Homogeneous Formation of NO and N_2O from the Oxidation of HCN and NH_3 at 600–1000°C

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The oxidation of HCN and NH_3 with CO, CH_4, or H_2 addition has been studied in the temperature range between 600 to 1000°C. In most of the tests 10% oxygen was used. The experiments were carried out under well-defined conditions in a flow tube reactor made of quartz glass. The effects of NO addition and oxygen level have been tested. To study the importance of O/H radicals in the reaction mechanism and to confirm previous studies, iodine was added in some tests. A detailed chemical kinetic model was used to analyze the experimental data. In general, the model and experimental results are in good agreement. The results show that under the conditions tested CO significantly promotes NO and N_2O formation during HCN oxidation. During NH_3 oxidation carbon-containing gaseous species such as CO and CH_4 are important to promote homogeneous NO formation. In the system with CH_4 addition, the conversion of HCN to N_2O is lower compared to the other systems. In the $HCN/NO/CO/O_2$ system NO reduction starts at 700°C and the maximum reduction of approx. 40% is obtained at 800°C. For the $NH_3/NO/CO/O_2$ system the reduction starts at 750°C and the maximum reduction is 50% at 800°C. Iodine addition shifts the oxidation of HCN, NO, and N_2O formation as well as NO reduction to higher temperatures. Under the conditions tested, it was found that iodine mainly enhances the recombination of the O-radicals. No effect on NO formation was found in the $HCN/CH_4/O_2$ system when oxygen was increased from 6% to 10%, but when oxygen was increased from 2% to 6% NO formation decreased. The role of hydrocarbon radicals in the destruction of NO is likely to become important at low oxygen concentrations (2%) and at high temperatures (1000°C). © 2000 by The Combustion Institute

NOMENCLATURE

c_k concentration of the species k [mol/m^3]

r_k recombination rate of the species k [mol/m^3s]

S surface of the reactor [m^2]

V_R volume of the reactor [m^3]

γ_k recombination efficiency of the species k [1]

ν_k velocity of the species k [m/s]

INTRODUCTION

Combustion is one of the sources of NO_x (i.e., NO and NO_2) and N_2O which are known as pollutant gases. NO_x causes acid rain and formation of ground level ozone, whereas N_2O contributes to the greenhouse effect and ozone layer depletion in the stratosphere. In combustion processes there are two possible nitrogen sources for NO_x and N_2O formation: the combustion air and/or the nitrogen in the fuel. At high combustion temperatures such as in flames, the nitrogen from the combustion air is the main source of NO_x formation (Zeldovich mechanism) [1]. In lower temperature combustion such as combustion of solid fuels (coal, biomass etc.) in grate furnaces or fluidized bed combustors, NO_x and N_2O originate mainly from the conversion of the nitrogen of the fuel (fuel-nitrogen) [2, 3].

The combustion conditions and fuel characteristic are the factors which affect the emissions of those nitrogenous pollutants. Under fluidized bed combustion (FBC) conditions, the NO and N_2O emissions originate from the nitrogen released with the volatiles and from nitrogen in the char [4]. In solid fuel combustion NO and N_2O are formed through complex reaction mechanisms involving many homogeneous and heterogeneous reactions. One of the major difficulties is the estimation of the contributions of these reaction routes [5]. The contribution of volatile nitrogen and char nitrogen to the emissions of NO and N_2O related to the type of coal has been studied in FBC [6–8]. In combustion of low-rank coals (high content of volatiles) the devolatilization stage is important for NO and N_2O formation. However, for high-rank coals char combustion gains importance.

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TABLE 1

The Selected Homogeneous Reactions in NO/N$_2$O
Formation and Destruction

Formation (through HCN/NH$_3$ oxidation)

R1	HCN + O → NCO + H
R2	HCN + OH → CN + H$_2$O
R3	CN + O$_2$ → NCO + O
R4	HCN + OH → HNCO + H
R5	HNCO + OH → NCO + H$_2$O
R6	NCO + NO → N$_2$O + CO
R7	NCO + O → NO + CO
R8	NCO + OH → NO + CO + H
R9	NCO + H → NH + CO
R10	NH$_3$ + OH → NH$_2$ + H$_2$O
R11	NH$_2$ + OH → NH + H$_2$O
R12	NH$_2$ + H → NH + H$_2$
R13	NH + H → N + H$_2$
R14	N + OH → NO + H
R15	NH + O → NO + H
R16	NH$_2$ + NO → N$_2$O + H$_2$
R17	NH + NO → N$_2$O + H
R18	NO$_2$ + O → NO + O$_2$
R19	NO$_2$ + H → NO + OH
R20	HNO → NO + H
R21	HNO + OH → NO + H$_2$O
R22	HNO + O → NO + OH

NO/N$_2$O Destruction

R23	N$_2$O + H → N$_2$ + OH
R24	N$_2$O + O → N$_2$ + O$_2$
R25	N$_2$O + OH → N$_2$ + HO$_2$
R26	N$_2$O + M → N$_2$ + HO$_2$
R27	NO + HO$_2$ → NO$_2$ + OH
R28	NO + NH$_2$ → N$_2$ + H$_2$O
R28	NO + NH$_2$ → N$_2$ + H$_2$O
R29	NO + NH$_2$ → N$_2$ + H + OH
R30	NO + NH$_2$ → NNH + OH
R31	NO + N → N$_2$ + O

HCN and NH$_3$ released during combustion as volatile species are the main sources of nitrogen for NO and N$_2$O formation by undergoing homogeneous gas-phase reactions. HCN has been found to be the more important homogeneous precursor than NH$_3$ for N$_2$O [9–11]. In HCN oxidation NCO was found as the main intermediate for N$_2$O formation through reaction R-6 [12]. It was found that during char combustion NO and HCN are primary products [13, 14].

There are thousands of reactions involved in the homogeneous mechanism [15] of NO and N$_2$O formation and destruction. Selected reactions from this mechanism which are discussed in the present work are listed in Table 1.

The heterogeneous and homogeneous chemistry may occur concurrently. Winter et al. [13] have studied the relative importance of the homogeneous and heterogeneous reaction paths during devolatilization and char combustion using iodine addition. It has been concluded that during devolatilization the homogeneous chemistry plays the dominant role for NO and N$_2$O formation and that during char combustion N$_2$O is formed in the gas phase from the heterogeneously formed NO and the HCN released from the char.

The present work investigates the homogeneous route of NO and N$_2$O formation through HCN and NH$_3$ oxidation in a temperature range between 600°C to 1000°C. Combustible gases H$_2$, CO, and CH$_4$ are used to represent the conditions during devolatilization. Since NO and HCN are found as primary products of the heterogeneous char combustion, the HCN/CO/NO/O$_2$ and NH$_3$/CO/NO/O$_2$ systems are used to simulate the gas-phase conditions around a burning char particle. The effect of oxygen is investigated in the HCN/CH$_4$/O$_2$ and NH$_3$/CH$_4$/O$_2$ systems. In order to study the importance of O/H radicals (O, OH, H, and HO$_2$) in the reaction mechanism and to confirm previous work [13], iodine is added in some tests. The experimental results are analyzed by a detailed chemical kinetic model.

EXPERIMENTAL

The tests were conducted in a well-defined flow tube reactor made of quartz glass (Fig. 1). The unit was designed to obtain the flexibility in changing residence time independently from temperature and flow-rate by changing the length of the reaction zone. The reactor consists of three separately in height adjustable reactant tubes and an adjustable carrier gas tube in the preheating zone, a reactor tube, and an adjustable sampling probe. The length of the reaction zone can be set by adjusting the position of reactant tubes and the sampling probe. The reactant gases and the carrier gas, flowing inside the reactant tubes and the carrier gas tube respectively, go downwards through the preheating zone. The flow-rate is controlled by mass-flow controllers. Additional components
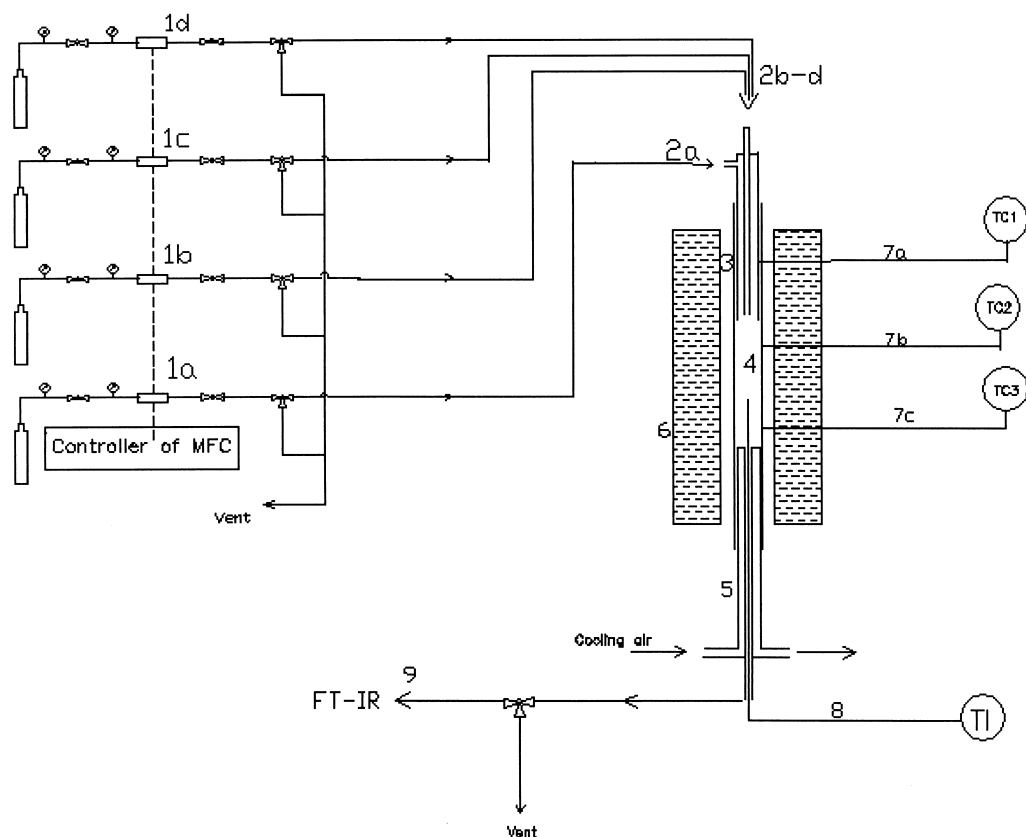
Fig. 1. The experimental setup of the test unit: 1a–d, mass-flow controllers; 2a, flow inlet for carrier gas and additional component; 2b–d, flow inlet for reactant gases; 3, preheating zone; 4, reaction zone; 5, quenched sampling probe; 6, heating shells; 7a–c, thermocouples connected to temperature controllers; 8, removable thermocouple; 9, sampling line to the FT-IR spectrometer.

such as O$_2$ and iodine are added into the carrier gas line. All the inlet gases are well mixed before entering the reaction zone. This is mainly achieved by the small holes on the tip of the reactant tubes.

The internal diameter of the reaction zone is 12 mm and in this work a length of 310 mm of the reaction zone was chosen (surface to volume ratio is 3.3 cm^{-1}). Since the reactor was designed to attain plug-flow conditions based on the dispersion model [16], residence time distribution tests have been done and plug-flow conditions were obtained. The reactor is heated by electrical heating shells with three temperature controllers. The temperature was measured with 3 Ni/Cr-Ni (K) thermocouples, 0.5 mm in diameter, positioned on the outer wall of the reactor. A uniform temperature profile can be maintained within ± 8°C along the reaction zone and almost isothermal

conditions can be achieved. One removable thermocouple was placed inside the reactor to measure the temperature inside the reactor.

The outlet gases from the reaction zone are quenched in a narrow air-cooled tube in the sampling probe. The gas analysis focused on the following species: N$_2$O, NO, CO, CH$_4$, CO$_2$, HCN, and NH$_3$ which were analyzed with a Fourier transform infrared radiation (FT-IR) spectrometer (BIO-RAD FTS 60A) in combination with a heated gas cell (Foxboro LV7, 223 cm^2 in volume and 7.25 cm optical path length). The maximum relative error for the measured species is ± 10% ranging on species concentrations and wave number.

Iodine was added to the reaction system by generating iodine vapor through sublimation of solid iodine in a flask warmed in a water-bath which then enriched the carrier gas. The tests

TABLE 2

The Reaction Systems and Experimental Conditions

No.	Reaction System	Reactants (ppm)/O_2(%)/I_2 (ppm)	τ-at 900°C (s)
1	HCN/O_2	262/10	0.289
2	$HCN/H_2/O_2$	260/333/10	0.289
3	$HCN/CO/O_2$	262/1254/10	0.289
4	$HCN/CH_4/O_2$	220/1020/10	0.306
		220/1020/6	
		220/1020/2	
5	$HCN/CO/NO/O_2$	263/1241/315/10	0.289
6	NH_3/O_2	242/10	0.289
7	$NH_3/H_2/O_2$	245/330/10	0.289
8	$NH_3/CO/O_2$	250/1250/10	0.289
9	$NH_3/CH_4/O_2$	200/1000/10	0.306
		200/1000/6	
		200/1000/2	
10	$NH_3/CO/NO/O_2$	254/1290/289/10	0.289
11	$HCN/CO/O_2/I_2$	260/1245/10/300	0.289
12	$HCN/CO/NO/O_2/I_2$	255/1242/305/10/212	0.289

were performed at atmospheric pressure in a temperature range between 600°C to 1000°C with residence times between 0.2 s to 0.3 s at 900°C. Table 2 shows the experimental conditions used for all tests.

REACTOR MODEL

The calculations were done using the plug-flow reactor model PFRCalc, which was optimized for the experimental setup. This program was developed to obtain concentration profiles as well as the degrees of conversion for each reaction with time. Because of the high surface to volume ratio of 3.3 cm^{-1}, the radical recombination reactions of O, H, OH, and HO_2 on the surface of the reaction tube were taken into consideration. To calculate the removal rate of the radicals, the following equation was used:

$$r_k = \nu_k \cdot \gamma_k \cdot \frac{S}{V_R} \cdot c_k$$

The velocity ν_k of the species k was calculated using the kinetic theory of gases. The recombination efficiency γ_k for the H and O atoms were taken from Kim and Boudart [17]. Due to lack of accurately measured values for the recombination probability of OH and HO_2 on quartz in literature, an estimated value of 10^{-2} for OH and 10^{-3} for HO_2 were taken [18].

To test the effect of the wall, tests with CH_4 and moist CO oxidation were done. The results show that the influence of radical recombination is of minor importance and overpredicted by the model, which is in accordance with the results of Kristensen et al. [18]. Therefore recombination was neglected for all further calculations.

Reaction Mechanism

The base reaction mechanism in these calculations was taken from GRIMECH 2.11 [15]. It includes 277 elementary reactions involving 49 species. It describes the oxidation of CH_4 and the oxidation of HCN. Because this mechanism is not optimized for pure H/N/O systems as NH_3 oxidation, its performance for this is not accurate. Therefore the reactions of the H/N/O system were replaced by reactions given by Glarborg et al. [19] with few changes given by Kjaergaard et al. [20]. Calculations for CH_4, HCN, and NH_3 oxidation and the thermal De-NO$_x$ process showed that the performance of each sub-mechanism is not influenced by the other. The effect of iodine is described by a mechanism taken from Babushok et al. [21]. This mechanism contains 58 reactions dealing with 9 iodine species. The rates of the reverse reactions were calculated using the thermodynamic data taken from the Sandia Thermodynamic Database [22] with changes for CN, NCO, HNCO, HOCN, and HCN as recommended by Glarborg and Miller [23]. The thermochemistry data for the iodine species were taken from Burgess et al. [24].

RESULTS AND DISCUSSION

Different Reaction Systems of HCN and NH$_3$ Oxidation

Different combustible gases—CO, CH$_4$, and H$_2$—have been used to study their effect on the oxidation chemistry of HCN and NH$_3$. The oxygen concentration was held constant at 10%. Nitrogen was the balance. Table 2 shows the experimental conditions used in all tests. The inlet concentrations of HCN range from 220 ppm to 262 ppm and 200 ppm to 254 ppm for NH$_3$.

In Figs. 2a–c the conversions of HCN to NO and N$_2$O are shown for the different reaction systems and compared to the modeling results. In all systems the conversion of HCN to NO increases with temperature (Fig. 2b). The addition of combustible gases, i.e., CO, CH$_4$, and H$_2$ into the HCN/O$_2$ system promotes NO formation. At 950°C, in the HCN/O$_2$ system 13% of HCN is converted to NO and increases to 16% by H$_2$ addition, 30% by CH$_4$ addition, and 35% by CO addition.

In the gas reburning chemistry hydrocarbon gases (CH$_4$, C$_2$H$_6$, etc.) are known to be effective in reducing NO and their efficiencies increase with temperature [25–27]. In that case NO, which is present under reducing conditions (the oxygen level is between 2000 ppm to 6000 ppm) and high temperatures ($>$1000°C), is converted to N$_2$, HCN, and NH$_3$. The present work is focused on the effect of hydrocarbons and other combustible gases on the formation of NO in the primary combustion zone. Under the present conditions HCN and NH$_3$, which are known to be released as volatile matter, were used as the sources of nitrogen at high oxygen levels (10%).

Due to the combustion of CO, CH$_4$, and H$_2$, the radical levels in the reaction systems increase. O and OH radicals convert HCN to NCO by reactions:

$$HCN + O \rightarrow NCO + H \tag{R-1}$$

$$HCN + OH \rightarrow CN + H_2O \tag{R-2}$$

$$CN + O_2 \rightarrow NCO + O \tag{R-3}$$

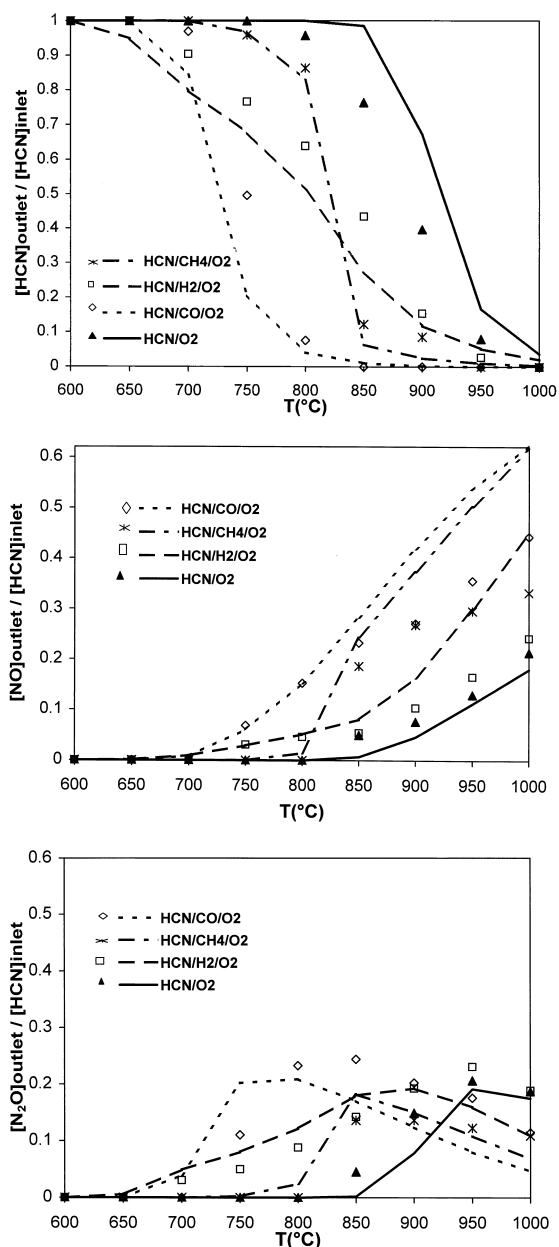NCO further reacts with O and OH radicals to produce NO by reactions:

Fig. 2. Conversion of HCN (a) to NO (b) and N$_2$O (c) in different reaction systems at 10% O$_2$. Lines show the modeling results, symbols show the experimental data. ($\diamond$) the HCN/CO/O$_2$ system, [HCN] inlet = 262 ppm, [CO] inlet = 1254 ppm. (*) the HCN/CH$_4$/O$_2$ system, [HCN] inlet = 220 ppm, [CH$_4$] inlet = 1020 ppm. ($\square$) the HCN/H$_2$/O$_2$ system, [HCN] inlet = 260 ppm. [H$_2$] inlet = 333 ppm. ($\blacktriangle$) the HCN/O$_2$ system, [HCN] inlet = 262 ppm. τ (at 900°C) = 0.289 s except for HCN/CH$_4$/O$_2$ system it is 0.306 s.

$$NCO + O \rightarrow NO + CO \tag{R-7}$$

$$NCO + OH \rightarrow NO + CO + H \tag{R-8}$$

Reaction R-1 and R-7 are the most dominant route for NO formation through HCN oxidation [12].

The modeling results are in good agreement at low temperatures for the HCN oxidation system. At high temperatures, in the systems with CO, CH_4, and H_2 the calculated NO formation is overpredicted. This difference may be partly caused by traces of water vapor present in the system resulting in a shift from O to OH radicals and less NO formation. Also it could be partly due to increased radical recombination with the reactor surface becoming more important at higher temperatures and giving a stronger effect in the experiments than in the model. However, in general the model is capable of representing the experimental results.

The results show that at high temperatures (>900°C) CO enhances NO formation stronger than the other gases whereas the least effect is found for H_2. In the $HCN/CO/O_2$ system the chain branching reaction (R-32) occurring during CO oxidation,

$$H + O_2 \leftrightarrow O + OH \qquad (R\text{-}32)$$

$$CO + OH \leftrightarrow CO_2 + H \qquad (R\text{-}33)$$

gives high O radical concentrations which favor R-7,

$$NCO + O \rightarrow NO + CO \qquad (R\text{-}7)$$

to form CO and produce more NO.

In the $HCN/CO/O_2$ system the concentration of O radical is higher than in the $HCN/CH_4/O_2$ and HCN/O_2 systems whereas it is less compared to the $HCN/H_2/O_2$ system. However, in the $HCN/H_2/O_2$ system the HCN oxidation starts early (at 700°C) and its conversion slowly increases with temperature. In this system an early formation of NO is found with lower rates compared to the other systems. The calculations show that H_2 is oxidized faster than HCN. Therefore, the O/H radicals in H_2 oxidation show an early high peak which then drops quickly while part of HCN still remains. This results in lower NO formation rates through reactions R-1 and R-7.

N_2O formation in all systems increases with temperature and then decreases after reaching its maximum concentration at 950°C for the
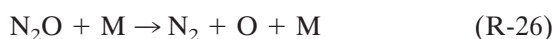
HCN/O_2 system and with H_2 addition and at 850°C for CO and CH_4 addition (Fig. 2 c). N_2O formation through HCN oxidation is mainly formed via the reactions:

$$NCO + NO \rightarrow N_2O + CO \qquad (R\text{-}6)$$

$$NH + NO \rightarrow N_2O + H \qquad (R\text{-}17)$$

where NH is formed directly from HCN or via

$$NCO + H \rightarrow NH + CO \qquad (R\text{-}9)$$

At high temperatures N_2O decreases partly because the thermal decomposition of N_2O becomes significant,

$$N_2O + M \rightarrow N_2 + O + M \qquad (R\text{-}26)$$

where M is a third body, as well as the destruction by O/H radicals

$$N_2O + H \rightarrow N_2 + OH \qquad (R\text{-}23)$$

$$N_2O + O \rightarrow N_2 + O_2 \qquad (R\text{-}24)$$

and partly because the N_2O formation route R-6 is slightly inhibited at high temperatures due to its lower activation energy compared to other product channels of NCO such as reactions R-7 and R-8 [28].

The addition of CO or CH_4 to the HCN/O_2 system shifts the N_2O concentration maximum towards lower temperatures, when enough radicals are present in the systems to produce NCO by HCN oxidation (R-1) and promote reactions R-6 and R-9, R-17 to form N_2O. The conversion of HCN to the maximum of N_2O in the HCN/O_2 systems and in the systems with CO and H_2 addition is nearly the same (about 22%) whereas it is only 14% in the system with CH_4 addition. Modeling results show the same behavior, although the conversion of HCN to the maximum of N_2O in the $HCN/CH_4/O_2$ system is only slightly lower than in the other systems. The calculations show that the H radical, which is known as the most important radical for destruction of N_2O via reaction (R-23) [29], is higher in the $HCN/CH_4/O_2$ system than in the other systems. Therefore, the maximum of N_2O is less in the $HCN/CH_4/O_2$ system compared to the other system. Also the selectivity of the reaction channel of NCO with NO to N_2O (R-6) in the $HCN/CH_4/O_2$ system is lower compared to the other systems. Hydrocarbons are known

to be effective in promoting NO to NO$_2$ [30] via reaction,

$$NO + HO_2 \rightarrow NO_2 + OH \qquad \text{(R-27)}$$
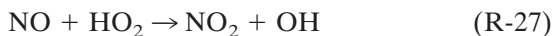
where HO$_2$ production is enhanced in the presence of hydrocarbon radicals through reactions,

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad \text{(R-34)}$$

$$CHO + O_2 \rightarrow CO + HO_2 \qquad \text{(R-35)}$$
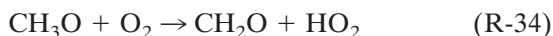
Further Bromly et al. [31] show the formation of NO$_2$ in the low-temperature CH$_4$ oxidation via the following reaction to be significant:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad \text{(R-36)}$$

Under the present conditions NO$_2$ is later converted back to NO:

$$NO_2 + O \rightarrow NO + O_2 \qquad \text{(R-18)}$$

$$NO_2 + H \rightarrow NO + OH \qquad \text{(R-19)}$$

Therefore, the lower concentration maximum of N$_2$O in the HCN/CH$_4$/O$_2$ system could be partly due to the competition between the destruction channels of NO to N$_2$O (R-6, R-17) and the formation of NO$_2$ (R-27, R-36). Further work is needed to confirm this by chemical kinetic modeling including low-temperature NO–hydrocarbon interactions.

Figures 3a–b show the conversion of NH$_3$ to NO in different reaction systems and the comparison with the model. In agreement with previous studies, the N$_2$O formation through NH$_3$ oxidation is hardly observed [9, 32]. This can be understood since NCO as the main intermediate precursor for N$_2$O formation is not present in the system. The experimental results show that CO and CH$_4$ promote the conversion of NH$_3$ to NO significantly whereas H$_2$ is much less effective. At higher temperatures (>900°C) the NH$_3$/O$_2$ system gives about 10% conversion of NH$_3$ to NO. The addition of CO or CH$_4$ to the system increases the conversion to 50% whereas only about 20% conversion is reached by adding H$_2$.

In the NH$_3$/H$_2$/O$_2$ system NH$_3$ was consumed earlier compared to the other systems; in consequence, NO formation starts already at lower temperatures (700°C). However, only little NH$_3$ is converted to NO; most of it reacts to N$_2$. It seems that H$_2$ can be an effective additive for
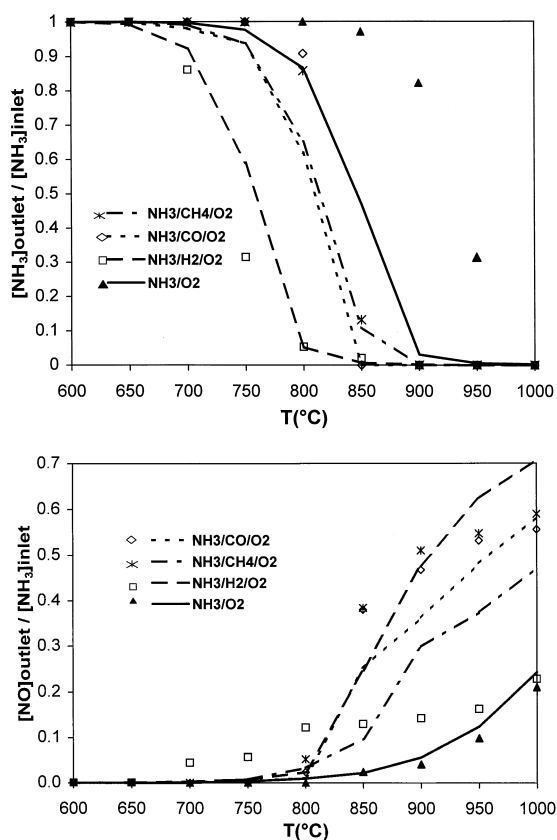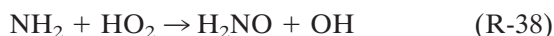

Fig. 3. Conversion of NH$_3$ (a) to NO (b) in different reaction systems at 10% O$_2$. Lines show the modeling results, symbols show the experimental data. ($\diamond$) the NH$_3$/CO/O$_2$ system, [NH$_3$] inlet = 250 ppm, [CO]inlet = 1250 ppm. (*) the NH$_3$/CH$_4$/O$_2$ system, [NH$_3$]inlet = 200 ppm, [CH$_4$]inlet = 1000 ppm. ($\square$) the NH$_3$/H$_2$/O$_2$ system, [NH$_3$]inlet = 245 ppm, [H$_2$]inlet =330 ppm. ($\blacktriangle$) the NH$_3$/O$_2$ system, [NH$_3$]inlet = 242 ppm. τ (at 900°C) = 0.289 s except for NH$_3$/CH$_4$/O$_2$ system it is 0.306 s.

decreasing NO formation (compare also with Lyon [33]).

The reaction sequence of NO formation through NH$_3$ oxidation starts with the oxidation of NH$_3$ with OH radicals to produce NH$_2$ and NH radicals (R-10 to R-12). The calculations show that under the present conditions NH$_2$ is converted to HNO via the following reaction routes:

$$NH_2 + O \rightarrow HNO + H \qquad \text{(R-37)}$$

$$NH_2 + HO_2 \rightarrow H_2NO + OH \qquad \text{(R-38)}$$

$$H_2NO \rightarrow HNO + H \qquad \text{(R-39)}$$

HNO is an important intermediate forming NO:

$$HNO \rightarrow NO + H \qquad (R\text{-}20)$$

$$HNO + OH \rightarrow NO + H_2O \qquad (R\text{-}21)$$

$$HNO + O \rightarrow NO + OH \qquad (R\text{-}22)$$

The model and the experimental results are in reasonable agreement except for the $NH_3/H_2/O_2$ and the NH_3/O_2 system. The model overpredicts NO formation in the $NH_3/H_2/O_2$ system and leads to lower conversions of NH_3 in the NH_3/O_2 system. The NO produced is a result of the competition between the destruction and the formation reactions. The relative turnovers for the $NH_3/H_2/O_2$ system show less destruction and higher NO formation compared to the other systems, thus more NO is produced. In contrast, the experiments show very low NO production rate even at higher temperatures. It is probably that traces of water vapor present in the system inhibit HNO formation via reaction R-37 which further will not form NO via reactions R-20 and R-22. Also high radical concentrations in the $NH_3/H_2/O_2$ system make the radical recombination with the reactor surface more important. However, the effect will not be strong enough to explain the obtained data satisfactorily. This discrepancy needs further investigation. The effect of H_2 compared to CO and CH_4 gases shows the importance of carbonaceous species for the formation of NO through NH_3 oxidation.

The Presence of NO in the Inlet Gases

Figure 4 shows the conversion of HCN to NO and N_2O in the system of $HCN/CO/NO/O_2$ with and without iodine and the comparison with the model. Without iodine addition, NO decreases with temperature and increases again at higher temperatures (>850°C), closely to its initial concentration. Under the present conditions the significant reduction of NO starts already at relatively low temperatures (700°C) and shows its maximum reduction of approx. 40% at 800–850°C. Kristensen et al. [34] found nearly the same behavior for the $HCN/NH_3/CO/NO/O_2$ system.

The conversion of N_2O is closely related to the reduction of NO and reaches its maximum at the maximum reduction temperature of NO. The calculations show that when NO is present
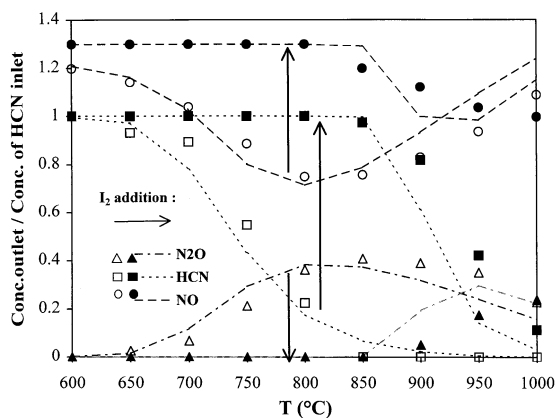

Fig. 4. Conversion of HCN in the $HCN/CO/NO/O_2$ system with I_2 addition, 10% O_2, 212 ppm I_2, $\tau = 0.289$ s (at 900°C). Lines show the modeling results, symbols show the experimental data. Experimental data without I_2, [HCN]inlet = 263 ppm, [CO]inlet = 1241 ppm [NO]inlet = 315 ppm: ($\square$) HCN, (O) NO, ($\triangle$) N_2O; with I_2, [HCN]inlet = 255 ppm, [CO]inlet = 1242 ppm, [NO]inlet = 305 ppm: ($\blacksquare$) HCN, ($\cdot$) NO, ($\blacktriangle$) N_2O. The arrows indicate the changes at 800°C by iodine addition.

in high enough concentrations reactions R-6 and R-17 are favored which are responsible for NO destruction, as well as N_2O formation,

$$NCO + NO \rightarrow N_2O + CO \qquad (R\text{-}6)$$

$$NH + NO \rightarrow N_2O + H \qquad (R\text{-}17)$$

In consequence, the maximum concentration of N_2O in the $HCN/CO/NO/O_2$ system is higher than in the $HCN/CO/O_2$ system.

By adding iodine to the $HCN/CO/NO/O_2$ system the oxidation of HCN and CO is shifted to higher temperatures. In comparison with the system without iodine, at a given temperature (e.g., 800°C), it can be seen that in the system with iodine addition the concentration of HCN is much higher, significantly more NO is present and N_2O drops to almost zero. In the system with iodine addition the concentration levels of the O/H radicals (O, OH, H and HO_2) are significantly lower, resulting in lower conversion rates (HCN, NO, CO) and lower formation rates (N_2O). The modeling results are in excellent agreement with the experimental results. More detailed explanations of the effect of iodine on the reaction system are given in the following section.
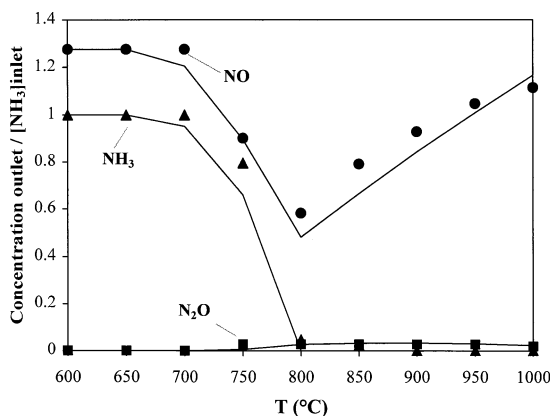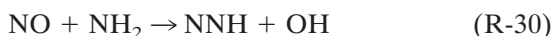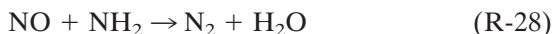
Figure 5 shows the conversion of NH_3 to NO

Fig. 5. Conversion of NH$_3$ in the system of NH$_3$/CO/NO/O$_2$, 10% O$_2$, [NH$_3$]inlet = 254 ppm, [CO]inlet = 1290 ppm, [NO]inlet = 289 ppm and τ = 0.289 s (at 900°C). Lines show the modeling results, symbols show the experimental data. (Δ) [NH$_3$], (O) NO, ($\square$) N$_2$O.

and N$_2$O in the NH$_3$/CO/NO/O$_2$ system (refer also to Alzueta et al. [35]) and the comparison with the model. For this system the model and the experimental results are in excellent agreement. Significant NO reduction starts at 750°C and reaches its maximum reduction of approx. 50% at 800°C. At higher temperatures the reduction decreases and the concentration of NO is again close to its initial concentration (at 1000°C). In comparison to the HCN/CO/NO/O$_2$ system (refer to Fig. 4), the maximum reductions in both systems are nearly the same and are reached at the same temperature (800°C). In the NH$_3$/CO/NO/O$_2$ system N$_2$O formation is hardly observed. The reaction mechanism of NO reduction by NH$_3$ (referred to as the selective noncatalytic reduction [SNCR] or thermal DeNO$_x$) has been investigated widely [36–38]. The key step in the reaction mechanism of that system is the reaction between NH$_2$ and NO which has three product channels,
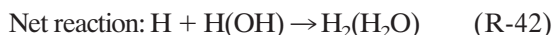
$$NO + NH_2 \rightarrow N_2 + H_2O \qquad (R\text{-}28)$$

$$NO + NH_2 \rightarrow N_2 + H + OH \qquad (R\text{-}29)$$

$$NO + NH_2 \rightarrow NNH + OH \qquad (R\text{-}30)$$

The present work shows that in the absence of NO in the inlet gases NH$_2$ is the main precursor for NO. When NO is added to the NH$_3$/CO/O$_2$ system, reactions R-28 to R-30 become dominant.

Comparison with Previous Studies

Halogen molecules, i.e., F$_2$, Cl$_2$, Br$_2$, and I$_2$ are well-known in the literature as flame inhibitors by catalyzing the recombination of O/H radicals (O, OH, H, and HO$_2$) resulting in a decrease of the pool of radicals [39, 40]. Their effect on CO oxidation and nitrogen chemistry in FBC has been studied [13, 41–45]. The radicals' concentrations are suppressed towards their equilibrium levels; this is due to the competition between the chain branching reaction

$$H + O_2 \rightarrow O + OH \qquad (R\text{-}32)$$

and catalyzed radical recombination by halides (X: Cl, Br, I, etc.) via cycle 1:

$$X + H + M \rightarrow HX + M \qquad (R\text{-}40)$$
$$\underline{HX + H(OH) \rightarrow H_2(H_2O) + X} \qquad (R\text{-}41)$$

Net reaction: H + H(OH) $\rightarrow$ H$_2$(H$_2$O) $\qquad$ (R-42)

and cycle 2:

$$X + X + M \rightarrow X_2 + M \qquad (R\text{-}43)$$
$$X_2 + H \rightarrow HX + X \qquad (R\text{-}44)$$
$$\underline{HX + H \rightarrow H_2 + X} \qquad (R\text{-}45)$$

Net reaction: H + H(OH) $\rightarrow$ H$_2$(H$_2$O) $\qquad$ (R-46)

Winter et al. [13] used iodine addition to significantly decouple the effect of homogeneous and heterogeneous chemistry in order to investigate the importance of NO and N$_2$O formation routes during devolatilization and char combustion of coal. A 10-mm single coal particle was burned in a laboratory-scale fluidized bed at 800°C and 10 kPa oxygen partial pressure. The concentration histories of NO, N$_2$O, and HCN during devolatilization showed that when iodine was added HCN increased, whereas NO decreased and N$_2$O dropped to almost zero. From these results it can be concluded that the oxidation routes of HCN are inhibited by the addition of iodine. Consequently less NCO and NO is formed resulting in a strong decrease of N$_2$O (R-6, R-17).

In Winter et al. [13], it is assumed that the addition of iodine only affects the chemistry in the gas phase. To support this hypothesis, in the present work iodine is added into the system of HCN/CO/O$_2$ (Fig. 6). This shows that by adding iodine the oxidation of HCN as well as NO and
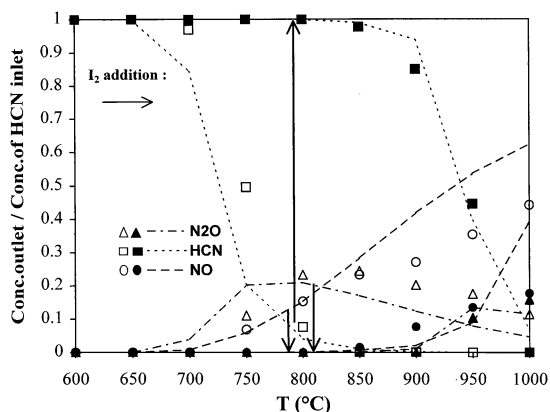
Fig. 6. Conversion of HCN in the system of HCN/CO/O_2 system with I_2 addition, 10% O_2, 300 ppm I_2, $\tau = 0.289$ s (at 900°C). Lines show the modeling results, symbols show the experimental data. Experimental data without I_2, [HCN]inlet = 262 ppm, [CO]inlet = 1254 ppm: (□) HCN, (O) NO, (△) N_2O; with I_2, [HCN]inlet = 260 ppm, [CO]inlet = 1245 ppm: (■) HCN, (·) NO, (▲) N_2O. The arrows indicate the changes at 800°C by iodine addition.

N_2O formation is shifted to higher temperatures. At 800°C the same trends are found (indicated by arrows) as in the previous work; HCN and CO increases whereas NO decreases and N_2O drops to almost zero. Figure 7 shows the time-dependent reactions' flux of radical recombination by iodine addition to the system of HCN/CO/O_2 at 900°C. The mechanism of O radical recombination can be described as follow:
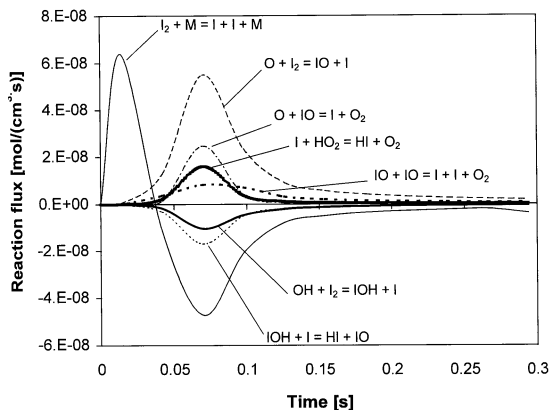

Fig. 7. (a) Reaction flux of radical recombination with I_2 versus residence time in the flow reactor. (b) The relative turnover of O radicals. The system: HCN/CO/O_2/I_2 at 900°C with 10% O_2, 300 ppm I_2, [HCN] inlet = 260 ppm, [CO]inlet = 1245 ppm.

$2I + M \leftrightarrow I_2 + M$	(R-47)
$O + I_2 \leftrightarrow IO + I$	(R-48)
$O + IO \leftrightarrow I + O_2$	(R-49)

Net reaction: $O + O \leftrightarrow O_2$ (R-50)

Under the present conditions the O radicals are the most affected radicals by iodine followed by OH, HO_2, and H. Modeling work shows that almost 50% of O radicals in the system are suppressed. Less O and OH radicals cause inhibition of HCN oxidation (R-1 and R-2) and NO formation (R-7 and R-8), inhibiting N_2O formation (R-6, R-17).

During char combustion Winter et al. [13] found that the addition of iodine results in an increase of HCN and NO whereas N_2O dropped to almost zero. To represent the gas-phase conditions around a burning char particle, iodine is added to the system of HCN/CO/NO/O_2 (Fig. 4). By adding iodine the temperature window of NO reduction shifts to higher temperatures as well as the HCN and CO oxidation and N_2O formation. At 800°C HCN, CO, and NO increase whereas N_2O is not observed. The oxidation of HCN (R-1 and R-2) is inhibited due to less O and OH radicals, consequently less NCO is formed. Furthermore, the destruction channels of NO via reactions R-6, R-17 are also inhibited resulting in no N_2O formation.

The changes of O/H radical concentrations due to iodine addition in the system of HCN/CO/NO/O_2 at 900°C are shown in Fig. 8. By adding iodine, ignition is delayed (<0.05 s), then the concentrations of the radicals increase with time but towards significantly lower level compared to the system without iodine addition. Especially the O radicals are reduced from approximately 23 ppm to 2 ppm, whereas OH is reduced from 6 ppm to 2 ppm, HO_2 from 0.26 ppm to 0.06 ppm, and H from 0.16 ppm to 0.03 ppm.

Effect of Oxygen

Three different oxygen concentrations (2%, 6%, and 10%) were used in the HCN/CH_4/O_2 and NH_3/CH_4/O_2 systems to study the effect of oxygen. Figure 9a shows the conversion to NO and N_2O in the HCN/CH_4/O_2 system for differ-
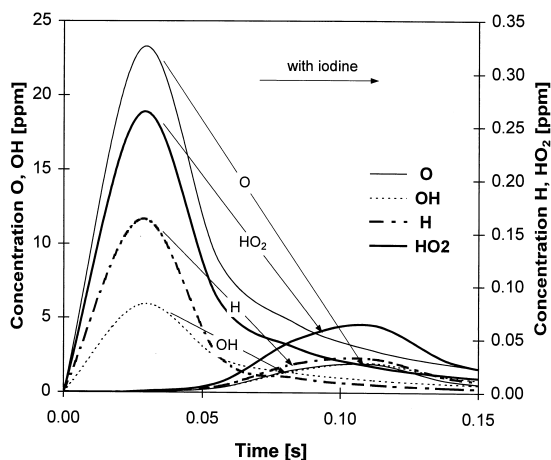
Fig. 8. Comparison of the calculated radical concentrations in the HCN/CO/NO/O$_2$ system with and without I$_2$ addition at 900°C versus residence time in the flow reactor. Reaction conditions: 10% O$_2$, 212 ppm I$_2$, [HCN]inlet = 255 ppm, [CO]inlet = 1242 ppm, [NO]inlet = 305 ppm and τ = 0.289 s (at 900°C). The arrows indicate the changes by iodine addition.

ent oxygen concentrations and compared to the modeling results. The model and the experimental results are in good agreement for N$_2$O formation whereas NO formation is overpredicted. This discrepancy is partly due to traces of water vapor present in the system resulting in a shift from O to OH radicals and less NO formation. The large discrepancy in the NO formation between 2 and 10 vol.% O$_2$ can also not be captured by the model

Increasing the oxygen concentration causes an earlier oxidation of HCN and CH$_4$. Therefore, at 850°C significant amounts of NO and N$_2$O are already formed for 6% and 10% oxygen whereas for 2% oxygen NO and N$_2$O are not observed yet. At higher temperatures N$_2$O is slightly increasing with increasing oxygen. The effect of oxygen on NO formation can be seen by increasing the oxygen concentration from 2% to 6% or up to 10%. In this case NO formation decreases. But when oxygen increases from 6% to 10%, no effect on NO formation was observed.

It seems that the difference in the radical pool is more significant between 2% oxygen and 6% or 10% oxygen compared to the difference between 6% and 10% oxygen. The calculations show that increasing the oxygen level from 2%
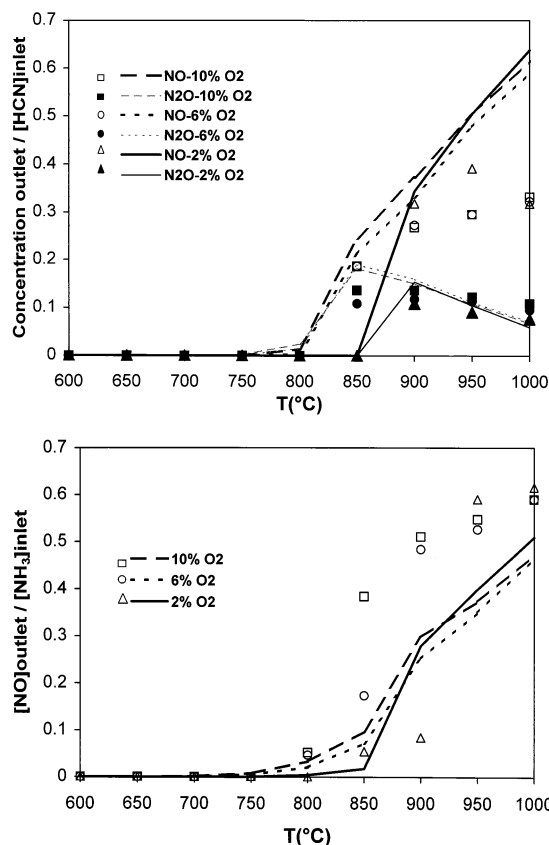

Fig. 9. Effect of O$_2$ concentration in the HCN/CH$_4$/O$_2$ system (a) and the NH$_3$/CH$_4$/O$_2$ system (b), τ = 0.306 s (at 900°C). Lines show the modeling results, symbols show the experimental data. (a): [HCN]inlet = 220 ppm, [CH$_4$]inlet =1020 ppm: ($\square$) NO at 10% O$_2$, (O) NO at 6% O$_2$, (Δ) NO at 2% O$_2$, ($\blacksquare$) N$_2$O at 10% O$_2$, ($\cdot$) N$_2$O at 6% O$_2$, ($\blacktriangle$) N$_2$O at 2% O$_2$. (b) [NH$_3$]inlet = 200 ppm [CH$_4$]inlet =1000 ppm; ($\square$) NO at 10% O$_2$, (O) NO at 6% O$_2$, (Δ) NO at 2% O$_2$.

to 10% gives lower H radical concentrations; thus the product channel of NCO destruction to NH (R-9) becomes of minor importance, in consequence more NCO is present in the system and reacts directly with NO to produce N$_2$O by reaction R-6. This results in higher N$_2$O and less NO in the system at 10% oxygen compared to 2%.

In the system at 2% oxygen a decrease of NO is found at 1000°C; the model might show the same behavior at higher temperatures. This could be due to the reduction of NO by hydrocarbon radicals. Alzueta et al. [46] and Glarborg et al. [47] concluded that under reburning conditions the hydrocarbon radicals are responsible for the NO destruction.

The NO formed through NH_3 oxidation at different oxygen levels is shown in Fig. 9b. Higher oxygen concentrations shift NO formation to lower temperatures as a result of more rapid consumption of NH_3 and CH_4. At high temperatures (950°C) the increase of oxygen from 2% to 6% or 10% decreases NO, whereas from 6% to 10% no significant differences were observed. This is the same behavior as in the HCN oxidation tests; however, the reduction of NO was not observed yet at 1000°C.

CONCLUSIONS

The effects of CO, CH_4, and H_2 have been tested on HCN and NH_3 oxidation. It was found that CO promotes the NO and N_2O formation through HCN oxidation significantly stronger than CH_4 and H_2. The system with CO addition produces more O-radicals than with CH_4 addition, consequently more NO and N_2O are formed via $HCN + O \rightarrow NCO + H$, $NCO + O \rightarrow NO + CO$, $NCO + NO \rightarrow N_2O + CO$. The highest O radical concentration is produced in the system with H_2 addition. Since the peak of O radicals in that system occurred early and drops while part of HCN still remains, NO formation is not promoted as strong as in the system with CO or CH_4 addition.

Carbon-containing gaseous species such as CO and CH_4 are important to promote homogeneous NO formation through NH_3 oxidation. Oxidation of those gases generates high amounts of O and HO_2 radicals (especially for CH_4) promoting NH_2 oxidation to HNO which further forms NO:

$$NH_3 \xrightarrow{O,OH} NH_2 \xrightarrow{O,HO_2} HNO \xrightarrow{O,OH} NO$$
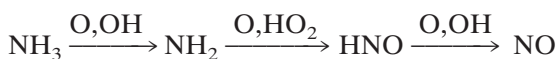
CH_4 addition gives lower conversions of HCN to N_2O compared to CO, H_2, and HCN oxidation without any additional gases. It is likely that N_2O destruction in this system is more dominant than in the other systems. Also it can be due to the competition between the destruction channels of NO to N_2O by reactions $NCO + NO \rightarrow N_2O + CO$, $NH + NO \rightarrow N_2O + H$ and the formation of NO_2 via reactions $NO + HO_2 \rightarrow NO_2 + OH$, and $CH_3O_2 + NO \rightarrow CH_3O + NO_2$. It is known that low-temperature CH_4

oxidation forms NO_2 mainly during the first stages of the combustion, which is later converted back to NO.

The experimental results show that H_2 is the least effective in enhancing NO formation through HCN and NH_3 oxidation. It is likely that H_2 can be an effective additive for decreasing NO formation.

HCN oxidation promotes NO and N_2O formation, whereas NH_3 oxidation forms NO and almost no N_2O. This confirms that $NCO + NO \rightarrow N_2O + CO$, $NH + NO \rightarrow N_2O + H$ are the main routes for N_2O formation whereas $NO + NH_2 \rightarrow N_2O + H_2$ is of little importance.

Significant reduction of NO has been observed when NO is present during the oxidation of HCN and NH_3. This is because the presence of NO at lower temperatures favors the destruction routes of NO such as $NCO + NO \rightarrow N_2O + CO$, $NH + NO \rightarrow N_2O + H$ and $NO + NH_2 \rightarrow N_2 + H_2O$.

The tests with iodine addition in the HCN/CO/O_2 system show that the oxidation of HCN and CO as well as NO and N_2O formation is shifted to higher temperatures. Consequently, at 800°C HCN and CO increases whereas NO decreases and N_2O drops to almost zero. This confirms previous work [13] that in the stage of devolatilization of coal the homogeneous chemistry plays the dominant role in NO and N_2O formation.

By adding iodine to the HCN/CO/NO/O_2 system, the temperature window for NO reduction shifts to higher temperatures as well as the HCN and CO oxidation and N_2O formation. Consequently, at 800°C HCN, CO, and NO increases whereas N_2O is not observed. This supports previous work [13] that during char combustion N_2O is formed in the gas phase.

The calculations show that under the present conditions in the HCN/CO/O_2 and HCN/CO/NO/O_2 system the O radical is the most attacked by iodine. The mechanism of O radical recombination is described as follows:

$2I + M \leftrightarrow I_2 + M$
$O + I_2 \leftrightarrow IO + I$
$O + IO \leftrightarrow I + O_2$
_____

Net reaction: $O + O \leftrightarrow O_2$
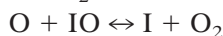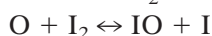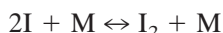
Increasing the oxygen concentration from 2% to 6% during HCN oxidation leads to a NO decrease. A further increase to 10% oxygen does not significantly affect NO. N$_2$O formation slightly increases by increasing the oxygen concentration. The calculations show higher oxygen levels result in less H radicals, thus the destruction channel of NCO via NCO + H → NH + CO becomes of minor importance, whereas NCO + NO → N$_2$O + CO is favored.

The calculations overpredict NO formation in some HCN oxidation tests and underpredict NO formation in some NH$_3$ oxidation tests. A good agreement with the experimental results for the NH$_3$/H$_2$/O$_2$ system has not been found. However, it is in excellent agreement with the experimental results for the HCN/CO/O$_2$ and HCN/CO/NO/O$_2$ system with and without iodine addition. In general, the model is in good agreement with the experimental work and is capable of representing the tests.

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