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PYROLYSIS OF BIOMASS AND COAL IN A BUBBLING FLUIDIZED-BED REACTOR; FATE OF FUEL-BOUND NITROGEN

H. Boerrigter
H. Bodenstaff
R.W.A. Wilberink
J. Kuipers
M. Geusebroek

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H.J. Veringa</td><td rowspan="2">ECN Biomass</td></tr>
<tr><td>Checked by:

J. Beesteheerde</td></tr>
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Justification

The work described in this report was part of the project "Nitrous Oxide Reduction in Circulating Fluidised Beds through Reburn" (REBED). This research was performed within the framework of the European Commission ECSC DG XIX project (contract number 7220-PR/054). Project partners were the Imperial College of Science Technology and Medicine (ISCTM) in London, Centro de Investigaciones Energeticas Medioambientales y Technologicas (CIEMAT) in Madrid, and Instituto Nacional de Engenharia e Technologia Industrial (INETI) in Lisboa. The ECN work was performed under ECN project number 7.2168.

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Combustion, Reburn, Circulating Fluidised Bed Combustor (CFBC), Puertollano Coal, Carbocol, Pine, Eucalyptus, Pyrolysis, Nitrogen, Nitrous Oxide, Ammonia, HCN, Char.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Circulating fluidised bed combustors (CFBC's) offer many advantages over conventional firing equipment at industrial scale, the most important being fuel tolerance and the little NO_x that is emitted. However, the future of the CFBC technology is threatened by possible release of significant quantities nitrous oxide (N_2O). Nitrous oxide is a 320 times more powerful greenhouse gas than CO_2.

The 'reburn' concept might prove to be a solution for this issue. Reburn, *i.e*. the addition of secondary fuel above the bed, has proven to be very successful in reducing NO_x emissions from conventional combustion plants. Application for the reduction of nitrous oxide emissions has equal potential. The objective of the project *"Nitrous Oxide Reduction in Circulating Fluidised Beds through Reburn"* (REBED) was to determine the manner by which reburn chemistry can be applied to reduce N_2O emissions from circulating fluidised bed combustion without incurring increased NO_x concentrations.

Four fuels were investigated in REBED, two coals (Puertollano coal and Carbocol) and two wood materials (Eucalyptus and Pine). During pyrolysis of the materials the main nitrogen-containing products are hydrogen cyanide (HCN), ammonia (NH_3), molecular nitrogen (N_2), tar-bound nitrogen, and char-bound nitrogen. HCN and NH_3 play an important role acting as gas-phase precursors for both N_2O and NO in the combustion process, while the majority of the N_2O is formed by (in)direct reactions of char. The ECN task in REBED was to perform pyrolysis experiments with the fuels to determine the fate of nitrogen in the fuel (fuel-bound nitrogen) as a function of four temperatures (600, 700, 775, and 885°C).

The pyrolysis experiments were performed in the ECN lab-scale bubbling fluidised bed reactor "WOB". In experiments with both Carbocol and Pine severe agglomeration occurred. Experiments with Puertollano coal and Eucalyptus proceeded smoothly. Overall mass balances of the experiments were prepared based concerning mass flows (feed, cyclone ash, soot, and bed build-up), gas analyses (CO, H_2, CO_2, CH_4, N_2, Ar, C_2H_4, C_2H_6, benzene, toluene, H_2S, and COS), Solid Phase Adsorption (tars), fuel and char composition (ultimate analysis), and wet-chemical analysis (NH_3, HCl, and HCN).

Based on the mass balances, the nitrogen distribution could be determined. The general trend is that at 600°C the majority of the nitrogen is bound to the char, while at increasing temperature more nitrogen is released as N_2. The other nitrogen containing compounds are formed in more-or-less constant fractions over the temperature range investigated. For Puertollano coal with a low volatile content, 50% of the nitrogen remains in the char and 41% is released as N_2 upon pyrolysis at 853°C. For Eucalyptus, 44% of the nitrogen remains in the char at 590°C decreasing to 6% at 845°C. At this high temperature, N_2 is the main nitrogen-containing compound (50%). Noticeable, compared to the coal, is the significant amount of tar-nitrogen (19%).

The results presented in this report can be used to optimise a system of CFBC operation with reburn to minimise N_2O formation without increasing the NO_x production.

The nitrogen distribution data were used to determine 'rules-of-thumb' for the prediction of the formation of N_2O (precursors). The fuels are compared based on their expected N_2O-emission when utilised as primary fuel (with a thermal input of 10 MJ) in a FBC at 850°C. Both coal fuels with relatively high nitrogen content produce a lot of NH_3, HCN, and especially char, all of which are notorious N_2O precursors. For Eucalyptus the production of NH_3 and HCN is

comparable but the char-N production is much lower due to the high volatile content. Pine produces the lowest amount of nitrogen compounds.

However, it should be realised that the reburn chemistry of the nitrogen compounds in the fluidised bed combustion determines the final N_2O and NO_x concentrations. The investigation of these issues was not included in the present study.

1. INTRODUCTION

To date, circulating fluidised bed combustors are increasingly applied at industrial scale for steam production. Circulating fluidised bed combustors (CFBC's) offer many advantages over conventional firing equipment at industrial scale, the most important being fuel tolerance and environmental cleanliness. The relative cleanliness arises from the little NO_x that is emitted compared to conventional suspension-fired coal combustion due to the lower process temperatures (typically about 850°C preventing the formation of thermal NO_x). However, the future of the CFBC technology is threatened by the fact that under the combustion conditions in fluidised beds significant quantities of nitrous oxide may be released. Nitrous oxide (N_2O) is a very destructive compound for stratospheric ozone as well as a powerful greenhouse gas, *i.e.* 320 times stronger than CO_2. In this light the N_2O issue is a real threat to the otherwise versatile and environmentally attractive CFBC technology. The 'reburn' concept might prove to be a solution for this issue. Reburn has proven to be very successful in reducing NO_x emissions from conventional combustion plants. Application for the reduction of nitrous oxide emissions has equal potential. This was the motivation to carry out the project *"Nitrous Oxide Reduction in Circulating Fluidised Beds through Reburn"* (REBED).

In REBED four European partners co-operated:
- Imperial College of Science Technology and Medicine (ISCTM) in London.
- Centro de Investigaciones Energeticas Medioambientales y Technologicas (CIEMAT) in Madrid.
- Instituto Nacional de Engenharia e Technologia Industrial (INETI) in Lisboa.
- Energy research Centre of the Netherlands (ECN) in Petten.

1.1 Background

1.1.1 Nitrous oxide

In coal and wood nitrogen is present as fuel-N in the form of heterocyclic aromatic structures (mostly of the pyrrolic and pyridinic type) in coals and as amino groups (*i.e.* from peptides) in the younger wood materials (see Figure 1).

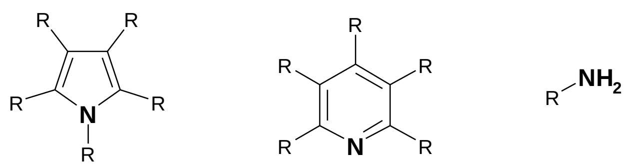


Figure 1 *General structures of pyrrolic, pyridinic, and amino groups. The R-groups can be a chemical group or represent a binding of a large aromatic structure*

During devolatilisation and pyrolysis of the materials the main nitrogen-containing products are hydrogen cyanide (HCN), ammonia (NH_3), molecular nitrogen (N_2), tar-bound nitrogen, and char-bound nitrogen. HCN and NH_3 play an important role acting as gas-phase precursors for both N_2O and NO in the combustion process. As the emissions of N_2O are closely coupled with formation of nitric oxide (NO) the chemical processes involving both gases should be considered together. Combustion of char is another source of nitrogen oxides. The relative contribution of NO_x/N_2O formed depends on the type of fuel, reaction temperature, excess oxygen level, etc. In Chapter 2 the background information on nitrous oxide (N_2O) is discussed in more detail.

1.1.2 Reburn principle

Reduction of NO and N_2O to molecular nitrogen (N_2) involves chemical reactions that constitute a powerful mechanism of NO_x/N_2O decomposition. The reduction can be heterogeneous, occurring on the (catalytic active) char surface, or take place in the gas phase. In the latter case, CO•, H•, and OH• radicals present in the combustion zone are particularly strong reducing agents for N_2O. The reburn principle is based on the injection of additional fuel in the downstream region of the flames to generate a region rich in radicals, creating a reactive environment.

In pulverised coal combustion the NO_x emissions are being reduced with reburn by addition of fuel at downstream locations. Under these conditions the reduction of NO_x is encouraged and the NO_x is preferentially reduced to N_2. A similar principle can be applied to fluidised bed combustion in order to reduce the more harmful emissions of N_2O. It is important to control the temperature of the reburn zone such that N_2O formation is minimised without an increased formation of NO_x. Furthermore, it is important to control the concentration of radicals so that NO_x is reduced to N_2 rather than forming new N_2O.

The reburn fuel can be any conveniently available material: (natural) gas, oils, biomass, and waste streams. In conventional combustors the technical requirements as the need for good mixing and short burnout times have tended to restrict the reburn fuel to natural gas. These restrictions do not apply for CFBC's and therefore a wide variety of solid fuels are potentially also acceptable. In general a reburn fuel should fulfil certain quality requirement as easy ignition, high reactivity, low nitrogen content, high volatile content, and good grindability.

1.2 Issue definition

The reburn technique has previously not been applied to circulating fluidised bed combustors. The main operational parameters influencing the formation and destruction of N_2O generated during fluidised bed combustion when making use of the reburn are unknown.

1.3 Objectives

The objective of the overall REBED project is to determine the manner by which reburn chemistry can be applied to reduce N_2O emissions from circulating fluidised bed combustion without incurring an increased NO_x concentration. The general objective of ECN within the REBED project is to provide insight in the pyrolysis process and pyrolysis products of the reburn fuels.

The specific ECN objective is to determine the fate of nitrogen in the fuel (fuel-bound nitrogen) as a function of the process temperature by performing pyrolysis experiments with the fuels. Pyrolysis is the thermal decomposition of a material and is the first step in combustion. Only the products of pyrolysis, *i.e.* the pyrolysis gas and char, react with combustion air and not the material itself. Knowledge about pyrolysis is essential to understand and predict the formation of N_2O and NO_x in combustion. When in the pyrolysis low amounts of NH_3 and HCN are formed the formation of nitrogen oxide compounds is also limited (see section 1.1.2). The obtained relations between fuel properties, process temperatures, and the fate of fuel-bound nitrogen are input for the computer model.

1.4 Project approach

1.4.1 Fuel selection

In the REBED project it was decided that Puertollano Coal would be the primary fuel for the CFBC experiments and that four materials would be tested as reburn fuel: Puertollano coal, Carbocol, Pine, and Eucalyptus. With respect to the selection of the primary fuel the consideration was that Puertollano coal is mined in Spain and therefore is of major interest for the Spanish and Portuguese project partners. Furthermore, both partners also have large experience with Puertollano coal.

All the four fuels would be tested for their reburn characteristics (*i.e.* as secondary fuel). Carbocol was selected, as it is readily available and frequently used in both countries, although imported from Columbia. The wood fuels (*i.e.* biomass materials) were included for two reasons: first the desire to make the CFB combustion of coal 'greener' by co-combustion of renewable biomass fuels. Secondly, to have a variety in compositions (C, H, N, O, ash) among the tested fuels. For example, Puertollano coal has high nitrogen and ash content, whereas the wood fuels have generally low nitrogen and ash content. Eucalyptus and Pine were selected as biomass fuels, as they are both readily available in Spain and Portugal.

1.4.2 Approach for ECN

In the original project work plan the following tasks were set for ECN:

1. Performing pyrolysis experiments with the four fuels in the lab-scale bubbling fluidised-bed reactor (WOB) to study product formation at different temperatures (amount and composition of pyrolysis gases, tar, and char).
2. Thermobalance (TGA) experiments to determine reactivity of selected pyrolysis chars with different gases and mixtures of gases (air, CO_2, NO, and N_2O).
3. Determine kinetic parameters from the TGA experiments.
4. Work meetings with the partners every six months.

In the ECN work plan it was foreseen to test both coal fuels at four temperatures (600, 700, 775, and 850°C) and the wood fuels at 700, 775, and 850°C in the lab-scale BFB. However, in the experiments with Carbocol at all four temperatures severe agglomeration was encountered. Due to this, all the experiments, except one, were terminated before sufficient data were collected. Also in the experiment with Pine at 850°C agglomeration occurred resulting in a premature termination of the experiment. Attempts to obtain useful data by repeating the experiments were unsuccessful.

Therefore, it was decided to omit further experiments with Carbocol. Considering the comparable properties of both wood fuels, it was also decided to omit the experiments with Pine at lower temperatures. The experiment with Eucalyptus at 600°C was included to be able to compare a coal and biomass fuel at all four temperatures.

The first results of determination of the kinetic parameters from TGA char reactivity experiments showed that data were comparable with data reported in literature. Therefore, it was decided that the data from literature would be used as input for the computer model to be prepared by ICSTM.

Revised ECN work plan - Due to the above-mentioned experimental situations and considerations the original ECN work plan was changed after consultations of, and in agreement with, the project partners. The effective ECN work plan as reported in this report was:

- Performing pyrolysis experiments in the lab-scale fluidised-bed reactor (WOB) to study product formation at different temperatures (amount and composition of pyrolysis gases, tar, and char). Tested were:

- Puertollano Coal at 600, 700, 775, and 850°C, experiments were performed in duplo;
- Eucalyptus at 600, 700, 775, and 850°C;
- Carbocol at 800°C;
- Pine at 850°C.

- Analysis of all four fuel materials.
- Work meetings with the partners every six months.

1.5 Intended results

The intended results of the ECN task in the overall REBED project are to providing input for (C)FBC modelling and selection of operation conditions. Specifically, this comprises data on:

- Product formation upon pyrolysis of the selected fuels at different temperatures.
- Mass balances of the pyrolysis experiments to determine the fate of fuel-bound nitrogen.

1.6 This report

This report describes the results of the ECN task of REBED and is the ECN contribution to the final report on the results of the overall REBED project. In Chapter 2 the subject of nitrous oxide (N_2O) is discussed in more detail. In Chapter 3 the experimental set-up, the fuel analyses, and the qualitative descriptions of the experiments are presented. In Chapter 4 the pyrolysis experiments are discussed. This comprises data on product formation upon pyrolysis of the selected fuels at different temperatures, mass balances, and the fate of fuel-bound nitrogen. Furthermore a comparison is made between the fuels for the production of N_2O precursors on an energy basis. Chapter 5 ends the report with concluding remarks.

2. NITROUS OXIDE

2.1 Mechanisms of N_2O formation and destruction

After several years the mechanisms of N_2O formation and destruction from fluidised bed combustion have been understood partly, although not fully and clearly. Many pathways to N_2O have been discovered and proven, which is illustrated in Figure 2. These pathways can be classified based on the four principles of N_2O formation:

- Homogenous oxidation of nitrogen-containing species (mainly HCN);
- Direct oxidation of char-N;
- NO reduction on the surface of char;
- Other pathways, for example reaction of NO with reduced $CaSO_4$ ($CaSO_R$).

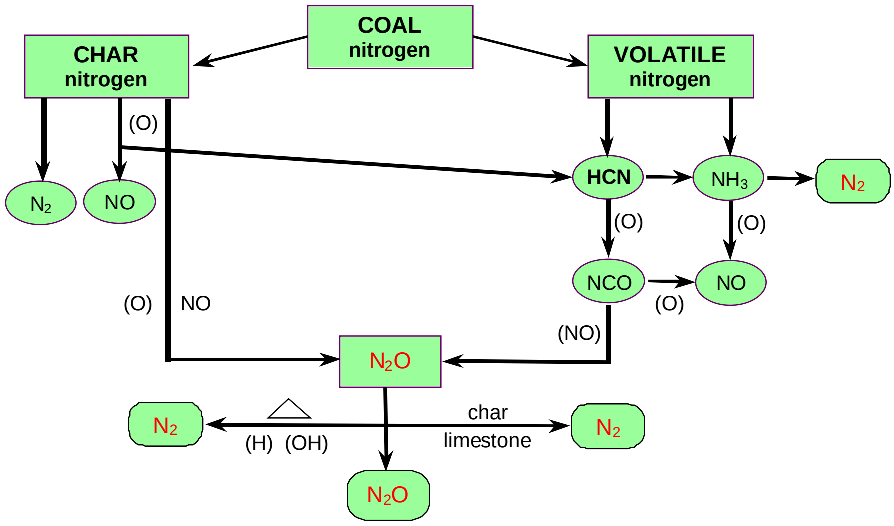


Figure 2 *Mechanisms of N_2O formation and destruction (from coal)*

2.1.1 Homogenous oxidation of nitrogen-containing species

The percentage of nitrogen released as volatiles is 1 to 20% of the fuel-N, dependent on the coal type, temperature, and heating rate [1]. In high-rank coals nitrogen is mainly released as HCN. In some cases the homogeneous oxidation of HCN to N_2O was reported to be as high as 60%, indicating that HCN is an important source of N_2O in coal combustion [2,3]. However, in the presence of solid materials such as limestone and char, the conversion of HCN to N_2O is generally lower than 10% or even less than 4% [4,5]. This phenomenon was attributed to a shift in the selectivity from N_2O formation to NO formation [4].

For a coal with a nitrogen content of 2%, and fixed-carbon content of 85%, the concentration of HCN released during devolatilisation will be between 5 and 150 ppm. Assuming a HCN concentration from devolatilisation of 150 ppm and a conversion of 10% of this HCN to N_2O in fluidised beds, the N_2O concentration from oxidation of HCN will not exceed 20 ppm. Only high-rank coals with a high nitrogen content and high volatiles content can potentially release considerable amounts of HCN as precursors for N_2O. However, this kind of coal is not widely available and thus very limited utilised. Therefore, for most coals the oxidation of the char-N to N_2O will be a more relevant pathway for N_2O formation.

2.1.2 N_2O from char-N

In experiments studying the conversion of char-N during char combustion in fixed bed reactors with batch supplies of chars, less than 5% of the char-N was converted to N_2O [6], although also values ranging from 1-17% have been reported [7]. This N_2O formation can be attributed to the conversion of char-N to N_2O by direct oxidation.

When fluidised bed reactors with a continuous feed of fuel were used, much higher conversions of char-N to N_2O (15-30%) were found [8,9]. The results do not only include char-N oxidation but also char-N conversion by other reactions, for example, the reaction of NO with char-N. NO has been found to enhance the conversion of char-N to N_2O. For combustion of char in fluidised beds, therefore, N_2O formation takes place via two pathways: via direct oxidation of char-N and via the reaction of NO with char-N.

In coal combustion, a large amount of NO is produced by oxidation of HCN and NH_3. This NO will also react with char-N to form N_2O. The amount of N_2O that originates from this pathway is comparable to the amount originating from the oxidation of HCN in the presence of bed material.

2.1.3 NO reduction & Reaction with $CaSO_4$

N_2O can also be produced by NO reduction on the surface of char in the absence of O_2, although only a few ppm of N_2O were found to be formed at an inlet NO concentration of 1000 ppm [10]. This indicates that this mechanism is less important than those discussed above. Another pathway for N_2O formation is the reaction of NO with reduced forms of $CaSO_4$ ($CaSO_R$). The rate of N_2O formation from this reaction is even faster than that from the direct oxidation of char-N in some cases [6]. The existence of this last reaction in FBC's has not been verified.

Figure 3 shows a rough indication of the contribution of the above-described pathways to N_2O formation during coal combustion [11].

2.2 Effect of operating conditions on N_2O emissions

In fluidised bed combustion the fuel type, excess air, temperature, and possible limestone additions are the main parameters that present an important influence on N_2O emissions [12,13]. The effect of each individual parameter is discussed below.

Fuel type - With increasing fuel nitrogen content, the partitioning of nitrogen to the volatile phase increases. Studies have shown that with such an increasing volatile content the conversion of fuel nitrogen to N_2O decreases [13,14,15,16] In coal fuels the nitrogen is mainly present as pyridinic or pyrrolic nitrogen. These structures favour the production of HCN (a precursor of N_2O) during devolatilisation.

Temperature - There is consensus that the conversion of fuel nitrogen to nitrous oxide decreases with increasing combustor temperature independent of the fuel. However, some studies show that when the temperature was raised from 800 to 900ºC, the outlet N_2O concentration initially increased and then decreased. At the lower temperature ranges, the outlet N_2O concentration was low because of the low rate of formation, and at the higher temperatures, it was low because of the high rate of decomposition.

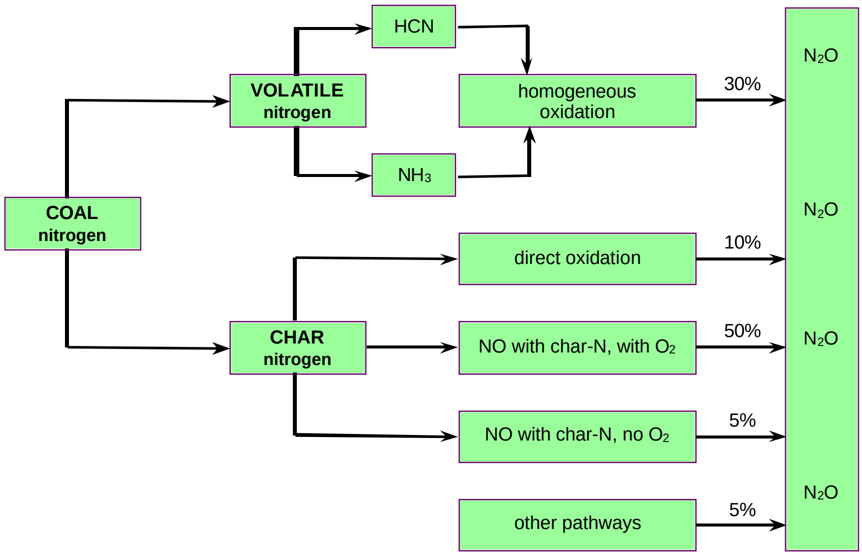


Figure 3 *A rough indication of the contribution of N_2O formation during coal combustion via various reactions pathways [11]*

Excess air - Increasing the amount of excess air leads to an increase in nitrous oxide emission [17]. Excess air and temperature also interact in relation to N_2O emissions. The effect of the excess air level is stronger at lower temperatures than at higher temperatures.

Limestone addition - Limestone addition has been demonstrated to have a beneficial effect on reduction of N_2O emissions. In some cases, however, no effect was observed while in other cases even an increase in N_2O was observed. The effect of limestone on N_2O emissions level therefore seems to be complex.

2.3 Technologies to reduce N_2O emissions in FBC

No mature N_2O control technologies are available at the moment. In general, the measures to minimise the emissions could be the following:

Pre-combustion measures - Pre-combustion treatment of fuels to reduce the nitrogen content of fuel before combustion is a viable option for fossil fuels. For example, Hydro-denitrification of heavy oil fractions before (catalytic) cracking is widely applied in oil refineries. However, in the case of coals and other solid fuels, denitrification processes are still under development and probably too expensive to be applied in the near future.

Combustion measures - In principal three methods can be considered:
1. Rising the bed temperature. This method takes advantage of the fact that at high temperatures (and low excess-air ratios) the N_2O emissions decrease. However, the two disadvantages of this measure are a higher NO emission and a lower efficiency of sulphur capture.
2. Changing the air supply to the combustor chamber. Low excess-air is common for both N_2O and NO_x reduction, but the reduction is quite moderate, so the potential of this method is limited.
3. Using catalysts in the combustion chamber. There are two steps in the conversion pathways from fuel nitrogen to nitrous oxide that can be influenced: (*i*) the conversion of volatile nitrogen compounds into N_2O and (*ii*) the decomposition of the N_2O that is formed. Materials like MgO and CaO shift the conversion of HCN into the direction of NO instead of N_2O. However, the N_2O reduction efficiency by this method is very small.

Post-combustion measures - Two applications of post-combustion measures can be envisaged: N_2O removal by fuel-gas injection or by catalytic decomposition of N_2O. The first one involves introduction of a gaseous fuel (natural gas, methane, etc.) downstream of a coal-fired zone to create an additional flame. Catalytic decomposition of N_2O has shown a lot of promise for N_2O abatement. Many materials like supported metal oxides and metal exchanged zeolites show catalytic activity for N_2O decomposition. N_2 and O_2 are the products of this decomposition. However, no mature catalytic N_2O removal measure exists to date.

Reburn - Among the most recent developments for reducing NO_x emissions from coal-fired systems are the reburning technologies [18,19,20]. Reburning involves the staged addition of fuel into two combustion zones. Firstly, into the primary combustion zone where the coal is fired. Secondly, in the reburn zone where additional fuel creates a reducing condition to covert the NO_x produced in the primary zone to molecular nitrogen and water. The reburning fuel can be gaseous (*e.g*. natural gas), solid (coal, char, wood) or liquid (residual oil). Above the reburn zone is a burnout zone in which overfire air is added to complete the combustion.
Reburning has been demonstrated in both pulverised coal and cyclone-fired boilers in order to reduce NO_x emissions, with both coal and natural gas as the reburning fuel. However, the utilisation of this technique in order to reduce the N_2O emissions in CFBC is new. Within the REBED project detailed studies are being undertaken into this subject.

3. PYROLYSIS EXPERIMENTS

3.1 Introduction

From the discussion in the previous Chapter it is clear that detailed information about the partitioning of nitrogen during combustion is essential to be able to model the formation of N_2O. The first step in thermal conversion of biomass and coal is pyrolysis. Due to the high temperature in a reactor the material decomposes into a char and a volatile phase consisting of gases, tars, and moisture. The pyrolysis products are the actual compounds that react with the oxygen from the combustion air.

The gaseous nitrogen-containing products that can be formed are N_2, NH_3, and HCN. Furthermore, a diversity of volatile organic compounds (*viz*. tars) is formed. Some of these tar compounds also contain nitrogen, for example pyridine. In Figure 4, the partitioning of nitrogen during pyrolysis is qualitatively illustrated. When quantitative information on the nitrogen partitioning is available, the amount of N_2 that can be formed in combustion can be predicted based on reaction kinetics of known paths (compare Figure 3). The green boxes indicate nitrogen compounds that can be detected and materials that can be analysed.

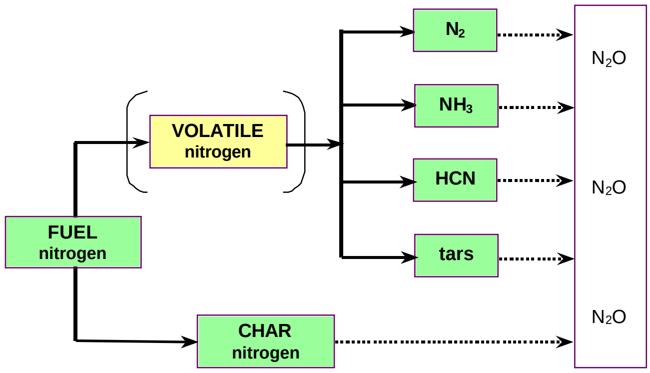


Figure 4 *Partitioning of nitrogen during pyrolysis*

In this Chapter the results are described of pyrolysis experiments with the four selected fuels. The most important result is information on the nitrogen partitioning, as this will be the input for the computer model.

3.2 Fuel properties

Four materials were tested in the present study: Puertollano coal, Carbocol, Pine, and Eucalyptus. These materials were selected to have a spectrum of the most important properties: ash content, nitrogen content, and H/C and H/O ratios. The Spanish Puertollano coal represents a high-ash, high-nitrogen content coal and was provided by CIEMAT (Madrid, Spain). Colombian Carbocol is a low-ash bituminous coal and was provided by INETI (Lisbon, Portugal). Eucalyptus and Pine (both also provided by INETI) are two wood/biomass materials with high volatile and low nitrogen content, with Pine containing almost no ash.

The materials were grinded when necessary and sieved prior to use. The fractions of 0.71-2.0 mm were used, except for Carbocol where the fraction of 0.5-2.0 mm was used. In case of Eucalyptus the material segregated upon sieving due to the agitation. Besides, the woody material, ‘fluffs’ were formed probably from the bark fibres. These fluffs were removed from the test samples, as they would cause feeding problems. The properties of the pre-treated materials are given in Table 1. These data are also recorded in the ECN public Internet database "Phyllis" [21].

Table 1 *Analysis of the four fuels*

Material [a]		Puertollano Coal	Carbocol	Eucalyptus	Pine
moisture	m%, a.r.	4.3	5.7	8.5	8.4
ash	m%, dry	36.91	7.45	3.28	0.44
C: carbon	m%, daf	72.19	83.58	52.02	53.37
H: hydrogen	m%, daf	4.96	4.71	5.00	5.53
N: nitrogen	m%, daf	1.93	1.68	0.42	0.22
O: oxygen	m%, daf	19.12	9.91	42.55	40.88
S: sulphur	m%, daf	1.80	0.12	0.006	0.001

[a] Normalised to 100%; a.r.: as received, dry: moisture free, daf: dry, ash free.

The ultimate analyses data from ECN deviate from the data obtained by CIEMAT for the same material, especially the carbon and oxygen values for Puertollano coal and Eucalyptus. Although the same analytical procedures were used, *viz*. the Best Practice Procedure. Evaluation during the progress meetings revealed that the CIEMAT data for Puertollano coals is based on an average of analysis data from many batches of coal and that the variation within the analysis series was large. The ECN data is based on one specific batch of coal that was used in the ECN experiments. The difference in the Eucalyptus analysis may be explained by the fact that the ECN analysis was performed on the pre-treated (sieved) material excluding the fluffs that were formed during sieving. The CIEMAT analysis was performed on the complete material.

3.3 Pyrolysis reactor "WOB"

The pyrolysis experiments were performed in the ECN lab-scale thermal conversion installation "WOB" (Dutch acronym for Fluidised Bed Installation for Biomass). The WOB is an atmospheric bubbling fluidised bed facility suitable for combustion, gasification, and pyrolysis experiments [22]. A schematic diagram of the installation is given in Figure 5. The inner diameter of the lower section is 74 mm (height 75 cm), of the upper section 108 mm, and the total inner height is 131 cm. Electrically heated walls both enable the simulation of adiabatic conditions and can provide the power needed for heat demanding processes like pyrolysis. In this way the reactor can be heated up to 900°C. Air, oxygen, argon, nitrogen, and steam can be added as fluidising medium. Temperatures in the bed are measured with four thermocouples and, furthermore, the temperatures under the gas distributor, and on the reactor wall in the bed are measured. Gas leaving the reactor passes a cyclone where dust, soot, and small sand particles are separated. From the gas after the cyclone a small volume can be withdrawn for analysis while the remainder being flared.

3.4 Experimental conditions

In the experiments, the bed consisted initially of 1 kg of sand (sieved river sand, 96.5 m% SiO_2, apparent density 2650 kg/m^3, bulk density 1600 kg/m^3) with a particle size of approx. 0.27 mm). For fluidisation in the pyrolysis experiments a flow of 10-15 L_n/min of argon was used. The temperature differences in the bed at stable operation conditions were generally within 4-7°C. The bunker was flushed twice with argon prior to the experiments to remove all the air and exclude air-nitrogen from the system. During the experiments an argon flow of 1 L_n/min was maintained over the bunker to prevent under-pressure and resulting air in-leak and back-flow of pyrolysis gas.

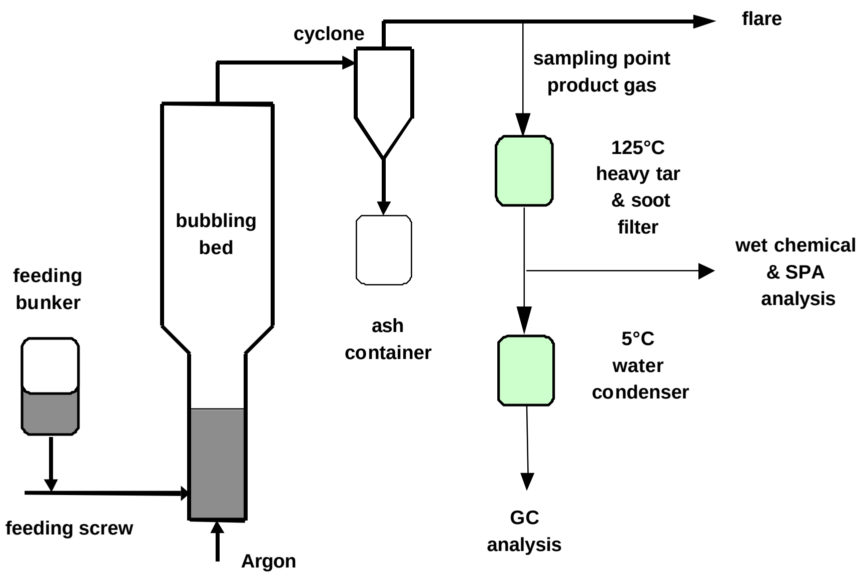


Figure 5 *Schematic representation of the ECN lab-scale thermal conversion installation "WOB" and the analysis points [22]*

The material was fed from the feeding bunker by means of a screw. Due to the high density of the coal materials the feeding rate at the lowest screw rotation speed was too high. Therefore, the feeding was performed with intervals: *x* seconds feeding followed by *y* seconds no feeding. The discontinuous feeding did not significantly influence the overall pyrolysis as was concluded from the stable gas composition.

The reactor was heated to the pyrolysis temperature and subsequently the feeding was started. Due to feeding of cold material the temperature first slightly decreased. The system was allowed to reach the desired temperature again and to stabilise. The stable condition was maintained for at least 60 minutes during which the gaseous products were continuously monitored and wet-chemical samples were taken. After each experiment the feed bunker was weighed to determine the exact feed mass flow. After the measuring period the feeding was switched-off and the reactor was allowed to cool down under nitrogen atmosphere. The amount of char and ash accumulated in the bed was determined by weighing of the bed material after the test and correcting this for the initial amount of sand present. For the bed material from experiments in which agglomeration occurred, the bed agglomerates were analysed.

3.5 Analysis

The gas for analysis passed first a filter at 125°C where the remaining dust and soot was captured and where the heavy condensable tars were removed (Figure 5). After the filter, periodically wet-chemical and SPA (Solid Phase Adsorption) samples were taken. The gas for on-line analysis was passed through a second filter to remove the majority of the water and the condensable organic compounds. On line the gases CO, CO_2, H_2, N_2, Ar, CH_4, C_2H_4, C_2H_6, benzene, and toluene were measured with two gas chromatographs. NH_3, HCl, and HCN were determined from wet samples in demiwater (for NH_3 and HCl) and 12 M NaOH solutions (for HCN).

3.6 Qualitative test performance

In the original work plan it was foreseen to test the selected fuels at four temperatures. In Table 2 qualitative descriptions of the pyrolysis tests are given. In the experiments with Carbocol severe agglomeration was encountered at all temperatures and only in the experiment at 775°C sufficient reliable data could be collected. Pine also gave agglomeration at 850°C and for that reason further experiments with Pine were omitted. Stable tests could be carried out with Puertollano coal, however, with some increase in the gasifier pressure caused by fouling in the pipe connecting the pyrolysis reactor and the cyclone. The high ash content of the fuel and the resulting relatively high dust-load of the gas induced this phenomenon. Experiments with Eucalyptus proceeded smoothly in any way.

Table 2 *Qualitative description of pyrolysis tests with the four selected fuels*

	Pyrolysis Temperature [°C]			
Fuel	600	700	775	850
Puertollano coal	stable test - pressure increase due to fouling	stable test - pressure increase due to fouling	stable test - pressure increase due to fouling	stable test - pressure increase due to fouling
Carbocol	agglomeration resulting in untimely abortion	agglomeration resulting in untimely abortion	more or less stable test for 1 h	agglomeration resulting in untimely abortion
Eucalyptus	smooth test	smooth test	smooth test	smooth test
Pine	not tested	not tested	not tested	more or less stable test for 1 h

The initial signs of agglomeration in the fluidised bed experiments are decreasing temperatures in the bed. At this stage the gas production is still stable and the composition of the gas is constant. The decreasing temperatures are caused by formation of agglomerates on the thermocouples due to which the heat transfer is limited. Upon further agglomeration the pressure in the reactor increases and temperatures start to oscillate. Ultimately the experiment is automatically aborted to prevent further pressure build-up. In the initial phase of agglomeration flow pulses with the fluidisation gas can destruct the early agglomerates and extent the experimental time.

In Figure 6 a photograph is shown of fouling in the WOB reactor due to the agglomerates at the wall and on the thermocouple in an experiment with Carbocol. In Figure 7 a photograph is shown of the larger agglomerates that were found in the bed after the experiment. Considering the diameter of the reactor of 7.4 cm, the size of the particles of approx. 3 cm is impressing. In Figure 8 agglomerates found in the bed after an experiment with Pine are shown.

Figure 6 *Bottom view of WOB after experiment with Carbocol. Fouling on the reactor wall resulting from agglomeration can be clearly seen. The small pipes are the thermocouples*

Figure 7 *Agglomerates found in the bed after the Carbocol experiment. Size of the larger agglomerates is approx. 3 cm*

Figure 8 *Agglomerates found in the bed material after an experiment with Pine*

4. RESULTS

In Appendix 1 the experimental information and analysis results of the pyrolysis experiments in the WOB are summarised.

4.1 Data interpretation

The purpose of the experiments was to determine the ‘fate’ of nitrogen upon pyrolysis and the quantitative partitioning into the compounds NH_3, HCN, N_2, and tars (SPA and heavy) and into the char. Therefore, overall mass balances had to be determined. For this the following step-wise procedure was followed:

• exact feed flow	:	back-weighing the feeding bunker.
• amount of solids (sum of char and ash) produced [g/h]	:	weighing the bed material after cooling of the reactor and correcting for the initial amount of sand *plus* the solids in the cyclone.
• amount of char produced [g/h]	:	ultimate analysis of sieve fractions of the solids.
• volatiles flow (gas + water)	:	feed flow *minus* solids produced *minus* heavy tars & soot produced.
• ash flow	:	feed rate *minus* char flow *minus* gas flow *minus* heavy tar & soot.
• gas flow (incl. SPA tars)	:	from gas analysis, based on the argon flow as reference.
• water flow	:	volatiles flow *minus* gas flow.

With this approach the major products were quantitatively determined. However, as some flows are calculated by difference, errors may accumulate and become significant. This is especially valid for the water flow as this value is used to close the balance. Similarly, this is valid for the ash flows as these values are derived from the difference between the feed and char flow. Relatively large errors can arise from small variations in the ultimate analyses of the solids fractions.

Subsequently, the normalised argon-free dry gas composition was determined from the gas analysis (with argon as reference), the SPA data, and the wet-chemical analysis. With the water flow the normalised argon-free wet gas composition could be determined from the dry gas composition. This composition represents the actual gas that is the product from the pyrolysis. With the information of the values of the product flows, the gas compositions, and the char and feed analysis, the mass balances for the elements carbon, hydrogen, oxygen, and nitrogen were determined. The mass balances over the WOB are presented in Appendix 2.

4.2 Primary product formation

In Figure 9 the formation of the solid (char, ash and soot), volatile (gases and tars), and water upon pyrolysis of the four feed materials at different temperatures is shown (in Appendix 2 the partitioning into the primary products is presented in more detail). For Eucalyptus the general trend is that with increasing temperature the amount of char decreases and more volatiles are formed. This indicates that at higher temperatures gasification of char with gas phase compounds is taking place. At increasing temperature from 589 to 700°C the amount of water produced decreases, whereupon further temperature increase the amount remains fairly constant (within the experimental uncertainty). Pine is showing a product formation very similar to Eucalyptus at the same temperature (845°C). For Puertollano coal the decrease in the amount of water produced is observed in the whole temperature range, resulting in an increasing fraction of gas produced as the solids fraction is fairy constant. Although the *absolute* amount of char formed decreases, indicating some gasification of char with gas phase compounds similar as observed for Eucalyptus. Compared to Puertollano coal, Carbocol has a higher volatile content, resulting in lower solid and higher volatiles yields.

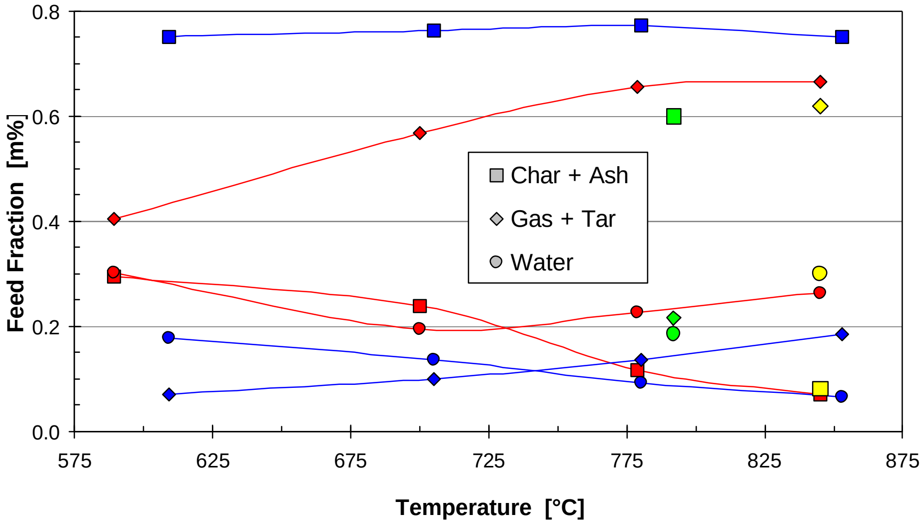


Figure 9 *Production of solid (• ; sum of char, ash, and soot) and gaseous (• ; sum of pyrolysis gas and tar) products, and water (•) upon pyrolysis at different temperatures. Feed materials shown coloured: Puertollano coal (blue), Carbocol (green), Eucalyptus (red), and Pine (yellow)*

4.3 Formation of gaseous compounds

The constitution of the gases that were produced upon pyrolysis of Puertollano coal and Eucalyptus at the whole temperature range are shown in Figure 10 and Figure 11, respectively. For the coal, the formation of most gases is independent of the temperature, exceptions being H_2O, H_2, and CO. This might be explained by the gasification of char (carbon) by H_2O to form H_2 and CO. However, at the highest temperature (853°C) the decrease in CO_2 also indicates some water-gas-shift activity. This is supported by the observation that the increase in the H_2 and decrease in the H_2O concentrations are less steep than the change in CO concentration.

For Eucalyptus the gas composition is independent of the temperature at temperatures above 700°C. When going from lowest investigated temperature of 583 to 700°C, the H_2 and CO concentrations increase at the expense of a decreasing H_2O concentration. Since the absolute amount of gaseous products and H_2O is increasing from 297 to 436 L_n/h, the constant gas compositions indicate that the gas phase is in equilibrium. The establishment of an equilibrium can be reasoned with an average residence time in the reactor of ~20 seconds at those conditions.

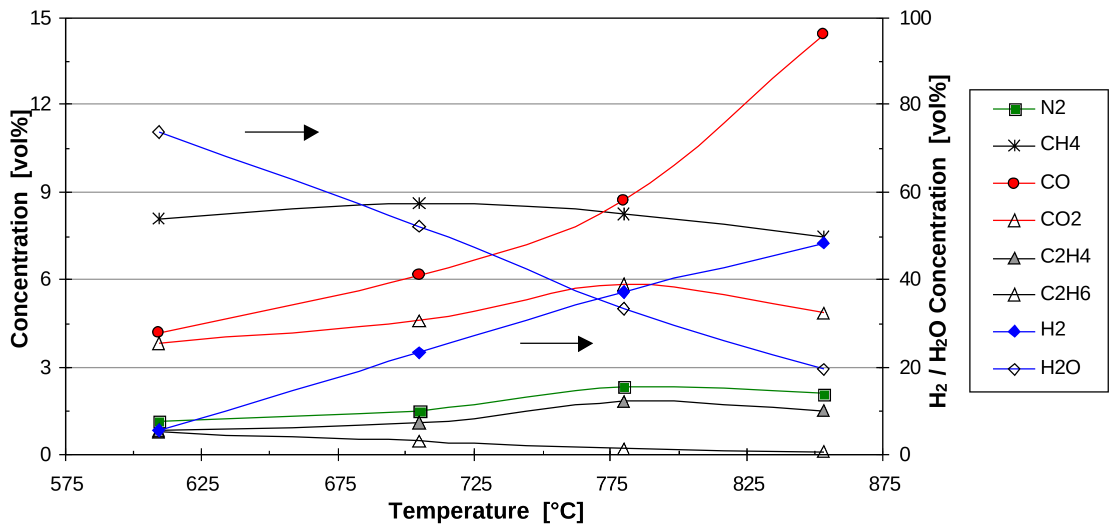


Figure 10 *Pyrolysis of Puertollano Coal at different temperatures. Gas concentrations in wet argon-free gas*

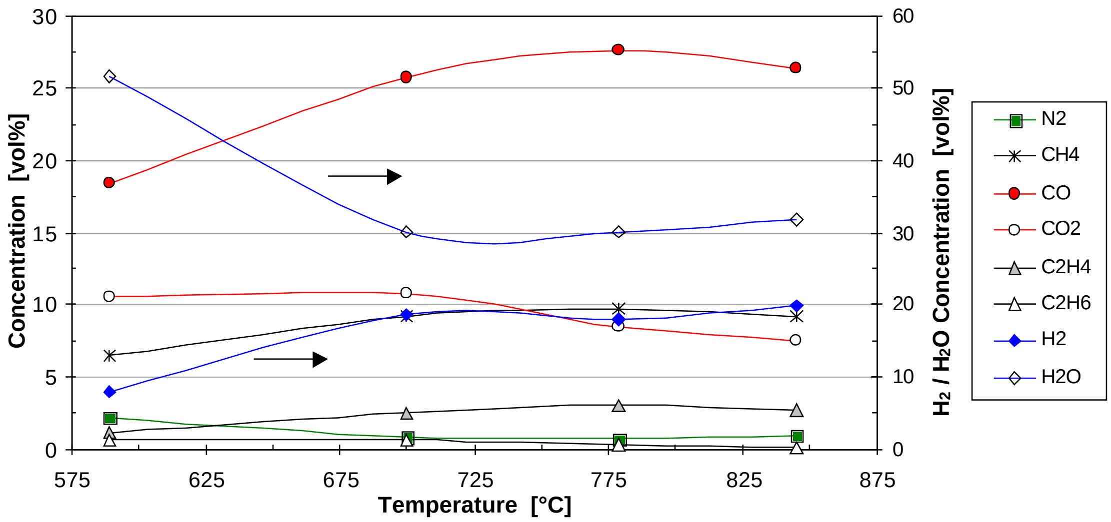


Figure 11 *Pyrolysis of Eucalyptus at different temperatures. Gas concentrations in wet argon-free gas*

4.4 Nitrogen distribution

From the wet-chemical analysis, the concentrations of NH_3 and HCN in the gas were determined. From the total amount of SPA tars the mass flow of nitrogen was calculated by assuming that SPA tars contain on average 3 m% nitrogen while the value of the naphthalene density was used for the average SPA tar density. The value of 3 m% nitrogen in the SPA tars is based on a large amount of gasification data at temperatures between 700-950°C. As at lower temperatures more heterocyclic tar compounds are formed (*e.g*. pyridine), this value of 3 m% might be slightly underestimating the nitrogen content in the 600°C SPA tars. The mass flow nitrogen in the char followed from the calculated char flow and ultimate analysis of the samples. For heavy tars also a nitrogen content of 3 m% was assumed and for soot a content of 0.4 m% was assumed. In principle the amount of N_2 followed from the gas analysis. However, in all experiments the nitrogen balance was well above 100%. For Puertollano coal with a high nitrogen content balance fits were 119 to 153%, whereas for the low nitrogen Eucalyptus and Pine fits of 300% up to 1200% (Pine) were found. These observations indicated leaking of nitrogen (*i.e.* N_2) into the system. The source of the nitrogen leak was determined to be 'false' air sucked into the sampling flow of the gas analysis. In the interpretation of the data, therefore, a 100% fit of the nitrogen mass balance was assumed and the N_2 mass flow being the fitting variable. Comparison of the fitted and the measured value for N_2 indicated an N_2 leak of 0.8 to 2.6 L_n/h (*i.e.* 1-3.3 L_n/h air), with some extremes of 6-8 L_n/h. On the total gas flows of 1 nm^3/h these leak flows are negligible, however, with the low nitrogen contents the effects on the nitrogen balances are significant.

Table 3 *Nitrogen partitioning during pyrolysis of the coal fuels at different temperatures. Values for the m% are based on nitrogen*

Fuel		Puertollano coal				Carbocol
Temperature	[°C]	609	705	780	853	792
N_2 (by difference)	[m%]	16.3	20.7	30.8	40.7	31.8
HCN	[m%]	0.98	~	1.38	1.72	3.03
NH_3	[m%]	11.4	17.9	15.1	5.87	9.38
SPA tar	[m%]	2.06	2.39	2.65	2.00	4.30
Char	[m%]	69.0	58.8	49.9	49.5	49.9
Heavy tar	[m%]	0.24	0.12	0.17	0.17	1.57
Soot	[m%]	~	0.13	0.01	~	0.01
TOTAL	*[m%]*	*100*	*100*	*100*	*100*	*100*

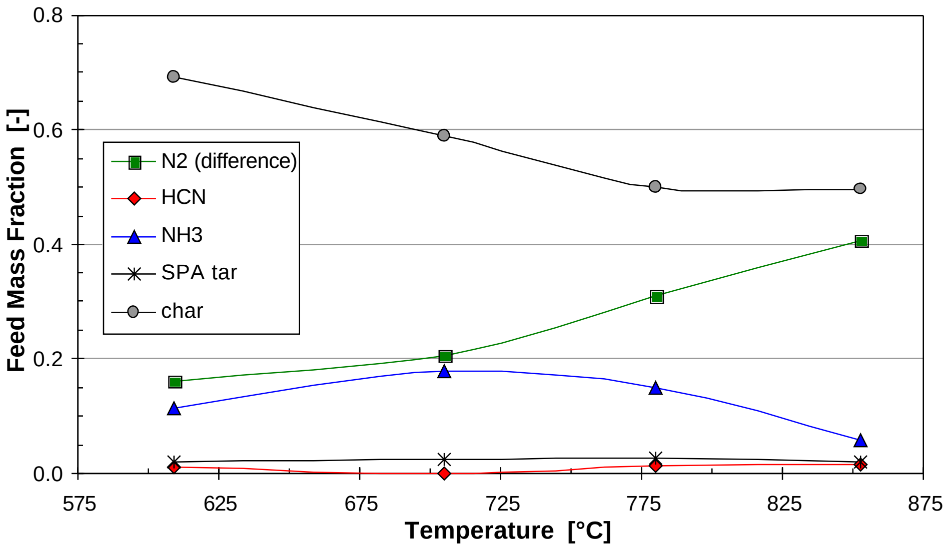


Figure 12 *Partitioning of nitrogen upon pyrolysis of Puertollano coal at four temperatures (mass fraction is based on nitrogen)*

In Table 3 the nitrogen partitioning for the coal fuels is shown and in Figure 12 the partitioning data of the major products are graphically presented for Puertollano coal. The major part of the nitrogen remains bounded in the char. With increasing temperatures, the fraction char-bounded nitrogen decreases due to increased devolatilisation and gasification of the char (*vide supra*). The second major product is N_2 of which the amount increased with temperature. NH_3 formation appears not to have a clear relation with temperature - the fraction being between 5.8 and 17.9 m%. HCN and SPA tars are minor products and the amounts in the heavy tars and soot are negligible. For Carbocol the fractions HCN and SPA tars are significantly higher compared to Puertollano coal.

In Table 4 the nitrogen partitioning for the wood fuels is shown and in Figure 13 the partitioning data of the major products are graphically presented for Eucalyptus. At 589°C the char accounts for most of the nitrogen. However, at increasing temperature the amount of char-bonded nitrogen decreases corresponding to the decrease of char formation (compare Section 4.2). At increasing temperatures most of the nitrogen is released as N_2 while the amounts of NH_3, HCN, and SPA tars formed are fairly constant over the whole temperature interval. The ratio of NH_3 and HCN is on average ~3.2. The formation of SPA tars is significant and even the second product in pyrolysis of Pine at 845°C. Char is a well-known catalyst for tar decomposition and for the low-char wood fuels this results in less tar decomposition and thus higher tar concentrations in the gas.

Table 4 *Nitrogen partitioning during pyrolysis of the wood at different temperatures. Values for the m% are based on nitrogen*

Fuel		Eucalyptus				Pine
Temperature	[°C]	589	700	779	845	845
N_2 (by difference)	[m%]	26.3	40.3	~	49.9	45.3
HCN	[m%]	2.19	3.71	5.96	4.86	2.92
NH_3	[m%]	12.1	6.28	13.0	15.9	11.8
SPA tar	[m%]	15.43	21.51	18.09	18.82	30.11
Char	[m%]	44.0	28.3	~	6.18	4.54
Heavy tar	[m%]	~	~	~	4.28	5.35
TOTAL	*[m%]*	*100*	*100*	*100*	*100*	*100*

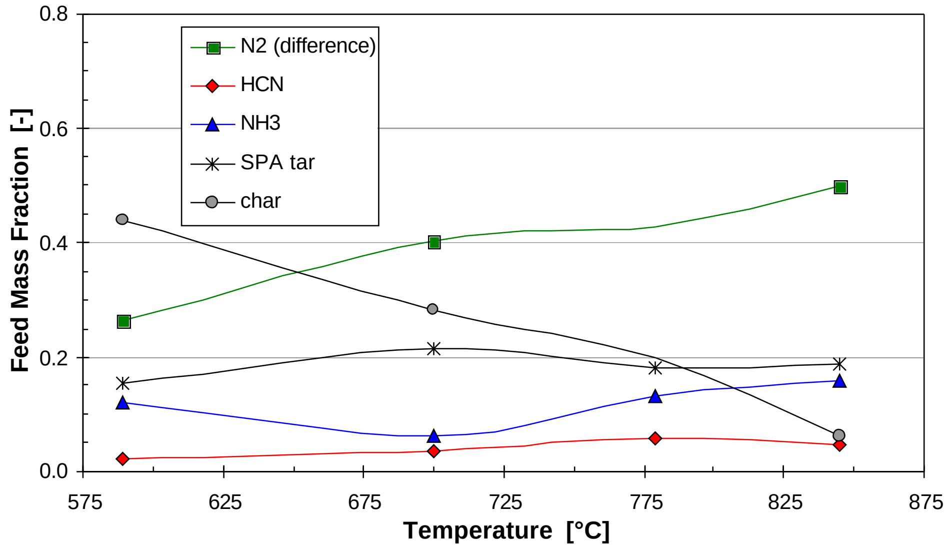


Figure 13 *Partitioning of nitrogen upon pyrolysis of Eucalyptus at four temperatures (mass fraction is based on nitrogen)*

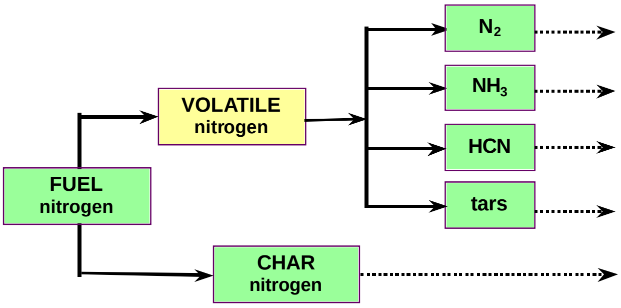
4.5 Application

The experimentally determined data on the nitrogen partitioning upon pyrolysis of the four fuels at different temperatures can be used as input for a modelling of (C)FBC's. With such a model the effect of reburn can be predicted and the real effect of reburn chemistry in circulating fluidised bed combustors (CFBC's) has to be demonstrated in practice. The investigation of these issues was not included in the present study.

However, the pyrolysis data can also be used to determine 'rules-of-thumb' to predict the formation of N_2O (precursors) when applying the fuels as primary fuel in (C)FBC's. In Section 2.2 the possible pathways of N_2O-formation via different precursors was discussed. The relative contributions of those pathways are a composition of the relative formation of the precursors (*i.e.* char and volatiles) and the rate of N_2O formation from these precursors. The values presented there are only for the specific coal investigated in that study.

In the current study the partitioning of nitrogen upon pyrolysis is determined for four fuels. With this information the fuels are compared based on their expected N_2O-emission when utilised as primary fuel in a CFBC at 850°C. For all fuels a thermal input of 10 MJ was set, requiring different amounts of fuel due to the variation in LHV. The masses of the individual nitrogen-containing compounds were determined from the partitioning data (Table 5).

Table 5 *Formation of nitrogen compounds per 10 MJ heating value. Partitioning of nitrogen (mass basis) upon pyrolysis at 850°C (Carbocol at 792°C). The value for nitrogen content in the dry fuel was calculated from the ultimate analysis value (on daf basis)*



Fuel		Puertollano coal	Carbocol	Eucalyptus	Pine
LHV (dry)	[MJ/kg]	19.4	30.1	17.9	17.5
Fuel (dry) per 10 MJ	[g]	516	333	558	573
N-content in dry fuel	[m%]	1.22	1.55	0.41	0.22
Partitioning in mass nitrogen	[g]				
N_2		2.56	1.64	1.13	0.57
NH_3		0.37	0.49	0.36	0.15
HCN		0.11	0.16	0.11	0.04
tars		0.14	0.30	0.52	0.44
CHAR nitrogen		3.11	2.58	0.14	0.06
Total amount of nitrogen	*[g]*	*6.29*	*5.17*	*2.27*	*1.25*

In spite of the higher N-content of Carbocol compared to Puertollano coal, the total amount of nitrogen is lower as less fuel is required for the 10 MJ input. Both wood fuels have a low production of nitrogen compounds due to the low nitrogen content in the feed materials. With Eucalyptus the amounts of NH_3 and HCN produced are in the same range as for the coals. However, the amount of char-N is on average 20 times lower. As the pathways of N_2O formation via char-N give the largest contribution, Eucalyptus is preferable over the coals. For Pine the production of nitrogen compounds is roughly two times lower compared to Eucalyptus which is in line with the two times lower nitrogen content in the fuel. Therefore, Pine seems to be most favourable (primary) fuel when a low production of N_2O precursors is desired.

However, practical considerations concerning behaviour in the fluidised bed and ability to feed the material in the reburn zone might prove to be more important decision criteria. Furthermore, the chemistry of the nitrogen compounds in the fluidised bed combustion determines the final N_2O and NO_x concentrations.

5. CONCLUSIONS

Within the REBED project, ECN performed pyrolysis experiments to determine the fate of nitrogen in the fuel (fuel-bound nitrogen) as a function of the process temperature. Knowledge about pyrolysis is essential to understand and predict the formation of N_2O (and NO_x) in combustion. The obtained relations between fuel properties, process temperatures, and the fate of fuel-bound nitrogen are input for modelling of (C)FBC's to be developed by ICSTM. The fuels tested in the lab-scale fluidised-bed reactor (WOB) were:

- Puertollano Coal at 600, 700, 775, and 850°C;
- Eucalyptus at 600, 700, 775, and 850°C;
- Carbocol at 800°C; and
- Pine at 850°C.

From the analysis of the composition of all process flows the overall mass balances were composed. The fate of nitrogen upon pyrolysis was determined from formation of different nitrogen-containing compounds.

The results presented in this report can be used to optimise a system of CFBC operation with reburn to minimise N_2O formation without increasing the NO_x production.

With the pyrolysis distribution data a comparison was made between the fuels, assuming an experiment in which the fuels were used as primary fuel with a thermal input of 10 MJ. Both coal fuels with relatively high nitrogen contents produce a lot of NH_3, HCN, and especially char, all of which are notorious N_2O precursors. For Eucalyptus the production of NH_3 and HCN is comparable but the char-N production is much lower due to the high volatile content. Pine seems the preferable fuel when the production of nitrogen compounds is the deciding criterion. However, based on their troublesome agglomeration behaviour in the fluidised bed experiments, utilisation as primary fuel in large-scale (C)FBC's might be a problem.

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APPENDICES

APPENDIX A EXPERIMENTAL RESULTS OF PYROLYSIS EXPERIMENTS IN THE WOB

	Fuel	[-]	Puertollano	Puertollano	Puertollano	Puertollano	Carbocol	Eucalyptus	Eucalyptus	Eucalyptus	Eucalyptus	Pine
	Average bed temperature (Tl 4, 5, 6)	[°C]	609	705	780	853	792	589	700	779	845	845
	Date	[-]	20-Sep-99	21-Sep-99	22-Sep-99	23-Sep-99	9-Feb-00	27-Jul-00	28-Jul-00	31-Jul-00	11-Feb-00	14-Feb-00
	Duration	[min]	58	66	62	117	122	59	59	59	157	132
	Argon flow	[nL/min]	10.89	10.89	10.89	10.89	15.88	11.00	11.00	11.00	10.89	10.89
1	Feed											
	Feed flow	[g/h]	420	420	420	420	542	410	413	391	422	442
	Particle size	[mm]	0,71 - 2,0	0,71 - 2,0	0,71 - 2,0	0,71 - 2,0	0,5 - 2,0	0,71 - 2,0	0,71 - 2,0	0,71 - 2,0	0,71 - 2,0	0,71 - 2,0
	Moisture content fuel	[m%]	4.3	4.3	4.3	4.3	5.7	8.5	8.5	8.5	8.5	8.4
	Ash content fuel	[m%; dry]	36.91	36.91	36.91	36.91	7.45	3.28	3.28	3.28	3.28	0.44
2	Ultimate Analysis of fuel											
	Source	[-]	ECN	ECN	ECN	ECN	ECN	ECN	ECN	ECN	ECN	ECN
	%C	[m%; daf]	72.19	72.19	72.19	72.19	83.58	52.02	52.02	52.02	52.02	53.37
	%H	[m%; daf]	4.96	4.96	4.96	4.96	4.71	5.00	5.00	5.00	5.00	5.53
	%N	[m%; daf]	1.93	1.93	1.93	1.93	1.68	0.42	0.42	0.42	0.42	0.22
	%O	[m%; daf]	19.12	19.12	19.12	19.12	9.91	42.55	42.55	42.55	42.55	40.88
	%S	[m%; daf]	1.80	1.80	1.80	1.80	0.12	0.006	0.006	0.006	0.006	0.001
3	Bed Material											
	Amount sand in bed	[g]	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
	Particle size sand	[mm]	circa 0.27	circa 0.27	circa 0.27	circa 0.27	circa 0.27	circa 0.27	circa 0.27	circa 0.27	circa 0.27	circa 0.27
	Type sand	[-]	??	??	??	??	??	??	??	??	??	??
4	After test											
	Amount of solids in bed	[g]	1294	1329	1314	1575	1624	1118	1096	1043	1067	1067
	- Sieve fraction < 350 mm	[g]	747	761	726	776	576	720	*736*	*732*	644	491
	- Sieve fraction 350 - 500 mm	[g]	301	293	328	314	330	231	210	204	283	305
	- Sieve fraction > 501 (500-710) mm	[g]	245	275	261	487	720	76	64	48	140	271
	- Sieve fraction > 710 mm	[g]	~	~	~	~	~	91	87	59	~	~
	Cyclone ash	[g/h]	8.4	18	20	20	16	1.2	0.96	1.8	2.8	4.8
	Total solids build-up	[g/h]	315	319	324	315	323	121	99	46	28	35
5	Volatile 'char' fraction (dry)											
	Sieve fraction < 350	[-]	0.026	0.026	0.026	0.026	0.058	0.04	0.02	0.050	0.022	0.032
	Sieve fraction 350 - 500	[-]	0.026	0.042	0.043	0.049	0.071	0.24	0.08	0.08	0.054	0.041

	Fuel	[-]	Puertollano	Puertollano	Puertollano	Puertollano	Carbocol	Eucalyptus	Eucalyptus	Eucalyptus	Eucalyptus	Pine
	Average bed temperature (Tl 4, 5, 6)	[°C]	609	705	780	853	792	589	700	779	845	845
	Sieve fraction > 500 (or 500-710)	[-]	0.50	0.48	0.44	0.46	0.55	0.39	0.24	0.26	0.37	0.17
	Sieve fraction > 710	[-]	~	~	~	~	~	0.51	0.31	0.28	~	~
	Cyclone ash	[-]	0.50	0.50	0.50	0.50	0.70	0.66	0.73	0.71	0.77	0.59
6	Char build-up											
	Sieve fraction < 350	[g/h]	20.3	18.1	18.3	10.3	16.4	29.3	16.5	37.1	5.4	7.1
	Sieve fraction 350 - 500	[g/h]	8.2	11.3	13.7	7.9	11.5	56.4	17.0	15.6	5.8	5.7
	Sieve fraction > 500 (or 500-710)	[g/h]	128.2	121.4	110.7	114.4	194.0	30.1	15.6	12.7	20.0	20.9
	Sieve fraction > 710	[g/h]	~	~	~	~	~	47.0	27.7	16.9	~	~
	Cyclone ash	[g/h]	4.2	9.0	10.0	9.9	11.4	0.8	0.7	1.3	2.2	2.8
7	Overall Mass Balance											
	In: Feed (ar)	[g/h]	420	420	420	420	542	410	413	391	422	442
	Out: Gas (incl water) (from 4 & 10)	[g/h]	104	99	96	105	217	289	314	345	393	406
	Out: Heavy Tar & Soot (from 10)	[g/h]	0.4	1.1	0.3	0.2	2.1	0.0	0.0	0.0	0.9	0.7
	Char build-up (from 6)	[g/h]	161	160	153	142	233	164	77	84	33	37
	Ash (difference char-total solids)	[g/h]	154	160	171	172	90	-42	21	-38	-5	-1
	Control: Ash expected	*[g/h]*	*148*	*148*	*148*	*148*	*38*	*12*	*12*	*12*	*13*	*2*
8	Gas Analysis (dry)											
	H_2O (in gas analysis at 5°C)	[vol%]	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
	H_2	[vol%]	0.84	4.07	6.59	10.21	9.16	2.85	6.97	7.32	9.10	8.94
	O_2/Ar	[vol%]	94.16	92.05	86.28	82.52	85.9	83.2	77.3	74.96	70.7	71.2
	N_2	[vol%]	0.17	0.27	0.42	0.44	0.70	0.79	0.32	0.31	0.45	0.92
	CH_4	[vol%]	1.20	1.51	1.47	1.57	2.63	2.32	3.48	3.94	4.22	3.85
	CO	[vol%]	0.62	1.08	1.55	3.03	2.41	6.57	9.68	11.17	12.10	12.28
	CO_2	[vol%]	0.57	0.81	1.03	1.03	0.77	3.77	4.05	3.44	3.44	2.91
	C_2H_4	[vol%]	0.12	0.20	0.32	0.32	0.75	0.40	0.95	1.23	1.27	1.24
	C_2H_6	[vol%]	0.12	0.08	0.04	0.02	0.09	0.22	0.22	0.12	0.05	0.05
	benzene	[ppmV]	243	442	898	1123	1455	667	2345	3898	4018	3985
	toluene	[ppmV]	272	370	412	338	893	822	1726	1598	733	639
	SPA tars (based on naphthalene)	[ppmV]	696	872	931	685	1710	1648	2184	1690	1813	1651
	NH_3	[ppmV]	1057	1790	1455	553	1025	354	175	334	421	178
	HCl	[ppmV]	5.0	8.3	3.7	3.4	2.8	40.8	8.8	20.0	69.2	15.5
	HBr	[ppmV]	0	0	0	0	0	0	0	0	0	0
	HCN	[ppmV]	90	0	133	162	331	64	103	153	128	44
	H_2S	[ppmV]	43	0	21	24	16	0	0	0	2	2
	Control Total	*[vol%]*	*98.88*	*101.26*	*98.93*	*100.28*	*103.83*	*101.33*	*104.47*	*104.11*	*102.90*	*102.89*

	Fuel	[-]	Puertollano	Puertollano	Puertollano	Puertollano	Carbocol	Eucalyptus	Eucalyptus	Eucalyptus	Eucalyptus	Pine
	Average bed temperature (Tl 4, 5, 6)	[°C]	609	705	780	853	792	589	700	779	845	845
9	Wet-chemical determinations											
	NH_3	[mg/nm^3]	803	1360	1105	420	779	269	133	254	320	135
	HCl	[mg/nm^3]	8.1	13.5	6.0	5.6	4.6	66.3	14.3	32.6	112.5	25.2
	HBr	[mg/nm3]	~	~	~	~	~	~	~	~	~	~
	complex CN	[mg/nm^3]	109	~	160	195	398.6	77.3	124.6	184.4	154.9	53.0
	H_2S (determined from SCN)	[mg/nm^3]	65	~	32	37	24.6	~	~	~	3.5	2.4
	H_2O (with P_2O_5)	[vol%]	~	~	~	~	6.2	~	~	~	7.4	9.3
10	Heavy Tar Filter (5°C)											
	Heavy Tar	[mg]	390	200	280	280	4150	~	~	~	2240	1580
	Soot	[mg]	0.4	1031	74.1	35.2	72.0	~	~	~	0.0	0.0
11	SPA analysis (dry gas)											
	Total	*[g/nm^3]*	*3.98*	*4.98*	*5.32*	*3.92*	*9.77*	*9.42*	*12.49*	*9.66*	*10.37*	*9.44*
	Pyridine	[mg/nm^3]						220	19	50		
	2-Mepyridine	[mg/nm^3]						8	14	10		
	3+4-Mepyridine	[mg/nm^3]						140	158	15		
	M/p-xylene (O-xylene/styreen?)	[mg/nm^3]	113	158	128	32	293	221	410	127	55	19
	O-xylene / styreen	[mg/nm^3]	85	149	132	40	362	275	1108	606	610	250
	Phenol	[mg/nm^3]	709	864	457	66	424	1313	1291	616	72	243
	O-cresol	[mg/nm^3]						501	456	29		
	Indene	[mg/nm^3]	278	229	274	169	590	192	963	1011	899	473
	M/p-cresol	[mg/nm^3]						975	714	86		
	Naphtalene	[mg/nm^3]	159	335	687	695	1330	204	1291	2129	3284	2800
	Quinoline	[mg/nm^3]						29	7	14		
	Isoquinoline	[mg/nm^3]						91	32	9		
	2-Me-naphtalene	[mg/nm^3]	118	236	302	159	68	103	360	270	141	138
	1-Me-naphtalene	[mg/nm^3]	81	161	167	66	64	136	277	177	89	83
	Biphenyl	[mg/nm^3]					438	12	82	114	187	158
	Ethenylnaphtalene	[mg/nm^3]					254	19	109	101	106	93
	Acenaphtylene	[mg/nm^3]	34	153	375	278	499	30	356	614	882	889
	Acenaphtene	[mg/nm^3]	16	17	37	83	55	17	21	20	46	61
	Fluorene	[mg/nm^3]	25	64	195	164	282	26	140	276	343	322
	Phenanthrene	[mg/nm^3]	22	81	316	292	364	17	175	424	695	698
	Anthracene	[mg/nm^3]	~	22	99	124	199	6	71	200	267	300
	Fluoranthene	[mg/nm^3]	~	21	134	210	166	5	46	150	287	331
	Pyrene	[mg/nm^3]	25	24	87	120	160	7	70	200	320	348

	Fuel	[-]	Puertollano	Puertollano	Puertollano	Puertollano	Carbocol	Eucalyptus	Eucalyptus	Eucalyptus	Eucalyptus	Pine
	Average bed temperature (Tl 4, 5, 6)	[°C]	609	705	780	853	792	589	700	779	845	845
	Benzo(a)anthrace	[mg/nm^3]	56	39	46	48	92	1	22	63	99	112
	Chrysene	[mg/nm^3]	284	255	100	266	88	1	21	57	102	104
	Benzo(b)fluorant	[mg/nm^3]	37	26	40	~	66	~	8	36	73	105
	Benzo(k)fluorant	[mg/nm^3]	31	25	60	~	28	~	3	17	29	40
	Benzo(a)pyrene	[mg/nm^3]	~	~	45	33	59	1	14	49	85	120
	Perylene	[mg/nm^3]	23	~	~	~	11	~	1	6	12	14
	Indeno(1,2,3-cd)	[mg/nm^3]	~	~	~	~	23	~	~	13	29	49
	Dibenz(a,h)anthr	[mg/nm^3]	~	~	~	~	11	~	~	1	8	13
	Benzo(ghi)peryle	[mg/nm^3]	19	~	~	~	15	~	~	5	20	40
	Unknown	[mg/nm^3]	1864	2123	1644	1074	3833	4869	4247	2166	1625	1634
12	Char Analysis [represented by sieve fraction > 500 mm] (dry, ash free)											
	[C]	[m%]	87.5	91.7	93.0	94.2	94.98	91.33	91.49	89.7	82.35	91.06
	[H]	[m%]	2.6	1.5	1.2	0.8	1.31	1.12	0.24	1.06	1.15	1.35
	[N]	[m%]	2.1	1.8	1.6	1.7	1.7	0.41	0.56	0.75	0.29	0.11
	[O]	[m%]	9.9	3.7	2.8	2.1	1.65	7.11	7.66	8.41	16.03	7.36
	[S]	[m%]	1.1	1.2	1.4	1.3	0.37	0.04	0.04	0.08	0.18	0.11
	ash (dry)	[m%]	35.4	39.6	45.5	44.0	43.17	53.99	74.58	74.96	61.82	82.21
	Source	[-]	Incolab	Incolab	Incolab	Incolab	Incolab	ECN	ECN	ECN	Incolab	Incolab

APPENDIX B BALANCES OF PYROLYSIS EXPERIMENTS IN THE WOB

Feed	[-]	Puertollano coal	Puertollano coal	Puertollano coal	Puertollano coal	Carbocol	Eucalyptus	Eucalyptus	Eucalyptus	Eucalyptus	Pine
Pyrolysis temperature	[°C]	609	705	780	853	792	589	700	779	845	845
Mass Balance (Ar free)											
Feed in (a.r.)	[g/h]	420	420	420	420	542	410	413	391	422	442
--> of which Moisture	[g/h]	18.1	18.1	18.1	18.1	30.9	34.9	35.1	33.2	35.9	37.1
Char out	[g/h]	161	160	153	142	233	164	77	84	33	37
Heavy Tars & Soot	[g/h]	0.4	1.1	0.3	0.2	2.1	0.0	0.0	0.0	0.9	0.7
Ash out	[g/h]	154	160	171	172	90	-42	21	-38	-5	-1
Volatiles out (= gas+H2O)	[g/h]	104.4	99.5	95.9	105.2	216.8	288.8	314.4	345.5	392.7	406.0
--> Pyrolysis Gas (from Ar balance)	[g/h]	29.9	42.0	57.4	77.8	116.8	165.4	234.2	256.6	281.2	273.8
--> H_2O (difference)	[g/h]	74.5	57.5	38.5	27.4	99.9	123.4	80.2	88.9	111.5	132.2
Total Volatiles out (incl. H_2O)	[nm^3/h]	0.125	0.137	0.144	0.175	0.323	0.297	0.332	0.367	0.436	0.455
		63	57	55	45	24	26	24	21	18	17
Relative Mass Balance (Ar free)											
Char	[m%]	38.30%	38.04%	36.32%	33.93%	43.06%	39.91%	18.75%	21.38%	7.93%	8.28%
Ash	[m%]	36.75%	38.00%	40.78%	40.99%	16.56%	-10.36%	5.12%	-9.74%	-1.19%	-0.30%
Heavy Tars & Soot	[m%]	0.10%	0.27%	0.08%	0.04%	0.38%	0.00%	0.00%	0.00%	0.20%	0.16%
Gas	[m%]	6.47%	9.15%	12.71%	17.78%	19.48%	38.51%	54.01%	63.35%	64.31%	59.92%
Water	[m%]	17.73%	13.68%	9.16%	6.52%	18.44%	30.10%	19.42%	22.74%	26.42%	29.92%
Tar	[m%]	0.65%	0.85%	0.95%	0.74%	2.08%	1.85%	2.70%	2.27%	2.34%	2.02%
TOTAL	*[m%]*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*
Char + Ash (incl. Heavy Tar & Soot)	[-]	75%	76%	77%	75%	60%	30%	24%	12%	7%	8%
Gas + Water (incl. Tar)	[-]	25%	24%	23%	25%	40%	70%	76%	88%	93%	92%
TOTAL	*[-]*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*	*100%*
Volatiles Balance (calcd Ar balance)											
Effective Ar flow	[nm^3/h]	0.65	0.65	0.65	0.65	0.95	0.66	0.66	0.66	0.65	0.65
Total Gas flow (dry; incl. Ar)	[nm^3/h]	0.69	0.72	0.75	0.79	1.15	0.80	0.89	0.92	0.95	0.94
Gas flow (dry; Ar free)	[nm^3/h]	0.033	0.065	0.096	0.141	0.199	0.144	0.232	0.257	0.298	0.291
Density Pyrolysis Gas (dry, Ar free)	[kg/nm^3]	0.91	0.64	0.60	0.55	0.59	1.15	1.01	1.00	0.95	0.94

Feed	[-]	Puertollano coal	Puertollano coal	Puertollano coal	Puertollano coal	Carbocol	Eucalyptus	Eucalyptus	Eucalyptus	Eucalyptus	Pine
Pyrolysis temperature	[°C]	609	705	780	853	792	589	700	779	845	845
Tar concentration (dry; Ar free)	[g/nm^3]	83	55	42	22	57	53	48	35	33	31
Tar concentration (wet; Ar free)	[g/nm^3]	22	26	28	18	35	25	34	24	23	20
Pyrolysis Gas (dry; Ar free)											
benzene	[vol%]	0.63	0.53	0.76	0.66	0.85	0.39	0.89	1.38	1.28	1.29
toluene	[vol%]	0.70	0.44	0.35	0.20	0.52	0.48	0.66	0.56	0.23	0.21
H2	[vol%]	21.63	48.69	55.82	60.37	53.71	16.49	26.48	25.87	29.03	28.99
N2	[vol%]	4.33	3.20	3.56	2.60	4.10	4.57	1.22	1.10	1.44	2.98
CH4	[vol%]	30.96	18.01	12.42	9.31	15.42	13.43	13.22	13.92	13.46	12.48
CO	[vol%]	15.99	12.96	13.13	17.92	14.13	38.02	36.77	39.47	38.60	39.82
CO2	[vol%]	14.62	9.64	8.74	6.07	4.52	21.82	15.39	12.16	10.97	9.44
C2H4	[vol%]	3.22	2.34	2.72	1.89	4.40	2.31	3.61	4.35	4.05	4.02
C2H6	[vol%]	3.02	1.00	0.35	0.13	0.53	1.27	0.84	0.42	0.16	0.16
SPA tars	[ppmV]	18002	10426	7890	4052	10025	9535	8296	5973	5784	5353
NH_3	[ppmV]	27343	21419	12322	3270	6013	2049	665	1182	1344	576
HCl	[ppmV]	129	99	31	20	17	236	33	71	221	50
HBr	[ppmV]	0	0	0	0	0	0	0	0	0	0
HCN	[ppmV]	2339	0	1124	957	1939	371	393	541	410	143
H_2S	[ppmV]	1106	0	178	144	95	0	0	0	7	5
Control Total	*[vol%]*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*
LHV (dry gas; Ar free)	[MJ/nm^3]	21.6	17.0	15.8	14.7	18.4	15.1	17.5	18.8	17.8	17.5
HHV (dry gas; Ar free)	[MJ/nm^3]	23.6	18.9	17.6	16.4	20.3	16.2	18.9	20.2	19.1	18.8
LHV (dry gas; with Ar)	[MJ/nm^3]	1.0	1.5	2.0	2.6	3.2	2.7	4.6	5.3	5.6	5.4
Pyrolysis Gas (wet; Ar free)											
benzene	[vol%]	0.16	0.25	0.51	0.53	0.52	0.19	0.62	0.96	0.87	0.83
toluene	[vol%]	0.18	0.21	0.23	0.16	0.32	0.23	0.46	0.39	0.16	0.13
H2	[vol%]	5.64	23.25	37.22	48.59	33.02	7.98	18.51	18.07	19.80	18.51
N2	[vol%]	1.13	1.53	2.38	2.10	2.52	2.21	0.85	0.77	0.98	1.91
CH4	[vol%]	8.08	8.60	8.28	7.49	9.48	6.49	9.24	9.73	9.18	7.97
CO	[vol%]	4.17	6.19	8.75	14.42	8.69	18.39	25.71	27.58	26.32	25.43
CO2	[vol%]	3.82	4.60	5.83	4.88	2.78	10.55	10.76	8.49	7.48	6.03
C2H4	[vol%]	0.84	1.12	1.82	1.52	2.70	1.12	2.52	3.04	2.76	2.57
C2H6	[vol%]	0.79	0.48	0.23	0.10	0.32	0.62	0.58	0.30	0.11	0.10

Feed	[-]	Puertollano coal	Puertollano coal	Puertollano coal	Puertollano coal	Carbocol	Eucalyptus	Eucalyptus	Eucalyptus	Eucalyptus	Pine
Pyrolysis temperature	[°C]	609	705	780	853	792	589	700	779	845	845
H_2O	[vol%]	73.91	52.25	33.32	19.52	38.52	51.64	30.08	30.13	31.80	36.14
SPA tars	[ppmV]	4698	4979	5261	3261	6164	4611	5800	4173	3945	3418
NH_3	[ppmV]	7135	10229	8217	2632	3697	991	465	826	916	368
HCl	[ppmV]	34	47	21	16	10	114	23	49	150	32
HBr	[ppmV]	0	0	0	0	0	0	0	0	0	0
HCN	[ppmV]	610	0	750	770	1192	179	275	378	280	91
H_2S	[ppmV]	289	0	119	116	58	0	0	0	5	3
Control Total	*[vol%]*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*	*100.0*
LHV (wet gas; Ar free)	[MJ/nm^3]	5.6	8.1	10.5	11.8	11.3	7.3	12.2	13.1	12.1	11.2
HHV (wet gas; Ar free)	[MJ/nm^3]	6.2	9.0	11.7	13.2	12.5	7.8	13.2	14.1	13.0	12.0
Carbon Balance (ash free)											
IN:	*[g/h]*	*183*	*183*	*183*	*183*	*395*	*189*	*190*	*180*	*194*	*215*
Feed	[g/h]	183	183	183	183	395	189	190	180	194	215
OUT:	*[g/h]*	*158*	*170*	*170*	*169*	*291*	*222*	*184*	*202*	*166*	*165*
CO	[g/h]	2.8	4.5	6.7	13.5	15.0	29.3	45.7	54.3	61.5	62.0
CO_2	[g/h]	2.6	3.4	4.5	4.6	4.8	16.8	19.1	16.7	17.5	14.7
CH_4	[g/h]	5.4	6.3	6.4	7.0	16.4	10.3	16.4	19.1	21.5	19.5
C_2H_4	[g/h]	1.1	1.6	2.8	2.8	9.4	3.6	9.0	12.0	12.9	12.5
C_2H_6	[g/h]	1.1	0.7	0.4	0.2	1.1	2.0	2.1	1.2	0.5	0.5
benzene	[g/h]	0.7	1.1	2.3	3.0	5.4	1.8	6.6	11.4	12.3	12.1
toluene	[g/h]	0.9	1.1	1.3	1.1	3.9	2.6	5.7	5.4	2.6	2.3
SPA tar	[g/h]	2.7	3.2	3.5	2.6	9.2	6.4	8.9	7.1	8.0	7.2
HCN	[g/h]	0.16	0	0.09	0.09	0.34	0.06	0.07	0.11	0.10	0.03
char	[g/h]	141	147	142	134	222	149	71	75	28	33
heavy tar	[g/h]	0.3	0.2	0.2	0.2	3.4	0.0	0.0	0.0	1.8	1.3
soot	[g/h]	0.00	0.95	0.07	0.03	0.07	0.00	0.00	0.00	0.00	0.00
Control Ratio	*[%]*	*86.6*	*92.6*	*92.9*	*92.5*	*73.5*	*117.7*	*97.0*	*112.4*	*85.6*	*76.9*
Hydrogen Balance (ash free)											
IN:	*[g/h]*	*14.6*	*14.6*	*14.6*	*14.6*	*25.7*	*22.0*	*22.2*	*21.0*	*22.7*	*26.4*
Feed	[g/h]	12.6	12.6	12.6	12.6	22.3	18.1	18.3	17.3	18.7	22.3
Moisture	[g/h]	2.0	2.0	2.0	2.0	3.5	3.9	3.9	3.7	4.0	4.2
OUT:	*[g/h]*	*15.9*	*14.9*	*14.4*	*15.4*	*33.1*	*23.2*	*24.0*	*27.6*	*32.2*	*33.5*

Feed	[-]	Puertollano coal	Puertollano coal	Puertollano coal	Puertollano coal	Carbocol	Eucalyptus	Eucalyptus	Eucalyptus	Eucalyptus	Pine
Pyrolysis temperature	[°C]	609	705	780	853	792	589	700	779	845	845
H_2	[g/h]	0.6	2.9	4.8	7.6	9.6	2.1	5.5	6.0	7.8	7.6
H_2O	[g/h]	8.3	6.4	4.3	3.1	11.2	13.8	9.0	9.9	12.5	14.8
CH_4	[g/h]	1.8	2.1	2.1	2.4	5.5	3.5	5.5	6.4	7.2	6.5
C_2H_4	[g/h]	0.2	0.3	0.5	0.5	1.6	0.6	1.5	2.0	2.2	2.1
C_2H_6	[g/h]	0.3	0.2	0.1	0.0	0.3	0.5	0.5	0.3	0.1	0.1
benzene	[g/h]	0.06	0.09	0.20	0.25	0.46	0.15	0.56	0.95	1.03	1.01
toluene	[g/h]	0.08	0.10	0.12	0.10	0.37	0.25	0.55	0.52	0.25	0.22
NH_3	[g/h]	0.121	0.189	0.159	0.062	0.161	0.040	0.021	0.041	0.054	0.023
HCl	[g/h]	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.001	0.003	0.001
HBr	[g/h]	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
HCN	[g/h]	0.003	0.000	0.005	0.006	0.017	0.002	0.004	0.006	0.005	0.002
H_2S	[g/h]	0.003	0.000	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.000
SPA tar	[g/h]	0.20	0.23	0.26	0.20	0.68	0.47	0.66	0.53	0.59	0.53
char	[g/h]	4.2	2.4	1.8	1.1	3.1	1.8	0.2	0.9	0.4	0.5
heavy tar	[g/h]	0.02	0.01	0.02	0.02	0.25	0.00	0.00	0.00	0.13	0.09
soot	[g/h]	0.000	0.010	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Control Ratio	*[%]*	*109.1*	*102.1*	*98.7*	*105.2*	*128.7*	*105.5*	*108.2*	*131.2*	*141.9*	*126.7*
Oxygen Balance (ash free)											
IN:	*[g/h]*	*64.5*	*64.5*	*64.5*	*64.5*	*74.3*	*185.3*	*186.7*	*176.8*	*190.8*	*197.8*
Feed	[g/h]	48.5	48.5	48.5	48.5	46.9	154.4	155.5	147.2	158.9	164.8
Moisture	[g/h]	16.0	16.0	16.0	16.0	27.4	31.0	31.2	29.5	31.9	33.0
OUT:	*[g/h]*	*93.0*	*72.5*	*59.8*	*57.9*	*127.0*	*205.8*	*190.1*	*203.7*	*234.2*	*243.0*
H_2O	[g/h]	66.1	51.0	34.2	24.3	88.8	109.6	71.2	79.0	99.0	117.4
CO	[g/h]	3.7	6.0	9.0	18.0	20.0	39.0	60.9	72.3	82.0	82.6
CO_2	[g/h]	6.8	9.0	12.0	12.2	12.8	44.8	50.9	44.5	46.6	39.2
SPA tar	[g/h]	0.34	0.39	0.43	0.33	1.14	0.78	1.10	0.88	0.98	0.89
char	[g/h]	15.9	5.9	4.3	3.0	3.9	11.6	5.9	7.0	5.4	2.7
heavy tar	[g/h]	0.04	0.02	0.03	0.03	0.42	0.00	0.00	0.00	0.22	0.16
soot	[g/h]	0.000	0.066	0.005	0.002	0.005	0.000	0.000	0.000	0.000	0.000
Control Ratio	*[%]*	*144.1*	*112.3*	*92.7*	*89.7*	*170.9*	*111.0*	*101.8*	*115.2*	*122.7*	*122.9*
Nitrogen Balance (ash free)											
IN:	*[g/h]*	*4.9*	*4.9*	*4.9*	*4.9*	*7.9*	*1.5*	*1.5*	*1.5*	*1.6*	*0.9*

Feed	[-]	Puertollano coal	Puertollano coal	Puertollano coal	Puertollano coal	Carbocol	Eucalyptus	Eucalyptus	Eucalyptus	Eucalyptus	Pine
Pyrolysis temperature	[°C]	609	705	780	853	792	589	700	779	845	845
Feed	[g/h]	4.9	4.9	4.9	4.9	7.9	1.5	1.5	1.5	1.6	0.9
OUT:	*[g/h]*	*5.9*	*6.5*	*7.7*	*7.5*	*15.6*	*9.3*	*4.4*	*4.7*	*6.1*	*11.3*
N_2	[g/h]	1.8	2.6	4.3	4.6	10.2	8.2	3.5	3.5	5.3	10.8
HCN	[g/h]	0.048	0.000	0.067	0.084	0.240	0.033	0.057	0.087	0.076	0.026
NH_3	[g/h]	0.559	0.875	0.738	0.287	0.746	0.184	0.096	0.189	0.250	0.105
SPA tar	[g/h]	0.10	0.12	0.13	0.10	0.34	0.24	0.33	0.26	0.30	0.27
char	[g/h]	3.4	2.9	2.4	2.4	4.0	0.67	0.43	0.63	0.10	0.04
heavy tar	[g/h]	0.01	0.01	0.01	0.01	0.12	0.00	0.00	0.00	0.07	0.05
soot	[g/h]	0.000	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Control Ratio	*[%]*	*119.9*	*132.6*	*156.4*	*152.8*	*196.3*	*612.8*	*289.3*	*321.9*	*390.4*	*1277.1*
N_2 (by difference)	[g/h]	0.8	1.0	1.5	2.0	2.5	0.4	0.6	0.3	0.8	0.4
In-leak of N2	[L/h]	0.8	1.3	2.2	2.1	6.1	6.3	2.3	2.6	3.6	8.4