncatalytic reduction of NO.

The influence of the N_2O decomposition was seen when the residence time was increased. At a residence time 65% longer than was used in Figure 7, the N_2O mole fraction at 1,370 K dropped from 22 ppm to below 10 ppm. When the reactor was run in the nonisothermal residence time mode ($\tau \simeq 2$ s), N_2O disappeared at high temperatures, leaving only a narrow peak of 3 ppm at 1,150 K (Hulgaard, 1991).

Increasing the NH_3/NO molar ratio increased the N_2O formation, though not proportional to the NH_3 concentration (Figure 8). In agreement with Figure 7, there is a pronounced level or a peak at 1,320-1,370 K. A few experiments were performed with quartz wool in the reactor in order to access

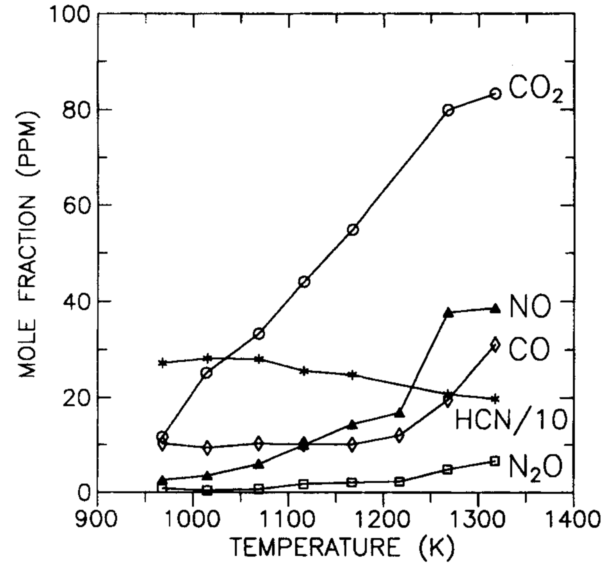

Figure 9. Oxidation of HCN.

Symbols used: N_2O (□); NO (▲); HCN (*); CO (◇); CO_2 (○); inlet mole fractions: 330 ppm HCN; 2.5% O_2; $\tau = 69/T$ s; N_2 carrier gas.

the influence of the quartz surface. No or only a minor influence on the N_2O level was observed.

In agreement with Duo (1990) and Lodders and Lefers (1985), the presence of a combustible, that is, CO, moved the NO-reduction profile towards lower temperatures (Hulgaard, 1991). The N_2O profile was moved accordingly.

Oxidation of HCN

As discussed previously, HCN may be a model component for urea in the SNR process and it is also formed during fuel pyrolysis in FBC.

Reaction of HCN in a dry mixture of N_2 and O_2 was found to be a slow process at low temperatures (Figure 9). At 1,200 K only 25% oxidation was observed with a residence time of 58 ms, and less than 20 ppm NO and 2 ppm N_2O was formed from 330 ppm HCN in the inlet. Less than 10 ppm N_2O was formed at any temperature in the interval 960–1,320 K. The outlet mole fractions of both NO and N_2O increased with the temperature.

Running the reactor in the nonisothermal long residence time mode caused HCN to be oxidized completely at temperatures above 1,200 K while significant amounts of N_2O were formed simultaneously (Figure 10).

From the survey by Miller and Bowman (1989) and the article by Kilpinen and Hupa (1991), it appears that the following sequence is important in the formation of N_2O: $HCN \rightarrow HNCO \rightarrow NCO$ followed by

$$NCO + NO \rightarrow N_2O + CO \qquad (3)$$

This sequence requires the presence of NO before N_2O formation occurs, which is in agreement with the experimental observations in Figures 9 and 10.

The NO profile in Figure 10 looks peculiar with a minimum at 1,220 K, supporting the idea of a shift in reaction mechanism. This, not being too conclusive and bearing the nonisothermal conditions in mind, an explanation could be that at temperatures below 1,200 K reaction 3 caused NO reduction to N_2O. At higher temperatures the oxidation of NCO to NO could be favored, for instance by reaction with O or OH radicals, the presence of which was favored by high temperatures:

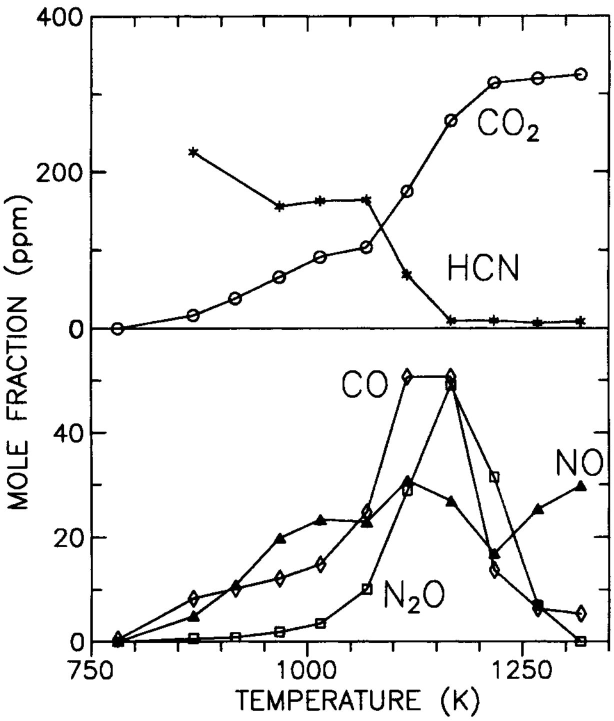

Figure 10. Oxidation of HCN, long residence time mode.

Symbols used: N_2O (□); NO (▲); HCN (*); CO (◇); CO_2 (○); inlet mole fractions: 330 ppm HCN; 2.5% O_2; $\tau = 2.8 \cdot 10^3/T$ s; N_2 carrier gas.

$$NCO + O \rightarrow NO + CO \qquad (4)$$

$$NCO + OH \rightarrow NO + CO + H \qquad (5)$$

Further supporting the importance of Eq. 3 is the almost coinciding of N_2O and CO peaks in Figure 10.

Compared to the dry reaction systems in Figure 9, HCN oxidation proceeded more readily with H_2O present (Figure 11). The amount of N_2O formed was also greater with H_2O than without. Furthermore, it is worth noting that the N_2O formation did not follow the HCN oxidation: only 5 ppm N_2O was observed at 1,220 K, at which temperature almost half of the HCN was oxidized.

In addition, the C mass balance was not closed by the sum of the mole fractions of CO, CO_2, and HCN, supporting the hypothesis that an important intermediate exists, presumably HNCO.

Oxidation of HCN in the presence of NO

The presence of NO in a dry mixture of HCN and O_2 (Figure 12), more than doubled the net formation of N_2O compared to what was the case with no NO present (Figure 9) over the temperature range 1,050–1,320 K.

The NO mole fraction was influenced to a limited extent by

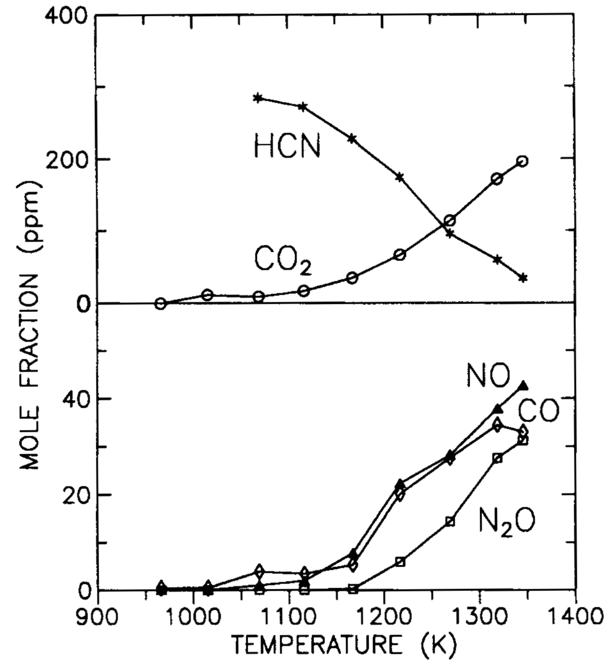

Figure 11. Oxidation of HCN with H_2O in the gas.

Symbols used: N_2O (□); NO (▲); HCN (∗); CO (◇); CO_2 (○); inlet mole fractions: 320 ppm HCN; 2.5% O_2, 3.0% H_2O; $\tau = 66/T$ s; N_2 carrier gas.

the formation of N_2O over the temperature range 970-1,220 K, and at 1,320 K about 20 ppm NO was reduced.

As was the case without NO, the presence of H_2O increased the oxidation rate of HCN and the N_2O formation rate at temperatures above 1,200 K (Figure 13).

The NO reduction was up to 30% at the temperature for maximum NO reduction, which was 1,320-1,350 K (or maybe higher). Compared to the dry case, the extent of NO reduction was thus much higher.

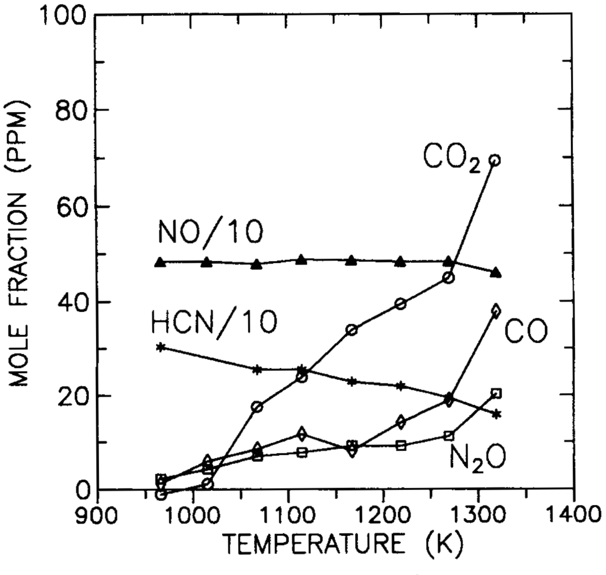

Figure 12. Oxidation of HCN with NO present.

Symbols used: N_2O (□); NO (▲); HCN (∗); CO (◇); CO_2 (○); inlet mole fractions: 311 ppm HCN; 475 ppm NO; 2.4% O_2, $\tau = 63/T$ s; N_2 carrier gas.

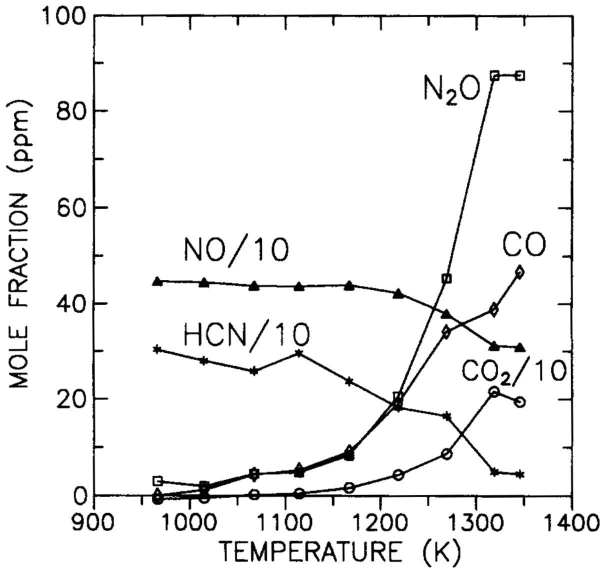

Figure 13. Oxidation of HCN with NO and H_2O in the gas.

Symbols used: N_2O (□); NO (▲); HCN (∗); CO (◇); CO_2 (○); inlet mole fractions: 303 ppm HCN; 447 ppm NO; 2.3% O_2; 2.7% H_2O, $\tau = 61/T$ s; N_2 carrier gas.

Running the reactor in the long residence time mode moved both the N_2O and the NO profiles towards lower temperatures (Figure 14). The N_2O outlet mole fraction peak at 1,140 K at 110 ppm corresponds to more than 70% of the N content of the injected HCN (not taking into consideration that one N in each N_2O molecule presumably originates from NO).

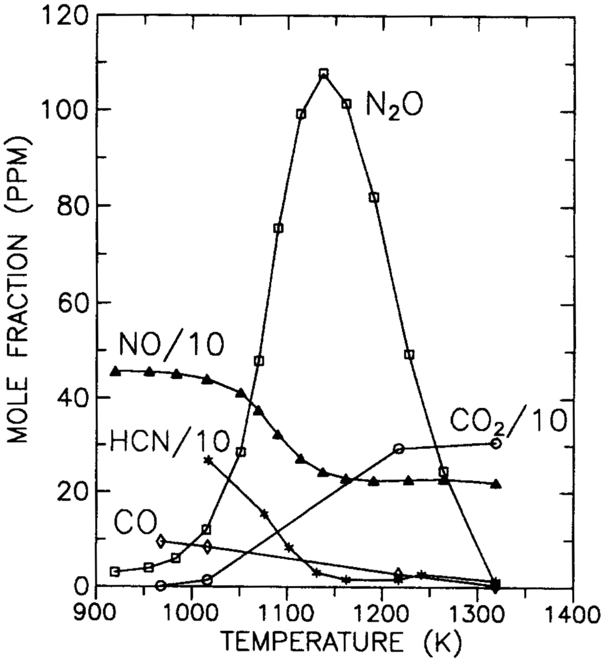

Figure 14. Oxidation of HCN with NO and H_2O present, long residence time mode.

Symbols used: N_2O (□); NO (▲); HCN (∗); CO (◇); CO_2 (○); inlet mole fractions: 303 ppm HCN; 456 ppm NO; 2.3% O_2; 2.7% H_2O; $\tau = 2.5 \cdot 10^3/T$ s; N_2 carrier gas.

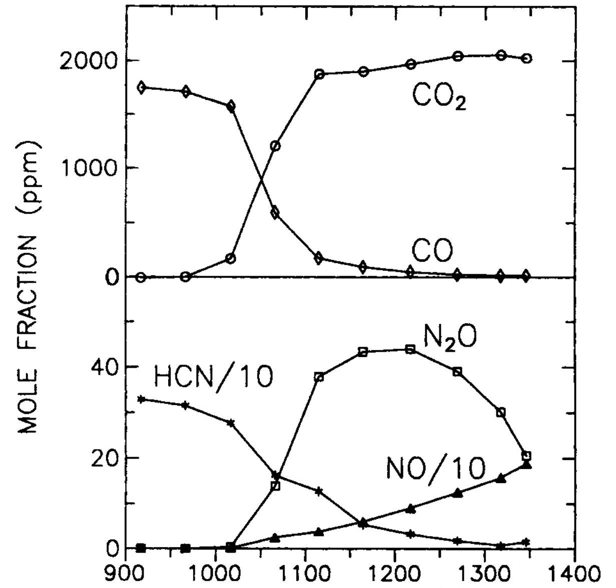

Figure 15. Oxidation of HCN with CO and H_2O present in the gas.

Symbols used: N_2O (□); NO (▲); HCN (*); CO (◇); CO_2 (○); inlet mole fractions: 318 ppm HCN; 1,710 ppm CO; 2.4% O_2; 2.8% H_2O; $\tau = 64/T$ s; N_2 carrier gas.

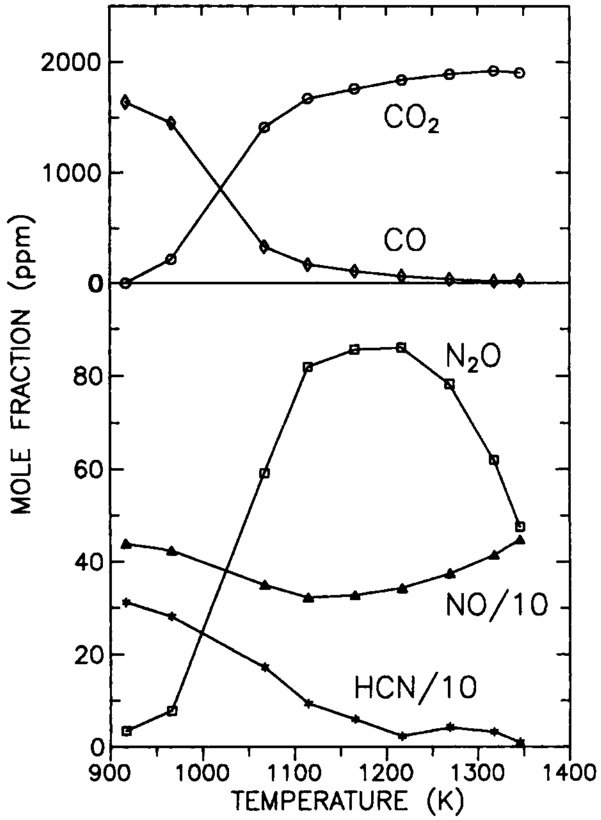

Figure 16. Oxidation of HCN with CO, NO, and H_2O present in the gas.

Symbols used: N_2O (□); NO (▲); HCN (*); CO (◇); CO_2 (○); inlet mole fractions: 298 ppm HCN; 2.3% O_2; 434 ppm NO; 1,620 ppm CO; 2.6% H_2O; $\tau = 60/T$ s; N_2 carrier gas.

The degree of NO reduction in the long residence time mode was about 230 ppm (Figure 14), corresponding to approximately 50% at any temperature above 1,150 K. This is a remarkably high reduction ratio, since the HCN/NO molar ratio in the inlet was only 0.65. The NO profile obtained in the long residence time mode was like the profile obtained under similar conditions with $NH_3 + NO + O_2$ (Hulgaard, 1991), in which the extent of the NO reduction rate was almost independent of the temperature above 1,120 K.

Oxidation of HCN in the presence of CO

With CO present during the oxidation of HCN in a dry gas and with a short residence time, the oxidation of HCN and the formation of N_2O proceeded at considerably lower temperatures than was the case without CO (Figure 15). An adiabatic temperature rise of less than 10 K due to the oxidation of 1,800 ppm CO and 328 ppm HCN cannot explain the large temperature differences.

With CO present HCN oxidation yielded more NO than N_2O (Figure 15). The measured N_2O mole fraction was the result of simultaneous formation and decomposition. At 1,320 K about 200 ppm NO was formed. Since little NO was formed during the decomposition of N_2O (Figure 2), and since only 330 ppm HCN was available, it is not likely that the total formation of N_2O at any temperature exceeded 50 ppm, which was the maximum exit value. If at high temperatures there must have been room for some N_2 formation together with the N_2O formation, it is therefore likely that the total production of N_2O decreased with increasing temperature at levels above 1,200 K.

In the long residence time mode, the N_2O profile peaked at 70 ppm at 1,050 K (Hulgaard, 1991), a temperature shift of about 100 K. This is a smaller shift than is seen when comparing the pure oxidation cases (Figures 9 and 10), in which it is about 200 K.

At a comparable residence time in the experiments of Houser et al. (1988), considerable oxidation of HCN and formation of N_2O were seen at reactor temperatures as low as 900 K, at which temperature little oxidation of HCN was seen in any of the $HCN + CO + O_2$ systems studied here. In the presence of large amounts of both CO and HCN (10 and 1%, respectively), a large adiabatic temperature rise in the experiments of Houser et al. is a plausible explanation for the great difference in results.

The profiles of NO, HCN, and N_2O in Figure 15 remained almost unaffected by the absence of H_2O, whereas the CO oxidation rate was lower at temperatures above 1,070 K.

Oxidation of HCN in the presence of both NO and CO

With a short residence time, the presence of both CO and NO combined the ability of NO to increase N_2O formation and the ability of CO to move the profile towards lower temperatures (Figure 16).

The influence of H_2O was largely limited to the CO oxidation rate, which is why only the figure with H_2O present has been included.

In Figure 16, the peak value for N_2O was within 5 ppm of the peak value obtained with NO and without CO (Figure 13), but the profiles of both N_2O and NO were shifted more than

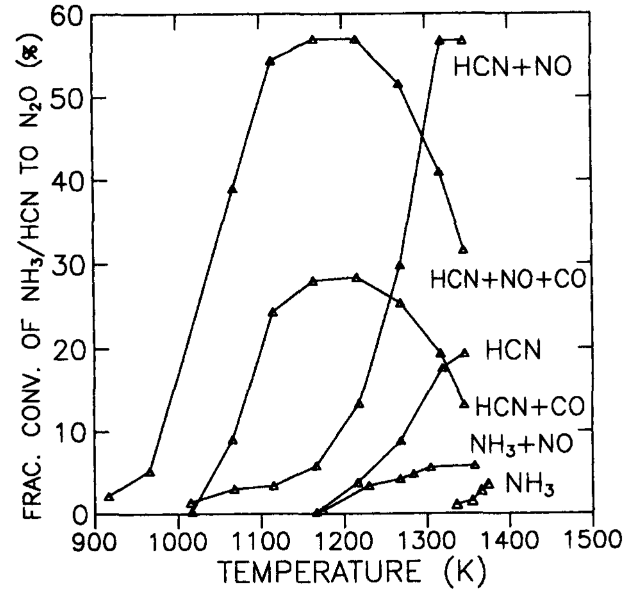

Figure 17. Comparison of the N_2O formation during oxidation of HCN and NH_3, obtained experimentally.

Conditions for HCN oxidation; approximate inlet mole fractions: 310 ppm HCN; 0 or 440 ppm NO; 0 or 1,750 ppm CO; 2.3% O_2; 2.7% H_2O; $\tau = 60 - 65/T$ s; conditions for NH_3 oxidation; inlet mole fractions: 770 ppm NH_3; 0 or 600 ppm NO; 2.6% O_2; 1.0% H_2O; $\tau = 70 - 73/T$ s; N_2 carrier gas.

150 K towards lower temperatures. The temperature for maximum N_2O net production coincides with the maximum NO reduction temperature. About 110 ppm NO was reduced, corresponding to 24%. At high temperatures almost no net reduction of NO took place.

It should further be noted that the profiles for HCN, CO, and CO_2 in Figure 16 are virtually identical to the ones obtained in the absence of NO (Figure 15).

Discussion of the Homogeneous N_2O Chemistry

N_2O profile

Figure 17 shows a comparison of the N_2O results from the oxidation of NH_3 and HCN. In the figure, the ordinate is the fractional conversion of NH_3 or HCN to N_2O. This ignores the supposition that one N in N_2O probably originated from NO in the experiments in which also NO was initially present, cf. the discussion in Hulgaard et al. (1991) where the major N_2O producing reactions were found to be $NH + NO \rightarrow N_2O + H$ and $NCO + NO \rightarrow N_2O + CO$. Since there are different inlet mole fractions of HCN and NH_3, the comparison in Figure 17 is fully correct only if the formation of N_2O could be considered to be first-order in the concentration of NH_3 or HCN. This is due to the fact that only in a first-order reaction is the relative change independent of the inlet concentration when the reaction takes place in a plug-flow reactor. Nevertheless, the main conclusions drawn from Figure 17 remain unchanged, if a reaction order in the range zero to two is assumed.

In Figure 17 it is worth noting that only a low percentage of NH_3 was converted into N_2O while the oxidation of HCN yielded up to 30% N_2O without NO present, and up to 60% with NO in the inlet. With CO present in the gas, the N_2O profile was moved towards lower temperatures in the case of both NH_3 and HCN oxidation. The height of the N_2O peak in the presence of CO was only slightly different from those obtained in the cases where no CO was present.

The reduction of NO

As regards the NO reduction, the temperature at which the maximum NO reduction was achieved was very different in the $HCN + NO + O_2 + H_2O$ and $NH_3 + NO + O_2 + H_2O$ systems. The NO reduction with NH_3 peaked at about 1,240 K (Figure 7), while the peak with HCN and a slightly longer residence time was at 1,320 K (or above) (Figure 13).

At first sight, NH_3 appears to be a better NO reducing agent than HCN when comparing Figures 7 and 13. The magnitude of the peak NO reduction was in the case of NH_3 more than 80% at an inlet NH_3/NO molar ratio of $\beta = 1.3$ (Figure 7). In the case of HCN, the magnitude was 25-30% with a molar ratio of $HCN/NO = 0.65$ and a residence time of 46 ms (Figure 13).

In this comparison, the molar ratio $NH_3/NO = 1.3$ is much higher than the molar ratio $HCN/NO = 0.65$, and the residence time is longer in the NH_3 case. Duo (1990) presented an NH_3 experiment more comparable to the HCN case using the same reactor as used here. He found a NO reduction of about 30% at $\beta = 0.5$, but there was a longer residence time, 76 ms. A longer residence time in the case of HCN would probably yield a higher NO reduction than found in Figure 13, since some HCN remains at 1,320-1,330 K. On this basis it is not obvious that NH_3 is a better reducing agent than HCN.

This does not mean that HCN is useful in a deNO$_x$ process, since HCN is too hazardous to handle in large quantities with respect to toxicity, flammability and the risk of polymerization. HCN could be used as a model compound for urea in laboratory experiments, since HCN and urea behave in a similar manner. This is most likely largely due to the fact that they have common oxidation paths, and relative to NH_3 they behave very similarly with respect to NO-reducing potential, peak NO-reduction temperature and N_2O production.

Another reason to compare the NO reducing potentials of NH_3 and HCN is that in both cases the presence of CO moved the NO reduction profile towards lower temperatures, and the shifts in the two cases were of comparable magnitude.

Another interesting feature is that the temperature for maximum NO reduction almost coincided with the peak N_2O temperature in the HCN + NO cases (Figures 13 and 16), but in the $NH_3 + NO$ case (Figure 7), the peak N_2O temperature was higher than the temperature of maximum NO reduction.

In HCN oxidation, Glass and Wendt (1982) proposed NO reduction solely by NH_2 at higher temperatures (1,400-2,000 K). They suggested a mechanism the basic content of which is

$$HCN + OH \rightarrow NH_3 + \text{products}$$
$$NH_2 + NO \rightarrow N_2 + H_2O$$

The experimental results in this work contradict the mechanism in that

(1) A significant N_2O production is found during HCN oxidation with or without NO present. Since N_2O is not produced

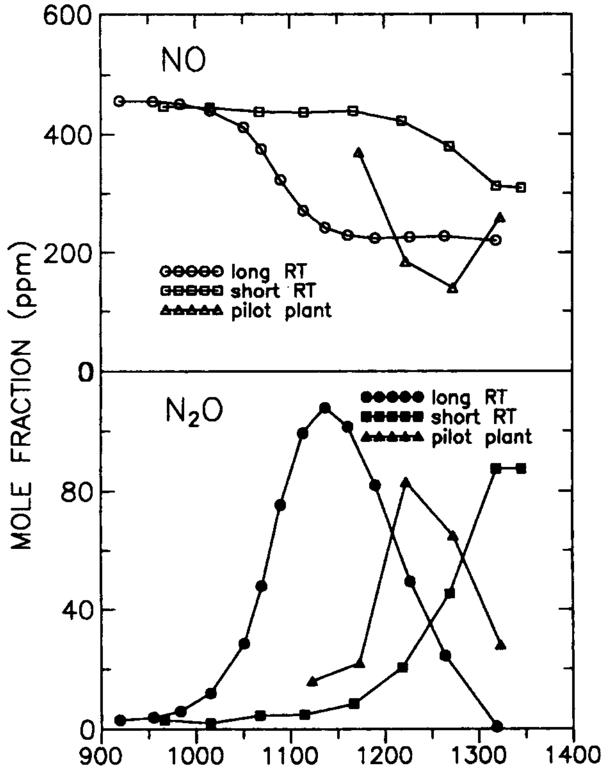

Figure 18. Comparison of NO presence in HCN oxidation and NO reduction by urea in the SNR process.

Oxidation of HCN with NO and H_2O in the gas; symbols: N_2O (■); NO (□); conditions: see Figure 13. Oxidation of HCN with NO and H_2O present, long residence time mode; symbols, N_2O (●), NO (○); conditions: see Figure 14; pilot-plant conditions: symbols: N_2O (▲); NO (△); inlet mole fractions (dry): 400 ppm NO; 260 ppm urea (N in urea/NO molar ratio: 1.3); 650 ppm SO_2; 6% O_2; 13% CO_2; cooling rate: 200 K/s.

in significant amounts from NH_3 oxidation, there must be other important oxidation pathways of HCN than through NH_3.

(2) A significant rate of HCN oxidation is found to occur only at temperatures higher than the optimum for homogeneous NO reduction by NH_3. Oxidation of NH_3 to NO is favored at high temperatures.

Comparison with the SNR process

A comparison of the results of the system $HCN + NO + O_2$ with the SNR results using urea as reductant in a pilot plant (Jødal et al., 1990) is interesting (Figure 18), since it is assumed that both urea and HCN form N_2O through the intermediate NCO. Jødal et al. proposed that urea decomposes into equal amounts of NCO and NH_2.

In the nonisothermal pilot plant of Jødal et al., 600 kg/h combustion gas was extracted at 1,100°C from a pulverized coal-fired utility boiler. The temperature was measured at the injection point for urea, after which the gas was cooled at a rate of about 200 K/s. The temperature for maximum NO reduction was about 1,273 K.

In one of the $HCN + NO + O_2$ experiments presented in Figure 18, the residence time was much shorter, and in the other it was longer than in the pilot-plant experiments. The 1,273 K pilot-plant temperature for maximum NO reduction fits in between the laboratory results, 1,150 K and 1,320 K.

The high levels of N_2O emissions from urea injection are related to the injection temperature (Figure 18). In full-scale systems a fairly low N_2O emission and extensive NO reduction should be obtainable at injection temperatures in a narrow band above 1,270 K, depending on the high-temperature residence time.

A remarkable difference between the laboratory experiments and practical combustion systems is that in the former, the gases were maintained at a constant or slowly increasing temperature, whereas in the latter the combustion gas was cooled.

Low levels of NO, HCN, and N_2O were obtained in the experiment (Figure 14) in which all reactant gases were premixed and heated slowly (>2 s) to temperatures above 1,200 K. In practical combustion systems, the temperature is usually decreasing in the post flame zone. This profile should be reversed in order to compare with the conditions of Figure 14. Realizing that this is rarely practicable in commercial boiler designs, it should be mentioned that a lengthy residence time (low cooling rate) is probably enough to improve the performance of the urea-based SNR-process regarding NO reduction and emissions of N_2O and NH_3.

Judging from the results which show that the injection of CO moves the temperature window of the SNR process towards lower temperatures, it appears that increasing the radical concentration to some extent is analogous to increasing the temperature.

An effect similar to increasing the temperature was obtained by Jødal et al. (1992) who injected natural gas downstream of the injection point of ammonia in a 135 MWe pulverized coal fired power plant. The emissions of NO and N_2O were not directly affected by the natural gas injection. However, the ammonia slip was reduced, and a fixed NH_3-emission allowance permitted an NH_3/NO molar injection ratio higher than could be used without methane injection, thus increasing the extent of NO reduction. This is based on the fact that usually the extent of NO reduction and the NH_3 emission increase with increasing NH_3/NO molar ratio (Jødal et al., 1992).

Homogeneous N_2O Formation and Decomposition in Fluidized Bed Combustion

Some of the main questions about the N_2O formation in FBC are:

(a) Is N_2O formed through homogeneous or heterogeneous reactions?

(b) Which volatile N-containing species are most important for N_2O formation?

(c) Are there any simple methods for reducing N_2O emissions?

Homogeneous or heterogeneous?

The profile of N_2O in a 2 MWt circulating fluidized bed was recorded by Hulgaard and Dam-Johansen (1992). They found that the N_2O formation relative to the consumption of O_2 was largest in the region immediately downstream of the secondary air inlet in the combustor. If it is assumed that the oxygen consumption in this zone was primarily due to oxidation of the volatiles, then this contributed significantly to the formation of N_2O.

One should bear in mind that oxidation of the volatiles need not consist of homogeneous reactions alone. The reactions could be solid-catalyzed or even gas-solid reactions.

In this study, the homogeneous oxidation of HCN and NH_3 was found to be very rapid in the presence of CO, with about 90% oxidation in 50 ms at a typical FBC temperature of 1,120 K. Catalytic reactions could play a role in the product distribution during the oxidation of HCN and NH_3, but this study indicates that the increase in the overall rate of oxidation should be considered negligible in the time scale of fluidized-bed combustion.

The formation of N_2O further downstream in the circulating FBC could be caused by either oxidation of the volatiles or by char oxidation. Since coal devolatilization is a relatively slow process, even for small particles (95% devolatilization in 21-54 s at 900°C for the 1.4 mm particles studied by Peeler et al., 1991), the coal particles could release some of their volatiles up along the riser in the CFBC, thereby contributing to the homogeneous formation of N_2O.

N_2O formation during char oxidation was seen by de Soete (1990). This could then be a significant source of N_2O in CFBCs. De Soete also detected HCN from char oxidation. Some of the N_2O believed to originate from char oxidation could in fact have been formed through the homogeneous oxidation of HCN. Even without HCN as an intermediate, one could speculate that NCO may be released from the surface, reacting homogeneously with NO to yield N_2O through reaction 3, $NCO + NO \rightarrow N_2O + CO$. Another hypothetical possibility is the reaction of NO with surface-bound NCO. The preliminary results obtained by Dam-Johansen et al. (1993) studying NO reduction over char withdrawn from a CFBC indicate that the homogeneous pathway is most likely.

De Soete (1990) did not find any N_2O formation from the reduction of NO on char or graphite surfaces in the absence of O_2. In the homogeneous formation of N_2O from HCN, O_2 is required in order to obtain the intermediate NCO. Therefore, the presence of O_2 is likely to be required for N_2O formation from bound or not-bound NCO derived from char.

This could explain the results of Åmand et al. (1991), who proposed simultaneous NO reduction and N_2O production through the riser part of a CFBC. The results of Åmand et al. could be caused either by the homogeneous reaction of NO with NCO, where NCO could be derived from the oxidation of HCN, tar, or char or by heterogeneous reactions of NO with char. The rate of N_2O formation through this mechanism could depend on the O_2 concentration. The mechanism could in this case be an explanation of the fact that N_2O emissions from FBC increase with increasing levels of excess air.

Detailed studies of the char-N oxidation mechanism are needed to reveal whether char oxidation yields N_2O directly, if NO reacts with char-bound N, or if N_2O formation occurs through the homogeneous reaction of NCO with NO. Studying the products of NO reduction during graphite oxidation is a possible means of revealing whether NO could be reduced to N_2O.

Another indication of the importance of the volatiles was presented by Wójtowicz et al. (1991), who found a significant difference between the N_2O levels found with char oxidation and with the oxidation of the parent coal. Combustion of an anthracite, a low-volatile coal, and a high-volatile coal yields much more N_2O than their corresponding chars. This indicates that the volatiles have a significant influence. However, the influence need not be purely homogeneous.

N_2O formation from the volatiles in FBC

In this study, the fractional conversion of HCN to N_2O was found to be much larger than the conversion of NH_3 to N_2O. Through modeling, NCO was found to be an important intermediate in N_2O formation from HCN (Hulgaard et al., 1991; Miller and Bowman, 1989). In FBC, the relative contribution of HCN and NH_3 to the N_2O formation involves estimates of the availability of HCN and NH_3.

Baumann and Möller (1991) found that the pyrolysis of coal under FBC conditions yielded 6-7% of the fuel N as NH_3 or HCN; the relative amounts depended on the fuel type. High-rank coals produced more HCN than low-rank coals. Large parts of the volatile N content of the coals were, however, released in the tar.

The decomposition/oxidation products of tar are also likely to depend on the fuel. In low-rank fuels, a large part of the N is bound in amino groups or amides (Baumann and Möller) which are likely to yield NH radicals rather than NCO. In the high rank coals N tends to be bound in N-heterocyclic compounds, which are likely to oxidize through NCO.

FBC results in the literature (Hulgaard and Dam-Johansen, 1992; Åmand and Leckner, 1991a), indicate that the N_2O emissions increase significantly with increasing levels of excess oxygen. For this reason, the experiment in Figure 16 was repeated with the O_2 mole fraction increased from about 2.3% to 5.5%. The influence of the excess oxygen was seen to be remarkably small, indicating that an O_2 level of 2.3% is already in great excess.

In FBC, the HCN evolved from pyrolysis experiences a very low oxygen concentration when there is a low level of excess air. During the oxidation of HCN in FBC, the local O_2 concentration is probably much lower than the 2.3 to 5.5% used in these experiments. Thus these experiments are not completely comparable with FBC conditions. In addition, during reducing conditions in FBC, HCN may be converted into NH_3 by hydrogenation (Baumann and Möller, 1991), and NH_3 forms less N_2O than the direct oxidation of HCN.

To assess the contribution of the pyrolysis products HCN and NH_3 to the formation of N_2O, a conservative assumption is that a maximum of 7% of the fuel N is released as HCN, and that this is converted quantitatively to N_2O. Assuming an N content of 1.6% in the coal, this would yield about 130 ppm N_2O, which is barely enough to account for the N_2O found by Hulgaard and Dam-Johansen (1992). Since some N_2 formation and N_2O decomposition is expected to occur, the HCN and NH_3 obtained through direct pyrolysis are therefore probably not the only sources of N_2O.

Another way to consider the availability of HCN and NH_3 is to measure the NH_3 and HCN inside the FBC. In the primary (substoichiometric) zone of a CFBC, Åmand and Leckner (1991b) found levels of up to 350 ppm NH_3 and 40 ppm HCN. Both dropped to below 10 ppm at the secondary air inlet. Assuming a conversion factor to N_2O of 0.06 for NH_3 and 0.60 for HCN (adopted from Figure 17 from the results with NO present, since NO was available due to the oxidation of NH_3, for example), this would yield only about 22 ppm N_2O. However, over the distance where HCN and NH_3 dropped from their peak values, only about 30 ppm increase in N_2O

was measured, so a homogeneous oxidation of NH_3 and HCN could provide most of the N_2O formed in this region.

In other parts of the reactor where oxygen is available, measuring the HCN and NH_3 profiles may underpredict the availability of volatile N_2O precursors. Both HCN and NH_3 are oxidized quickly, so that the measured concentrations where oxygen is present represent only a fraction of the amounts produced. In addition, HCN and NH_3 might be adsorbed on surfaces as a first step in catalytic conversion. NCO and HNCO are possible precursors for N_2O, of which no measurements in FBCs are known to exist.

When considering the availability of HCN and NH_3 in the reactor, it should be remembered that the sampling and analysis of HCN and NH_3 are not simple tasks. They are both liable to catalytic conversion over a hot filter during sampling, and the subsequent analysis usually consists of solution in aqueous solutions in which cyanide ions, for example, are susceptible to complex formation, thereby escaping analysis.

Reduction of N_2O emissions from FBC

The rate of N_2O decomposition found previously for the $N_2O + N_2$ system should be regarded as a lower limit to the rate in practical systems, since large radical concentrations and catalytic surfaces are likely to be present, causing an increased decomposition rate.

At 1,120 K the pseudo first-order rate constant is $k_{obs} = 0.13$ s^{-1}. Assuming a 2-s residence time and plug flow at this temperature, a decomposition of 23% should be expected. Two seconds corresponds roughly to the time needed to pass from the top of the riser to the exit of the cyclone in a conventional CFBC. In the CFBC experiment reported by Hulgaard and Dam-Johansen (1992) and in the profile reported by Åmand et al. (1991), no significant decrease in N_2O was found from the top of the reactor to the exit. Provided the temperature was maintained at 1,120 K over the cyclone, this indicates that the N_2O formation balances the N_2O decomposition in this region, or possibly even indicates inhibition of the N_2O decomposition by an unknown mechanism. Even at a temperature of 1,070 K a decomposition of 7-8% should be observed during a two-second residence time.

In future designs, one could bear in mind that, judging from the rate constant at 1,120 K, N_2O decomposition could take place in the exit duct of an FBC if the residence time at high temperatures could be increased.

Even better would be to increase the temperature and radical concentrations in the top of the reactor by means of gas injection as had been tried successfully by Gustavsson and Leckner (1991), although the expected N_2O decomposition was not achieved. Other injection gases, other injection methods, a lower particle load and a longer residence time prior to cooling than used by Gustavsson and Leckner might improve the results. For instance, H_2 might be a useful gas, since N_2O decomposition through a reaction with H and OH radicals consists of very rapid reactions. Since a high radical concentration enhances N_2O decomposition, it would probably improve the process to ensure good mixing by injection of the gas through many nozzles instead of just one burner. The question is how large an amount of gas one should use.

From the results in Figures 4 and 5, it appears that the injection of small amounts of either H_2, CO or NH_3 increases the N_2O decomposition rate to some extent, when the residence time is short. This is probably due to a rapid increase in the radical concentrations. The influence of these gases is probably minor at long residence times. Therefore, one should not expect injection of small amounts of H_2, CO, or NH_3 to cause extensive N_2O decomposition in FBCs. For significant N_2O decomposition to occur the amounts injected should be large enough to cause a significant temperature rise.

An alternative to the decomposition of N_2O is to minimize its formation. The results presented in this article strongly indicate that NO must be present for homogeneous N_2O formation to take place. For this reason, reducing the in-bed formation of NO should be a viable way to reduce N_2O emissions. Reducing the in-bed NO level could be obtained by lowering the temperature and the oxygen level in this region. Supporting this hypothesis are the results presented by Johansen et al. (1992), who lowered the N_2O emissions from their modified CFBC to 10 mg/MJ by maintaining low oxygen levels and temperatures in the dense bed.

Conclusions

In laboratory experiments of the homogeneous oxidation of NH_3 and HCN, it was shown that the fractional conversion of HCN to N_2O is much larger than that of NH_3. During oxidation there are strong indications that any significant formation of N_2O is dependent on the presence of NO. For this reason, it is not surprising that N_2O formation is enhanced by the addition of NO to the reactant gases.

The influence of CO is to move the profiles of all reacting species towards lower temperatures. The oxidation rates of NH_3 and HCN, and hence the formation of NO and N_2O, are increased at low temperatures through an increase in the radical pool caused by the oxidation of CO.

The presence of H_2O also causes an increase in the radical pool, although one which is much smaller than the oxidation of CO. Therefore, H_2O has a slight effect on the very simple systems such as $HCN + O_2$, but no significant effect on the oxidation of NH_3 and HCN when CO is present.

The rate of N_2O decomposition relative to the rate of thermal decomposition is increased by the increase in the radical pool caused by the presence of a combustible component.

The laboratory results obtained in the systems $NH_3 + NO + O_2$ and $HCN + NO + O_2$ are comparable to the respective pilot- and full-scale SNR process results with NH_3 and urea. This applies to both the position and magnitude of the NO-reduction window and the N_2O peak.

It was found that a large part of the N_2O emission observed during coal fired circulating fluidized-bed combustion can be explained by the homogeneous oxidation of NH_3 and HCN.

The most viable means of reducing N_2O emissions from FBCs is probably to decrease the amount of excess air or to increase the cyclone temperature by means of fuel injection. Reducing the amount of NO initially formed in the bed is also likely to reduce N_2O emissions.

Acknowledgments

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