

HCN oxidation in an O₂/CO₂ atmosphere

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Abstract

HCN is the main intermediate product generated during the NO reduction reburning process. The present work aims to evaluate the oxidation behavior of HCN under oxy-fuel combustion conditions, which is a promising CO₂ capture technology characterized by presenting an O₂/CO₂ combustion atmosphere instead of air. With this purpose, an experimental and a kinetic modeling study of the oxidation of HCN (1000 ppm) under CO₂ diluted conditions, in the 900-1450 K temperature range and for different stoichiometries, has been performed. The gas reaction products have been quantified and the main differences compared to those of traditional air-fired combustion are presented.

Introduction

Oxy-fuel combustion is a CO₂ capture technology for fossil fuel combustion systems, including existing and new plants [1]. This technology requires the removal of the nitrogen from the air prior to combustion, as the fuel is burned with pure oxygen together with a fraction of the flue gases. The flue gas recycling is needed to dilute the oxygen fed and thus control the boiler temperature. Without nitrogen dilution, the flue gas is mainly composed of CO₂ and H₂O, allowing to manage a highly concentrated CO₂ stream ready for sequestration once water is removed. Nevertheless, some important pollutants, like NO, may also appear during the combustion and should be removed prior the CO₂ storage.

Several authors have studied NO reduction under oxy-fuel combustion conditions, both experimentally [2-7] and by modeling [8-10]. The main conclusion is that oxy-fuel combustion technology has a higher potential for reduction of NO_x emissions compared to air combustion processes. This reduction is mainly due to absence of thermal NO, as there is no nitrogen. Another important contribution is the removal of recycled NO through fuel reburn reactions when it returns to the furnace.

During this process, NO is mainly reduced into HCN and NH₃ by the reactions with hydrocarbon radicals from the fuel [11, 12], either from the primary fuel or even from a secondary fuel added specifically after the main combustion to improve NO reduction when a reburning technology is included in the system [13, 14]. Finally, with the adequate conditions these intermediates should be converted to N₂.

HCN oxidation under traditional combustion with air has been studied earlier, as reviewed by Dagaut et al. [15]. Nevertheless, despite of the importance of HCN as the main intermediate product obtained during the reduction of NO, its oxidation regime in a CO₂ atmosphere has not been addressed until now.

The objective of this work is to study the behavior of the HCN oxidation under typical oxy-fuel combustion conditions, that is highly diluted in CO₂ instead of N₂, including an experimental study and simulation with a literature mechanism [15]. Previously, a comparison is made between O₂/CO₂ and air combustion results.

Experimental

The experiments of HCN oxidation have been carried out in an experimental installation consisting basically of a gas feeding system, a reaction system, and a gas analysis system. The apparatus is described in detail elsewhere [e.g. 16, 17] and only a brief description is given here.

A quartz flow reactor of 8.7 mm internal diameter and 200 mm in length is placed in a three-zone electrically heated oven, which ensures an isothermal temperature throughout the reaction zone within ± 10 K. Gases are led to the reactor from gas cylinders by separate streams, resulting in a constant concentration of 1000 ppm of HCN and a varying amount of O₂ which depends on the stoichiometry considered for each experiment. The mixture contains 75% of CO₂ in volume to represent oxy-fuel conditions and the balance is closed with Ar, as an inert gas. In addition, a fix quantity of water vapour (0.7%) is fed by saturating the argon stream through a bubbling water system at room temperature. A total gas flow rate of 1000 mL (STP)/min is kept constant during the experiments, leading to a gas residence time as a function of the reaction temperature, $t_r(s) = 195/T$ [K]. At the outlet of the reaction zone, the product gas is cooled by means of external refrigeration with air. The gas analysis equipment consists of a Gas Chromatograph equipped with TCD and FID detectors (to measure CO, CO₂, N₂ and H₂), a continuous IR analyzer for NO concentration, and a FTIR spectrometer, where HCN, N₂O and HNCO are measured. For the experiments diluted in CO₂, it is not possible to detect HNCO by FTIR analysis as its peak is hidden by the too wide CO₂ peak that appears at

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nearby wavelengths. Therefore, the concentration of HNCO is calculated by applying a nitrogen balance at each temperature, considering that during HCN oxidation only N₂, NO, N₂O and HNCO are formed in a significant amount, a hypothesis validated by the model predictions. The uncertainty of the measurements is estimated as $\pm 5\%$. For the air-fired experiments, the conditions are exactly the same as for oxy-fuel combustion conditions except for the CO₂, which is replaced by N₂ to dilute the mixture. In both cases, because the mixture is highly diluted, low heat is released during the reaction and isothermal conditions can be assumed. The experiments are carried at atmospheric pressure covering the 900-1450 K temperature range and for different excess air ratios (λ), ranging from very fuel-rich ($\lambda=0.2$) to fuel-lean conditions ($\lambda=2$). Table 1 lists the conditions of the performed experiments.

Table 1: Matrix of experimental conditions (Residence time is a function of temperature, t_r (s) = 195/T [K]).

Set	λ	[HCN] (ppm)	[O ₂] (ppm)	[H ₂ O] (%)	[N ₂] (%)	[CO ₂] (%)	[Ar] (%)
1A	0.2	1000	350	0.7	-	75	Bal.
1B	0.2	1000	350	0.7	75	-	Bal.
2A	0.7	1000	1225	0.7	-	75	Bal.
2B	0.7	1000	1225	0.7	75	-	Bal.
3A	1	1000	1750	0.7	-	75	Bal.
3B	1	1000	1750	0.7	75	-	Bal.
4A	2	1000	3500	0.7	-	75	Bal.
4B	2	1000	3500	0.7	75	-	Bal.

Results and discussion

Comparison of HCN oxidation for CO₂ and N₂ atmospheres

In order to evaluate the differences between oxy-fuel and air-fired combustion, the oxidation of HCN is analyzed as a function of the bath gas. The mixture is diluted in CO₂ to represent typical oxy-fuel combustion conditions and a N₂ dilution is used for simulating air-fired combustion.

Figure 1 shows the results obtained under stoichiometric conditions ($\lambda=1$), sets 3A and 3B in Table 1, although similar trends are observed for all the stoichiometries studied. Solid symbols represent results in CO₂ dilution and open symbols denote N₂ dilution. The results include the HCN behavior and the output concentrations of the main product gases found in quantitative amounts during its oxidation, i.e. CO, NO, N₂O and HNCO.

As can be seen in Figure 1a, the onset temperature of HCN conversion is similar for both cases studied, around 1075 K, and the HCN conversion increases with rising temperature. It has been pointed out in several studies [e.g. 18, 19] that the main responsible of the chemical effects of CO₂ replacement of N₂ in air is the reaction:



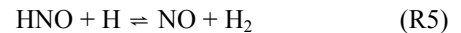
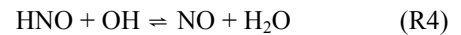
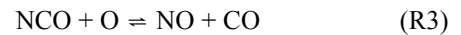
The CO₂ present will compete with O₂ for atomic hydrogen, which is the main chain branching reaction in combustion processes:



As the importance of reaction R1 increases in the presence of high levels of CO₂, less chain carriers are formed by reaction R2 due to the competition for H radicals between CO₂ and O₂, which leads to a lower HCN burning rate for the CO₂ dilution. This trend is confirmed in Figure 1, where more conversion of HCN is attained at any temperature when diluting with N₂. In addition, HCN presents conversions of 100% in the N₂ case but it is not totally consumed in CO₂, even at the higher temperatures studied.

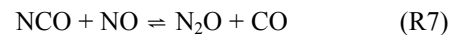
The onset of CO formation occurs in parallel with the decrease in HCN concentration, Figure 1b. In N₂, the CO concentration profile reaches a maximum, around 1275 K, and subsequently, its concentration decreases gradually as it is oxidized to CO₂. However, when CO₂ replaces N₂, the CO formation increases with the temperature throughout the entire temperature range. The strong increase in CO concentration in the presence of high levels of CO₂ is mainly due to increased importance of the CO₂+H reaction (R1) at these conditions, where CO represents the main product.

As shown in Figure 1c, NO is obtained as a minor product during HCN oxidation. In both experiments compared, the NO concentration increases with the temperature, reaching stabilization at high temperatures or even a slightly decrease of the NO formed. The formation of NO is much higher in the N₂ experiments. During the oxidation of HCN, different nitrogen-containing radicals are formed, like NCO, HNO and NH. The production of NO occurs primarily by the oxidation of these radicals [15]:



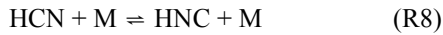
The higher HCN conversion found for N₂ dilution leads to a higher formation of N-radicals, which is therefore accompanied by more NO formation.

Another important product formed in the oxidation of HCN is N₂O. The profile of N₂O concentration is similar in both cases, increasing its concentration with the temperature until reaching a maximum and subsequently decreasing (Figure 1d). The main differences are the location of the N₂O maximum, which appears 50 K shifted to lower temperatures with N₂ dilution, and the amount of N₂O formed, which is twice as much in this case due to the higher formation of the NCO radical from HCN. The reaction NCO+NO represents the main source of N₂O [15]:



HNCO is also included among the main products originated during HCN oxidation. The trend of this compound is similar to the N₂O profile explained above, reaching a maximum of HNCO concentration, at 100 K lower temperature with N₂ (Figure 1e). Nevertheless,

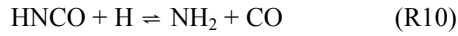
the concentration of HNCO obtained using CO₂ is much higher. With the presence of high CO₂ concentrations, the thermal isomerisation of HCN is favoured:



The HNC formed reacts with OH producing HNCO [20]:



Additionally, with N₂ dilution, most of the HNCO formed by reaction R8 is consumed due to the greater availability of hydrogen, through the high temperature reaction [15]:



The differences detected between these two configurations highlight the importance of the study of the HCN oxidation in a CO₂ atmosphere.

HCN oxidation in an O₂/CO₂ atmosphere

A study of the oxidation of HCN under CO₂ diluted conditions has been carried out at atmospheric pressure in the 900-1450 K temperature range. In addition to temperature, the influence of the air excess ratio has been analyzed for a given HCN concentration of 1000 ppm, ranging from very reducing ($\lambda=0.2$) to oxidizing conditions ($\lambda=2$).

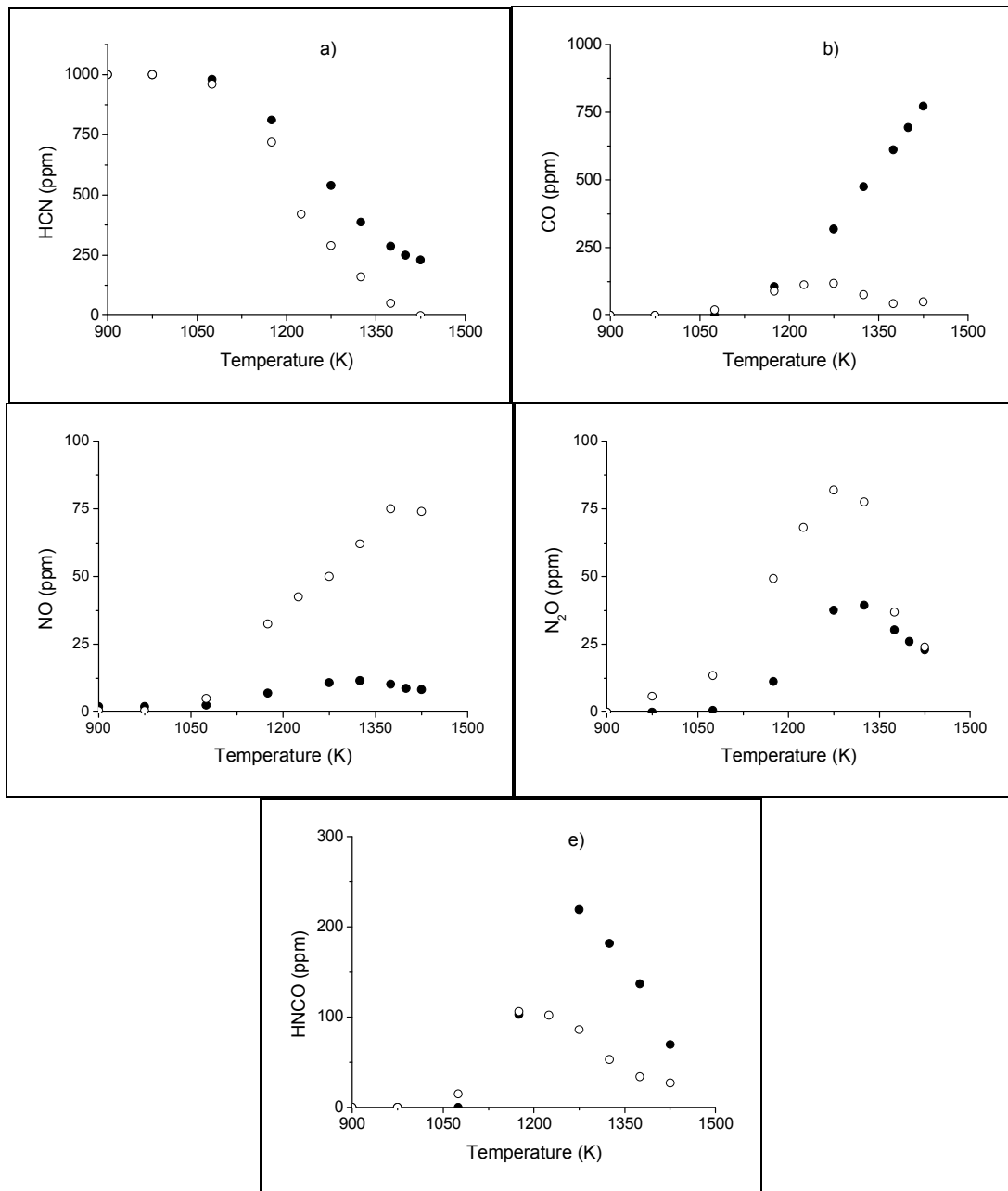
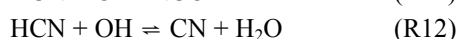
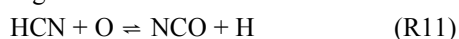


Figure 1: Experimental results of the main output gases as a function of temperature: a) HCN, b) CO, c) NO, d) N₂O, e) HNCO. Solid symbols denote experiments with CO₂ dilution and open symbols denote experiments with N₂ dilution.

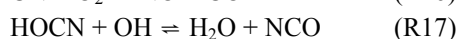
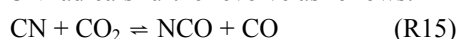
The experimental results have been analyzed in terms of a detailed gas-phase chemical kinetic model. The comprehensive reaction mechanism used for the modeling study was developed by Dagaut et al. [13] for the oxidation of HCN in air combustion, based on a review of the formation and destruction routes of HCN and the thermochemistry of HCN-related species. Minor modifications have been done to take into account the chemical effect of the presence of high CO₂ concentrations. Calculations are performed using the PFR Model of Chemkin-Pro software [21]. The reverse rate constants were obtained from the forward rate constants, and the thermodynamic data were taken from the same source as the mechanism. The full reaction mechanism includes 41 species and 250 elementary reversible reactions.

Figure 2 shows the experimental and calculated results of HCN concentration and the concentration profiles of the main products obtained during its oxidation, as a function of the temperature and for different excess air ratios, specifically for the conditions of the experiments 1A, 2A, 3A and 4A in Table 1. Experimental data are shown in open symbols and calculations as lines. Overall, the applied mechanism provides a reasonable good agreement between modeling predictions and experimental results, even though the computed profiles are shifted to lower temperatures for most of the compounds analyzed. The model is able to reproduce the experimental trends, except for the results at very fuel-rich conditions ($\lambda=0.2$), where significant discrepancies are found.

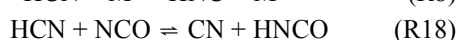
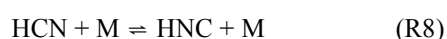
It can be seen in Figure 2a that the onset temperature of HCN conversion is similar for all the stoichiometries studied, around 1075 K. For any temperature, as the mixture becomes more fuel-lean, the HCN consumption is higher. An increase in the availability of O₂ increases the formation of radicals, favoring the HCN removal, mainly with OH and O radicals, through the reactions:



CN and HOCN radicals further evolve as follows:

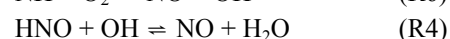
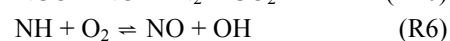
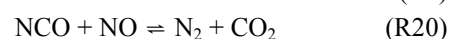
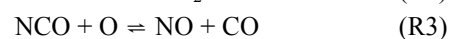
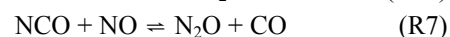
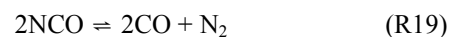


The HCN/HNC isomerization reaction, as well as the HCN+NCO reaction path, also have an important contribution during the HCN oxidation in a CO₂ atmosphere:

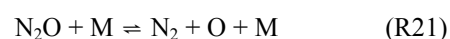


Independent of the oxygen availability, HCN does not present complete conversion, even at the highest temperatures of the study. The model calculations for HCN conversion as a function of the temperature are slightly over-estimated at any stoichiometry.

The increase in the HCN conversion with the increase in the excess air ratio leads to a higher formation of CO, NO, N₂ and N₂O, as shown in Figure 2b-2e. The formation of the main products takes place through reactions involving different radicals generated during the HCN oxidation, primarily NCO:



Additionally, a significant amount of CO is formed through the competitive reaction CO₂+H (reaction R1) under high levels of CO₂. This reaction is the main responsible for the differences obtained between oxy-fuel and air-fired combustion. Regarding N₂O profiles, the decrease observed at the highest temperatures studied in all the experiments performed is basically due to its dissociation to N₂ and O:



While the CO and N₂O concentration profiles show more formation in the modeling compared to the experiments for all temperatures and stoichiometries analyzed, the model calculations of the NO and N₂ concentrations are under-predicted.

Experimental HNCO concentration was calculated by means of a nitrogen balance at each temperature, considering HCN, NO, N₂, N₂O and HNCO as the only N-containing products obtained during HCN oxidation. The simulation predictions do not fit well the values based on experimental results, primarily at high temperatures. An attempt to explain the HNCO behavior in the CO₂ atmosphere shows that the HNC isomer plays a key role for the formation of HNCO. HNC reaction pathways are not clear at present [13, 22] and therefore it is not possible to conclude on the HNCO fate for the present conditions.

To sum up, Figure 3 displays the major reaction pathways of the HCN oxidation under high CO₂ dilution conditions, derived from the Reaction Path Analyzer Tool of the Chemkin-Pro software. The reaction net differentiates for the different excess air ratios tested, although the predominant paths of HCN oxidation are similar for all the stoichiometries.

Conclusions

An experimental and simulation study of the oxidation of HCN in a CO₂ atmosphere has been carried out under flow reactor conditions in the 900-1450 K temperature range and for different stoichiometries, ranging from very-fuel rich to fuel-lean environments. Especial emphasis is given to the differences with traditional air-fired combustion results performed in the same experimental setup.

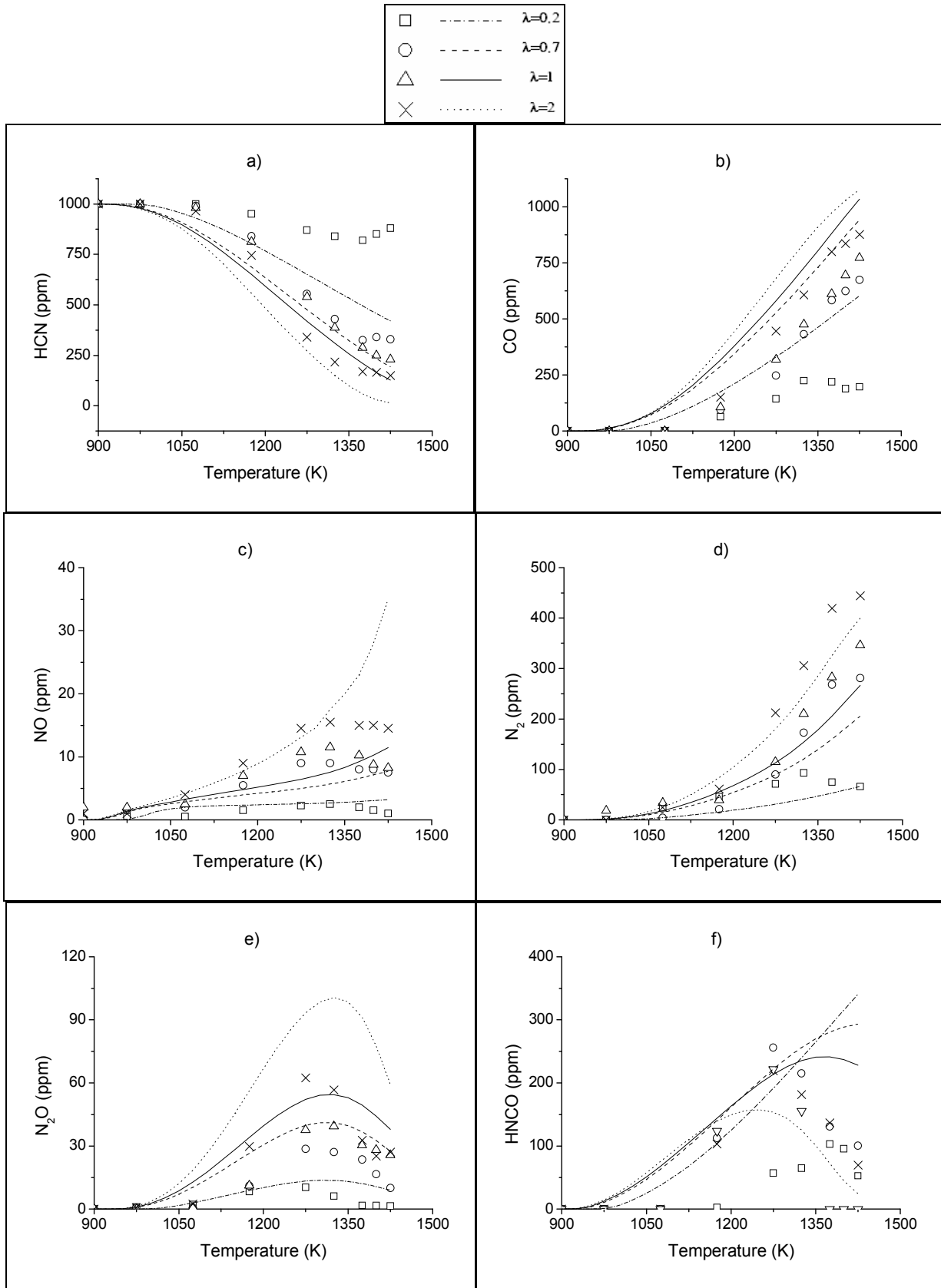


Figure 2: Experimental (open symbols) and simulation (lines) results of the main output gases as a function of temperature and the stoichiometry. a) HCN, b) CO, c) NO, d) N₂, e) N₂O f) H₂CO. The inlet conditions correspond to sets 1A, 2A, 3A and 4A in Table 1.

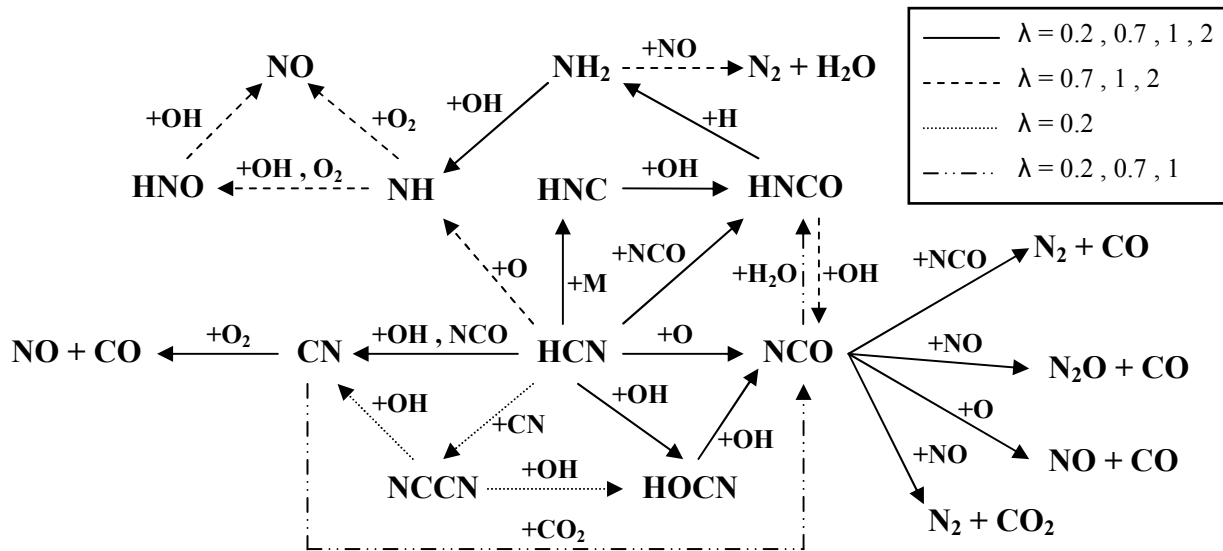


Figure 3: Major reaction pathways of the oxidation of HCN under oxy-fuel combustion conditions for different excess air ratios. Calculations are made with the Reaction Path Analyzer Tool from Chemkin-Pro.

The high levels of CO_2 present will compete with O_2 for atomic hydrogen, through the $\text{CO}_2 + \text{H} = \text{CO} + \text{OH}$ reaction, reducing the formation of chain carriers via $\text{O}_2 + \text{H} = \text{O} + \text{OH}$. This competition leads to a lower HCN burning rate, a higher CO formation and lower NO and N_2O formation compared to air combustion. With regard to the stoichiometry influence under CO_2 diluted conditions, the higher availability of oxygen increases the HCN conversion, leading to a greater formation of the main products (including CO, NO, N_2 and N_2O). Nevertheless, the onset temperature for reaction is similar at any stoichiometry studied. The literature chemical kinetic model applied [15] reproduces reasonably well the experimental trends, except for the very fuel-rich experiments and the HNCN concentration profile, which will require further improvement.

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References

- [1] B.J.P. Buhre, L.K. Elliott, C.D. Sheng, R.P. Gupta, T.F. Wall. *Prog. Energy Combust. Sci.* 31 (2005) 283-307.
- [2] E. Croiset, K.V. Thambimuthu. *Fuel* 80 (2001) 2117-2121.
- [3] H.K. Kim, Y. Kim, S.M. Lee, K.Y. Ahn. *Proc. Combust. Inst.* 31 (2007) 3377-3384.
- [4] K. Okazaki, T. Ando. *Energy* 22 (1997) 207-215.
- [5] Y. Hu, S. Naito, N. Kobayashi, M. Hasatani. *Fuel* 79 (2000) 1925-1932.
- [6] H. Liu, R. Zailani, B.M. Gibbs. *Fuel* 84 (2005) 833-840.
- [7] K. Andersson, F. Normann, F. Johnsson, B. Leckner. *Ind. Eng. Chem. Res.* 47 (2008) 1835-1845.
- [8] E.H. Chui, M.A. Douglas, Y. Tan. *Fuel* 82 (2003) 1201-1210.
- [9] J. Park, J.S. Park, H.P. Kim, J.S. Kim, S.C. Kim, J.G. Choi, H.C. Cho, K.W. Cho, H.S. Park. *Energy Fuels* 21 (2007) 121-129.
- [10] F. Normann, K. Andersson, B. Leckner, F. Johnsson. *Fuel* 87 (2008) 3579-3585.
- [11] T. Nozaki, S. Takano, T. Kiga, K. Omata, N. Kimura. *Energy* 22 (1997) 199-205.
- [12] Y. Hu, N. Kobayashi, M. Hasatani. *Fuel* 80 (2001) 1851-1855.
- [13] R. Bilbao, A. Millera, M.U. Alzueta. *Ind. Eng. Chem. Res.* 33 (1994) 2846-2852.
- [14] M.U. Alzueta, P. Glarborg, K. Dam-Johansen. *Combust. Flame* 109 (1997) 25-36.
- [15] P. Dagaut, P. Glarborg, M.U. Alzueta. *Prog. Energy Combust. Sci.* 34 (2008) 1-46.
- [16] M. Abián, C. Esarte, A. Millera, R. Bilbao, M. U. Alzueta. *Energy Fuels* 22 (2008) 3814-3823.
- [17] M.U. Alzueta, R. Bilbao, M. Finestra. *Energy Fuels* 15 (2001) 724-729.
- [18] F. Liu, H. Guo, G. J. Smallwood, Ö. L. Gülder. *Combust. Flame* 125 (2001) 778-787.
- [19] P. Glarborg, L. L. B. Bentzen. *Energy Fuels* 22 (2008) 291-296.
- [20] A. Dean, J. Bozzelli. In: W.C. Gardiner Jr, editor. *Gas-phase combustion chemistry*. New York Springer (2000) Chapter 2.
- [21] Chemkin-Pro. Reaction Design, Inc.
- [22] M.C. Lin, Y. He, C.F. Melius. *Int. J. Chem. Kin.* 24 (1992) 1103-1107.