

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 49

EFFECT OF FUEL COMPOSITION ON THE CONVERSION OF FUEL-N TO NITROGEN OXIDES IN THE COMBUSTION OF SMALL SINGLE PARTICLES

BY
Jouni Hämäläinen

Academic Dissertation
for the Degree of
Doctor of Philosophy



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Preface

This work was carried out at the Department of Chemistry, University of Jyväskylä, and at the Technical Research Centre of Finland, VTT, during the years 1991-1994. I wish to express my sincere gratitude to Associate Professor Tummavuori, under whose supervision this work was carried out. His invaluable guidance, support and encouragement have been deeply appreciated. At the outset an agreement for cooperation was concluded between the University of Jyväskylä and VTT and for that I express my warm thanks to Prof. Dan Asplund.

I am deeply grateful to Dr. Martti Aho, my closest colleague at VTT, who willingly shared with me his understanding of combustion chemistry, and offered encouragement and constructive criticism when this was needed.

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I am grateful to Dr. Kathleen Ahonen for revising the language of the manuscript.

My greatest debt of gratitude is to my wife Katriina and daughter Vilma, who provided the kind of support and patience that only family can. To them go my very warmest thanks.

Jyväskylä, April 1995

Jouni Hämäläinen

to Katriina and Vilma

Abstract

Older fuels produce more N_2O in fluidized bed combustion than younger fuels. In this study the effect of fuel composition on the formation of nitrogen oxides was examined with solid fuels and model compounds at 1073 K, the temperature typical of fluidized bed combustion. Differences in the release of HCN and NH_3 were investigated under pyrolysis conditions, and the formation of nitrogen oxides (NO , N_2O and NO_2) was determined in combustion. All experiments were performed in an entrained flow reactor. HCN and NH_3 were determined by ion selective electrodes, and HCN was also measured by standard method. Nitrogen oxides were detected and measured with an FT-IR spectrometer.

The experiments showed fuel oxygen to play an important role in the formation of NH_3 from fuel-based HCN during pyrolysis stage and, therefore also in the formation of N_2O . As the fuel-O/fuel-N ratio increased, as it does with younger fuels, conversion of HCN to NH_3 was enhanced and the ratio of NH_3 /HCN in the pyrolysis gases increased. In model compound studies, phenolic OH-groups in particular were found to increase the conversion of HCN to NH_3 . The importance of the fuel-O/fuel-N ratio has also been demonstrated in studies carried out in pilot scale combustors.

It is proposed that, with older fuels, HCN remains inactive during pyrolysis stage and is able to reach the combustion zone, where it readily can oxidize to N_2O . In low rank fuels, where the oxygen concentration is higher, there are more oxygen-containing radicals available to convert fuel-based HCN to NH_3 . Moreover, in lower rank fuels the aromaticity in the fuel is lower and the tars lighter, which facilitates the release of nitrogen. Thereby, more HCN is released during early pyrolysis, and reactions between HCN and oxygen-containing radicals, mostly OH, to produce NH_3 become more probable. It is particularly this

fast volatile-N which has been found to evolve as NH_3 during pyrolysis. In the combustion zone NH_3 reacts mostly to NO . The formation of NO_2 was insignificant in the combustion conditions studied in this work.

LIST OF ORIGINAL PAPERS

This thesis is based on the following publications:

1. Hämäläinen, J.P., Tummavuori, J.L and Aho, M.J., Determination of NH₃ in pyrolysis gases by ammonia selective electrode, *Talanta* 40 (1993) 1575.
[https://doi.org/10.1016/0039-9140\(93\)80371-W](https://doi.org/10.1016/0039-9140(93)80371-W)
2. Aho, M.J., Hämäläinen, J.P. and Tummavuori, J.L., Conversion of peat and coal nitrogen through HCN and NH₃ to nitrogen oxides at 800 °C, *Fuel* 72 (1993) 837.
[https://doi.org/10.1016/0016-2361\(93\)90088-J](https://doi.org/10.1016/0016-2361(93)90088-J)
3. Aho, M.J., Hämäläinen, J.P. and Tummavuori, J.L., Importance of Solid Fuel Properties to Nitrogen Oxide Formation Through HCN and NH₃ in Small Particle Combustion, *Combustion and Flame* 95 (1993) 22.
[https://doi.org/10.1016/0010-2180\(93\)90049-9](https://doi.org/10.1016/0010-2180(93)90049-9)
4. Hämäläinen, J.P., Aho, M.J. and Tummavuori, J.L., Formation of nitrogen oxides from fuel-N through HCN and NH₃: a model-compound study, *Fuel* 73 (1994) 1894.
[https://doi.org/10.1016/0016-2361\(94\)90218-6](https://doi.org/10.1016/0016-2361(94)90218-6)
5. Hämäläinen, J.P. and Aho, M.J., Effect of fuel composition on the conversion of volatile solid fuel-N to N₂O and NO, accepted to *Fuel*.
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CONTENTS

PREFACE

ABSTRACT

LIST OF ORIGINAL PAPERS

1. INTRODUCTION	9
<i>1.1 The problem of nitrogen oxides</i>	9
<i>1.2 Scope of the study</i>	10
2. COMPOSITION AND COMBUSTION OF SOLID FUELS	10
<i>2.1 Ranking and chemical composition of solid fuels</i>	10
<i>2.2 Structural analysis of fuels</i>	11
<i>2.3 Analytical methods and functionalities of oxygen, sulfur and nitrogen in fuels</i>	12
<i>2.3.1 Oxygen and sulfur in fuels</i>	13
<i>2.3.2 Nitrogen in fuels</i>	14
<i>2.4 Combustion of solid fuels</i>	16
<i>2.4.1 Combustion stages</i>	16
<i>2.4.2 Release of fuel nitrogen and oxygen</i>	19
<i>2.4.3 Conversion of fuel-N to nitrogen oxides</i>	21
3. EXPERIMENTAL WORK	25
<i>3.1 Construction of the entrained flow reactor and determination of NO and N₂O</i>	25
<i>3.2 Determination of HCN and NH₃</i>	26
<i>3.3 Effect of (fuel-O)/(fuel-N) ratio and nitrogen functionality on HCN/NH₃ and N₂O/NO ratios</i>	29
<i>3.4 Conversion of model-compound N to HCN and NH₃ and to N₂O and NO</i>	32
<i>3.5 Effect of fuel structure on the conversion of volatile fuel-N to N₂O and NO</i>	35
4. CONCLUSIONS	41
5. REFERENCES	43

Erratum

Page	Is	Should be
Name page	...Natural Science...	...Natural Sciences...
Page 27, line 13	...particular produce...	...particular produced...
Page 31, line 9	The fuels with...	The fuel with...
Page 40, line 3	...range the the experiments...	...range than the experiments...
Paper I, page 1577		
Fig. 2. caption	...11, data-logger...	...12, data-logger...
Fig. 2. caption	...11, data-logger...	...11, gas washing bottles...
Fig. 2. caption	...12, computer HP 9845.	...13, computer HP 9845.
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second paragraph, line 7	...values of s_A and s_Bvalues of s_E and s_S ...
second paragraph, line 8	...value of s_Bvalue of s_S ...
Paper I, page 1579		
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Paper III, page 27, right column		
first paragraph, line 7	...mostly from ammonia,...	...mostly from hydrogen cyanide,...
Paper IV, 1896, left column		
first paragraph, line 5	...the N_2 was <0.05%.	...the N_2 was <0.5%.

1. INTRODUCTION

1.1 The problem of nitrogen oxides

World energy consumption continues to increase despite the current recession. Today about 85% of the world's energy is produced by combustion processes. Unfortunately, this production brings with it serious environmental problems among them the emissions of sulfur (SO_x) and nitrogen oxides (NO_x), which are precursors of acid rain, and the participation of nitrogen oxides in the formation of photochemical smog. Some combustion processes also produce significant amounts of nitrous oxide (N_2O), a gas that contributes to stratospheric ozone depletion and global warming.

Sulfur oxide emissions can be reduced to an acceptable level by flue gas scrubbing or in fluidized bed combustion (FBC), by capturing SO_2 in the form of sulfate in the bed material. Emissions of nitrogen oxides (N_xO_y) can be decreased by changing the combustion conditions (temperature, oxygen concentration in the combustion zone) or by reducing NO to N_2 in postcombustion controls. Although the postcombustion controls such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR), tend to be more expensive, the use of these methods will certainly become more widespread in the future as regulations tighten. The stack gas controls may sometimes increase N_2O emissions. In older power plants the regulations regarding NO_x are usually now met by changing the combustion technique to one more environmentally favourable. Significant improvement of these techniques depends, of course, on a sound understanding of the formation of nitrogen oxides.

1.2 Scope of the study

Fuel bound nitrogen is the major source of the nitrogen oxides emitted from modern power plants. The mechanisms involved in the formation of NO_x and N_2O are not completely known, however, despite the many results that have recently been published. In particular, the effect of fuel composition on the formation of N_xO_y in fluidized bed combustion is not well understood. It was to throw light on these problems that the present work was undertaken. First the suitability of the methods employed in the determination of NH_3 and HCN was evaluated¹ and then the effect of fuel composition on the conversion of fuel nitrogen through HCN and NH_3 , to N_xO_y was studied with real fuel samples and with model compounds.^{2,3,4,5}

2. COMPOSITION AND COMBUSTION OF SOLID FUELS

2.1 Ranking and chemical composition of solid fuels

The formation of peat and coal from plant matter via biochemical and geochemical processes, otherwise known as coalification,⁶ involves the progressive transformation of plant matter through peat, lignite/brown coal and subbituminous and bituminous coals to anthracite coals. If not separately mentioned, the whole series, from peat to anthracite, is intended when 'fuels' are discussed below.

Fuels are complex mixtures of molecules,⁷ with major elements carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S). The inorganic part of the fuel is referred to as ash. Fuels are often classified by ranking system where the rank is a measure of the degree of coalification. As the fuel rank changes the relative concentration of these elements, the

chemical composition and many properties of the fuel change. Relative to the younger, lower rank fuels, the higher-rank fuels have lower hydrogen and oxygen contents and higher carbon content along with lower porosity and moisture content.^{6,8,9}

The fuel structure is difficult to define, because the carbon network is made up of non-repeating monomer units.¹⁰ At the least, fuels can be described in terms of structural parameters such as¹⁰

size distribution of the macromolecules

degree and type of cross linking

carbon aromaticity

average size of condensed aromatic units

number of hydroxyl groups

2.2 Structural analysis of fuels

The structures of fuels have traditionally been studied by chemical methods including pyrolysis (or thermal degradation), acylation, reductive alkylation, hydrolysis, oxidative degradation and fluorination of the material.^{10,11} One obvious disadvantage of these methods is that the structure of the material may change during the degradation so that the fragments found no longer represent the original structure of the material. More common today are direct methods of analysis such as ¹³C CP/MAS (cross polarization/magic angle spinning) nuclear magnetic resonance (n.m.r),¹² solid state ¹H n.m.r., Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS or 'ESCA').¹³

Analytical studies have shown that increasing rank implies a loss of aliphatic and hydro-aromatic structures⁶ a reasonable finding since fuel rank is a measure of the approach to pure graphitic structure. ¹³C NMR and IR methods, as well as various chemical analyses, have also shown that the carbon aromaticity in fuel increases with the carbon content and fuel rank.¹⁴ The aromatic carbon content of a low-rank fuel may be as low as 30 - 40% of the total carbon content, while for a high-rank fuel it may be 90 - 95%.^{14,15}

2.3 Analytical methods and functionalities of oxygen, sulfur and nitrogen in fuels

The most abundant heteroatoms (the major elements except C and H) in fuels are oxygen, nitrogen and sulfur. Some of the old procedures are still useful for the analysis of oxygen-containing functional groups. For example, Ihnatowich's¹⁶ and Schafer's¹⁷ methods, both based on cation exchange, have been used for the determination of carboxylic oxygen in fuel. Carboxylic oxygen content can also be calculated by measuring the amount of carbon dioxide evolved under standard hydrogenation conditions.¹⁷ Kröger's method, based on the reaction between coal and hydroxylamine hydrochloride, has been employed for the determination of carbonyl oxygen, and acetylation in a basic medium followed by non-aqueous potentiometric titration¹⁷ has been used in the determination of fuel hydroxyl groups.¹⁶ Later FT-IR was found to be a powerful method for determining oxygen-containing groups, particularly because of its sensitivity in detecting the changes in oxygen functionality,¹³ for example during pyrolysis of fuel.¹⁸ FT-IR has also been used for direct determination of the carboxylic,^{19,20} ester, ether^{17,20} and carbonyl groups¹⁶ in fuel. Unfortunately, absorption of water may mask the O-H stretching bands,^{13,16} an effect which has been evaluated in some studies.²⁰ ¹³C n.m.r. has been used for indirect measurement of fuel oxygen.^{12,17,20,21}

Nitrogen functionalities have conventionally been studied by thermal degradation of the fuel followed by chemical analysis.²² The original functionalities of nitrogen in fuels are assumed to be identical with those found in pyrolysis and extraction products. Functionality of fuel nitrogen has been difficult to determine by direct methods because the nitrogen concentration is very low. XPS has recently been found to be informative, although the method suffers from the limited energy separation and large XPS peak widths for the different forms of nitrogen.¹⁴ Other direct methods useful for the characterization of fuel nitrogen are FT-IR and potentiometric titration.^{22,23,24} FT-IR has been applied for the determination of non-basic N-H (pyrrolic)²³ and potentiometric titration for the measurement of basic nitrogen (pyridinic).^{23,24,25} At the moment, non-aqueous titration is being used as a parallel method to XPS.^{23,25,26,27} Recently, X-ray absorption near-edge spectroscopy (XANES) has been introduced for characterization of the chemical forms of nitrogen in coals.^{14,28}

Methods for the investigation of sulfur in coal are X-ray techniques like XANES and XPS,^{29,30,31} and reduction methods.^{14,29,32} The temperature-programmed reduction (TPR) method relies on the reduction of the various forms of organic sulfur in fuel to hydrogen sulfide at characteristic temperatures.²⁹

2.3.1 Oxygen and sulfur in fuels

The principal heteroatom in most fuels is oxygen, varying in content from 1 to 2 wt% in anthracites to more than 20 wt% in brown coals⁹ and as much as 35 wt% in dry peat. The concentration of organic oxygen is usually calculated by subtracting the sum of the other

chemical components (C, H, N, S and ash) from 100 wt%, which means that the value obtained reflects all the errors incurred in figuring out the other values.

The major oxygen-containing functional groups are phenolic hydroxyl (-OH), free carboxylic (-COOH), carboxylate (-COO⁻) and carbonyl (=CO).³³ The lower rank fuels may also contain ether, quinone, methoxyl and heterocyclic structures attached to aromatic systems.⁶ Several studies have shown that the relative amount of carboxylic groups decreases and that of phenolic hydroxyls increases with increasing rank of the parent fuel.^{17,21,34} At the same time, however, the total concentration of the two groups decreases along with the total oxygen content.^{17,35}

Most of the sulfur in fuel is in organic form. Both spectroscopic and reductive methods indicate an almost linear increase in the proportion of aromatic sulfur with fuel rank, from ~50% at 70 wt% carbon to virtually 100% at 90-95 wt% carbon.²⁹ The aromatic sulfur in fuel occurs in thiophenic structure, while the aliphatic sulfur is present in (saturated) sulfides, sulfoxides and sulfones. Inorganic sulfur occurs in coals in the forms of sulfide, elemental sulfur, and sulfate.¹⁴

2.3.2 Nitrogen in fuels

The nitrogen content is independent of fuel type and normally varies between 0.5 and 3 wt%. According to Russian sources, most of the nitrogen in peat (28 - 58% of total nitrogen) can be presumed to exist as protein amino acid, as in the original plant.³⁶ Older non-aqueous potentiometric titration and extraction studies have shown that a significant portion of the nitrogen may occur in amino groups even in coals.²² Contrary to this, the

newest spectroscopic methods have suggested that only a minor part of the fuel nitrogen is present in amino groups,^{14,23,37} and XPS studies find it instead in pyrrolic- and pyridinic-type ring structures^{23,38} with peaks 400.2 eV and 398.8 eV, respectively. These heterocyclic nitrogen compounds are considered to be important in linking together the subunits of the macromolecular fuel structure.²³ Sometimes a component at a binding energy near 401.4 eV is required to get an acceptable fit in the XPS spectra.^{38,39} The binding energy at this location represents to quaternary nitrogen, but evidence for the presence of significant amounts of such a functionality in fuels is presently insufficient.³⁹ According to Kelly, such a high energy component could also arise from a conjugated pyridinic imine system.³⁹ Yet another possible reason for that component source would be the oxidation of pyridinic nitrogen to N-oxide during sample preparation.³⁸

Even if the intensity of this peak of 401.4 eV is combined with that of the pyridinic peak near 398.6 eV to provide an estimate of the total content of nitrogen in 6-membered rings, the pyrrolic nitrogen still predominates in all low-rank and bituminous coals.³⁸ However, the proportion of pyridinic nitrogen increases with coal rank.^{27,37,40}

It bears emphasis that XPS is a surface sensitive method of analysis with a penetration of only ~5 nm.²⁹ Since the surface composition of a material will not be representative of the bulk composition because of interaction of a freshly exposed surface with the local environment, sample for XPS analysis must always be prepared with extreme care under an inert atmosphere.³⁸

Recently, XANES studies have produced interesting results regarding the nitrogen functionality in coals. Pyrrolic nitrogen was found to be the dominant nitrogen fraction in all coals, as with XPS, but there was an apparent increase in this fraction as the oxygen

content of the coal diminished.¹⁴ Furthermore, in the lowest-rank coals, there was a strong correlation between rank and pyridone fraction, whereas the pyridine fraction was very small. Pyridone was concluded to be converted into pyridine with increasing fuel rank, since pyridine was found to be the second most abundant nitrogen type in high rank coals. All coals studied contained small but significant amounts of aromatic amine, but no evidence was found of saturated amines.¹⁴

2.4 Combustion of solid fuels

2.4.1 Combustion stages

The combustion of a solid fuel particle is a complicated process involving several stages (Fig. 1) which may, however, overlap if combustion occurs at low temperature, oxygen content is high or particle size is small.⁴² In addition, the overlapping increases with increasing fuel rank. Five phases may be distinguished:⁴¹

1. Heating and drying (phase 1). During this phase heat is transferred to the fuel particle, causing water evaporation. As the temperature of the particle increases some bond-breaking may occur.

2. Devolatilization and gas-phase combustion (phases 2,3,4). Devolatilization rate and physical behaviour of the fuel during these phases depend on fuel type and particle size, and on pyrolysis conditions.^{41,43,44} The content of volatiles varies from a few per cent up to 70 - 80% of the total particle weight. The mass of volatiles evolved decreases with increasing fuel rank and increases with increasing final temperature and heating rate.⁴¹ The major volatile species produced by primary pyrolysis of solid fuels are CO, H₂O, CO₂ and

hydrocarbons such as CH_4 , aliphatics and tars. Tars are defined as fuel volatiles (other than water) that condense at room temperature.⁴⁵

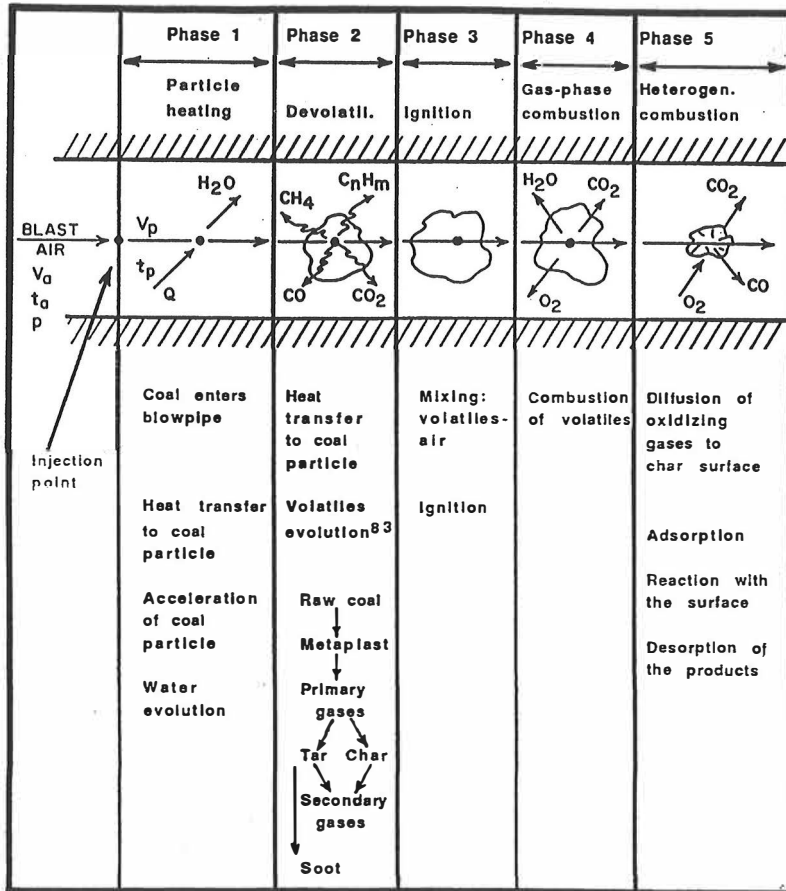


Fig. 1. Combustion phases of a solid fuel particle after Hutny.⁴¹

Combustion of the volatiles is affected by several factors, including oxygen concentration in the surrounding atmosphere, particle size, mixing, temperature, heat transfer and fuel composition. The ignition temperature depends on the combustible fraction of the volatiles in the fuel. After ignition, the heat transfer accelerates rapidly, which further intensifies devolatilization and combustion.⁴¹ Combustion of volatiles is perhaps the most poorly

understood stage of solid fuel combustion. Smoot and Smith have proposed a model of volatiles combustion consisting of the following phases:⁴³

- (1) release of volatiles,
- (2) condensation and repolymerization of tar in char pores,
- (3) evolution of hydrocarbon cloud, through small pores, from moving particles,
- (4) cracking of hydrocarbons to lower molecular weight hydrocarbons with local production of soot,
- (5) condensation of gaseous hydrocarbons and agglomeration of soot particles,
- (6) macromixing of devolatilization products with air,
- (7) micromixing of volatiles cloud with oxygen,
- (8) oxidation of gaseous species to combustion products, and
- (9) heat transfer from reacting fluids to the char particles.

3. Char combustion (phase 5). Char is the fuel residue after devolatilization. It is enriched in carbon and depleted in oxygen and hydrogen, and still contains some nitrogen and sulfur and most of the mineral matter. The char particle is often spherical and may be very porous. It can be oxidized by direct contact with oxygen at sufficiently high temperature, in which case the reaction between the char and the oxygen is thought to be heterogeneous, with gaseous oxygen diffusing to and into the particle, absorbing and reacting on the particle surface. The nature of the char and the burning rate of the char are dependent on the type of fuel and on the pyrolysis conditions.^{43,44} Of course the char burning rate depends in part, on the size of the particle and the nature of its pore structure.⁴¹ Normally this heterogeneous reaction is much slower than the devolatilization process.⁴³

2.4.2 Release of fuel nitrogen and oxygen

Part of the fuel nitrogen is released with the volatiles during pyrolysis, while the rest is retained in the char residue. At low gas temperatures ($T \leq 1100$ K) a delay occurs between the release of coal nitrogen and volatiles, suggesting that nitrogen evolution is delayed until ring rupture occurs.^{46,47,48} At temperatures below 1200 K the general trend is for the char to be enriched in nitrogen relative to the parent coal,^{46,47} or the nitrogen content is about the same independent of the coal type and test conditions.⁴⁶ However, at higher temperatures ($1250 \leq T \leq 1600$ K) the opposite trend prevails: the nitrogen content is lower in the char than in the parent coal.^{46,47} The nitrogen content in tar is the same as in the parent coal, suggesting that tar is a primary devolatilization product.^{47,48}

Coal nitrogen seems to evolve initially in heavy tar molecules, which are released without substantial change in molecular structure.⁴⁷ The amount of nitrogen evolved is proportional to the amount of tar released.^{47,49} It has further been reported that secondary gas-phase pyrolysis of tar nitrogen-containing aromatic species leads to the formation of HCN, NH_3 and N_2 .^{50,51,52} With high rank coals HCN is the second most abundant devolatilization product after tar-N, while the relative importance of NH_3 grows with decreasing fuel rank. In general, the evolution of HCN exceeds that of NH_3 with bituminous coals, but is weaker than NH_3 evolution with subbituminous and brown coals.^{54,55} HCN and NH_3 are not produced in significant quantities at temperatures between 873 and 973 K.^{38,47} In this temperature range fuel-N is released as pyridine, alkyl-substituted pyridines, pyrroles, quinolines, acridines and carbazoles.³⁸ At higher temperatures (1073 K) the amounts of complex organic nitriles such as cyanoacetylene and the amounts of HCN and NH_3 increase. At higher temperatures still, yields of NH_3 decrease, while those of HCN continue to increase.³⁸

The relative concentrations of the nitrogen-containing intermediates (HCN and NH₃) have been attributed to the original fuel nitrogen functionality. In model compound studies of the pyrolysis of heterocyclic aromatics, the major product was HCN.^{56,57,58} As the decomposition studies with model compounds have shown no formation of NH₃, the origin of NH₃ has been difficult to explain. It has been suggested that heterocyclic species produce HCN, and that other functional groups such as amines may be responsible for NH₃ production.^{50,55} Analysis of the functional groups in coals provides no support of this explanation, however, since amino groups do not occur in large amounts in coals. In lieu of this the decomposition of organic-rich sedimentary rock has been suggested as a possible source of NH₃.³⁸ Alternatively, Wendt and Bose propose that the difference in N-speciation is due to the different chemical environment (produced by the fuel itself) in which fuel evolves in the gas phase, or due to the chemical composition of the fuel.^{59,60}

The rank-dependent differences in reaction rates of fuels are related to their oxygen functionalities.⁴⁵ The oxygen-containing species begin to decompose at low temperatures and oxygen is initially lost faster than carbon.⁶¹ Oxygen loss of two subbituminous and bituminous coals during pyrolysis was nearly complete at fast heating rates (10⁴ - 10⁵ K/sec) at temperatures between 1300 and 1750 K.⁶¹ On that basis the oxygen functional groups were assumed to be relatively loosely bound. During pyrolysis at temperatures from 900 to 1150 K Nelson found the coal oxygen to evolve as CO, CO₂, phenol, cresols and water.⁶² At higher temperatures even the most stable phenols decomposed. The yields of CO increased sharply as the temperature was raised above 900 K, whereas CO₂ concentration was constant. The CO₂ is assumed to originate from carboxylic acids, which decompose at low temperature. Methoxy groups, hydroxyl groups and furans are thought to be CO sources at higher temperature.⁶²

In a study of the decomposition of aromatic hydrocarbons, Bruinsma et al.⁶³ found that the substituents in the phenyl ring generally decreased the thermal stability of those compounds. The thermal stability of benzene derivatives with a functional group containing one oxygen increased in the sequence methoxy < carbaldehyde < hydroxy. In phenol decomposition, the major products were cyclopentadiene and CO and, at higher temperatures (> 1020 K), benzene.

2.4.3 Conversion of fuel-N to nitrogen oxides

After the volatile nitrogen-containing intermediates (NH_3 , HCN) have been formed, they will further react to N_2 , NO, N_2O or NO_2 (Fig. 2) depending on 1) the local combustion environment (temperature and stoichiometry),⁶⁴ 2) fuel type^{49,65} and 3) the addition of limestone or other sorbents in fluidized bed combustion.⁶⁶

It is fair to assume that in fluidized bed combustion, the only contribution to final $\text{N}_2\text{O}/\text{NO}$ emissions comes from fuel-bound nitrogen. Although the effects of fuel type on the $\text{N}_2\text{O}/\text{NO}$ chemistry have been extensively studied, few conclusions have been drawn, though clearly the emissions of N_2O increase with increasing fuel rank. The effect of fuel properties on the formation and destruction of nitrogen oxides has been explained by (1) the elemental composition of the fuel, (2) consistency^{59,60} and content of volatile matter,⁶⁸ (3) the composition and content of mineral matter, (4) the chemical nature of bound nitrogen and other elements (functional groups) and (5) the physical characteristics of the char surface (pore structure).⁶⁷

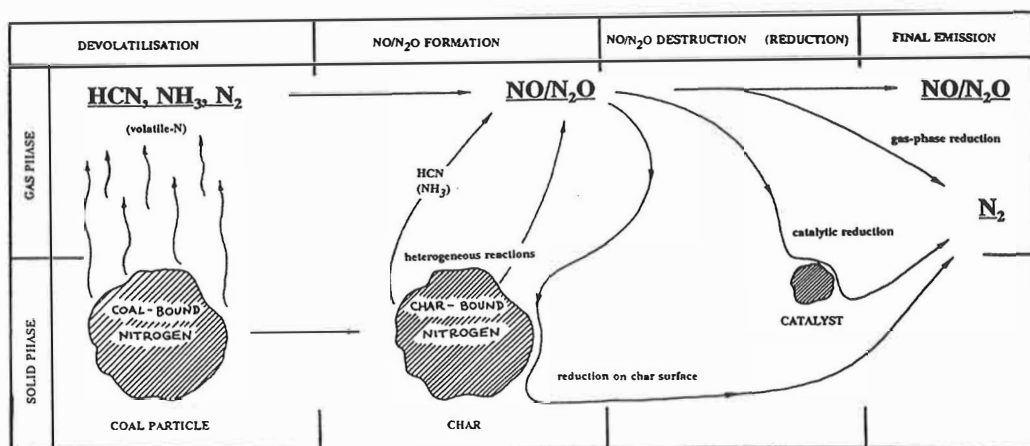


Fig. 2. Conversion of fuel nitrogen in solid fuel combustion.⁶⁷

The relative concentrations of NH₃ and HCN are very important in the formation of nitrogen oxides. Kramlich et al. injected NH₃, HCN and acetonitrile into the postflame gases and found that N₂O was preferentially formed from cyano species, whereas very little N₂O was released during NH₃ injection. Likewise other studies have shown that HCN is the major precursor in the formation of N₂O in the temperature range of fluidized bed combustion.^{48,69,70,71} The main formation pathway is thought to be



The effect of temperature on the N₂O and NO emissions is clear and has not incited any controversy in the literature. As the temperature increases (~1200 K), the emission of N₂O significantly decreases because the key intermediate (NCO) is then rapidly removed by radicals⁶⁹



and N_2O is quickly reduced through the reaction⁷⁰



At the same time, the NO emissions increase with temperature because the reactions (3), (4) and (5) result in NO formation; finally, above 1500 K, the oxidation of air nitrogen to NO becomes significant.⁶⁷ At lower temperatures (~1000-1200 K) reactions (3), (4) and (5) are slow enough that NCO reacts instead to N_2O via reaction (2).⁶⁷

Since HCN is the major intermediate in the formation of N_2O , the emissions of N_2O remain low in low rank fuel where the fuel-nitrogen is converted during devolatilization mainly to NH_3 instead of HCN. The porous structure of low rank fuel chars has also been thought to be important in the heterogeneous reduction of N_2O to N_2 .⁷² Other factors affecting the formation of nitrogen oxides are the additives used, for example limestone added to capture SO_2 in fluidized bed combustion.⁷³ Gavin and Dorrington found the addition of limestone and dolomite in fluidized bed combustion to increase the emissions of NO, while decreasing those of N_2O .⁶⁶ Relevant to this, Kasaoka et al. have reported that CaO has a high catalytic activity for the hydrolysis of HCN to NH_3 .⁶⁶ A possible role for CaO is, therefore, to catalyse the reaction of HCN to NH_3 or NH_2 radicals, thereby excluding the formation of NCO, which is a necessary intermediate for the formation of N_2O .⁶⁶ The further reaction of NH_3 to NO is known to be promoted by lime.⁶⁶ In contrast to Gavin and Dorrington, Mann and co-workers report that the addition of limestone has only a marginal effect on N_2O emissions.⁷³

Earlier it was thought that volatile-N was the major source for emissions of N_2O . Later studies, particularly ones in circulating fluidized bed (CFB), have shown that some N_2O

may be formed from char-N heterogeneously. The route by which char nitrogen is converted to N_2O is not clear, but some possibilities have been suggested: 1) char-N is oxidized to N_2O through oxidized surface sites, 2) char-N reacts with NO in the manner $NO + (CN) \rightarrow N_2O + (C)$, 3) char-N is gasified to HCN and NH_3 , which are oxidized to NO and N_2O .⁶⁷ Moritomi contends that char-N is the primary source of N_2O formation,⁷⁵ but Åmand et al.⁸³ suggest char-N has of only minor importance in the formation of N_2O . Åmand et al. found that the N_2O concentration increases with the bed height, in contrast to the NO concentration which decreases. In view of this they emphasize the importance of heterogeneous formation of N_2O and suggest that the N_2O emissions originate from the reduction of NO on the char surface. De Soete found only 1 - 6% of char-N to be converted to N_2O in a laboratory fixed bed reactor.⁷⁴

The contribution of char-N to the formation of N_2O is difficult to discover because the amounts of volatiles are clearly higher in combustion conditions than when measured by standard method (slow heating rate). As well, pyrolysis and char combustion may sometimes overlap, in which case part of the fuel-N will be devolatilized during the char combustion (slow volatile-N) and be released in the upper part of the bed. Char originated N_2O would then be overestimated in CFB combustion.

3. EXPERIMENTAL WORK

3.1 Construction of the entrained flow reactor and determination of NO and N₂O

The experiments were performed in an atmospheric entrained flow reactor. The maximum operating temperature produced by an electrical gas preheater is 1173 K, but higher temperatures can be reached by adding CO to the reaction gas as an extra source of heat. All experiments of the study were performed at 1073 K. The temperature distribution in the reaction zone was within ± 15 K of 1073 K, and the gas velocity was 4 ms^{-1} in the reactor tube (inner diameter 0.1 m and length 2 m). With solid fuels, the particle heating rate is of the order $10^4 \text{ }^\circ\text{C/s}$ and the solid/gas mixing occurs perfectly within 100 ms. This was found in an earlier experiment where N₂O and the reaction gas were mixed at 923-1093 K.

Nitrogen oxides (NO, N₂O, NO₂) formed in oxidizing experiments were determined with an FT-IR spectrometer (Perkin-Elmer 1760). The gas sample was taken with a vertically mobile water- and N₂-cooled probe, and quenched to about $150 \text{ }^\circ\text{C}$ within a few milliseconds.⁷⁶ The dried gas sample was led to the spectrometer equipped with an adjustable long-path gas cell (0.75-20.25 m). The optical path length used was 6.75 m and the detection limits achieved were 5 ppm for NO, 1 ppm for N₂O and 0.3 ppm for NO₂. The spectral ranges used for the determination were $1880\text{-}1790 \text{ cm}^{-1}$, $1404\text{-}1235 \text{ cm}^{-1}$ and $1660\text{-}1561 \text{ cm}^{-1}$ for NO, N₂O and NO₂, respectively. Disturbing overlappings, for example of water, which has strong absorption bands in the same spectral range as N₂O, were distinguished with a programme developed at VTT.⁷⁷ The program can eliminate any disturbing components whose concentrations can be calculated from the spectrum.

3.2 Determination of HCN and NH₃

To reveal the formation and destruction pathways of NO and N₂O, the amounts of HCN and NH₃ must be determined in the pyrolysis and combustion gases. HCN and NH₃ are generally determined, as here, by absorbing the gaseous components into solutions and measuring them by ion selective electrodes.^{51,54,55,59-61,78-83} Other techniques have been used as well, such as argentometry⁸³ (Liebig-Deniges method) and titration⁸⁴ in the determination of CN⁻ and titration⁸⁴ for NH₄⁺. The trend in analytical work today is towards ON LINE analyses and several new methods of analysing HCN and NH₃ are under development. Gas chromatography-mass spectrometry and FT-IR spectroscopy are increasingly being used in basic research, and both have been applied in model compound studies to determine the decomposition products of N-containing heterocycles^{56-58,85,86} and in pyrolysis studies of coals.⁵⁰ In pyrolysis studies, the use of FT-IR is complicated by the absorption of hydrocarbons such as acetylene and ethylene in the same spectral range as HCN and NH₃.⁸⁷ As with absorption methods, the sample for FT-IR analysis must be transferred from the combustion chamber to a cooler space, and reactions may take place during the transfer, with reduced reliability of the results. Such reactions can, however, be minimized by rapid cooling of the sample gas at the top of the probe. The best option is, of course, to make *in situ* determinations. For example, NH₃ has been measured in the gases of a power plant by photoacoustic laser spectroscopy.⁸⁸ In this method the most serious problem is the presence of dust-like impurities that absorb light; particularly in fluidized bed combustion, the passage of light is nearly totally hindered.⁸⁹ The sensitivity of photoacoustic spectroscopy for interesting gaseous components of combustion is reported to be at ppb-level.⁹⁰

In this work, NH_3 was determined by ion selective electrode and HCN by a Finnish standard method (SFS 3039)⁹¹ and electrode method. The standard method was particularly time-consuming. However, as they are not sensitive to background changes, the methods were suitable for this work. The NH_3 and HCN were sampled simultaneously by connecting the gas washing bottles in tandem, the first bottle being for NH_3 and the second for HCN. The absorption solutions were 0.01M HNO_3 for NH_3 and 0.01M NaOH for HCN. A part of the HCN was observed to be absorbed into the acidic solution (in the first bottle) and a part of the solution in the first bottle was therefore reserved for the determination of HCN. The volume of the absorption solutions was normally 0.3 dm³ and the sampling rate of gas was 0.167 dm³/s. Fuel feeding rate was adjusted to 0.2 - 0.25 g/s and was kept as stable as possible. All samples were dried, milled and sieved to a particle size of < 63 μm before experiments.

Peats in particular produce dark-coloured absorption solutions containing an abundance of organic compounds (pyrolysis products). If the concentration of those pyrolysis products is high enough, they may penetrate through the membrane of the NH_3 electrode and render it useless. This danger was minimized by measuring NH_3 in the gas phase. Because coal and lignite samples had lower content of volatiles they could be analysed directly from the liquid phase. The bark samples were also analysed directly in liquid phase because the nitrogen content was low and the electrode determination limit is considerably lower in liquid phase. The lowest limit for NH_3 electrode is $(5.0 \pm 0.35) \cdot 10^{-4}$ M in gas phase and $(5.0 \pm 0.25) \cdot 10^{-6}$ M in liquid phase. The corresponding NH_3 concentrations in flue gas are about 50.0 ± 3.5 ppm_{vol} and 0.50 ± 0.025 ppm_{vol}, respectively, with sampling parameters as follows: sampling time = 420 s, sampling rate = 0.167 dm³/s, volume of sampling solution = 0.3 dm³ and $V_m = 24.789$ dm³/mol (at 298.15 K and 1 bar). The overall repeatability

of the determination of HCN and NH₃ (including sampling and determination) was studied by statistical methods and found to be within 13%.

The determination limit for HCN with the standard method is $(1.5 \pm 0.075) \cdot 10^{-6}$ M. This corresponds to about 0.3 ppm_{vol} HCN in the pyrolysis gases calculated with the same sampling parameters as with NH₃ above. The drawback of this method is the long time required for analysis. An attempt was therefore also made to measure HCN by CN⁻ selective electrode, a method less sensitive than the standard method but much faster. A reasonable determination limit for the electrode is $8.0 \cdot 10^{-6}$ M (1.7 ppm_{vol} HCN).

The most serious problem in the determination of HCN was sample stability. Even the standard solutions lost cyanide during storage when the concentration of cyanide in solution was low (below $5 \cdot 10^{-5}$ M). Probably the loss was due to cyanide adhering to the walls of the container. Some researchers point to another problem: that sulfur can convert cyanide to thiocyanate if the samples are exposed to air,^{92,93} and Berman and co-workers suggest solving this problem by removing sulfur by precipitation before storing the sample.⁹⁴ In our case the sulfide concentrations were low ($< 1.5 \cdot 10^{-4}$ M or < 5 ppm S), and as the conversion of cyanide to thiocyanate first requires the formation of polysulfides from the sulfide, sulfur was not considered a significant problem in our measurements.

3.3 Effect of (fuel-O)/(fuel-N) ratio and nitrogen functionality on HCN/NH₃ and N₂O/NO ratios

During primary pyrolysis volatile nitrogen is evolved in tar compounds, which in the second stage of pyrolysis decompose to lighter species including HCN. In addition, the low rank fuels produce considerable NH₃ during pyrolysis and the early stages of combustion. Some researchers have claimed that the amine nitrogen in fuels is responsible for the high NH₃ conversions associated with low rank fuels.^{50,95} However, in this work the amine nitrogen content was found to be low even in low rank fuels. The measurement of nitrogen functionality by XPS showed the amine nitrogen content normally to account for 1 wt% or less of the total nitrogen concentration. In barks and peats the dominant nitrogen functionality was pyrrolic nitrogen. In coal and lignite the proportion of pyrrolic nitrogen was clearly decreased relative to peats, while the quaternary and oxidized nitrogen content became significant.

Contrary to the earlier common belief that the formation of N₂O depends only on fuel rank, Aho et al. have demonstrated that the fuel-O/fuel-N ratio has an effect on the N₂O/NO ratio in flue gases: the N₂O/NO ratio decreases with the O/N ratio.⁷⁶ The effect of the fuel-O/fuel-N ratio on the formation of N₂O and NO through HCN and NH₃ was studied first by pyrolysing several fuels with different O/N ratios, 7 to 150, to define the conversion of fuel-N to NH₃ and HCN. Then, the same fuels were combusted and the conversion of fuel-N to nitrogen oxides was measured. The HCN/NH₃ and N₂O/NO ratios increased sharply as the fuel O/N ratio decreased from 20 to 7. At higher O/N ratios than 20 (up to 150), the ratios of HCN/NH₃ and N₂O/NO remained nearly constant (Fig. 3) and the concentrations of HCN and N₂O were low in pyrolysis and combustion gases, respectively.

The pyrolysis studies were done at 1073 K, at which temperature the decomposition rate of tars is probable quite low and, therefore, the conversions of fuel-N to HCN and NH_3 were low. If, as suggested by Saastamoinen⁴², pyrolysis and combustion overlap for small particles the particle temperature could rise as much as several hundred degrees during devolatilization. And this means that, with oxygen present, the actual devolatilization rate would be higher than it was in the pyrolysis tests at 1073 K.

The nitrogen functionality seems to be less important than the fuel-O/fuel-N ratio in the chemistry of conversion of fuel-N to NH_3 , HCN and nitrogen oxides. This was seen with lignite and coal, which have nearly the same nitrogen functionalities, but the HCN/ NH_3 and $\text{N}_2\text{O}/\text{NO}$ ratios are considerably higher for coal (Fig. 3).

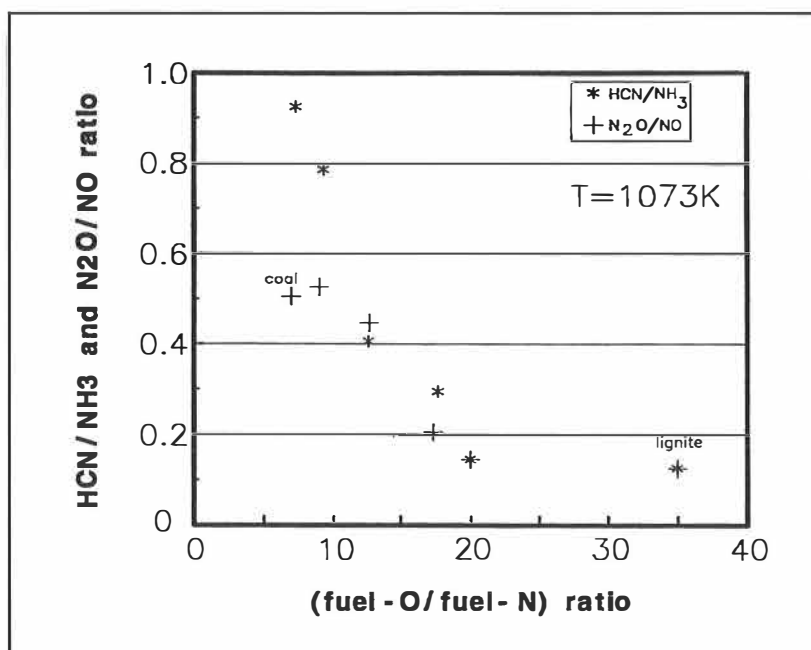


Fig. 3. Effect of fuel O/N ratio on the conversion of fuel-N to HCN and NH_3 and to N_2O and NO.

The dependency of the conversion of fuel-N to N_2O on the ratio of fuel-O/fuel-N has been demonstrated in a number of studies.^{65,75,96,97,98} Hiltunen et al.,⁹⁷ for example, have measured emissions of N_2O from different fuels in several boilers. The emissions decreased with increasing temperature as expected, but there were also marked differences in N_2O emissions between the fuels. Since the nitrogen contents in the fuels varied it was difficult to compare the fuels directly, and the reconstruction in Fig. 4 shows instead the conversions of fuel-N to N_2O . The volatile nitrogen content of these fuels varies also. The conversion of fuel-N to N_2O is seen to be lowest for fuels with high O/N ratio, and the conversion decreases with the O/N ratio. The fuels with O/N ratio 7.6 show surprisingly high conversion to N_2O , perhaps because of the high sulfur content (Table 1), 4.4%. De Soete has suggested that the reactions of sulfur species with nitrogen species can increase the emissions of N_2O in fluidized bed combustion.⁶⁹ It is also interesting to see that if coal is combusted together with fuel of high oxygen content the conversion of fuel-N to N_2O decreases (coal*+oil shale). Ultimately the conversions of fuel-N to N_2O were below 10% with all fuels combusted.

Table 1. Analysis of fuels combusted in different boilers (Hiltunen et al.).⁹⁷

Fuel type	O/N	Vol.	Ash	C	H	N	S	O
coal	4.7	28.5	19.1	69.5	4.0	1.2	0.6	5.6
coal*	2.5	34.0	15.1	72.6	4.8	2.0	0.4	5.1
coal*+75% oil shale	33	46.0	44.0	38.1	3.1	0.4	1.2	13.2
peat+wood waste	25	70.6	6.7	54.3	5.6	1.3	0.2	31.9
coal	7.6	41.6	11.3	69.1	4.9	1.2	4.4	9.1
coal	3.7	6.4	38.6	56.1	1.5	0.7	0.5	2.6
coal	5.9	42.9	14.7	66.1	4.6	1.4	4.9	8.3
coal	0.7	14.0	9.4	80.6	4.6	2.4	1.3	1.7
coal	7.0	38.4	12.9	67.6	3.7	1.9	0.5	13.4

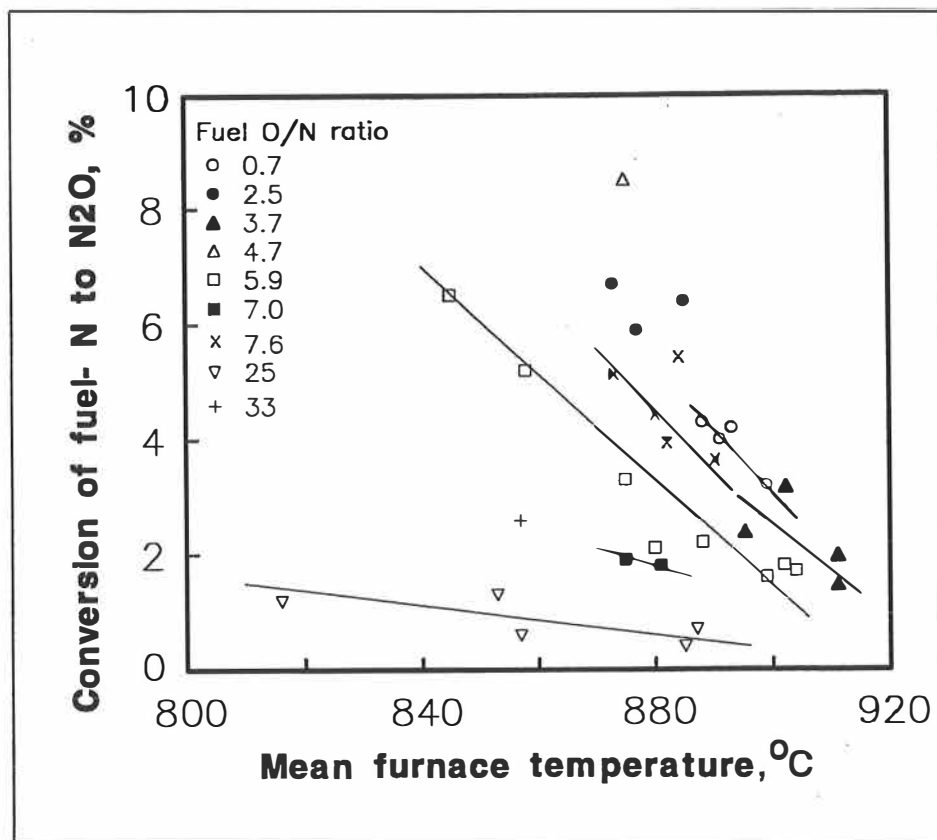


Fig. 4. Conversion of fuel-N to N₂O. Drawn from the experimental data of Hiltunen et al.⁹⁷

3.4 Conversion of model-compound N to HCN and NH₃ and to N₂O and NO

Besides real fuel samples, the effect of the fuel-O/fuel-N ratio on the formation of nitrogen oxides was studied with model compounds. In contrast to fuels the structure of model compounds is exactly known and the reactions occurring during the pyrolysis stage are more easily recognized. The model compounds were of pyridine, pyrrole and amine type with different numbers of oxygen-containing functional groups (hydroxyl and carboxyl groups) and were selected to represent the nitrogen-containing structural units in fuels. The

model compound sample for pyrolysis and combustion experiments was prepared by fixing the nitrogen content of the sample to 3 wt% by diluting the model compound with activated carbon and kaolin ($\text{SiO}_2 + \text{Al}_2\text{O}_3$). Samples were diluted to eliminate the effect of the different nitrogen contents of the model compounds and to obtain sufficient precision in the sample feeding rate. The degradation of the model compounds was studied in inert atmosphere to reveal the conversion of model-compound N to HCN and NH_3 . The formation of N_xO_y was investigated in combustion experiments.

The experiments in inert atmosphere showed that it is not simply the fuel-O/fuel-N ratio that determines the conversion of fuel-N to HCN and NH_3 , because when the model compound contained OH groups in the ring structure the conversion of HCN to NH_3 increased, and when the number of OH groups in the ring increased, the conversion of HCN to NH_3 increased further. Because of a high heating rate (10^4 °C/s), the phenolic OH groups were probably first to split off, producing OH-radicals.⁶³ Kinetic calculations have shown OH-radicals to be important in the gas phase chemistry,^{69,99,100,101} and particularly if the OH-radical concentration is high relative to the O concentration, the fuel-N based HCN is likely to be converted to NH_3 . The carboxylic groups in the structure of the model compounds did not have a marked effect on the HCN/ NH_3 ratio and it can be assumed that a large part of the COOH groups decompose directly to CO_2 . With amino-type compounds the conversion of model-compound N to NH_3 was high, as expected.

Redlich et al. have observed a broad general increase of phenolic oxygen content with increasing total oxygen content¹⁷ (Fig. 5a). If the fuel O/N ratio of their fuels is plotted as a function of the fuel OH/N ratio, a good correlation is obtained (Fig. 5b). This suggests that the actual fuel property controlling the formation of $\text{N}_2\text{O}/\text{NO}$ from volatile-N is not pure O/N ratio but the fuel OH/N ratio.

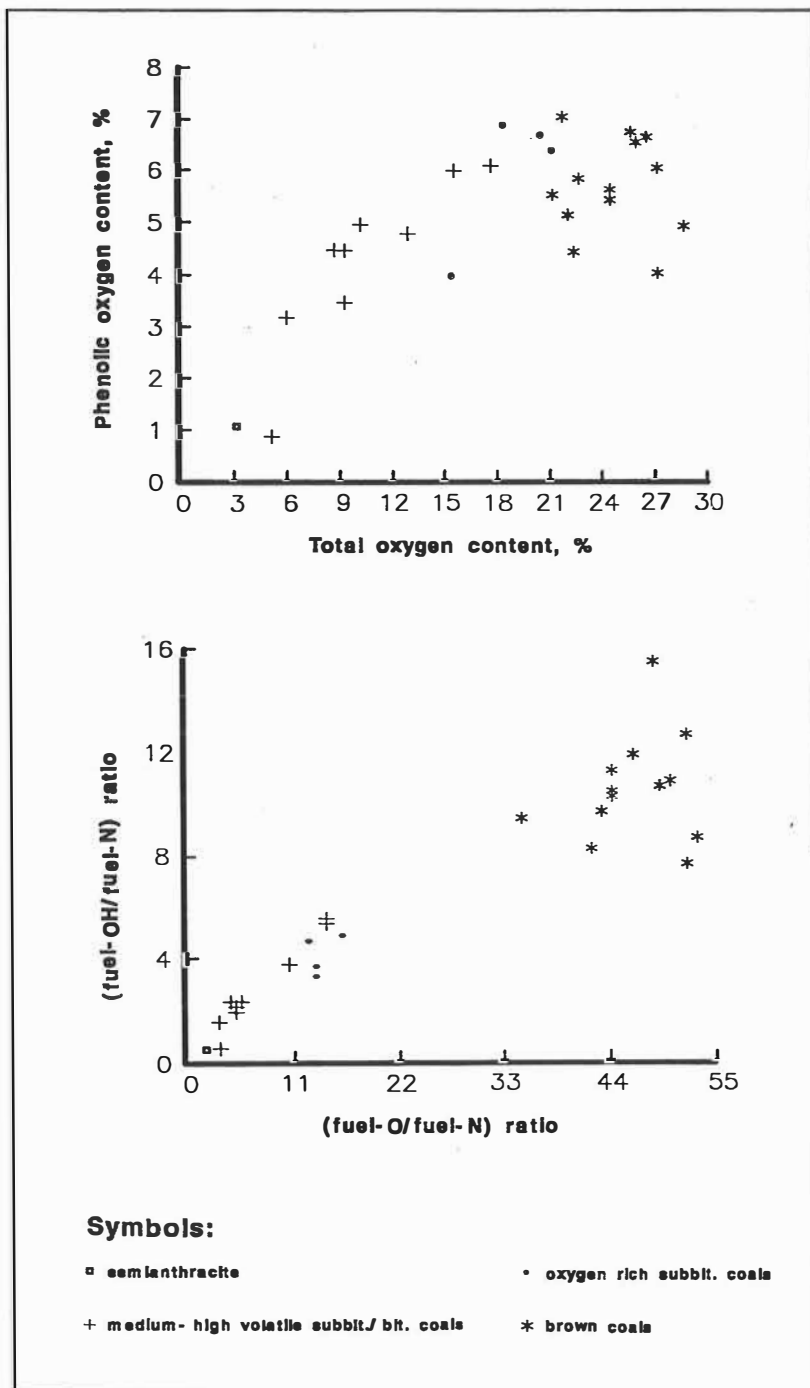


Fig. 5. a) The relationship between oxygen present as phenolic groups and total oxygen in Australian coals (wt% dmmf basis, figure drawn from data of Redlich et al.).¹⁷ b) Correlation between (fuel-O/fuel-N) ratio and (fuel-OH/fuel-N) ratio (Redlich et al.).¹⁷

The ratios of nitrogen oxides (fuel-N \rightarrow N₂O / fuel-N \rightarrow NO) recorded in combustion experiments for the model compounds did not follow the ratios of HCN/NH₃ found in degradation experiments. Probably this was due to the simpler structure of the model compounds relative to real fuels, which meant that also the pyrolysis or degradation stage was simpler. When a fuel particle pyrolyses, the volatiles flow out from the particle and simultaneously char is formed. With model compounds it is merely a case of chemical bonds breaking, and the char formation is negligible. Therefore oxygen is not at all hindered from reaching the nitrogen-containing species during combustion and the reaction



which is the most important pathway in the formation of N₂O, becomes predominant (at least when the combustion occurs at high oxygen concentration (20% O₂) as in these experiments). The simple structure of the model compounds was not a disadvantage because the goal of the experiments was to determine the effect of the oxygen-containing groups on the conversion of HCN to NH₃.

3.5 Effect of fuel structure on the conversion of volatile fuel-N to N₂O and NO

In studies on the structure of brown coal, Hüttinger and Michenfelder and Redlich et al. came to similar conclusions regarding the oxygen-containing groups in solid fuels.^{17,102} On the basis of their studies, Hüttinger and Michenfelder have proposed a structural model for brown coal with chemical composition C₂₇₀H₂₄₀O₉₀N₃S. As the nitrogen content in that structure is low relative to the value in real fuels, the model is redrawn in Fig. 6, modified to composition C₂₃₂H₂₀₂O₆₈N₆S. In this model the nitrogen content is increased to 2.0% so

as better to represent the nitrogen functionalities in fuels. The studies of Redlich and co-workers were taken into consideration in adjusting the concentrations of the oxygen-containing functional groups. In other respects the modified model structure is that proposed by Hüttinger and Michenfelder. The model compounds pyrolysed in my study closely resemble the building blocks of the brown coal. In the modified structure the phenolic oxygen content is 31% of the total oxygen concentration, the O/N ratio is 13 and the OH/N ratio 4.

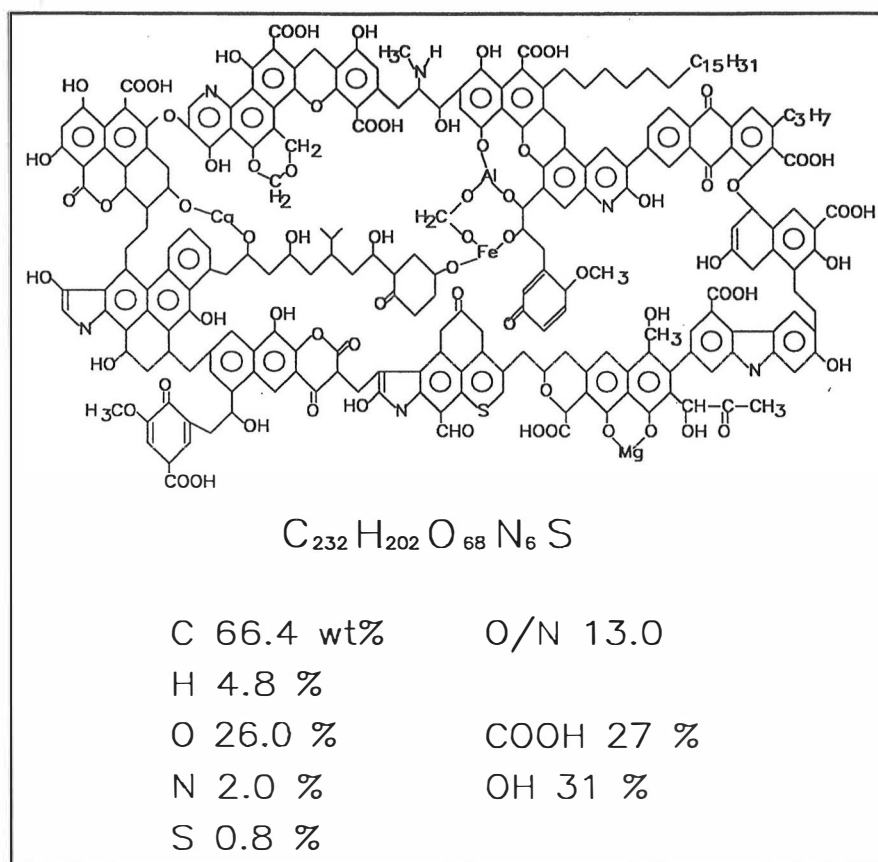


Fig. 6. Structure of brown coal, presented in part, modified after the model proposed by Hüttinger and Michenfelder.¹⁰²

It is possible that a part of the HCN species and OH radicals produced during devolatilization stage of the fuel come together inside the fuel particle, and react to NH_3 (Fig. 7). If the evolution and combustion of volatiles prevent oxygen from reaching the particle surface this reaction is also feasible near the particle surface.

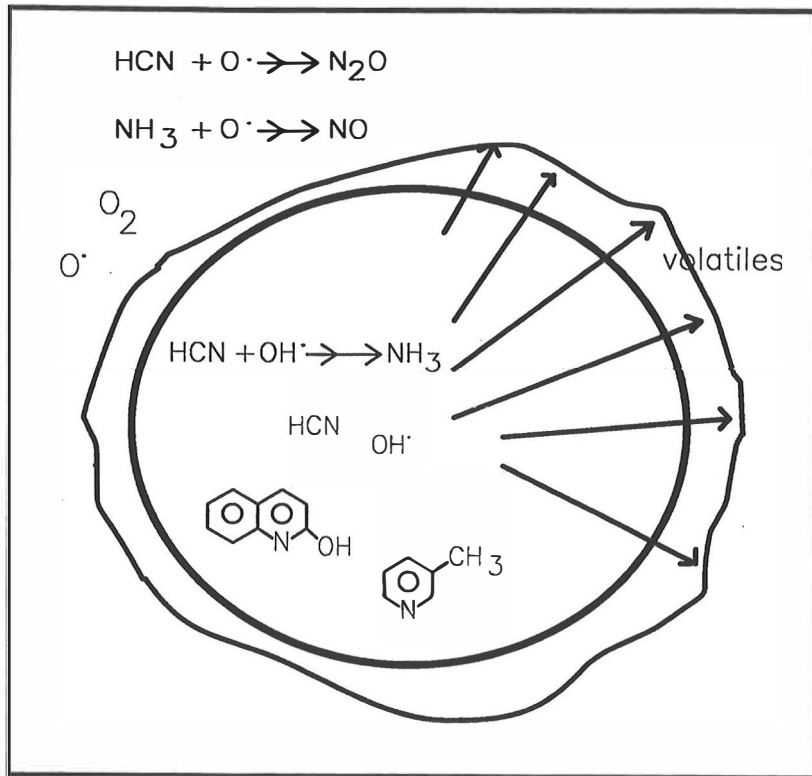


Fig. 7. Conversion of HCN to NH_3 inside a single fuel particle.

The results of the experiments with the entrained flow reactor indicate that the conversion of HCN to NH_3 occurs mostly inside the fuel particle, for the following reasons:

- variation in particle size between 63 and 250 μm did not affect the conversion of fuel-N to N_2O and NO. If the reaction were outside, one would expect the larger particle size to favour the conversion of HCN to NH_3 outside the fuel particle, near the surface, since the

amount of pyrolysis gases flowing out through the particle surface would then be greater and it would be difficult for oxygen to penetrate to the particle surface.

- with small particles (100-200 μm) the conversion of fuel-N to N_2O and NO at 1073 K depended on the fuel O/N ratio even at 18% O_2 .

- calculations showed that oxygen can reach the surface of a small burning fuel particle at low temperatures (< 1373 K).

Strong evidence has been presented that, under FBC conditions, N_2O is formed mainly from cyano species released as volatile-N.⁶⁷ However, although the volatile content decreases, the formation of N_2O increases with increasing fuel rank. This means that, with high rank fuels, most of volatile-N will travel as HCN to the oxidizing region and form N_2O . Because the fuel structure also becomes more aromatic with increasing rank, the thermal stability of the fuel increases and the release of fuel-nitrogen becomes more difficult. Therefore the amount of slow volatile-N to total volatile-N increases as the fuel rank increases (Fig. 8). The time interval between the liberation of fuel oxygen and fuel nitrogen also increases in older fuels, while the overall oxygen concentration decreases. All these factors contribute to making the conversion of HCN to NH_3 unfavourable.

In contrast, with low rank fuels the N_2O emissions are low even though the volatile-N content is high, because the fuel-based HCN is efficiently converted to NH_3 by the OH radicals (Fig. 8). The structure of the low rank fuels is less aromatic, the liberation of fuel nitrogen less hindered and the reaction of HCN with OH-radicals more probable. The finding that the quantity of NH_3 was increased and that of HCN reduced by raising the pressure⁵¹ supports the above interpretation, because pressure inhibits diffusion of volatile products through the particle.¹⁰³

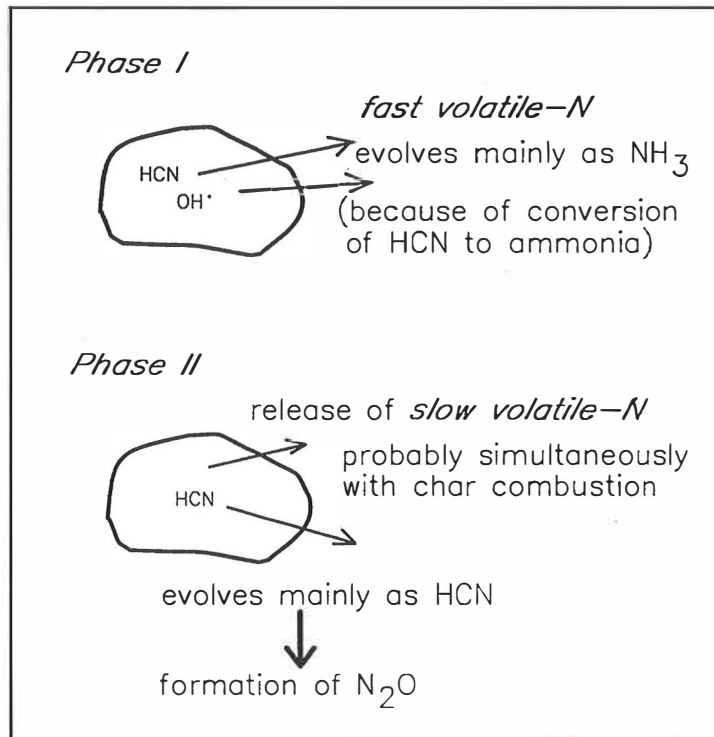


Fig. 8. Release of volatile fuel-N during pyrolysis.

The reaction pathways of fuel-based HCN to NH₃ are shown in Fig. 9. If the fuel O/N ratio is low, probably the fuel OH/N ratio is low too, and the conversion of fuel-based HCN to NH₃ remains small. In this case HCN can reach the oxidative combustion zone and react with oxygen to form NCO, which is the most important intermediate in the formation of N₂O. As the fuel O/N ratio increases, the conversion of HCN to NH₃ increases through reactions that first produce HNCO, either directly or through HOCN (Fig. 9). HNCO can react with H· producing NH₂, which can further convert to NH₃.^{99,100,104} NH₃ can also be formed through NCO. In this reaction route, NCO reacts with H and forms HNCO or NH, which are the intermediates in the formation of NH₃.^{69,99} Kinetic calculations carried out by Kilpinen et al.⁹⁷ have shown that, in reducing conditions (reburning), the most important reaction pathway in the conversion of HCN to NH₃ is the

reaction sequence that produces HNCO through HOCN .⁹⁹ In a secondary pathway HNCO is produced by direct reaction between HCN and OH radicals. However, this kinetic modelling was performed in a higher temperature range than the experiments in this study.

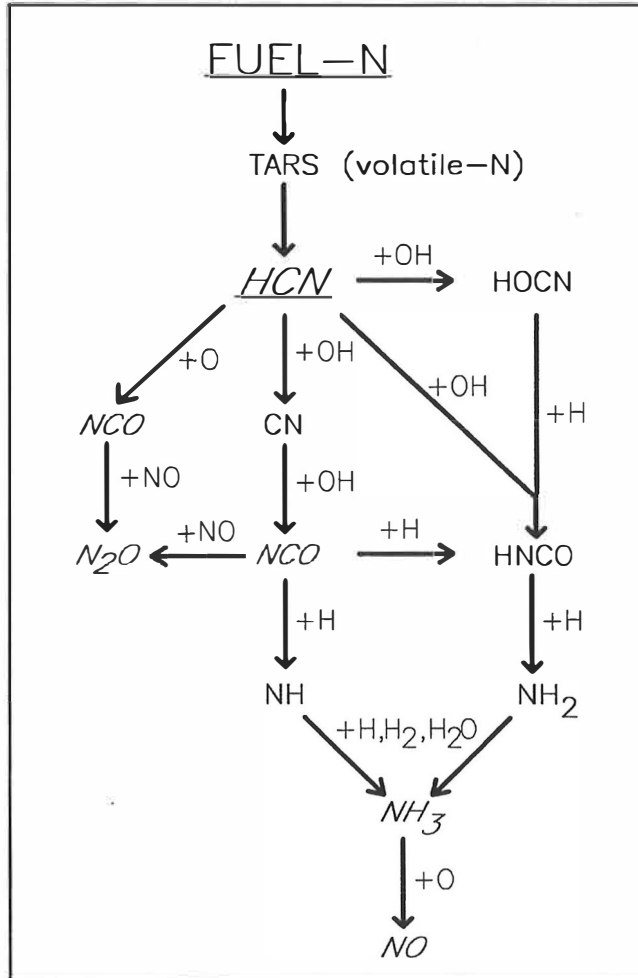


Fig. 9. A simplified scheme of the conversion of volatile fuel-N. If the fuel O/N ratio is low, HCN can reach the oxidizing combustion zone and the formation of N_2O is possible.

4. CONCLUSIONS

The ON-LINE determination of gaseous components such as HCN and NH₃ in pyrolysis gases is difficult by spectroscopic methods because of the disturbing presence of hydrocarbons and particulates. Measuring HCN and NH₃ in absorption solutions as was done here gave accurate results, though the methods were time-consuming.

Although it is the most important stage in the formation of pollutants from solid fuels, pyrolysis is not a well understood process. In this work, the effect of fuel composition on the formation of nitrogen oxides was studied by pyrolysing and combusting several fuel samples, and the conversion of fuel-N to HCN and NH₃ was studied with model compounds. It was found that the oxygen-containing functional groups, and particularly the OH-groups, are important in the formation of nitrogen oxides from fuel-N. The concentration of OH-groups decreases with decreasing total oxygen concentration in the fuel, and if the fuel O/N ratio decreases, probably the OH/N ratio decreases too.

Because the HCN + O· reaction is much faster than the HCN + OH· reaction, the latter is important only at low oxygen concentrations.¹⁰⁰ Calculations have shown that, with small particles, oxygen can reach the particle surface at low temperatures (< 1373 K).⁴² Under these conditions, the reaction between HCN and OH· can be important only inside the fuel particle. The experiments made on particles varying in size between 63 and 250 μm showed that size does not affect the conversion of fuel-N to N₂O and NO.⁷⁶ Larger particle size would favour the reaction between OH-radicals and HCN also outside the particle because the amount of volatiles flowing out through the particle surface would be greater and it would be more difficult for oxygen to penetrate to the particle surface. With small particles (100-200 μm) the conversion of fuel-N to N₂O and NO was found depend on the

fuel O/N ratio even at 18% O₂ at 1073 K, where the oxygen certainly reaches the particle surface. All these findings suggest that the conversion of HCN to NH₃ occurs primarily inside the fuel particle in the conditions studied in this work.

Much remains to be done. If the pyrolysis and combustion stages are overlapping the particle temperature begins to increase during devolatilization. A study of the temperature effect on the release of fuel nitrogen and on the relative concentrations of NH₃ and HCN would therefore be in order. In future the use of the pressurized combustion techniques will almost certainly increase, and the effect of pressure on the conversion of fuel nitrogen to NH₃ and HCN will need to be clarified. Model compounds create an interesting and informative way of studying the reaction pathways in conversion of fuel-N to NH₃ and HCN. The pathways could be studied by pyrolysing the model compounds in a small-scale pyrolyser and analysing the N-containing intermediates with gas chromatography-mass spectrometry.

One further important matter deserving of study is the combustion of material with high oxygen content, for example biomass, with coal (blended fuels) in fluidized bed. Feasibly, fuel with high oxygen content could create conditions in the bed suitable for the conversion of fuel-based-N to NH₃, so rendering the formation of N₂O unfavourable.

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