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DISSERTATION

Experimental Investigations of selected Elements Behaviour during Biomass Pyrolysis and Gasification

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Inmitten von Schwierigkeiten liegen günstige Gelegenheiten.

Albert Einstein

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Dedicated to Marcus

Kurzfassung

Die Verwendung von Biomasse wird heutzutage als Lösung vieler umwelttechnischer Probleme gesehen, vor allem bei der Reduktion von Treibhausgasen und der Einsparung von fossilen Brennstoffen zeigen sich dessen Vorteile.

Bei der Verwertung von Biomasse, wie Pyrolyse, Vergasung und Verbrennung, werden zuerst die flüchtigen Bestandteile freigesetzt. Die Menge sowie die Zusammensetzung dieser flüchtigen Bestandteile sind von vielen Faktoren wie z.B. Temperatur, Feuchtigkeit der Biomasse, Aufheizrate, Partikelgröße, Vorhandensein bestimmter Elemente und vielem mehr abhängig. In der Literatur wurde schon einiges über das Verhalten von Biomasse bei der thermischen und chemischen Umsetzung in Form von der Freisetzung von Teeren usw. berichtet, nicht jedoch über jene von anorganischen Verbindungen wie Schwefelwasserstoff etc. Die Verringerung der Emissionen von Stickoxiden, Alkalimetallen, Chlor- und Schwefelverbindungen sowie auch von Schwermetallen ist sowohl für den Umweltschutz als auch für die störungsfreie Betriebsweise einer Anlage von größter Bedeutung.

Ziel dieser Arbeit war es, das Verhalten verschiedener Elemente während der Pyrolyse und der Vergasung zu untersuchen. Hierzu wurden zwei Arten von Wirbelschichten verwendet, eine im Labormaßstab und eine Kleinanlage, wobei beide elektrisch beheizt wurden.

Die Anlage im Labormaßstab mit welcher die Untersuchungen der Pyrolyse durchgeführt wurden war mit einem diskontinuierlichen Fördersystem für die Biomasse ausgestattet. Der Effekt der Temperatur auf das Verhalten der Elemente (C,H,....) sowie deren Verteilung in der Gas- und Feststoffphase wurde evaluiert. Insgesamt wurden drei verschiedene Arten von Biomasse herangezogen: Holz, Getreide und Hanf. Die Pyrolyse wurde in einem Temperaturbereich zwischen 300 und 850°C untersucht, wobei Stickstoff als Fluidisierungsgas und Quarzsand als Bettmaterial verwendet wurde. Die Biomasse und Kohleproben wurden mittels ICP_AES und Röntgenfluoreszenz analysiert. CO und CO₂ wurden während der Messung online detektiert und die Menge an flüchtigen Bestandteilen während der Pyrolyse ermittelt.

Das Verhalten der Elemente während der Pyrolyse ist komplex und wird von vielen Faktoren beeinflusst wie zum Beispiel Temperatur, Druck, Verweilzeit der Partikel im Reaktor, das Vorhandensein anderer Elemente (z.B. beeinflussen Chlor und Schwefel die Verflüchtigung von Metallen), Wassergehalt usw. Basierend auf den Resultaten von Experimenten sind Elemente wie Hg, Cd und Pb die flüchtigsten Metalle. Alkalimetalle werden nach der Pyrolyse vor allem i n der Kohle gefunden. Dies konnte auch bei Temperaturen von über 800°C und mit ca. 70 m-% Alkalimetallen beobachtet werden. Chlor und Stickstoff verflüchtigen sich bei Temperaturen von 800°C und konnten zu über 70% in der Gasphase

wieder gefunden werden. Im Gegensatz dazu fanden sich Elemente wie Cr, Cu, Mg, Mn, Zn, Al, Li und Sn wieder vor allem in der Kohle.

Das Vergasungsverhalten der Elemente wurde in der Kleinanlage in Technikum des Institutes realisiert, welche mit einer kontinuierlichen Förderanlage für die Biomasse ausgestattet war. Der Einfluss verschiedener Betriebsbedingungen wie Luft zu Brennstoff Verhältnis (ER), Temperatur, Feuchtigkeit der Biomasse, Bettmaterial und Additive wurde evaluiert. Gemahlene Holzpellets mit verschieden Wassergehalt (6,7; 15,8 und 21,5 m-%) wurden als Brennstoff eingesetzt. Die Vergasung erfolgte bei Temperaturen von 750 bis 850°C und ER wurde zwischen 0,3 und 0,4 variiert. Insgesamt kamen drei Bettmaterialien zum Einsatz: Quarzsand, Olivin und Kalzit. Sättigungsschlamm aus der Zuckerverarbeitung wurde als Zusatz zum Brennstoff in einem Verhältnis Schlamm/Holz = 1/7 untersucht. Der Teergehalt, die Freisetzung von NH₃ und H₂S, sowie die Gaszusammensetzung wurden gemessen.

Die Auswirkung der Temperatur auf die Gehalte von NH_3 und Teer waren nicht so signifikant wie jenes des ER Betriebes. Bei hohem ER wurden niedrigere Teergehalte und NH_3 Konzentrationen beobachtet. Weiters resultierte ein niedrigerer Heizwert des Produktgases, welcher mit dem geringeren Gehalt an CH_4 und CO begründbar ist.

Sowohl bei der Verwendung von Quarzsand als auch Olivin belief sich der NH₃ Gehalt in etwa auf denselben Wert, 254 und 242 ppm. Bei Kalzit wurde eine Konzentration von 296 ppm gemessen. Schon größere Unterschiede gab es beim Teergehalt im Fall der verschiedenen Bettmaterialen. Bei der Verwendung von Quarzsand entstanden 7,2 g/Nm³, bei Olivin nur 6,3 g/Nm³ und bei Kalzit überhaupt nur mehr 1,5 g/Nm³. Der Heizwert der entstandenen Gase betrug bei Quarzsand als Bettmaterial 9,27 MJ/Nm³ bzw.7,14 und 7,47 MJ/Nm³ bei Verwendung von Olivin bzw. Kalzit.

Weiters wurde beobachtet, dass sich eine höhere Feuchtigkeit des eingesetzten Holzes zu einer Verringerung des gemessenen NH_3 Gehaltes führte während der N_2 Gehalt stieg. Der Teergehalt in der Gasphase sank mit zunehmender Feuchtigkeit. Negativ wirkte sich die Feuchtigkeit jedoch auf den Heizwert aus, welcher sich bei einem Feuchtigkeitsgehalt von 21,5 m-% in etwa halbierte.

Das Zumischen des Sättigungsschlammes zum Brennstoff wurde in einem Verhältnis von Schlamm/Holz = 1/7 realisiert. Der resultierende Teergehalt betrug in diesem Fall nur mehr 68% der Messung mit reinem Holz. Andererseits stieg jedoch der gemessene Anteil an NH₃ von 254 ppm auf 391 ppm an was womöglich auf den Schlamm zurückzuführen ist.

Abstract

Biomass thermal utilisation is widely seen as a part of environmental problems solution, especially the accumulation of greenhouse gases in the atmosphere and saving fossil fuels.

The first step of each thermal conversion process (pyrolysis, gasification, combustion) is a release of volatiles. Amount and composition of volatiles is dependent on many factors, such as temperature, fuel moisture, heating rate, particle size, presence of some elements etc. There is some information available in literature about the behaviour of organic matter during the thermochemical conversion but not so much about the inorganic one. The lowering of nitrogen, chlorine, sulphur, alkali and some heavy metals emissions is very important for the environment and also for the proper work of conversion units without damages or malfunction in the plant itself.

The aim of this work was to study elements and their inorganic compounds behaviour under the pyrolysis and gasification conditions using two types of fluidized bed reactors. The laboratory scale fluidized bed reactor used during the biomass pyrolysis was equipped with a batch feeding system and was electrically heated. The effect of the temperature on the elements behavior (C, H, N, Cl, S, K, Na, As, Cd, Hg, Pb, Cr, Cu, Mg, Mn, Zn, Al, Fe, Li, Ni, Sn) their distribution to the gas or solid phase was studied. Three types of biomass were used: wood, corn and hemp. The pyrolysis experiments were performed at temperatures of 300-850°C. Nitrogen was used as a fluidizing agent and the bed material was formed by silica sand.

The biomass and the char samples were analysed using ICP_AES and X-ray fluorescence method. CO and CO_2 were measured on-line during the pyrolysis process. The amount of volatiles rising during pyrolysis process was defined.

The elements behaviour during the pyrolysis is a complex process, influenced by many factors, such as temperature, pressure, residence time of a biomass particle in the reactor, presence of other elements (e.g. chlorine and sulphur influence the volatilization behaviour of metals), biomass moisture, etc. Based on the results from experimental work, it is possible to say that elements such as Hg, Cd and Pb are the most volatile metals. Alkali metals after the pyrolysis process were mostly found in the char. Even at temperature of 800°C, about 70 w-% of alkali metals were found in the char. Chlorine and nitrogen released into the volatiles, at temperature of 800°C, it was more than 70 w-% found in the gas phase. Elements such as Cr, Cu, Mg, Mn, Zn, Al, Li and Sn were found mostly in the char.

During the biomass air gasification the small scale fluidized bed reactor with the continuous feeding system and electrical heating was used. The effects of different operation conditions: air to fuel ratio (ER), temperature, moisture of the fuel, type of the bed material and the effect of an additive were studied. Milled wood pellets with different moisture (6.7; 15.8 and 21.5

w-%) were used as a fuel. Gasification process was performed at temperatures of 750 and 850°C, ER was varying between 0.3 and 0.4. Three types of the bed materials were used: quartz sand, olivine and calcite. The saturation sludge from sugar industry was used as an additive to the fuel (ratio sludge/wood = 1/7). The amount of tars, NH₃, H₂S and the gas composition were measured during the biomass gasification.

The effect of the temperature on the NH₃ and tars amounts was not as significant as in the case of ER. With higher ER the lower tar and NH₃ concentrations were detected. Higher ER caused also lower heating value of the product gas because of lower concentrations of CH₄ and CO. The NH₃ content using the quartz sand and the olivine was nearly the same, 254 and 242 ppm respectively. Using the calcite, 296 ppm of the NH₃ was detected in the gas. The amount of tars in the case of quartz sand was 7.2 g/Nm³. Lower amount, 6.3 g/Nm³ was measured using olivine and only 1.5 g/Nm³ of tars was detected using calcite as a bed material.

The gas heating value of 9.27 MJ/Nm³ was measured when the quartz sand was used as the bed material. The lower values 7.14 and 7.47 MJ/Nm³ was measured in the case of the olivine and the calcite respectively. With higher moisture of the wood, the lower NH₃ content in the gas phase was measured. It was 254, 82.67 and 50 ppm. But the higher contents of N₂ were measured in the product gas with rising moisture. The tar content in the gas phase decreased with the rising moisture. 7.2, 4.9 and 3.3 g/Nm³ were the values of the tars measured in the gas using the wood with 6.7, 15.8 and 21.5 w-% of the fuel moisture. With the rising moisture of the wood, the heating value of 9.27 MJ/Nm³ was produced, but using the wood with moisture of 6.7 w-% the gas with heating value of 9.27 MJ/Nm³.

The saturation sludge from sugar industry was added to the fuel, ratio sludge/wood =1/7. As expected the tar content using this additive was reduced to 68 % of the origin amount using only clean wood. On the other hand the NH₃ content in the gas phase rose from 254 ppm to 391 ppm using the sludge as an additive. It is possible that the sludge supports the formation of NH₃.

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1. Aim of the work

Biomass energy has the potential to greatly reduce greenhouse gas emissions and to save fossil fuels for next human generations. There are many ways how to produce and use energy from biomass. In this work the attention is paid to the thermochemical conversion of the biomass, pyrolysis and gasification respectively.

Biomass contains not only elements, which are important for the energetic use (C, H, O), but also elements, which are undesirable and their emissions, releasing during the thermochemical processes are harmful for the environment and/or can cause serious problems and damage of conversion units (S, Cl, N, alkali metals, heavy metals). The behaviour of such undesirable elements and the factors, which influence their behaviour is therefore of great interest. The effect of the temperature, biomass type, biomass moisture, catalytic effect of the bed materials and additive during the biomass pyrolysis and gasification were experimentally investigated.

At the beginning of this dissertation thesis the literature review concerning the selected elements (S, N, Cl, alkali metals, trace elements) behaviour during biomass pyrolysis and gasification can be found.

Experimental work, biomass pyrolysis as well as gasification, was performed at department of Technical Chemistry of University of Technology Vienna.

During the biomass pyrolysis three different types of fuels were used: wood, corn and hemp and the effect of temperature on distribution of selected elements into gas or solid phase was experimentally investigated. The amount of volatiles releasing during biomass pyrolysis was also measured. The aim of the pyrolysis experiments was to determine the temperature when the thermochemical conversion process is already wholly finished but the most of undesirable elements such as nitrogen, chlorine, sulphur or alkali metals remain in char (solid phase). The biomass pyrolysis process was performed at temperature range between 400 and 850°C.

At temperature of 800°C more than 20 w-% of origin nitrogen were detected in wood char, 20 w-% in corn char and less than 5 w-% were found in hemp char after the pyrolysis process. At the same temperature, nearly 50 w-% of origin sulphur were detected in wood char, about 3 w-% in corn char and 40 w-% were found in hemp char. Chlorine distribution in char after pyrolysis at 800°C was also by each fuel different. About 30 w-% of origin chlorine were detected in wood char, 2 w-% in corn char and nearly 50 w-% of origin chlorine remained in hemp char after the pyrolysis process. Potassium content in char was still high even at temperature of 800°C. 70 w-% of origin potassium amount were detected in wood char, 90 w-% in corn char and about 80 w-% were found in hemp char.

Different temperatures, ER, fuel moistures, bed materials and fuels were used during biomass gasification process to determine their effect on behaviour of nitrogen, NH_3 and N_2 formation respectively, tar formation and gas composition.

The effect of temperature was not as significant as in case of ER. With higher ER, lower NH_3 and higher N_2 amounts were detected in gas. Also the tar content and heating value of the gas were lower at higher ER.

Higher fuel moisture caused higher ER what is explained further in this work.

Three different bed materials were used during biomass gasification: quartz sand, olivine and calcite. The catalytical effect of the bed material on tar formation in case of olivine and calcite was observed. NH₃ content in gas was not significantly reduced using olivine or calcite as bed materials.

Two different biomass fuels were used during the experimental work. Clan wood and wood mixed with saturation sludge from sugar industry. The catalytical effect of the sludge on tar formation was expected. Using the sludge as an additive caused that tar content in gas was about 30% lower.

2. Introduction

Overview Energy supply

The future energy supply of mankind is characterised by increasing energy demand of the growing population, the limitation of fossil fuels and the impacts of the energy utilisation on the environment. One possibility how to solve these problems is the use of renewable energy, such as wind and solar energy, utilisation of biomass etc. Today, biomass already contributes about 6 to 17 % to the world's energy supply and it is considered to be one of the key renewable energy resources of the future.

Mankind uses biomass energy or "bioenergy", the energy from organic matter, for thousands of years, ever since people started burning wood to cook food or to keep warm. And today, wood is still our largest biomass energy resource. But many other sources of biomass can now be used, including plants, residues from agriculture or forestry, and the organic component of municipal and industrial wastes. Even landfills gases can be used as a biomass energy source. Biomass refers to all forms of plant based material that can be converted into usable energy, such as wood, sugarcane, crop and forestry residues.

Biomass offers considerable flexibility of fuel supply due to the range and the diversity of fuels which can be produced at small or large scales, in a centralised or dispersed manner. It can be burnt directly, converted to liquid fuels, anaerobically digested to produce biogas, or thermally converted (pyrolysis, gasification).

Today, a lot of research and development programmes aim at developing biomass gasification and pyrolysis technologies. The overall objective is to produce an energy source which can be fed into the modern gas turbines.

2.1.2 Use of biomass - environmental impacts

The use of bioenergy has the potential to greatly reduce our greenhouse gas emissions. Biomass generates about the same amount of carbon dioxide as fossil fuels, but every time a new plant grows, carbon dioxide is actually removed from the atmosphere. The net emission of carbon dioxide will be zero as long as plants continue to be replenished for biomass energy purposes. These energy crops, such as fast-growing trees and grasses, are called biomass feedstocks. The use of biomass feedstocks can also help to increase the profits of the agricultural industry.

Acid rain, which can damage lakes and forests, is a by-product of the combustion of fossil fuels, particularly coal and oil. The high sulfur content of these fuels together with hot

combustion temperatures result in the formation of sulfur dioxide (SO₂) and nitrous oxides (NO_x), when they are burned to provide energy. The replacement of fossil fuels with biomass can reduce the potential for acid rain. Biomass generally contains less than 0.1% sulfur by weight compared to low sulfur coal with 0.5 - 4% sulfur. Lower combustion temperatures and pollution control devices such as wet scrubbers and electro-static precipitators can also keep emissions of NO_x to a minimum when biomass is burned to produce energy.

2.2 Biomass composition

Biomass could be divided into these types:

- waste biomass (biomass from wood industry or agriculture) and energy crops (fast growing plants)
- vegetation biomass or biomass from animal breeding

The attention in this work is paid to vegetation biomass, such as wood, hemp, corn, etc. The basic biomass components are biopolymers such as cellulose, hemi-cellulose and lignin.

Cellulose is the principal component of the biomass cell walls. Cellulose is a linear polymer of β -(1 \rightarrow 4)-D-glucopyranose units in $\frac{4C_1}{C_1}$ conformation. Structure of cellulose is shown in the following figure.



Figure 2.2-1 Structure of cellulose

In contrast to cellulose that is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is composed of shorter molecules than cellulose and makes up a large part of wood. It is easily hydrolyzed by dilute acid or base. Some monomers of hemi-cellulose are shown in the figure 2.2-2.



Figure 2.2-2: Monomers of hemi-cellulose

Lignin can be thought to be the glue that holds the wood (cellulose and hemicellulose) together. Lignin is important because it gives rigidity to the cells so that a tree can grow large and tall. The structure of the wood lignin is shown in the figure 2.2-3



Figure 2.2-3: Partial structure of a hypothetical lignin molecule from European beech (*Fagus sylvatica*)

An average composition of biomass could be formulated as $C_6H_{10}O_5$. Vegetation biomass consists of many chemical elements. These elements could be divided into following groups:

- 1. major elements (concentration > 1 w-%)
- 2. minor elements (concentration 0.1 1 w-%)
- 3. trace elements (concentration <0.1 w-%)

Major elements are carbon, oxygen and hydrogen. Further are for plants important minor elements such as nitrogen, sulphur, potassium, phosphor, calcium, magnesium and chlorine.

The term "trace elements" refers to chemical elements present in a natural material at concentrations < 0,1 w-%. Trace elements may then cover the whole periodic table of the elements after Ca (atomic number 20), although the elements beryllium (Be, atomic number 4) and boron (B, atomic number 5) should be included as well. A sub-class of the trace elements are "heavy metals", with a density of approx. 5000 kg/m³ or higher, such as Cd, Pb, Hg, Zn and Cu.

Table 2.2-1 shows	an elementary	biomass c	composition
	2		1

С	Н	0	Ν	Р	K	Na	S	Ca
40-47	6	40-44	0.1-5	0.05-0.8	0.3-5	0.02-0.5	0.05-0.8	0.3-5
Si	Mg	В	Cl	Cu	Fe	Mn	Zn	
0.05-3	0.05-1	0.005-	0.02-1	0.0002-	0.005-	0.002-	0.001-	
		0.01		0.002	0.1	0.03	0.01	

Table 2.2-1: Elementary biomass composition (dm) [w-%] (Kaltschmitt M.,2001)

2.2.1 Importance of some elements for biomass growth

Carbon, oxygen and hydrogen

Cellulose, hemicellulose and lignin mainly consist of carbon, oxygen and hydrogen, which are the most important elements in thermochemical utilisation processes. During the biomass oxidation, which is an exothermical reaction, energy is released. This energy release is caused by oxidation of carbon and hydrogen, oxygen affords the reaction. Therefore, the carbon and hydrogen content is responsible for the calorific value of the dry matter.

Nitrogen

Nitrogen is an essential nutrient for the growth of biomass. It is fixed into biomass mostly in organic form as biopolymers, proteins, alkaloids, etc. Nitrogen content in biomass is very different. Herbal biomass with higher proteins content contains more nitrogen than lignocellulose material such as woody biomass. High nitrogen content could be found in generative organs f.e. corn kernels. Rape, maize, sunflower and hemp straw are the typical biomass types, where high nitrogen content can be detected.

During the thermochemical process of biomass nitrogen is mostly conversed into HCN, NH_3 , NO, N_2O_3 or N_2O , which are released into the gas phase. Nitrogen oxides are harmful for the respiratory system and devastate forests.

Sulphur

Sulphur is an important element in biomass body. It is fixed in proteins, amino acids and enzymes. Sulphur is important by metabolism processes. It is also an important substance of fertilizers.

Sulphur compounds release into the gas phase during thermochemical process (pyrolysis, gasification, combustion) in form of alkali sulphates and SOx (SO₂ and SO₃), which could be modified in atmosphere into H_2SO_4 .

Chlorine

Chlorine plays a very important role during the oxygen supply for the biomass. Chlorine reacts with hydrogen during the thermochemical conversion and HCl, which is formed during the process releases to the gas phase. HCl, besides H_2SO_4 , causes acid rain.

Alkali metals

Potassium is important for water regime of the biomass, the taste of fruits and it has also antifreeze effect. The role of sodium is not really clear, but it is supposed that it takes part in the metabolism processes.

2.3 Conversion technology – energetic use of biomass

The simplest, cheapest and most common method of obtaining energy from biomass is direct combustion. Any organic material with a water content low enough to allow a sustained combustion can be burned to produce energy. The heat from the combustion can be used to provide process heat, water heating or by the use of a steam turbine, electricity. In the developing countries, many types of biomass such as dung and agricultural wastes are burned for cooking and heating.

Virtually all biomass products can be converted into commercial fuels, suitable to substitute the fossil fuels. These fuels can be used for transportation, heating, electricity generation, etc. Wood and many other similar types of biomass which contain lignin and cellulose, (agricultural wastes, cotton gin waste, wood wastes, peanut hulls etc.) can be converted during thermochemical processes into solid, liquid or gaseous fuels. Pyrolysis, used to produce charcoal since the dawn of civilization, is still a common thermochemical conversion process of biomass to produce commercial fuel.



Figure 2.3-1: History of charcoal

During the pyrolysis, biomass is heated in the absence of air and breaks down into a mixture of liquids, gases and a residual char. If wood is used as the feedstock, the residual char is what is commonly known as charcoal. With more modern technologies, pyrolysis can be carried out under a variety of conditions to capture all the components, and to maximize the output of the desired product (char, liquid or gas).

There are three main possibilities of biomass conversion technologies:

- Thermochemical conversion
- Biochemical conversion
- Physicochemical conversion

2.3.1 Thermochemical conversion

Heating up and drying

The first step of each biomass thermochemical conversion is heating up and drying. At temperature up to about 200°C the biomass particle is heated up and during this step free bond water and water bond in organic matter is transformed into steam which releases from the biomass particle. This process is endothermic and it is necessary to donate energy.

The biomass particle cell wall could be cracked by extremely high heating rates, this can happen especially in the case of the wood from needle-leaved trees. Biomass macromolecules

are not decomposed yet. The decomposition of macromolecules starts with rising temperature over 200°C.

Pyrolysis

Biomass pyrolysis is the thermal conversion of biomass particles in the absence of an externally supplied oxidizing agent (air, O₂, H₂O, CO₂, etc.). During this process the biomass macromolecules are decomposed. An important step during biomass pyrolysis is the release of volatiles. Devolatilization starts at temperatures of about 200°C and ends about 500°C. Pyrolysis products are mostly char, tars and low molecular gases. Factors such as heating rate, temperature, pressure and reaction time strongly influence the amount and composition of the formed products.

Gasification

Gasification is the complete thermal breakdown of the biomass particles into a combustible gas, volatiles and ash in an enclosed reactor (gasifier) in the presence of any externally supplied oxidizing agent (air, O_2 , H_2O , CO_2 , etc.) when equivalent ratio (ER) is < 1.

ER = 1 if the stoichiometric amount of oxidising agent is present. Stoichiometric amount is the theoretical amount of air or any other oxidizing agent required to burn the fuel completely. Gasification is an intermediate step between pyrolysis and combustion.

Gasification is a two-step, endothermic process. During the first step the volatile components of the fuel are vaporized at temperatures below 600°C by a set of complex reactions. No oxygen is needed in this phase of the process.

Hydrocarbon gases, hydrogen, carbon monoxide, carbon dioxide, tar and water vapour are included in the volatile vapours. Char (fixed carbon) and ash are the by-products of the process which are not vaporized. In the second step, char is gasified through the reactions with oxygen, steam and hydrogen. Some of the unburned char is combusted to release the heat needed for the endothermic gasification reactions.

Main gasification products are gas, char, and tars. Gasification products, their composition and amount are strongly influenced by gasification agent, temperature, pressure, heating rate and fuel characteristics (composition, water content, granulometry). Gaseous products formed during the gasification may be further used for heating or electricity production. The main gas components are CO, CO_2 , H_2O , H_2 , CH_4 and other hydrocarbons.

Combustible gas, produced during gasification can be cleaned and used for the synthesis of special chemical products or for the generation of heat and/or electricity. Specific hydrogen – carbon monoxide mixtures (because of the production method or the final use) have the designation water gas, cracked gas, and methanol synthesis gas or oxo-synthesis gas.

The fundamental reactions of the synthesis gas chemistry are the methanol synthesis, Fischer – Tropsch synthesis, oxo-synthesis (hydroformylation) and methane synthesis; further synthesis gas reactions are being developed.

Gasification has the unique characteristic of being such a technology that can even convert waste (from MSW to agricultural or crop residues, like coconut shells, rice husks, straw, wood residues, bagasse, etc.) to a useful and high quality energy source. It is known how complicated the disposal of any kind of waste is, nowadays due to environmental regulations and legislations. Gasification gives the advantage of separating the noxious substances from the fuel gas prior to the combustion.

Combustion (oxidation)

Products from pyrolysis and gasification processes are fully oxidized during the combustion process. For fully oxidation presence of the sufficient amount of oxygen is necessary (min. ER = 1). Oxygen must be well mixed with the gases formed during the combustion process. By this process heat is discharged and the temperature in conversion reactor rises up. With rising temperature reaction kinetics rises exponentially. Combustion products after fully oxidation are ash, CO₂ and H₂O. The heat produced during this exothermical process can be used directly or converted into mechanical or electrical energy.

2.3.2 Main pyrolysis reactions



Activation energies: $k_1 < k_2 < k_3$ (k_4 at temperatures $< 650^{\circ}$ C)

Figure 2.3.2-1: Schematic description of the main pyrolysis reactions

During the reaction k_1 , products such as char, CO₂ and H₂O are observed. This pyrolysis reaction is performed under the lower temperature range. At higher temperatures, the reaction k_2 proceeds. The main products are liquids and this temperature rate responds the flash pyrolysis. During the following reaction k_4 can be these liquid products converted into the gas by secondary cracking process. At very high temperatures (reaction k_3) biomass is converted into the gas, where CO, H₂ and CH₄ are the main gas components.

Primary devolat	ilizati	on		
		Primary tar (CH _x O _y)		
Biomass	\rightarrow	CO, CO ₂ , CH ₄ , C ₂ H ₄ , H ₂ O		[eq.2.3.3-1]
		Carbon		
Tar cracking an	d refo	rming		
		Secondary tar		
Primary tar	\rightarrow	CO, CO ₂ , CH ₄ , C ₂ H ₄ , H ₂		[eq. 2.3.3-2]
Homogenous gas	s-phas	e-reactions	ΔH	
Secondary tars	\rightarrow	C, CO, H ₂		[eq. 2.3.3-3]
$H_2 + 0,5 O_2$	\rightarrow	H_2O	-242 kJ/mol	[eq. 2.3.3-4]
$CO + 0,5 O_2$	\rightarrow	CO_2	-283 kJ/mol	[eq. 2.3.3-5]
$CH_4 + 0,5 O_2$	\rightarrow	$CO + 2 H_2$	-110 kJ/mol	[eq. 2.3.3-6]
$CH_4 + CO_2$	\rightarrow	$2 \text{ CO} + 2 \text{ H}_2$	+247 kJ/mol	[eq. 2.3.3-7]
$CH_4 + H_2O$	\rightarrow	$CO + 3 H_2$	+206 kJ/mol	[eq. 2.3.3-8]
$\rm CO + H_2O$	\rightarrow	$CO_2 + H_2$	-40,9 kJ/mol	[eq. 2.3.3-9]
Heterogenous re	action			
$C + O_2$	\rightarrow	CO_2	-393,5 kJ/mol	[eq. 2.3.3-10]
$C + 0,5 O_2$	\rightarrow	СО	-123,1 kJ/mol	[eq. 2.3.3-11]
$C + CO_2$	\rightarrow	2 CO	+159,9 kJ/mol	[eq. 2.3.3-12]
$C + H_2O$	\rightarrow	$CO + H_2$	+118,5 kJ/mol	[eq. 2.3.3-13]
$C + 2 H_2$	\rightarrow	CH_4	-87,5 kJ/mol	[eq. 2.3.3-14]
[eq. 2.3.3-4]		H ₂ – Combustion (oxidation)		
[eq. 2.3.3-5]		CO - Combustion (oxidation)		
[eq. 2.3.3-6]		CH ₄ - Combustion (oxidation)		
[eq. 2.3.3-7]		Dry reforming reaction		
[eq. 2.3.3-8]		Steam reforming methanisation		
[eq. 2.3.3-9]		Water-gas-shift reaction		
[eq. 2.3.3-10]		Oxidation of carbon		
[eq. 2.3.3-11]		Partial oxidation		
[eq. 2.3.3-12]		Boudoard equilibrium		
[eq. 2.3.3-13]		Water gas reaction (steam		
		reforming)		
[eq. 2.3.3-14]		Methane production reaction		

2.3.3 Main gasification reaction

Table 2.3.3-1: Main reactions during biomass gasification (Ising, 2002)

2.4 Pyrolysis technologies

Based on the process temperatures, heating rates and final products, pyrolysis technologies can be divided into:

- flash pyrolysis
- slow pyrolysis

Flash pyrolysis is relatively new technology for producing liquid products, bio-oils used as energy sources for further use.

The aim of the flash pyrolysis is the maximal yield of the liquid final products and that is why it is necessary keep to the following terms:

- very fast heating up of the biomass particles (heating rates higher than 1000°C/s)
- the residence time of the final products in the reactor shorter than 1 s
- fast and effective removing of the liquid products

Flash pyrolysis is performed in special reactors:

- stationary fluidized bed reactors
- circulating fluidized bed reactors
- reactors with ablative effect
- vacuum reactors

Figure 2.4-1 gives a flash-pyrolysis reactors overview.



Figure 2.4-1: Flash-pyrolysis reactors: a - stationary fluidized bed reactor, b - circulating fluidized bed reactor, c, d, e - reactors with ablative effect, f - vacuum reactor (Hofbauer, 2003)

Slow pyrolysis is used for production of char coal and is used for many years (history of charcoal – figure 2.3-1), but today slowly pyrolysis loses its importance.

2.5 Gasification technologies

Gasification process takes place in a conversion unit usually called gasifier. There are several types of gasifiers.

Gasifiers can be classified:

- according to the oxidant
- air-blown gasifiers
- oxygen/steam gasifiers
- according to the heat supply for gasification:
- autothermal gasifiers
- allothermal gasifiers

- according to the design of fuel bed:

- fixed bed gasifiers
- fluidized bed gasifiers
- entrained flow gasifiers

- according to pressure:

- atmospheric gasifiers
- pressurized gasifiers

- according to the fuel gas end use:

- heat gasifiers
- power gasifiers

Heat gasifiers are used to power external burners in boilers, kilns or dryers. Power gasifiers are coupled to the internal combustion engines or gas turbines for shaft power producing.

Classification	Туре	Mode of contact
Dense phase	Updraft	Solid moves down, gas moves up
reactors - Fix	Downdraft	Solid moves down, gas moves down
bed gasifier	Cocurrent	Both solid and gas move in the same direction
	Countercurrent	Solid and gas move in opposite directions
	Crosscurrent	Solid moves down, gas moves at right angles
	Variations	Stirred bed; Two stage gasifier
	Moving bed	Mechanical transport of solid. Low temperature
		processes. Includes: multiple hearth, horizontal moving
		bed, sloping hearth, and screw/auger kiln.
Lean Phase	Bubbling	Low gas velocity, inert solid stays in reactor.
reactors -	fluidized-bed	
fluidized-bed	Fast fluidized-	Inert solid is elutriated with product gas and recycled.
gasifier and	bed	
entrained-bed	Circulating	Inert solid is elutriated, seperated, and recirculated.
gasifier	fluidized-bed	This sometimes also refers to fast fluidized-bed or twin
		reactor system.
	Entrained flow	Usually no inert solid. Highest gas velocity, can be
	bed	operated as a cyclonic reactor.
	Twin	Steam gasification and /or pyrolysis occur in the first
	fluidized-bed	reactor. Char is combusted in the second reactor to heat
		the fluidising medium for recirculation. Either can be
		any type of fluidized-bed, although the combustor is
		often a bubbling fluidized-bed.

Table 2.5-1: Classification of biomass gasifiers



B -biomass P - producer gas

Figure 2.5-1: Different types of gasifiers

The composition of the gas and the level of undesirable components (tars, dust, ash content) produced during biomass gasification process are dependent on many factors such as feedstock composition, reactor type and operating parameters (temperature, pressure, ER).

	Tempera	ture [°C]					MW	el
	Reaction	Exit gas	Tars	Particulates	Turn	Scale-up	min	max
					down	ability		
Downdraft	1000	800	v. low	moderate	good	poor	0.1	1
Updraft	1000	250	v. high	moderate	good	good	1	10
Stationary	850	800	mediu	high	good	good	1	20
fluidized			m					
bed								
Circulating	850	850	low	v. high	good	v. good	2	100
fluidized				_		_		
bed								
Entrained	1000	1000	low	v. high	poor	good	5	500
flow								

 Table 2.5-2: Typical gasifier characteristics (Bridgwater, 1995)

Compound		Air gasification	Steam gasification
СО	Vol. %	10-15	20-25
CO ₂	Vol. %	10-15	20-25
H ₂	Vol. %	15-20	30-40
CH ₄	Vol. %	3-5	6-12
N ₂	Vol. %	45-55	1-5
LHV	MJ/Nm ³	4-6	10-14

Table 2.5-3: Typical composition of a dry product gas during the biomass gasification

Typical composition of a dry gas produced during the biomass gasification process is shown in table 2.5-3. As can be seen, the concentration of the gas compounds during air and steam gasification is completely different.

During the air gasification, air is used as a fluidizing agent (air contains about 78 vol.-% of nitrogen), that is why the nitrogen concentration in the product gas is very high contrary to steam gasification. Nitrogen in the product gas during the steam gasification originates from the fuel and its concentration is low.

On the other hand the higher amount of hydrogen in the product gas can be found during the steam gasification. The hydrogen found in the product gas does not originate only from the fuel as in the case of air gasification but also from the steam (H_2O).

2.6 Pyrolysis and gasification using fluidized bed reactors

Fluidized bed is formed by the bed material particles (quartz sand, olivine, calcite, dolomite etc.) if the resistance strength of the gas flow coming into the reactor (from the bottom of the reactor) equals the mass weight of all particles. This term can be expressed using the following formula.

$$\Delta \mathbf{P} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{H}_{\mathrm{L}} \cdot (1 - \varepsilon_{\mathrm{L}}) \cdot (\rho_{\mathrm{p}} - \rho_{\mathrm{g}}) \cdot \mathbf{g} \qquad [\mathrm{eq.}\ 2.6\text{-}1]$$

А	Cross-section area of fluidized bed	$[m^2]$
H_L	Height of the bed at minimum fluidization velocity	[m]
$\epsilon_{\rm L}$	Porosity at minimum fluidization velocity	[-]
g	Gravitation parameter	$[m/s^2]$

Pressure loss is independent on the velocity of the gas flow; it means it is constant in each place of the fluidized bed.

$$\Delta \mathbf{P} = (1 - \varepsilon_{\mathrm{L}}) \cdot (\rho_{\mathrm{p}} - \rho_{\mathrm{g}}) \cdot \mathbf{g} \cdot \mathbf{H}_{\mathrm{L}} \qquad [\mathrm{eq.}\ 2.6\text{-}2]$$

Minimal fluidization velocity is the velocity of the gas coming into the reactor, which is necessary for fluidization of the bed material.

$$U_{\rm L} = \frac{\mu}{\rho_g d_{sv}} \left[\sqrt{33.7^2 + 0.0408.Ar} - 33.7 \right]$$
 [eq. 2.6-3]

Ar =
$$\frac{\rho_g d_{sv}^{3} (\rho_p - \rho_g) g}{\mu^2}$$
 [eq. 2.6-4]

U_L	Minimal fluidization velocity	[m/s]
μ	Dynamic viscosity	[kg/ms]

 ho_g Density of gas $[kg/m^3]$

$$U_{s} = \sqrt{\frac{4}{3} \cdot \frac{\rho_{p} - \rho_{g}}{\rho_{g}} \cdot \frac{d_{p} \cdot g}{C_{w}}}$$
[eq. 2.6-5]

[m/s]

C_W	Resistance parameter of spherical partical	[-]

Terminal velocity

 U_{S}

		Pyrolysis	Gasification		
Bed material		Quartzsand	Quartzsand	Olivine	Calcite
Particle diameter	[mm]	0.315	0.25	0.25	0.25
Density of bed material	$[kg/m^3]$	2600	2600	2900	2710
Temperature	[°C]	850	850	850	850
Density of gas at 850°C	$[kg/m^3]$	0.304	0.301	0.301	0.301
Viscosity at 850°C	[Pas]	0.0000442	0.0000442	0.0000442	0.0000442
Ar	[-]	124	61	69	64
UL	[m/s]	0.035	0.022	0.024	0.023
U _{S0}	[m/s]	2.21	1.53	1.68	1.59
Re	[-]	4.79	2.61	2.86	2.71
Cw	[-]	7.24	12.08	11.14	11.68
Us	[m/s]	2.21	1.53	1.68	1.59

Table 2.6-1 shows the values used during experimental work when biomass pyrolysis and gasification were performed at 850°C.

Table 2.6-1: Values used during experimental work

Ar – Archimedes number

Re-Reynolds number

3 Elements behaviour during the thermochemical conversion processes – literature overview

The behaviour of elements during thermochemical conversions, respective their distribution into gas, liquid and solid phase after the conversion process is a complex process which is influenced by many factors. Such factors are: conversion temperature, pressure, heating rate, equivalent ratio, oxidizing agent (air, oxygen, steam...), moisture of the fuel, particle size, fuel composition, residence time of the fuel particle in the conversion unit etc.

The most important step in the elements behaviour is the volatiles release. The conditions of the devolatilization influence largely the distribution of each element in the gas, solid or liquid phase.

In this work the attention was paid to the following elements: sulphur, nitrogen, chlorine, alkali and some heavy metals, which are the most harmful ones for environment, may disturb the conversion process and may cause serious damage of the conversion units.

3.1 Sulphur

Sulphur is an important element in the biomass structure; it is fixed in proteins, amino acids and enzymes. Sulphur is important for the metabolism processes. It is also an important substance of fertilizers.

Sulphur and its compounds released in higher concentrations into the atmosphere cause acid rain, which damages lakes and forests. Sulphur can cause serious corrosion problems in the conversion units and finally, sulphur can deactivate catalysts in the conversion units.

Biomass contains less than 0.1 w-% of sulphur and in comparison with a low sulphur coal, which has a sulphur content of approximately 0.5-4 w-%, the sulphur content in untreated biomass is negligible. That is why there are no serious problems expected, when clean natural woody biomass is used during the thermochemical conversion process.



Figure 3.1-1: Sulphur content in different types of biomass (Hofbauer, 2003)

Sulphur from biomass after the thermical conversion is mostly found as H_2S , COS, CH₃SH, CS₂, SO₂, and mercaptanes. Sulphur is also bond in form of sulphides (FeS, ZnS, MnS, PbS, Ni₃S₂ and Cu₂S). FeS and ZnS are the major sulphides.

Kuramochi at al.,(2005) predicted the behaviour of H_2S during the gasification of several biomass types (demolition wood, verge grass, sewage sludge, bio-dried wood by composting, railroad ties and cacao shells) at various temperatures from 400 to 1200°C using the thermodynamic equilibrium model based on a free energy minimization.

The conditions used during the calculations were:

- Air-blown circulation fluidized-bed gasifier
- ER = 0.32 0.43
- Pressure 0.1 MPa

The results of their calculations can be seen in the following figures.



Figure 3.1-2: Equilibrium concentration of H₂S calculated for biomass gasification: (a) demolition wood, (b) verge grass, (c) sewage sludge, (d) bio-dried wood, (e) railroad ties, (f) cacao shells

As can be seen in the figure, the concentration of H_2S produced during the biomass gasification is dependent on the biomass type, which means the sulphur concentration in biomass and gasification temperature. Maximum concentration of H_2S varied between 97 and 4000 ppm. From the feedstock composition and the calculations of H_2S emissions, a linear relationship between the maximum value of H_2S concentration and the sulphur content of the feedstock for all fuels was observed. This implies that the maximum concentration can be easily predicted based on the feedstock composition data and also that the sulphur in the feedstock is almost completely transformed to H_2S . At high temperatures (750 – 850°C) the H_2S concentration in the gas was constant (except sewage sludge) and proportional to the sulphur content of the feedstock.

On the other hand, differences in behaviour of H_2S among the biomass fuels were observed at lower temperatures. It means that not all of the reasons for the differences could be demonstrated based only the feedstock composition.

During the gasification process not only H_2S was formed but also sulphides such as: FeS, ZnS, MnS, PbS, Ni₃S₂ and Cu₂S. FeS and ZnS were the major sulphides. Kuramochi et al., (2005) deduced, that the retention of sulphur to those sulphides allowed the suppression of H_2S production at low temperatures.

Sulphur in product gas was measured during the biomass gasification in gasification plant in Güssing (Siefert, 2004). Figure 3.1-3 shows the scheme of the plant in Güssing.



Figure 3.1-3: Scheme of gasification plant in Güssing

Figure 3.1-4 shows the sulphur content in product gas in gasification plant in Güssing. The sulphur content in the product gas was measured after heat exchanger, after filter and after scrubber.



Summe aus H2S - Schwefel und Mercaptan - Schwefel im Produktgas

Figure 3.1-4: Sulphur content in product gas in Güssing plant (Siefert, 2004)

As can be seen in figure 3.1-4 the content of sulphur in product gas is about 200 mg/Nm³.

From literature review it can be concluded:

- Sulphur is fixed in biomass in proteins, aminoacids and enzymes
- During thermochemical processes sulphur is bond as H₂S, COS, CH₃ SH, CS₂, SO₂, mercaptanes and sulfides (FeS, ZnS, MnS, PbS). H₂S is the major compound.
- H₂S amount produced during gasification is dependent on sulphur content in biomass, process temperature and metal content in biomass (Fe, Zn, Pb, Ni, Cu, etc.)
- Sulphur can cause serious corrosion problems in the conversion units because of formation of H_2SO_4 , environmental problems (acid rain) and it is also able to deactivate the catalysts.

3.2 Nitrogen

Nitrogen is an essential nutrient for the biomass growth. It is incorporated in biomass as biopolymers, in a wide variety of structures such as proteins, DNA, RNA, alkaloids, porphyrin and chlorophyll (Tian et. al., 2004). Both the aliphatic and the heteroaromatic N-containing structures may be found in biomass. The concentration of nitrogen varies widely with the biomass type. While the nitrogen content of wood may be very low (much less than 1 w-%), the nitrogen content in a sewage sludge many be up to 8-9 w-%. An overview of different biomass types and their nitrogen content is shown in figure 3.2-1.



Figure 3.2-1: Nitrogen content in different types of biomass (Hofbauer, 2003)

The conversion of biomass nitrogen during the thermochemical processes has been studied in the last years. A large number of the model compounds believed to represent the typical Ncontaining structures in biomass. While it is known that both biomass properties (Ncontaining structures) and reaction conditions affect the distribution of the biomass nitrogen during its thermochemical conversion, the exact mechanisms of the biomass-nitrogen conversion remain imperfectly understood. The future widespread use of the biomass as a renewable energy source needs a better understanding of the conversion mechanism of the biomass nitrogen into NO_x and their precursors (HCN, NH_3) as well as into N_2 .

During the gasification biomass nitrogen is mostly conversed into NH_3 , HCN and N_2 or heavy aromatic compounds, while a smaller part of nitrogen remains in a solid char. Independent of the type of gasified feedstock, more NH_3 is formed than other nitrogen containing compounds in most gasifiers. The measured amount of NH_3 in the gas phase during the gasification seems to be dependent on the nitrogen content in biomass. The lower NH_3 concentration can be found in the gas during the wood gasification (wood contains about 1 w-% of nitrogen) and higher in the gas produced during the peat or coal gasification (peat and coal contain about 1.5-3 w-%).

The fraction of biomass nitrogen, which is converted into NH_3 is dependent on several parameters such as gasification temperature, heating rate, pressure, residence time of fuel particles in the conversion reactor and the nitrogen functionality in the fuel structure. In peat and wood gasification most of the fuel nitrogen is released during the pyrolysis stage. On the other hand during the coal gasification most of nitrogen remains in the char after the pyrolysis and releases during the char gasification stage (Leppälahti et al., 1994).

The pyrolysis studies of the model compounds have shown that the nitrogen from pyridine and pyrrole structures releases in form of HCN and from proteins and aminoacids in form NH₃.

Nitrogen chemistry in gasification

Schematically the reaction steps of the fuel nitrogen are presented in the following figure.



Figure 3.2-2: Behaviour of the nitrogen compounds during the gasification and combustion

During biomass pyrolysis and gasification processes nitrogen occurs in the gas mostly in form NH_{3} , HCN, HNCO and N_{2} . The most important NO_{x} precursors formed during the pyrolysis and gasification of biomass are NH_{3} and HCN.

There are three major routes of NH₃ formation:

- 'hydrolysis' of N-containing structures in the solid phase during the primary pyrolysis
- thermal cracking and gasification of the solid nascent char
- thermal cracking and reforming of volatile-N.

Tian et al. (Tian, 2004) studied the formation of NO_x precursors during the biomass (cane trash) and coal pyrolysis and gasification. Figure 3.2-3 shows some selected results.



Figure 3.2-3: HCN and NH₃ yields from the pyrolysis and gasification of cane trash (Tian et al., 2004)

It can be seen in the figure that under the pyrolysis conditions HCN is the dominant specie, whilst during the gasification it is NH₃.

The same result was presented by de Jong et al. (de Jong, 2003) in their study concerning pyrolysis of Miscanthus. They published, that during the pyrolysis of Miscanthus HCN and HNCO were found to be the major N-products, while the NH₃ fraction was detected to a minor extent.

Biomass devolatilization takes place already at temperatures lower than 600°C and at 700°C volatiles would have been swept out of the reactor. This means that the thermal cracking of volatiles might not have been taken place to the extents to produce significant amounts of HCN and NH₃. Formation of HCN during the pyrolysis and gasification may mainly originate from less stable organic structures. These N-containing structures might be relatively small heteroaromatic ring systems in the char.

Formation of NH₃ during pyrolysis and gasification at fast heating rates is shown in figure 3.2-4.


Figure 3.2-4: NH₃ formation during the pyrolysis and gasification conditions (Tian et al., 2004)

About 5% of the fuel nitrogen was converted into NH_3 during biomass pyrolysis at 400°C. The formation of NH_3 from the biomass at 400°C at both slow and fast heating rates is believed to have originated from the amino groups or similar structures (proteins).

The most important requirement for the formation of NH₃ from the solid char is the presence of H radicals to hydrogenate the char-N for form NH₃.

Figure 3.2-5 shows HCN yield as a function of temperature during the pyrolysis and gasification of the can trash in the fluidized bed reactor at a fast heating rate.



Figure 3.2-5: HCN yield during the pyrolysis and gasification conditions (Tian et al., 2004)

As it can be seen in the figure, slightly more HCN was measured during the pyrolysis of cane trash.

Zhou et al. (Zhou, 2000) studied the release of the fuel-bond nitrogen during biomass gasification using four types of biomass. They were interested in effect of ER and temperature during the biomass pyrolysis.

Effect of the temperature

Gasifier temperature was varied between 750 and 950°C for leucaena and between 700 and 900°C for sawdust at a constant ER of 0.25. The high levels of NH_3 in the product gas suggested that it might be the major nitrogenous species formed when the biomass was pyrolysed rapidly after the entering the gasifier. The conversion of NH_3 to N_2 is the dominant thermochemical process which determines the final fate of FBN (fuel-bound nitrogen) in the gas phase under the gasification conditions.

Temperature [°C]					
	750	800	850	900	950
N(NO _x)/N _{fuel} , %	0.06	0.04	0.02	0.02	0.01
N(NH ₃)/N _{fuel} , %	63.5	48.74	25.81	13.49	10.48
N(HCN)/N _{fuel} , %	0.11	0.09	0.08	0.07	0.07
N(char)/N _{fuel} , %	7.7	5.2	2.0	2.0	1.2
N(N ₂)/N _{fuel} , %	38.6	69.9	80.3	88.7	85.7

Table 3.2-1: The distribution of FBN among the nitrogenous species NH_3 , N_2 , NO and HCN during the gasification of leucaena at ER = 0,25 (Zhou et al., 2000)

As can be seen in table 3.2-1 the sum of nitrogen compounds in the gas e.g. at 800°C is 123.97 %. The authors (Zhou et al., 2000) did not explain exactly the reason of the sum higher than 100%.

Effect of the equivalent ratio

Contrary to the temperature, the ER did not significantly impact the concentrations of the nitrogenous species in gasified biomass.

Temperature [°C]						
	750	800	850	900	950	
	N(NH ₃)/N _{fuel} , %					
ER=0.18	63.1	50.5	27.6	12.8	10.6	
ER=0.25	63.5	40.5	24.0	16.0	18.2	
ER=0.32	47.2	44.7	27.6	11.0	17.4	
	N(N ₂)/N _{fuel} , %					
ER=0.18	37.8	67.8	97.6	108.2	114.9	
ER=0.25	38.6	69.9	80.3	88.7	85.7	
ER=0.32	42.3	51.0	67.8	81.0	90.6	

Table 3.2-2: The fuel nitrogen distribution into NH_3 and N_2 as a function of ER and temperature (Leucaena) (Zhou et al., 2000)

Effect of the feedstock

Figures 3.2-6 and 3.2-7 show the influence of the feedstock on NH_3 and NO production. In the feedstock tests, the gasifier temperature was set at 800°C and ER of 0.25.



Figure 3.2-6: NH₃ concentration for four types of the feedstock (Zhou et al., 2000)



Figure 3.2-7: NO concentration of four feedstocks (Zhou et al., 2000)

Feedstocks used by Zhou contained between 0.08 (sawdust) and 2.51 w-% (leucaena) of fuel bond nitrogen. The amount of NH₃ is clearly impacted by the nitrogen content of the feedstock. The NH₃ content for gasified sawdust was only about 400 ppm, in comparison with the approximately 18000 ppm of NH₃ detected for leucaena.

The results indicated that NO levels are inversely affected by the fuel nitrogen content. Sawdust, which has the lowest nitrogen content, produced a gas with the highest NO concentrations.



NO and HCN concentrations vs temperature (ER = 0.25, leucaena). Nitrogen species concentration vs temperature (ER = 0.25, sawdust

Figure 3.2-8: Nitrogen species during the biomass gasification (Zhou et al., 2000)



 NH_3 and N_2 concentrations vs temperature (ER = 0.25, leucaena).

Figure 3.2-9: NH_3 and N_2 concentrations during the biomass gasification (Zhou et al., 2000)

The major gas-phase nitrogenous species generated during the biomass gasification include NH_3 , N_2 , NO_x and HCN. Most of the fuel-bond nitrogen in the feedstock is converted to NH_3 and N_2 during the gasification. HCN and NO_x are present at very low concentrations in the product gas. N_2 appears to be produced primarily by the thermochemical conversion of NH_3 . Concentrations of the nitrogen species generally depend strongly on the temperature and weakly on the equivalence ratio over the range of conditions examined. As the temperature increases the amount of NH_3 decreases sharply while the amount of N_2 rises.

Nitrogen in form NH_3 was measured in product gas in gasification plant in Güssing. Figure 3.2-10 shows the results from measurements.



Figure 3.2-10: NH₃ in product gas measured in Güssing (Siefert, 2004)

 NH_3 was measured after heat exchanger, after filter and after scrubber. As can be seen in the figure 3.2-10 the amount of NH_3 measured after scrubber was about 700 mg/Nm³.

From literature it can be concluded:

- Nitrogen is incorporated in biomass as biopolymers, in a wide variety of structures such as proteins, DNA, RNA, alkaloids, porphyrin and chlorophyll
- The concentration of nitrogen varies widely with the biomass type. While the nitrogen content of wood may be very low (much less than 1 w-%), the nitrogen content in a sewage sludge many be up to 8-9 w-%
- During the gasification biomass nitrogen is mostly conversed into NH₃, HCN and N₂ or heavy aromatic compounds, while a smaller part of nitrogen remains in a solid char.
- Independent of the type of gasified feedstock, more NH₃ is formed than other nitrogen containing compounds in most gasifiers. The measured amount of NH₃ in the gas phase during the gasification seems to be dependent on the nitrogen content in biomass, gasification temperature, heating rate, pressure, residence time of fuel particle in the conversion reactor and the nitrogen functionality in the fuel structure
- The pyrolysis studies have shown that nitrogen from pyridine and pyrrole structures (less stable structures) releases in form of HCN and from proteins and aminoacids in form NH₃

- There are three major routes of NH₃ formation: 'hydrolysis' of N-containing structures in the solid phase during the primary pyrolysis, thermal cracking and gasification of the solid nascent char and thermal cracking and reforming of volatile-N.
- The most important requirement for the formation of NH₃ from the solid char is the presence of H radicals to hydrogenate the char-N for form NH₃

3.3 Chlorine

Chlorine content in biomass varies between 0.005 w-% (wood) and 1.5 w-% (maize). The chlorine content in biomass can be influenced by closeness of the sea, fertilizers and leaching by the rain. Figure 3.3-1 shows the chlorine content of several types of biomass.



Figure 3.3-1: Chlorine content in biomass (Hofbauer, 2003)

Emission of the hydrogen chloride is the third most important contribution to the global acidification from human activities. The first two are SO_2 and NO_x . HCl is a local pollutant, contrary to the other two, since it is easily dissolved in rain droplets and, therefore, usually falls down near the emission source. The major part of the estimated global contribution of

HCl to the atmosphere is evaporation from seas. Even with a redeposition of 90% HCl to the seas, the estimated emission will reach approximately 120 Mt/year. The hydrogen chloride emission from combustion and gasification processes has been calculated to 3,5 Mt/year (Björkman et al., 1997).

The other source of HCl in the atmosphere is methyl chlorine (CH₃Cl), which reacts with the OH radical and forms HCl. The main emission producers of CH₃Cl are microorganisms, marine plants on the sea and burning of the vegetation on land. The total amount of HCl produced from CH₃Cl in the atmosphere has been estimated to 4 Mt/year. Chlorine together with alkali metals has been shown to play an important role in the deposits formation during the biomass thermochemical conversion processes.

The distribution of chlorine between gas, liquid and solid phase during the biomass conversion processes (pyrolysis, gasification and combustion) is dependent on the pressure and the temperature.

Björkmann et al. (Björkmann, 1997) studied the chlorine distribution during the biomass gasification. Thermodynamic calculation of the peat pressurized gasification (10 bar) showed that at 800°C the gas phase was dominating. Furthermore, the composition of the gas phase is also dependent on the temperature. The dominating Cl-containing compound below 600°C was HCl (g) but above 800°C KCl (g) dominated, followed by NaCl (g).

Major Cl-containing compounds released during gasification of biomass (switch grass) at 800°C are HCl and KCl, which are formed both in the devolatilization and in the char combustion phase.

Björkmann et al. (Björkmann, 1997) deduced based on the experimental work that chlorine release is independent on the heating rate and pyrolysis/gasification conditions (different gasifying atmospheres: N_2 , $N_2 + 10\%$ H₂O, $N_2 + 2\%$ O₂, CO₂)

Increased pressure also did not significantly affect the chlorine release reactions. At elevated pressures the chlorine reactions were slower but still significant amount of chlorine released at the higher temperatures.

It is known, that about 90% of chlorine, which is in the biomass mostly bond as KCl (especially grass) is water soluble. KCl is also one of the most stable alkali containing compounds in the gas phase at higher temperature (800°C and above) under gasification and combustion conditions. In many cases, the amount of the alkali vaporized during biomass thermal conversion is more dependent on the amount of available chlorine to form stable vapours than by the amount of alkali in the fuel.

The main part of the chlorine in biomass is in an inorganic form and therefore should not vaporize appreciably below the melting point of the corresponding salt (around 700°C).

Contrary to this hypothesis, the results from practical work showed that during biomass pyrolysis about 80% of chlorine evaporated already at 400°C. One possible explanation for chlorine release is that KCl reacts with steam formed from the biomass itself to give a gaseous HCl and KOH. Equilibrium calculations showed that this formation is small. But if an acidic oxide is added (e.g. SiO₂), the formation of HCl (g) is significant and coupled to the formation of potassium silicates. The proposed reaction is shown below:

$$2\mathrm{KCl} + n\mathrm{SiO}_2 + \mathrm{H}_2\mathrm{O}(\mathrm{g}) \rightarrow \mathrm{K}_2\mathrm{O}(\mathrm{SiO}_2)_n + 2\mathrm{HCl}(\mathrm{g}) \qquad [\mathrm{eq. 3.3-1}]$$

This reaction seems to be important already at 400°C. It means that even if the chlorine in biomass is bond as inorganic salt, it can leave at temperatures below the corresponding melting point of the salt during pyrolysis process. The amount of HCl(g) and potassium silicate increases with temperature and steam concentration. HCl can cause corrosion problems in operation systems during the conversion process.

Björkmann et al. (Björkmann, 1997) deduced based on their work that the chlorine release reactions are governed by the solid phase and cannot be induced by gas phase reactions only.

Jensen et al. (Jensen, 2000) provided further experimental work concerning the chlorine behaviour during the straw pyrolysis. Straw contains 0.1-1.1 w-% of chlorine.

At temperatures of 200-400°C, much of the original organic straw matrix is destructed and the chlorine is probably released from the original binding sites and transferred into the liquid tar phase and further to the gas phase as HCl, or reacts with K on the char surface. Chlorine releases in two steps. Jensen et al. (Jensen, 2000) reported that at temperatures between 200 and 400°C 20-60% of chlorine was released. At temperatures of 400-700°C no significant amount of chlorine was released. At temperature between 700-900°C almost all chlorine retaining in the biomass is released into the gas phase. Chlorine releases in form of HCl or bond with potassium as KCl. The work presented by Jensen et al. showed that chlorine bond as KCl released to the gas phase at temperature between 680-830°C.



Figure 3.3-2: Chlorine release to gas phase and total volatiles (Jensen et al., 2000)

Jensen et al. (Jensen, 2000) performed pyrolysis tests also under a lower heating rate, about 25 °C/min. The chlorine release at 500°C was 12-14%. These experiments indicated that applying a low heating rate or a large sample size results in a significantly reduced Cl release.

Kuramoshi et al. (Kuramoshi, 2005) predicted the behaviour of HCl during gasification of selected residual biomass fuels by equilibrium calculation. They used elements content of biomass types such as demolition wood, verge grass, sewage sludge, bio-dried wood, railroad ties and cacao shells in the calculations.

They deduced from the calculations that not the entire chorine in the feedstock is transformed to HCl. During gasification chlorine almost forms solid KCl at low temperatures of up to 550-600°C. Formation of KCl leads to lower HCl emission at low temperatures. Besides solid KCl, the formation of NaCl is expected to contribute to the removal of HCl. At higher temperatures, the solid KCl is partially transformed to vapor phase as KCl gas. The rest of chlorine is transformed to HCl and NaCl gases.

Figure 3.3-3 shows the distribution of chlorides under gasification conditions at different temperatures.



Figure 3.3-3: Distribution of chlorides under gasification conditions at different temperatures (a=demolition wood, b=verge grass)

Besides KCl, also $K_2Si_aO_b$ was observed during gasification and $KAlSi_xO_y$ when aluminium was present.

The HCl emission depends further on the ratio K/Si in the biomass and also the ratio Si/Ca is considered to be an important factor in the reduction of HCl emission during gasification in the presence of aluminium. Finally, the following composition is desired for low HCl emission:

- 1. K/Cl » (or >) 1
- 2. K/Si » 1 for biomass fuels without aluminium
- 3. Si/Ca < 1 for biomass fuels with aluminium

If the K content is lower than the content of either Al or Si in feedstock such as in sewage sludge, the HCl emission is relatively higher in all temperature ranges due to lack of KCl. Although KCl forms easily during gasification in the presence of potassium, it should be noted that there is a specific composition that makes the formation of KCl impossible (see the following figure).



Figure 3.3-4: Phase diagram at 600°C (Kuramoshi et al., 2005)

In the grey area, no solid KCl is formed. Lower content of K causes the increase of the KCl decomposition area.

Kuramoshi et al. (Kuramoshi, 2005) studied the mixing effect of potassium-rich biomass for the reduction of HCl. The potassium-rich biomass with low chlorine content (e. g. cacao shells) can lead to much lower HCl emission (below 0.1 ppm) during gasification. However, the potassium-rich biomass with the high content of chlorine and silicon (e.g. verge grass), can not provide low emission of HCl. They expected that addition of cacao shells to the demolition wood with relatively low content of chlorine and silicon has the potential to reduce the HCl emission. During gasification, when the cacao shells were added to the demolition wood, the similar amount of HCl was produced as in the case, when only cacao shells were gasified and HCl emission was noticeably reduced. Using this blending effect, gasification without dechlorination equipment could be carried out for limited biomass fuels with low content of chlorine and silicon. The effect also induces several economical advantages, such as low capital and running cots, as well as the reduction of the poisonous and hazardous gas.

Chlorine content in product gas, which was measured in gasification plant Güssing is shown in figure 3.3-5.

Chlorgehalt im Produktgas



Figure 3.3-5: Chlorine content in product gas (Siefert, 2004)

Chlorine content was in Güssing plant measured after heat exchanger, before and after scrubber. Chlorine was detected in form HCl.

From literature it can be concluded:

- Chlorine content in biomass varies between 0.005 w-% (wood) and 1.5 w-% (maize). The chlorine content in biomass can be influenced by closeness of the sea, fertilizers and leaching by the rain
- Emission of the hydrogen chloride is the third most important contribution to the global acidification from human activities. The first two are SO₂ and NO_x. HCl is a local pollutant, contrary to the other two, since it is easily dissolved in rain droplets and, therefore, usually falls down near the emission source
- The distribution of chlorine between gas, liquid and solid phase during the biomass conversion processes (pyrolysis, gasification and combustion) is dependent on the pressure and the temperature.
- About 90% of chlorine, which is in the biomass mostly bond as KCl (especially grass) is water soluble
- Chlorine releases in form of HCl or bond with potassium as KCl or sodium NaCl
- Although KCl forms easily during gasification in the presence of potassium, there is a specific composition that makes the formation of KCl impossible (see figure 3.3-4)

3.4 Alkali metals

Alkali compound emissions during thermochemical conversion of biomass cause problems such as agglomeration, slagging (formation of sintered deposits on the heat transfer surfaces or refractories subjected to radiative heat transfer), fouling (deposition of ash on the convective heat transfer section of the steam generator at temperatures below the melting point of the ash) and metal corrosion in the conversion process systems. Understanding the behavior of alkali metals emissions from the biomass fuels is very important for the solving these problems.

Alkali metals are in fossil fuels and the biomass bound organically and inorganically in form of salts such as chlorides, sulphates or hydroxides. In biomass potassium is found especially in the fast growing parts of trees, in the straw, grass and in corn hulls. Much of this alkali is present in water-soluble or ion-exchangeable forms. (Straw harvested after a wet summer contains significantly lower alkali.) Sodium is often incorporated as sandy inclusions or as NaCl from seawater.

The following table presents alkali content in some fossil, biomass and waste-derived fuels.

	Coal	Lignite	Peat	Wood	Straw	RDF	Sew.
				saw dust			sludge
Na	100-1500	100-300	400	40	100-5000	3000-	2000
						5000	
K	50-3000	100-1000	700	300-500	5000-	2000-	6000
					10000	3000	

Table 3.4-1: Alkali concentrations in some fossil fuels and waste-derived fuels (in mg/kg, dry) (Zevenhoven, Kilpinen, 2001)

Typical levels of K in biomass such as straw are five times higher than those found in coal. Na concentrations are usually higher in coal than in the biomass. It can be the reason why the potassium behaviour is in focus of interest of many authors more often than the sodium behaviour.

3.4.1 Sodium

The most important sodium vapor phase species are NaOH and NaCl. Under high temperature and reducing conditions in a flame, elemental Na is the most common specie, except for the high chlorine coal (Srinivasachar et al., 1990). After the release of sodium in form of NaOH, Na or NaCl it may react with the char and ash-forming matter to produce silicates and sulphur compounds, and later NaCl and Na₂SO₄ can be formed. Slagging and fouling result from the low-melting point of silicates and sulphates.

3.4.2 Potassium

Potassium content in biomass varies in a wide range from 0.03 w-% (wood) to 2.5 w-% (straw). Potassium can be found in biomass as dissolved salts in the moisture or as a cation attached to carboxylic and other functional groups, which is highly mobile. It is most possibly bond to chlorine as KCl if chlorine is available in biomass fuels. The most possible potassium compounds released from the biofuels are KCl, K_2SO_4 and KOH.

Potassium releases to the gas phase in two stages. The first stage is at temperature range of 200°C to 500°C. The potassium release at lower temperatures can be well coupled to biomass devolatilization and insensitive to the chlorine content in the biomass. In this first stage the organic bond potassium releases following the devolatilization of the biomass constituents, cellulose, hemicellulose and lignin. In the second stage at temperatures above 500°C, the potassium releases at full speed, depending on chlorine presence in the fuel. In this stage, potassium releases in form of KCl and KOH.

Organic and inorganic bond potassium can be determined experimentally based on the solubility in a series of increasingly aggressive solvents. Those materials soluble in water are soluble salts and loosely bonded material. Those soluble in ammonium acetate solvent are the organic bounded materials (ion exchangeable by ammonium acetate). Those materials soluble in hydrochloric acid are typically carbonates or sulphates. Those materials not soluble in any of these solvents are commonly in the form of oxides, silicates or sulfides.

Jensen et al. (Jensen, 2000) investigated the transformation and release of potassium to the gas phase during straw pyrolysis. They assumed that potassium in the biomass exists as ions bound onto oxygen-containing functional groups in the organic matrix, or as discrete KCl particles. It has been demonstrated that the presence of potassium in the straw modifies the final distribution of the evolved gas, tar and char, showing that potassium strongly interacts with the organic matrix. During the pyrolysis the original binding sites of K may be destroyed and K may be released to the gas phase, bound to mineral particles or bound to the organic matrix of the char.

It is possible that K binds to non-volatile minerals during the pyrolysis process. Both the binding of the K to the char matrix and the reaction of K with SiO_2 may prevent the release to the gas phase at low temperatures. Release to gas phase of potassium as a function of pyrolysis temperature during the straw pyrolysis can be seen in figure 3.4.2-1.



Figure 3.4.2-1: Potassium release to the gas phase during the straw pyrolysis (Jensen et al., 2000)

A few experimental investigations of alkali release during the biomass pyrolysis have been published. The main gas-phase products containing chlorine or potassium were HCl during the volatile combustion phase and KCl and KOH during the char combustion phase. Also K^+ was detected by the mass spectrometer, possibly originating from the release of K, KOH or K_2SO_4 .

No quantification of the total release of potassium bond in straw was published yet, but the relative release of KCl (compared to the total K content in the switch grass) was measured by Dayton et al. (Dayton, 1995) to be approximately 23% at a combustion temperature of 1100°C.

A quantification of potassium release from wood ash as a function of temperature has been carried out by Misra et al. (Misra, 1993). The ash was prepared by oxidation at 500°C. Most potassium was released from the ash between 800-1300°C.

Yu et al. (Yu, 2000) provided modelling of potassium release during the straw pyrolysis. They published that potassium fixed as KOH evaporated at temperature of 800°C and hold a whole vaporization rate as the temperature was kept about 900°C. KCl vaporization, on the other hand, started at a higher temperature of about 850°C and hold a low vaporization rate under the same condition. After vaporization, KOH may be converted into KCl by reaction with HCl depending on chlorine content in biomass.

They observed that only a small amount of potassium released during the biomass devolatilization stage due to the limited content of organic bond potassium in the fuel (in the case of straw about 13%). The main potassium release occurred at a higher temperature (above 800°C) by means of vaporization of potassium compounds. The pyrolysis temperature, the fuel properties and the residence time influenced significantly the potassium release to the

gas phase. It means that the lower pyrolysis and gasification temperatures (under 900°C) offer a great advantage when biofuels with a high alkalis content are treated.

Olsson and Pettersson (Olsson, Pettersson, 1998) assumed that alkali metals are the key elements in the formation of ultra fine primary particles. The main alkali compounds released from the fuel are chlorides, which are substantially converted to condensed-phase sulfates in the presence of SO₂. At low SO₂ concentrations, the formation of primary particles decreases in extent due to the high vapor pressure of alkali chlorides. Thus, the aerosol size distribution of the product gas from gasification depends on the relative M/Cl/S ratio, where M denotes alkali metals. Biomass combustion has been found to produce a submicron mode with a mean diameter around 0.3 μ m and these particles consist almost of KCl and K₂SO₄ in the case of straw.

Olsson and Pettersson (Olsson, Pettersson, 1998) also published that for the fluidized bed materials, the alkali metal emissions for the agglomerated material above 600°C is lower than for unagglomerated.

Limits of the maximum tolerable alkali metal concentration in product gas

For the limits of the maximum tolerable alkali metal concentrations at the entry to a gas turbine, different sources have stated values of 24 ppbw (Bedick, 1990), 50 ppbw (Newby, 1994) and 110 ppbw (Pintsch and Gudenau, 1991). These values are based on experiences from fossil fuels.

The current industrial gas turbine specification limit for alkali metal compounds in the product gas entering the combustion chamber is of the order of 0.1 ppm by weight (Kurkela et al., 1995).

Removal of alkali metals from gas phase

Alkali metals emission from the filter ash and fluidized bed materials during the gasification of biomass was studied by Olsson and Pettersson (Olsson, Pettersson, 1998). They suggested that the most straightforward way of removing alkali compounds from the fuel gas is to lower the temperature, since vapor phase alkali compounds condense in the temperature interval of 400-550°C (Hallgren, 1996).

Salo and Mojtahedi (Salo, Mojtahedi, 1998) studied the fate of alkali and trace elements during the biomass gasification. They also lowered the temperature of the gas to get a gas with very low alkali compounds content. The results of their work can be seen in figure 3.4.2-2.



Figure 3.4.2-2: Results from the gasification test rig of the Technical Research Centre of Finland (Salo and Mojtahedi, 1998)

The points at the right hand side of figure 3.4.2-2 correspond with the concentrations measured before the gas cooler (750-900°C) and those at left side are the results of measurements from the same test runs but after the gas cooler (400-550°C). As can be seen in the figure, the alkali content of the product gas was reduced to 0.05-0.1 ppm when the gas was cooled and filtered at 400-500°C even if different fuels were used.

Although effective, the energy loss makes this method less attractive and higher gas temperatures are desired. In this case, alkali vapours may be removed by sorbents such as activated bauxite in the form of injected particles (Lippert et al., 1992). Alternatively, advanced high-pressure-high-temperature ceramic barrier filters may be used for the capturing of alkali compounds as well as removing particulate matter.

Since the 1980s several aluminosilicates, clay-like materials have been tested for the removal of alkali from gases at high temperatures. Materials such as emathlite and kaolinite can be used in two ways for this purpose (Uberoi et al., 1990):

- by injection as powdered sorbent into the combustion or gasification zone
- in a separate fixed bed reactor with the sorbent through which the gas stream is flown

	SiO ₂	Al ₂ O ₃	(Na, K) ₂ O	(Ca, Mg)O	P ₂ O ₅	Others
		[W-%]				
Emathlite	~ 69	~ 8	~ 1	~ 9	~ 3	~ 10
Kaolinite	~ 51	~ 44	~ 0	~ 0	~ 0	~ 5
Bauxitic Kaolinite	~ 36	~ 58	~ 0	~ 0	~ 0	~ 6
Attapulgite	~ 62	~ 10	~ 1	~ 10, ~ 5	~ 1	~ 2
Ca-montmorillonite	~ 54	~ 18	~ 2	~ 5, ~ 13	~ 0	~ 8

Table 3.4-2: Typical compositions of aluminosilicates sorbents for the alkali removal from gases at 600-100°C (Wilson et al., 1996)

The table above gives some averaged compositions of various materials that have proven to remove alkali from the hot coal conversion streams. Maximum sorption capacities are $\sim 25\%$ alkali for kaolinite and 15% for bauxites and emathlite.

The alkali removal is supported by water but hindered (except for kaolinite) by HCl (Schultz et al., 1995), (Uberoi et al., 1990) (Alk = Na or K)

$$AlkCl + H_2O + Al_2O_3.xSiO_2(s) \le 2 AlkAlO_2.xSiO_2(s) + 2 HCl$$
 [eq.3.4.2-1]

From literature review it can be concluded:

- Alkali metals are bound in biomass organically and inorganically in form of salts such as chlorides, sulphates or hydroxides. In biomass potassium is found especially in the fast growing parts of trees, in the straw, grass and in corn hulls. Much of this alkali is present in water-soluble or ion-exchangeable forms
- The most important sodium vapor phase species are NaOH and NaCl. Under high temperature and reducing conditions in a flame, elemental Na is the most common specie
- After the release of sodium in form of NaOH, Na or NaCl it may react with the char and ash-forming matter to produce silicates and sulphur compounds, and later NaCl and Na₂SO₄ can be formed
- Potassium content in biomass varies in a wide range from 0.03 w-% (wood) to 2.5 w-% (straw).
- Potassium can be found in biomass as dissolved salts in the moisture or as a cation attached to carboxylic and other functional groups, which is highly mobile.
- Potassium is most possibly bond to chlorine as KCl if chlorine is available in biomass fuels. The most possible potassium compounds released from the biofuels are KCl, K₂SO₄ and KOH

- Potassium releases to the gas phase in two stages. The first stage is at temperature range of 200°C to 500°C. The potassium release at lower temperatures can be well coupled to biomass devolatilization and insensitive to the chlorine content in the biomass. In this first stage the organic bond potassium releases following the devolatilization of the biomass constituents, cellulose, hemicellulose and lignin. In the second stage at temperatures above 500°C, the potassium releases at full speed, depending on chlorine presence in the fuel. In this stage, potassium releases in form of KCl and KOH
- Alkali compound emissions during thermochemical conversion of biomass can cause problems such as agglomeration, slagging, fouling and metal corrosion in the conversion process systems
- Limit for alkali metals compounds in the product gas entering the combustion chamber is of the order of 0.1 ppmw
- There are two possibilities of removal of alkali metals from gas phase: to lower the gas temperature or using of alkali sorbents (emathlite, kaolinite, bauxitic kaolinite, attapulgite or Ca-montmorillonite)

3.5 Trace elements

Within the European Union 13 elements of highest concern are As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Sn, Tl and V. Emissions of these elements are regulated for waste incinerators and cement plants.

Table 3.5-1 gives an overview of the trace elements concentrations in some fossil fuels, waste-derived fuels and in wood.

	Coal	Peat	MSW	RDF	Wood	Waste	Waste	Sew.
						wood	paper	sludge
Hg	0.02-3	~ 0,07	< 15	1-10	0.01-0.2		~ 0.08	0.5-10
As	0.5-10	1-3	0.5-500	~ 3	~ 0.2			0.1-100
В	5-100		< 0.5				~ 0.5	
Be	0.1-10	~ 0.1	1-40	~ 1			~ 0.8	
Cd	0.05-10		< 100	1-10		~ 0,5	~ 0.7	1-10
Со	0.5-20	1-2	< 20		~ 0.1			~ 5
Cr	0.5-60	0.5-2	< 1500	50-250	~ 1	1-4	~ 6	~ 100
Cu	5-60	~ 10	< 2500	< 1000	0.5-3	~ 15	~ 18	200-
								700
Mn	5-300	30-100	< 1000	~ 250	10-1000		~ 27	~ 200
Ni	0.5-100	5-10	< 5000	10-100	~ 0.5	< 20	~ 7	~ 50
Pb	1-300	1-5	< 2500	100-500	1-20	< 50	~ 8	100-
								300
Sb	<1		< 80	< 5			~ 5	100-
								500
Se	0-3	~ 1	< 10	3-6	~ 0.2		~ 0.08	
Sn	<10		3-10	~ 500			~ 8	
Tl	~1							
V	1-100	5-50			~ 2			
Zn	1-1000	~ 20	~ 2 w-%	300-800	5-150	< 30	~ 150	~ 1000

Table 3.5-1: Trace element concentrations in some fossil fuels and waste-derived fuels (in mg/kg, dry) (Zevenhoven, Kilpinen, 2001)

As can be seen in the table, wood is a relatively "clean" fuel concerning the trace elements, but treated wood, which is e.g. covered with protecting coat of chromated copper arsenate (CCA wood) contains ~ 15 ppmw of Cr, ~ 5 ppmw of Cu and ~ 10ppmw of As (Helsen and van de Bulck, 2000). Sewage sludge is a rather "dirty" fuel, with trace elements concentrations higher than coal or RDF.

Many factors influence whether and in what form a trace element will be found in the gaseous or the solid phase. The most important factors are:

- how the trace element is bond in fuel
- temperature and pressure during the conversion process
- oxidizing or reducing conditions
- the presence of halogens, most important is the presence of chlorine
- the presence of compounds that can act as sorbents, e.g. calcium

Element/Compound	Boiling point [°C]
F	-188,1
Cl	-34,1
Se	217
SeO ₂	317
Hg	357
As ₂ O ₃	465
As	613
MoO ₃	796
Zn	907
Sb ₂ O ₃	1155
B ₂ O ₃	1800
CoO	1800
Mn	1960
Cu	2570
Ni	2730
Со	2870
Cr ₂ O ₃	3000-4000
Мо	4660

The boiling point of element is also not negligible. Table 3.5-2 gives an overview of the boiling points of several trace elements.

Table 3.5-2: Boiling point of trace elements and their compounds

Based on the data showed in the table 3.5-2, F is the most volatile and Mo the less volatile element. In fact the volatility of trace elements is influenced by the presence of other elements, esp. chlorine and sulphur.

Many studies showed that the trace elements may be classified in three classes as shown in the following figure.



Figure 3.5-1: Classification of the trace elements according to their behaviour during gasification (Couch, 1995)

This classification combined with information of toxicity and harmful effects on process equipment gives the first indications which of the trace elements need special attention. This classification of trace elements is connected to the concept of enrichment. The relative enrichment factor (RE) of an element in an ash is defined as

$$RE = \frac{element \ concentration \ in \ ash}{element \ concentration \ in \ fuel} x \ \frac{\% \ ash \ in \ fuel}{100}$$
[eq. 3.5-1]

For elements class I, RE \sim 1 for bottom ash and fly ash, for class II RE < 0.7 for bottom ash and RE \sim 1.3-4 for fly ash, for class III RE << 1 for bottom ash and RE >> 10 for fly ash. These numbers are based on pulverised coal combustion (Kema, 1997).

Particle size was found to have no effect on the vaporisation of trace elements (Senior et al., 1998). It is mainly the temperature that influences where the elements will be found (in gas or in solid phase).

The oxidizing or reducing conditions are also very important for the behaviour of trace elements. Many species are more volatile in the reducing than in the oxidizing atmosphere.

Limits of the maximum tolerable trace metal concentration

Environmental standards are imposed for the most toxic trace element emissions in Europe and will be regulated in the US under the Clean Air Act Amendments by the US Environmental Protection Agency (EPA). An emission rate of 0.05 mg/Nm³ for Hg, 0.05 mg/Nm³ for Cd and 0.5 mg/Nm³ for the other nine trace metals have been proposed for the EU member countries. (Salo and Mojtahedi, 1998)

Trace elements removal

Sorbent	Element	Temperature range
Based on zeolites	Ца	low tomporatures
Impregnated with suppurimpregnated with iodidesAg and Hg ion exchanged	ng	up to 400°C
 Based on activated carbon activated carbon activated carbon impregnated with S, Cl, iodides oxidised activated carbon 	Hg at higher temperatures also Cd, Pb	low temperatures, up to 300°C
 Siliceous materials Mg, Ca, Al silicates Mixed silicates, silicates fly ash mixtures, impregnated siliceous materials 	V, Pb, Ni, Zn at low temperatures also Hg, Cd	high temperatures 600- 1000°C low temperatures <100°C

 Table 3.5-3: Sorbents for the removal of trace elements from the gas streams

 (CINEMAT, 1998)

Based on alumina		
 activated alumina gel alumina coated steel wool alumina impregnated with alkali carbonate or phosphated 	Pb	up to 700°C
Calcium compounds		
 hydrated lime/fly ash limestone/fly ash, limestone/silica hydrated lime+Sn, limestone, calcium chloride 	Hg, Zn, V, Ni at low temperature As at high temperature	Hg at up to 300-400°C V, Ni, As at high temperatures
Other materials		
 MgO, Mg(OH)₂ Cr, Ni compounds Fe compounds, e. g. blast furnace dust 	Hg, V, Ni, Pb, As	V, Ni at up to 550°C As at high temperatures

Table 3.5-3: Sorbents for the removal of trace elements from the gas streams (CINEMAT, 1998)(continue)

As and Se may be removed by calcium. For fuels or waste materials with more than 0.1 w-% of Ca (and with oxygen in the gas phase!), As is almost completely removed as calcium arsenate (Kema, 1997):

$$3 \text{ CaO} + \text{As}_2\text{O}_3 + \text{O}_2 <=> \text{Ca}_3(\text{AsO}_4)_2$$
 [eq.3.5-2]

Se and As can be removed from flue gases at 350-600°C by calcium based sorbents, forming CaSeO₃ and Ca₃(AsO₄)₂ provided that SO₂ has been removed to low concentrations upstream, to prevent competitive sulphation of the sorbent (Ghosh-Dastidar et.al., 1996).

Thermodynamic calculations and the experimental work showed that at low temperatures the major Se species in the typical flue gases are H_2Se and $SeCl_2$, at higher temperatures S, Se and SeO₂ (Yan et al., 2001). Se can be removed from gases by activated carbon at 125-250°C. Removal efficiency increases with gas moisture content (Se reacts with the sorbent as H_2SeO_3) and internal surface of the sorbent but decreases with temperature, indicating a physiosorption mechanism.

Sorbents such as silica, alumina, kaolinite, limestone, emathlite, bauxite, titanium have been widely tested for trace elements control at 400-1000°C by direct injection into the gas or in packed or fluidized beds. Based on the thermodynamic calculations (at 400-1400°C), alumina may be a good sorbent for As, Be and fairly active for Cd and Ni, silica may be a good sorbent for Cd, Pb and Hg, whilst titanium may be a good sorbent for Cd and Pb. Experiments with kaolinite injection showed a high removal efficiency for Pb, which was much less active when excess chlorine was present. Other tests showed that kaolinite effectively removes Ni, Cd and Pb, again limited by presence of Cl. Also limestone can be used to capture Pb and Cd species, and Sb, Hg, Se and As as well (Biswas and Wu, 1997).

3.5.1 Heavy metals

A sub-class of the trace elements are heavy metals, with a density of approx. 5000 kg/m^3 or higher, such as Cd, Pb, Hg, Zn and Cu.

The devolatilization of heavy metals on the grate at temperature range of $677-1327^{\circ}C$ was studied by Sørum et al. (2003). They used MSW, which is well known to have a higher content of the heavy metals. Heavy metals may be harmful to the environment and humans when exposed to concentrations above what can be found in the natural environment.

They calculated an equilibrium distribution of As, Cd, Cu, Cr, Hg, Ni, Pb and Zn at reducing conditions (ER= 0.6). The results of the calculations are shown in figure 3.5.1-1.



Figure 3.5.1-1: Equilibrium distribution of As, Cd, Cu, Cr, Hg, Ni, Pb and Zn at reducing conditions on the grate (Sørum et al., 2003)

When interpreting the results it is important to know the equilibrium distribution of chlorine and sulphur, since these species will affect the distribution of the heavy metals.



Figure 3.5.1-2: Chlorine (a) and sulphur (b) balances at reducing conditions (Sørum et al., 2003)

As can be seen in the figure above, chlorine is present as $CaCl_2$ (cr = solid condensed phase) and gaseous HCl (g) up to 777°C. From 777°C, HCl (g) is the dominating specie. The sulphur distribution for the reducing conditions is dominated by CaS (cr) and H₂S (g) up to 997°C, where H₂S dominates. Minor amounts of COS (g), SO₂ (g) and HS (g) were also observed. The sulphur and the chlorine contents in the fuel influence the volatility of some heavy metals, especially Cu, Ni and Pb.

Arsenic; As is present as AsO (g) with only a small amount of As_2 (g) below 777°C. Arsenic release is strongly dependent on the MSW composition (especially Ca content) and operation conditions. The behaviour of arsenic under oxidizing conditions is completely different (Sørum et al., 2003)

Cadmium; Cd (g) is the stable phase for Cd under the reducing conditions at temperature range of 677-1327°C. This distribution was also observed by Frandsen et al. (Frandsen, 1994).

Chromium; Cr does only to a very small degree volatilise under the given temperature range (950-1550 K). This is also observed in the practice in the real combustion plants. About 95 wt-% of Cr remains in the bottom ash. CaO.Cr₂O₃ (cr) is the dominant specie for the both reducing and oxidizing systems. In the reducing conditions, the CrOOH (g) oxide is barely present above 1277°C. The equilibrium distribution for Cr is not significantly influenced changing from the reducing to the oxidizing conditions.

Copper; The volatile behaviour of Cu is largely altered when changing from reducing to oxidizing conditions. At reducing conditions, Cu is present as the sulphides in the solid phase as CuS.FeS (cr) up to 927°C and Cu₂S (cr, l) from 927°C. From 1077°C, the amounts of Cu (g) and CuH (g) increase. Values found in literature (Rigo and Chandler, 1994), (Brunner, Mönch, 1986) reported that 89-96 wt-% of Cu remained in the bottom ash.

Mercury; Hg is present as Hg (g) under the reducing conditions at the whole temperature range.

Nickel; The major part of Ni is present as the stable condensed elemental Ni (cr, l) for reducing system at 677-1327°C. Small amounts of chlorides in the gas phase and Ni (g) were observed above 1127°C. Rigo and Chandler (Rigo, 1994) reported that about 98 wt-% of Ni remained in the bottom ash.

Lead; At lower temperatures (< 1227°C) under the reducing conditions, Pb (g) and lead chlorides are dominating. Above 777°C, the amount of Pb (g) increases gradually. The literature reports a large variation in the volatility of Pb. Reported values of the fraction of Pb remaining in the bottom ash, varied from 58 to 94 wt-% (Sørum et al, 1997), (Brunner, Mönch, 1986), (Barton et al., 1990).

Zinc; At 677°C the silicate 2ZnO.SiO₂ (cr) was the dominant specie under the reducing conditions. However, it gradually decreased with the increasing temperature to zero at 827°C, from where Zn (g) was the dominant stable phase. A minor amount of ZnCl₂ (g) was observed from 677 to 977°C. The experimental work of Rigo and Chandler (Rigo, 1994) and Sørum et al. (Sørum, 1997) showed that 37-86 wt-% of Zn remained in the bottom ash. Since chlorides of Zn in deposits were highly unwanted in the boiler, efforts should be made to decrease the volatility for Zn on the grate. The influence of the different parameters such as temperature, availability of sulphur and chlorine and ER on the volatility are therefore of the great importance for Zn.

All heavy metals species used in calculations of Sørum et al. (Sørum, 2003) can be found in appendix.

From literature review it can be concluded:

- Within the European Union 13 elements of highest concern are As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Sn, Tl and V. Emissions of these elements are regulated for waste incinerators and cement plants.
- Many factors influence whether and in what form a trace element will be found in the gaseous or the solid phase. The most important factors are: how the trace element is bond in fuel, temperature and pressure during the conversion process, oxidizing or reducing conditions, the presence of halogens, most important is the presence of chlorine and the presence of compounds that can act as sorbents, e.g. calcium
- The most volatile trace elements are: Hg, Br, Cl, F (figure 3.5-1)
- Limits of the maximum tolerable trace metal concentration: 0.05 mg/Nm³ for Hg, 0.05 mg/Nm³ for Cd and 0.5 mg/Nm³ for the other nine trace metals have been proposed for the EU member countries
- Trace elements can be removed from the gas streams using sorbents based on zeolites, based on activated carbon, siliceous materials, based on alumina, calcium compounds or other materials (Mg, Cr, Ni or Fe compounds)

- A sub-class of the trace elements are heavy metals, with a density of approx. 5000 kg/m³ or higher, such as Cd, Pb, Hg, Zn and Cu
- Cd (g) is the stable phase for Cd during thermochemical conversion process under the reducing conditions
- Cr remains mostly in char during the thermochemical conversion process
- Cu is present as sulfides in the solid phase during pyrolysis and gasification, at higher temperatures, the amounts of Cu (g) and CuH (g) increase
- Hg (g) is the stable phase for Hg during pyrolysis and gasification
- Ni is present as the stable condensed elemental Ni (cr, l) during pyrolysis and gasification (up to 1600 K), small amounts of nickel chlorides in the gas phase and Ni (g) were also observed
- Pb is present as Pb (g) or lead chlorides. Reported values of the fraction of Pb remaining in the bottom ash varied from 58-94 w-%
- At lower temperatures Zn is bond as silicate 2ZnO.SiO₂ (cr), Zn (g) was observed at higher temperatures. 37-86 wt-% of Zn was observed in the bottom ash during the thermochemical conversion process

4 Pyrolysis

The first step of each thermal conversion process (pyrolysis, gasification, combustion) is a release of volatiles. Amount and composition of volatiles is dependent on many factors, such as temperature, fuel moisture, heating rate, particle size, presence of some elements etc.

The distribution of selected elements into volatiles or solid phase after pyrolysis at different temperatures was investigated. There is some information available in literature about the behaviour of organic matter during the thermochemical conversion processes but not so much about the inorganic one.

Three different biomass fuels were chosen for these experiments: wood, hemp and corn. Wood presented the woody biomass, which is well spread and very often used during the industrial thermo conversion processes, because of its purity in case of undesirable elements. Hemp and corn, biomass fuels with higher content of chlorine, nitrogen and alkali metals, were used to determine the process conditions (e.g. process temperature), when most of the undesirable elements and their compounds remain in the char and do not disturb the conversion process and/or cause damages of conversion unit.

4.1 Characteristics of used biomass materials

4.1.1 Wood

Untreated beech wood in a cube form (7x7x7 mm) was used in this experimental work. Elemental analysis of the wood can be seen in table 4.1.1-1. Two methods of elements detection were used: ICP-AES and X-ray fluorescence analysis. The data from literature in the last column offer the possibility of comparison.

	a	b	c
Element	[mg/kg]	[mg/kg]	[mg/kg]
Cl			50
S	500	58	60
Hg	<3	<1	0.01
Cd	1-2	<1	0.01
Pb	1-2	<1	0.4
Cr	1-2	<1	2.4
Cu	4	<1	1.2
Zn	4	<1	11.1
Ni	1-2	<1	0.3
Sn	8	<1	0.1
K	2600	1530	380
Na	30	<1	8.5
Li	1-2	<1	
Mg	220	208	300
Ca	800	1140	1210
Al	NA	<1	64
Si	NA	<1	470
PO ₄ ³⁻	NA	37	
SO4 ²⁻	NA	<1	
Cl	NA	<1	
Ti	NA	<1	1.9
Mn	NA	109	56
Fe	NA	<1	50
Sr	NA	29	5.1

Table 4.1.1-1: Elemental analysis of the wood before pyrolysis (dm)

NA...not analysed

- a...detection method: ICP-AES
- b...detection method: X-ray fluorescence analysis
- c...literature (Hasler et al., 1995), (www.ecn.nl/phyllis)

Note: The gray fields in the table define the values which were not used in the calculations because of their big deviation from literature data.

	[w-%]
С	42.98
Н	4.8
Ν	0.19
0	36.61
ash	0.27

Table 4.1.1-2: C-H-N-O analysis and ash content of the wood (dm)

Moisture of wood samples used during pyrolysis was 8.5 w-%.

The C, H and O content are responsible for the calorific value of the dry matter.

To determine the amount of C, H, N, and S, a furnace is heated to a temperature of 1000°C. Approximately 1 mg of sample is placed inside a silver capsule and is completely combusted and is dropped into the furnace. Using infrared detection method it the weight percent of carbon, hydrogen, and sulfur measured, while nitrogen is measured using thermal conductivity detection.

4.1.2 Corn and hemp

Besides wood barley corn (8x3 mm) and hemp in a pellet form (15x4 mm) were used in this work. Elemental analysis of the corn and hemp can be seen in table 4.1.2-1. X-ray fluorescence method was used for the elements detection.

	Corn	Hemp
	[w·	-%]
Na	0.011	0.048
Mg	0.093	0.415
Al	0.038	0.556
Si	0.401	1.470
PO ₄ ³⁻	0.723	2.050
SO ₄ ²⁻		1.360
S ²⁻	0.146	
Cl-	0.131	0.143
K	0.560	1.080
Ca	0.077	2.040
Ti	< 0.001	0.024
Cr	< 0.001	< 0.001
Mn	< 0.001	0.022
Fe	0.008	0.212
Ni	< 0.001	< 0.001
Cu	< 0.001	< 0.001
Zn	< 0.001	0.005
Br-	< 0.001	< 0.001
Rb	< 0.001	< 0.001
Sr	< 0.001	0.009

Table 4.1.2-1: Elemental analysis of corn and hemp (dm)

	Corn	Hemp			
	[w-%]				
С	43.480	40.520			
Η	6.470	5.400			
Ν	1.820	2.010			
0	46.042	42.636			
ash	5.300	6.900			

Table 4.1.2-2: C-H-N-O and ash analysis of corn and hemp (dm)

Moisture of corn and hemp samples used during pyrolysis was 8.85 and 6.40 w-%.

4.2 Pyrolysis conversion unit

Biomass pyrolysis tests were performed using a laboratory scale stationary fluidized bed reactor (diameter 35 mm, height 240 mm) made of a quartz glass (in the case of the wood pyrolysis) or of a stainless steel (corn and hemp pyrolysis). The electrical heating shells of the fluidized bed reactor produced a uniform temperature around the fuel particles. A quartz glass frit served as a distributor (porosity 00). A fluidized bed of silica sand (granulometry 250 to 315 μ m) was used. The reactor operated in the range of bubbling and slugging fluidization. Nitrogen was used as a fluidizing agent during pyrolysis process and cooling down period. Air was used during heating up period only. Samples were fed into the reactor in a batch form with a spoon. The reactor was covered with insulation material (see photos).



Figure 4.2-1: Laboratory scale stationary fluidized bed unit

1,2...Air and nitrogen; 3,4...Mass flow controllers; 5...Preheating; 6...Electrical heating shells; 7...Ni/Cr-Ni thermocouples for fluidized bed and freeboard; 8...To the chimney; 9...Product gas cooler; 10...NGA2000; 11 ...Fuel feeding

Figure 4.2-2 shows the upper part of the fluidized bed reactor made of glass, where the wood pyrolysis took place. During the heating up period and the pyrolysis process the reactor was covered with insulation material, what can be seen in the following figure.



Figure 4.2-2: Photo of the quartz glass reactor



Figure 4.2-3: The reactor covered with insulation material

The second type of reactors, made from steel which was used during the corn and hemp pyrolysis can be seen in figure 4.2-4.


Figure 4.2-4: The steel reactor used during corn and hemp pyrolysis

The biomass samples were fed into the reactor in a batch form with the spoon. The details of the feeding system are shown in figure 4.2-5.



Figure 4.2-5: Feeding system of the reactor

4.3 Experimental procedure

The pyrolysis tests were performed at different temperatures, in case of wood it was 300-800°C, in case of hemp and corn, 400-850°C. At each temperature three runs were carried out. Air was used as a fluidizing agent only during the heating up period. About 15 minutes before starting the experiment, nitrogen was switched on and at the same time air was switched off. Biomass was fed into the reactor in a batch form, weight of 1 g.

After the devolatilization of biomass, the heating shells were switched off and the reactor slowly cooled down. During the cooling phase the bed material was fluidized with nitrogen. The reactor was opened and the char taken out when the temperature in the fluidized bed decreased to 70 °C. Bed material (silica sand) and biomass char samples were separated with a sieve. The char samples were sent to the specialized laboratories to analyze the composition of elements.

4.4 Measurements methods and methods of elements detection

The content of CO, CO_2 and O_2 was measured using NGA 2000 and data recorded using Labtech software. The CO_2 and CO measurements were performed by non-dispersive IR method. This measurement technique is based on the difference of the IR absorption of a probe gas and a reference gas. Only gases with a dipole moment can be measured. The O_2 measurements use the paramagnetic characteristic of the O_2 molecule.



Time [s]

Figure 4.4-1: CO amount produced during wood pyrolysis at temperature of 800°C

The CO amount releasing during the wood pyrolysis is shown in figure 4.4-1. As can be seen in the figure the maximal measured amount of CO (peak) was 16000 ppm and the devolatilization time was about 34 s. Devolatilization time was defined as a time, when the CO concentration reached 10%-value of the peak, in this case 1600 ppm of CO.

The rest figures of CO, CO_2 amounts produced during the wood pyrolysis process can be found in appendix.

The elements detection was performed in two specialised laboratories using two different methods: ICP-AES and X-ray fluorescence analysis.

ICP-AES is the atomic emission spectrometry with inductively coupled plasma. The plasma is formed by argon gas flowing through a radiofrequency field, where it is kept in a state of partial ionisation. This allows to reach very high temperatures (10 000°C). At high temperature, most elements emit light of characteristic wavelengths which can be measured and used to determine the concentration. The dissolved solid sample mixed with water is introduced into the plasma as a fine droplet aerosol. Light from the different elements is separated into different wavelengths. This technique permits analysis of up to 40 elements. The detection limit is at $\mu g/l$ in aqueous solutions.

X-ray fluorescence method is based on the irradiation of the pulverised sample with X-ray radiation. It is followed by the electron ejection from inner shells of atoms. The atoms are than unstable and electrons from the outer shells are transferred into inner shells. During this process (photoelectric effect) energy is released in form of the lines of X-ray spectrum, which is characteristic for each atom. Intensity of the lines depends on the concentration of the element in the sample. Chemical bonds do not influence wavelengths of X-ray spectrum.

4.5 Results of biomass pyrolysis experiments

From the pyrolysis experiments described above the following information is deduced:

- the amount of volatile matter produced during the pyrolysis at different temperatures
- devolatilization time dependent on the pyrolysis temperature
- results of elements behaviour, their distribution into the gas or solid phase after the pyrolysis process respectively.

The "green" biomass is in literature very often divided into two groups: woody and nonwoody biomass. One of the reasons for this division is the ash content, which is in the case of untreated wood the lowest one of all biomass types. Also the content of some elements such as chlorine, sulphur or alkali metals is in the wood is very low.

The different ash content of the biomass, different elements composition and two different pyrolysis reactors (made of glass or steel) used in this work were the reasons for the division to wood pyrolysis and corn and hemp pyrolysis.

4.5.1 Wood pyrolysis

The wood pyrolysis tests were performed at temperatures of 300, 400, 500, 600, 700 and 800°C. Each wood sample was weighted before and after pyrolysis test and based on the weight of particles (dm), the amount of volatile matter was determinated.

At each temperature three runs were carried out and one of the three runs was chosen as a representative one for the determination of CO and CO_2 contents at each temperature. Based on the curve of CO the end of devolatilization was determined.

The wood particles were fed into the reactor with a spoon. The weight of the wood samples was 0.31 - 0.37 g. A similar weight of wood samples was used to have a possibility of comparison of the amount of CO and CO₂ produced during the pyrolysis process.

The samples of the wood before pyrolysis and the char after pyrolysis process are shown in figure 4.5.1-1. As it can be seen, with rising temperature the size of particles became smaller. The reason was the higher amount of volatile matter at higher temperature.



Figure 4.5.1-1: Wood samples before and after pyrolysis process

Volatile matter, CO and CO₂

The amount of volatile matter produced during the wood pyrolysis was calculated as the difference between the weight of the dry samples before and after the pyrolysis. Results can be seen in the figure 4.5.1-2. For comparison data from wood pyrolysis using muffle furnace were added.

It can be seen that the temperature strongly influences the release of volatiles. As expected the amount of volatile matter rose with a rising temperature.



Figure 4.5.1-2: Volatile matter released during the wood pyrolysis

The heating rate during the pyrolysis process was not measured, but it is known, that the heating rate in fluidized bed reactors is commonly higher than in the muffle furnaces, because of the heat transport to the fuel particle. Figure 4.5.1-2 shows that the difference of the volatiles amount releasing in the fluidized bed and the muffle furnace was nearly the same. It was assumed, based on these results that the hating rate does not influence the amount of volatiles produced during the pyrolysis process. As the particles are large the limiting for hating up is the heat conduction in the particle.

	Temperature [°C]					
	300 400 500 600 700 800					
Particle weight [g]	0.34	0.31	0.36	0.34	0.37	0.35
CO [ppm]	425	1390	1800	3250	12000	16000
CO ₂ [vol.%]	0.08	0.17	0.21	0.22	0.45	0.45
Time CO [s]	194	110	79	52	40	38
Time CO ₂ [s]	130	54	51	37	41	37

Table 4.5.1-1: The highest levels (peaks) of releasing CO and CO₂, devolatilization time and the wood sample weight

The end of the devolatilization was defined as the time, when the CO value reached 10 % of the peak (see figure 4.4-1). It can be seen in table 4.5.1-1, that the volume of releasing CO and CO_2 was dependent on the temperature. With the rising temperature also the concentrations CO and CO_2 rose in the gas and the devolatilization time was shorter. This fact is shown in figure 4.5.1-3.



Figure 4.5.1-3: Dependency of the devolatilization time on the temperature during pyrolysis

Elemental analysis

Samples of pyrolysed wood were sent into a laboratory where the elements content was detected. In tables 4.5.1-2 and 4.5.1-3 the results of analysis are shown.

Temperature	С	Н	Ν	S	Cl
[°C]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
400	714100	34600	2650	<200	<100
600	818700	22100	2840	<200	<100
800	807400	9600	2430	<200	<100

Table 4.5.1-2: C-H-N-S-Cl analysis of pyrolysed wood

Temperature	400°C	400°C	600°C	800°C	800°C
	a	b	a	a	b
Element	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
S	3000	160	3900	2800	<10
Hg	<2	<1	<2	<2	<1
Cd	<1	<1	<1	<1	<1
Pb	<1	<1	<1	<1	<1
Cr	1	<1	1	1	<1
Cu	4	<1	9	6	<1
Zn	4	20	1	3	<10
Ni	2	<1	8	4	<1
Sn	8	<1	20	50	<1
Κ	2300	4590	3000	2300	7420
Na	50	69	100	140	<10
Li	<1	<1	<1	<1	<1
Mg	500	1170	700	1300	2110
Ca	2900	2730	2900	5100	5250
Al		243			58
Si		320			339
PO ₄ ³⁻		116			233
Cl-		<10			<10
Mn		207			377
Fe		186			<10

Table 4.5.1-3: Elemental analysis of pyrolysed wood

- a...detection method: ICP-AES
- b...detection method: X-ray fluorescence analysis

Behaviour of elements

Carbon

The wood samples contain 42.98 w-% of carbon. 59.26 w-% of the origin carbon were detected in the char after the pyrolysis process at 400°C and 40.74 w-% released into the gas phase. At temperature of 600°C 41.54 w-% of origin carbon were detected in char and 58.46 w-% came into volatiles. At temperature of 800°C 26.45 w-% of origin carbon were found in wood char and 73.55 w-% released to volatiles. Figure 4.5.1-4 shows the carbon behaviour during the wood pyrolysis



Figure 4.5.1-4: Carbon distribution in char and volatiles after wood pyrolysis

Hydrogen

The wood used in this investigation contains about 48000 mg/kg (4.8 w-%) of hydrogen. During the pyrolysis process at temperature of 400°C 79.77 w-% of hydrogen released into the volatiles and 20.23 w-% were found in the wood char. With rising temperature the content of the hydrogen remaining in the char decreased. At 600°C 7.90 w-% and at 800°C only 2.22 w-% of the origin hydrogen remained in the wood char.



Figure 4.5.1-5: Hydrogen distribution in the char and volatiles after pyrolysis

Nitrogen

The nitrogen content in the clean wood sample was 1900 mg/kg. The analysis after the pyrolysis process showed that at temperature of 400°C 63.02 w-% of the origin nitrogen

remained in the char and 36.98 w-% leaved into the volatiles. At 600°C 41.29 w-% of nitrogen remained in the char and 58.71 w-% released into the volatiles and at 800°C only 22.81 w-% of origin nitrogen were detected in the char and 77.19 w-% released into the volatiles.



Figure 4.5.1-6: Nitrogen distribution in the char and volatiles after the pyrolysis process

Nitrogen in the volatiles is bond mostly as HCN and NH_{3} , these are two important gaseous NO_x precursors formed during the pyrolysis of biomass. The formation of NH_3 requires the presence of a condensed phase (s) formed by carbonaceous materials rich in hydrogen.

The thermally less stable N-containing structures are mainly responsible for the formation of HCN, the thermally more stable N-containing structures may be slowly hydrogenated by the H radicals to NH₃. The formation of HCN and NH₃ are controlled by the local availability of the radicals, particularly the H radicals, in the pyrolysis solid.(Li et al., 2000)

Sulphur

The sample contains about 60 mg/kg of sulphur. After the pyrolysis process at temperature of 400°C 95.12 w-% of the origin sulphur were still found in the char and only 4.88 w-% released into the volatiles. At 600°C 27.30 w-% of sulphur leaved to the volatiles and 72.70 w-% remained in the char. At 800°C 53.07 w-% of the origin sulphur leaved into the volatiles and 46.93 w-% were found in the wood char.



Figure 4.5.1-7: Sulphur distribution in the char and volatiles after the pyrolysis process

It was found in the literature (Sørum et al., 2003) that the sulphur distribution for the reducing conditions is dominated by H_2S (g) and CaS (cr=solid phase) up to 1270K. Minor amounts of COS (g), SO₂ (g) and HS (g) were also observed.

Chlorine

The chlorine content in the clean wood is about 50 mg/kg. The chlorine in the biomass strongly influences the behaviour of other elements. In the presence of Cl and S the volatilisation temperatures of some heavy metals, especially Cd, Cu and Pb are lower than in the absence of these elements and their species. The evaporation tests performed by Lindt et al. (Lindt, 1999) showed that without chorine, virtually no evaporation of the heavy metals was observed, whereas the tests with chlorine clearly showed significant evaporation following the behaviour of the ashes.

The results after the pyrolysis process at 400°C showed that 71.34 w-% of the origin chlorine remained in the char and 28.66 w-% released into the volatiles. At a temperature of 600°C 43.62 w-% of chlorine remained in the char and 56.38 w-% of the origin chlorine released into the volatiles. At 800°C 28.16 w-% of the origin chlorine remained in the wood char and 71.84 w-% leaved into the volatiles.



Figure 4.5.1-8: Chlorine distribution in the char and volatiles after the pyrolysis process

Jensen et al. (Jensen, 2000) published that during the straw pyrolysis at temperatures of 200 to 400°C about 20-60% of Cl were released to the gas phase. At 700-830°C the rest of the chlorine from the char is released. This chlorine release to gas phase shows the figure 4.5.1-9. To have a possibility of the comparison of the chlorine release from the straw and the wood, results from wood pyrolysis were added into the figure from literature.



Figure 4.5.1-9: The comparison of Cl released into the gas phase (straw and wood) (Jensen et al., 2000)

Chlorine can cause the corrosion problems in the operation systems because of the HCl formation during the conversion process.

Potassium

Potassium content in the wood sample is about 380 mg/kg. Jensen et al. (2000) presented that during the straw pyrolysis at temperatures between 200 and 400°C potassium is bound as KCl and K_2CO_3 and at temperature of 400-700°C no significant amounts of K was released to the gas phase. From 700°C all KCl evaporated. At this temperature, K also reacts with silicon and potassium silicates are generated. From 830 to 1000°C, K_2CO_3 is decomposed and potassium is released as KOH or as free K atoms. Possibly, K can also be released from the char matrix. Above 1000°C, K may be released to the gas phase from the char matrix and from potassium silicates. By limiting the temperature in the pyrolysis reactor to 700°C a significant release of K could be prevented.



Figure 4.5.1-10: Potassium distribution in the char and volatiles after the pyrolysis process



Figure 4.5.1-11: Comparison of K release; straw and wood pyrolysis (Jensen et al., 2000)

Figure 4.5.1-11shows potassium release during straw and wood pyrolysis. As can be seen in the figure higher potassium amount was found in the gas phase during wood pyrolysis. At temperature of 800°C it was about 32 w-% in case of wood pyrolysis. The reason could be a higher amount of chlorine content in straw. Potassium bond with chlorine forms KCl which is very stable and remains in the solid phase.

Sodium

Sodium content in the clean wood is about 8.5 mg/kg. Using ICP-AES 30 mg/kg. were detected. Sodium content in the wood is about 10 times lower than the content of potassium. In comparison with potassium the release of sodium is negligible.

Arsenic

The content of arsenic in the clean wood is usually very low, approximately 0.1 mg/kg. This value is already below the detection limit of the two methods used (ICP-AES and X-ray fluorescence analysis). The detection limit of these methods was about 1 ppm. Devolatilization of heavy metals on a grate was studied by Sørum et al. (Sørum, 2003). Under reducing conditions, arsenic were present as AsO (g) with only a small amount of As₂ (g) below 1050 K. Under the oxidizing conditions As is stable as $Ca_3(AsO_4)_2$ (cr) up to approximately 1300 K. From 1300 K to 1400 K the stable form of As gradually changes to AsO (g). Volatility of As is strongly dependent on the fuel composition and operational parameters such as air/fuel ratio and temperature. The amount of arsenic devolatilized from the clean wood is negligible. It is important in the case of the treated wood with arsenic salts (protection coating). Then the arsenic content it the treated wood is much higher and therefore also arsenic release.

Cadmium, Mercury, Lead

Based on the results from analysis it was not possible to determine the behaviour of these elements. The content of these elements in the clean wood is very low. Clean wood usually contents less than 0.1 mg/kg of cadmium, 0.01 mg/kg of mercury and about 0.4 mg/kg of lead. But from the literature (Cioni et al., 2002), (Faaij et al. 1997) it is well known, that these elements are the most volatile ones of all heavy metals. Mercury found in the fly ash and the flue gas is likely to be in the elemental form. In the gasification reactions, the presence of HCl or Cl_2 may cause that some of the elemental mercury forms $HgCl_2$. (Klein, 2002)

Chromium

Chromium content in the clean wood is about 2.4 mg/kg. Using detection methods (ICP-AES and X-ray fluorescence method) lower values were found. It was less than 1 mg/kg what was below the detection limit. That is why the results from analysis could not be used for calculations and only data from literature are presented.

It was found in the literature (Sørum et al., 2003) that chromium does only to a very small degree volatilise under the given temperature range. About 95 w-% of chromium remains in the bottom ash. CaO.Cr₂O₃(cr) is the dominant specie for the reducing and oxidizing systems. In the reducing system, the CrOOH (g) oxide is barely present above 1550 K. The equilibrium distribution for Cr is not significantly influenced changing from reducing to oxidizing conditions. The gasification of Miscanthus was performed by Ünal et al. (not published yet).

They observed that during the gasification Cr, Fe and Ni was accumulated in the bed material, but the largest mass fraction was found in the fly ash.

Copper

The amount of copper in wood is about 1.2 mg/kg. Using ICP it was found 4 mg/kg of copper and using X-ray fluorescence method less than 1 mg/kg of copper in the wood samples. The behaviour of copper strongly depends on the temperature, oxidizing and reducing conditions and the chlorine presence. It is known from the literature (Sørum et al., 2003) that under the reducing conditions (ER = 0.6), Cu is present as CuS.FeS (cr) (up to 1200 K) in the solid phase and Cu₂S (cr,l) (from 1200 K). A gradual increase of CuCl (g) was observed from approximately 1200 K. Sørum et al. (2003) reported that more than 80 wt% of Cu remained in the bottom ash.

Magnesium

Magnesium content in the wood is about 300 mg/kg. Using ICP 220 mg/kg and using X-ray fluorescence method 208 mg/kg were found. Based on the analysis results there was assumed that most of Mg remained in the char. Even at 800°C 83.20 w-% of the origin magnesium were found in the char.

Manganese

The volatilization of manganese is strongly dependent on the chlorine presence. At higher temperature (about 1000°C) manganese can be present as gaseous MnCl₂. At temperatures lower than 1000°C most of manganese remains in the char.

Zinc

The zinc content in the wood is 11.1 mg/kg. Using ICP and X-ray fluorescence lower values in the char of 4 mg/kg and less than 1 mg/kg., respectively were detected. The results from analysis are shown in figure 4.5.1-12.



Figure 4.5.1-12: Zinc distribution in the char and volatiles after pyrolysis

Using X-ray fluorescence method 64.27 w-% of zinc were found in the wood char after the pyrolysis at 400°C. After the pyrolysis at a temperature of 800°C 12.68 w-% of zinc were detected in the wood char.

Zinc appears as 2ZnO.SiO2 (cr) up to 950 K, and at about 1100 K Zn (g) is a dominant phase. A minor amount of $ZnCl_2$ (g) was observed from 950 to 1250 K. 37-86 w-% of Zn remained in the bottom ash. Zn behaviour is strongly influenced by different factors such as temperature, availability of sulphur and chlorine, and fuel/air ratio. (Sørum et a., 2003)

Aluminium, Iron. Lithium, Nickel, Tin

The values of these metals are too low to detect them in biomass using these two analytical methods. It is known from literature (Faaij et al., 1997) that these metals mostly remain in the char.

4.5.2 Corn and hemp pyrolysis

The corn and hemp pyrolysis tests were performed using the same stationary fluidized bed unit as for the wood pyrolysis described before. But in case of the corn and hemp pyrolysis the fluidized bed reactor made of stainless steel was used. The temperature of the fluidized bed was varied between 400°C and 850°C. Nitrogen was used as a fluidizing agent during the pyrolysis process; air was used as a fluidizing agent during the heating up period. The biomass particles were fed into the unit in a batch form with the spoon. In the following figures the corn and hemp samples before the pyrolysis and char samples after the pyrolysis performed at different temperatures can be seen.



Figure 4.5.2-1: Corn before and after the pyrolysis process at different temperatures



Figure 4.5.2-2: Hemp before and after the pyrolysis process at different temperatures

The pyrolysis tests were performed at 400, 500, 600, 700, 800 and 850°C. About 15 minutes before starting the experiment, nitrogen was switched on and at the same time air was switched off. The biomass samples were fed into the reactor in a batch form with a weight of 1 g. After the biomass devolatilization, the heating shells were switched off and the reactor slowly cooled down. During the cooling phase the bed material was fluidized with nitrogen. The reactor was opened and the char taken out when the temperature in the fluidized bed was decreased to 70 °C. The bed material (silica sand) and the char samples were separated with a sieve. Each biomass sample (dry) was weighted before and after the pyrolysis tests to determine the amount of volatiles. The char and fresh biomass samples were sent to a laboratory to analyze the composition of elements. X- ray fluorescence method was used for the elements concentration detection.

Volatile matter

The volatile matter of the biomass was calculated as a difference between the weight of the dry sample before and after pyrolysis. Results are shown in figure 4.5.2-3.



Figure 4.5.2-3: Amount of the volatile matter during the corn and hemp pyrolysis

It can be seen in the figure that the temperature strongly influences the release of the volatiles. As expected the amount of the volatile matter rose with a rising temperature. The amount of the volatiles releasing during the corn pyrolysis is higher as the amount of the volatiles rising during the hemp pellets pyrolysis. The reason can be the different material composition of these two biomass types.

Elemental analysis

The elemental analysis of the corn and hemp pellets is shown in the following table. Values for oxygen were calculated.

	Corn	Hemp		
	[w-%]			
С	43.480	40.520		
Н	6.470	5.400		
Ν	1.820	2.010		
0	46.042	42.636		
Na	0.011	0.048		
Mg	0.093	0.415		
Al	0.038	0.556		
Si	0.401	1.470		
PO ₄ ³⁻	0.723	2.050		
SO ₄ ²⁻		1.360		
S ²⁻	0.146			
Cl-	0.131	0.143		
K	0.560	1.080		
Ca	0.077	2.040		

	Corn	Hemp
Fe	0.008	0.212
Ni	< 0.001	< 0.001
Cu	< 0.001	< 0.001
Zn	< 0.001	0.005
Br-	< 0.001	< 0.001
Rb	< 0.001	< 0.001
Sr	< 0.001	0.009

 Table 4.5.2-1: Elemental analysis of the corn and hemp before the pyrolysis (referred to dm)

	Corn	Hemp	
	[w-%]		
ash (dm)	5.300	6.900	
moisture	8.850	6.400	

Table 4.5.2-2: Moisture and ash content of the corn and hemp

Behaviour of elements

The content of elements in samples before and after pyrolysis was detected using X-ray fluorescence analysis. The amount of the volatile matter was used by the determination of the elements behaviour, their distribution into gas or solid phase, during the pyrolysis process. The distribution of elements into the solid or gas phase is different by each element and it is influenced by many factors (process temperature, heating rate, pressure, etc.). The effect of temperature on elements distribution was investigated during the pyrolysis process.

Carbon

Carbon is the basic element in the biomass body. Biomass contains up to 50 w-% carbon. About 43.5 w-% of carbon was detected in the corn and about 40.5 w-% in the hemp. CO, CO_2 , CH_4 and other hydrocarbons are the most important carbon components releasing during the thermochemical processes. Figure 4.5.2-4 shows the carbon distribution in the volatiles and char after the pyrolysis of corn and hemp.



Figure 4.5.2-4: Carbon distribution into volatiles and char after corn and hemp pyrolysis

As it can be seen in the figure with the rising temperature the amount of carbon in the char decreases at a temperature of 800°C about 30 w-% of the origin carbon were found in the hemp char, but only 20 w-% were detected in the corn char after the pyrolysis process. These results correspond well with the figure 4.5.2-3, where the amount of the volatile matter releasing during the pyrolysis process can be seen. The figure 4.5.2-3 shows, that after the biomass pyrolysis about 75 w-% of the origin hemp sample mass released into the volatiles. In the case of the corn it was about 85 w-% of origin corn sample mass released into the volatiles.

Hydrogen

5.4 w-% of hydrogen in the hemp and about 6.5 w-% in the corn samples were detected using X-ray fluorescence method. Hydrogen is one of the most volatile elements released into the volatiles during the thermochemical process. Figure 4.5.2-5 shows that after the biomass pyrolysis at a temperature of about 800°C only very small amounts of hydrogen were detected in the char. They were 3.5 w-% of the origin hydrogen found in the hemp char and only 1.5 w-% in the corn char. It can be seen in this figure that even at a temperature of 400°C about 85 w-% of the hydrogen were released into the gas phase.



Figure 4.5.2-5: Hydrogen distribution after the corn and hemp pyrolysis

Nitrogen

Nitrogen is an essential nutrient for the growth of biomass. It is fixed in the biomass mostly in the organic form as biopolymers, proteins, alkaloids, etc. The content of nitrogen in biomass varies in a wide range between 0.1 w-% (wood) and 9 w-% (sewage sludge). The nitrogen content in corn was 1.820 w-% and in hemp 2.010 w-%.



Figure 4.5.2-6: Nitrogen distribution after corn and hemp pellets pyrolysis

As expected, with the rising temperature also the amount of nitrogen in volatiles rose. The figure above shows, that at a temperature of 400°C about 60 w-% of the origin nitrogen were found in corn char and less than 20 w-% in hemp char. At 800°C these amounts decreased to about 20 w-% of nitrogen in the corn char and only about 3.5 w-% in the hemp char.

Sulphur

Sulphur is fixed in biomass mostly in proteins and enzymes. Sulphur compounds released into the gas phase during the thermochemical processes are the precursors of SO_x , which can be transferred in atmosphere into H_2SO_4 . Under reducing conditions sulphur can be found mainly as CaS (solid phase) and H_2S (g) up to 1270K. At higher temperatures H_2S (g) is the dominating specie.

In the biomass and the char samples sulphur can be present in the solid phase in form SO_4^{2-} or S^{2-} . It was also found that in the corn before pyrolysis sulphur was fixed in form of S^{2-} and after the corn pyrolysis sulphur remained in char in the same form. Whereas in the hemp pellets sulphur was fixed as SO_4^{2-} and after pyrolysis up to 600°C it was found in the same form, but after pyrolysis at temperatures higher than 700°C sulphur was detected as S^{2-} .



Figure 4.5.2-7: Sulphur distribution after the pyrolysis process

The distribution of sulphur into char and volatiles is shown in figure 4.5.2-7. As can be seen in the figure 95 w-% of origin sulphur were found in volatiles during corn pyrolysis and only 5 w-% remained in the corn char. At temperatures between 600 and 850°C the amount of sulphur, which remained in corn char was constant. On the other hand in case of hemp even at temperature of 850°C about 40 w-% were still found in hemp char.

Chlorine

Chlorine content in corn was 0.131 w-% and in hemp 0.143 w-%. Chlorine is one of the elements (sulphur too), which influence the behaviour of other elements, esp. metals. Figure 4.5.2-8 shows the distribution of chlorine in gas and solid phase after pyrolysis.



Figure 4.5.2-8: Chlorine behaviour during the corn and hemp pellets pyrolysis

The higher alkali metal concentrations in the fuel increase the sintering ability of the fuel. If we compare the content of K and Cl in both the fuels (corn and hemp), we can see that the Cl content in the corn and hemp is similar whereas the potassium content in the hemp is about two-times higher than the potassium content in corn. This could be a reason, why even at 850°C about 45 w-% of chlorine were still left in hemp char. Hemp contains also higher amounts of sodium, which is known to lower the sintering temperatures. The comparison of the results from the corn and hemp pyrolysis with literature data can be seen in figure 4.5.2-9.



Figure 4.5.2-9: Comparison of Cl release during the pyrolysis of different types of biomass (Jensen et al., 2000)

As can be seen, the experimental results from this work correspond well with literature data (straw pyrolysis) (Jensen et al., 2000).

Potassium

Alkalis content varies in biofuels in a wide range depending on the biomass sources. Agricultural residues such as straw are high in the alkalis content, followed by grass. Woody biomass has a low content of alkalis.

The samples of corn and hemp contained 0.560 w-% and 1.080 w-% of potassium respectively.

The following figure shows the distribution of potassium after the pyrolysis process.



Figure 4.5.2-10: Potassium distribution after the pyrolysis process

As can be seen in the figure more than 80 w-% of potassium remained in the solid phase even at temperature of 850°C.

Figure 4.5.2-11 shows a comparison of the results from this work with literature. As it can be seen the results from experimental work correspond well with literature data.



Figure 4.5.2-11: Comparison potassium release with literature data (Jensen et al., 2000))

4.6 Biomass pyrolysis - Conclusions

Investigations of elements behaviour during the wood, corn and hemp pyrolysis were performed. Using two detection methods (ICP and X-ray fluorescence method) the amount of elements remaining in wood char was defined. The results were compared with data from literature.

The elements behaviour is a complex process influenced by many factors. It is strongly dependent on the type of element bonds in the pyrolysed material, which means that it is important if the metal is bound in the organic constituents or in the mineral matrix. The concentration of the element in the biomass material is also not negligible. Temperature, presence of sulphur and chlorine and oxidizing/reducing conditions are further important factors.

At the temperature of 800°C 26.45 w-% of origin **carbon** were found in wood char, in case of corn it was about 20 w-% and about 30 w-% of origin carbon were found in hemp char. Figure 4.6-1 shows an overview of carbon distribution in biomass char at 400, 600 and 800°C.



Figure 4.6-1: Amount of origin carbon in biomass char after pyrolysis at different temperatures

At the temperature of 800°C only 2 w-% of origin **hydrogen** were found in wood char, 1.5 w-% of hydrogen were detected in corn char and 3.5 w-% of origin hydrogen remained in hemp char after pyrolysis process. Hydrogen distribution in biomass char after pyrolysis is given in figure 4.6-2.



Figure 4.6-2: Amount of origin hydrogen in biomass char after pyrolysis at different temperatures

Nitrogen is bond in the volatile matter mostly as HCN and NH_3 during the pyrolysis and gasification process. These are two important precursors of NO_x . At 800°C only 23 w-% of origin nitrogen were found in wood char, 20 w-% were found in corn char and only 3.5 w-% of origin nitrogen remained in hemp char after pyrolysis process. Figure 4.6-3 gives an overview about nitrogen left in biomass char after pyrolysis process.



Figure 4.6-3: Amount of origin nitrogen in biomass char after pyrolysis at different temperatures

Sulphur as well as chlorine influences the behaviour of other elements and during pyrolysis process releases in form H_2S (g). Elemental analysis of the biomass samples before and after pyrolysis process showed that sulphur in the fresh biomass and in the char was present in form SO_4^{2-} or S^{2-} . About 47 w-% of sulphur were found in the wood char after pyrolysis at 800°C. In case of corn 3 w-% were detected and about 40 w-% were still left in hemp char. The distribution of sulphur after pyrolysis at 400, 600 and 800°C shows figure 4.6-4.



Figure 4.6-4: Amount of origin sulphur in biomass char after pyrolysis at different temperatures

Chlorine content in the biomass strongly influences the behaviour of other elements (especially metals). Based on the results from measurements, about 28 w-% of origin chlorine were found in wood char at temperature of 800°C. At the same temperature only 3 w-% were detected in corn char and about 48 w-% were found in hemp char. The reason why at

temperature of 800°C 48 w-% of origin chlorine were still left in hemp char can be higher content of potassium fixed in hemp. The higher alkali metal concentrations in the fuel increase the sintering ability of the fuel. Chlorine distribution in biomass char after pyrolysis is shown in figure 4.6-5.



Figure 4.6-5: Amount of origin chlorine in biomass char after pyrolysis at different temperatures

Figure 4.6-6 shows the results from corn pyrolysis in muffle furnace.



CI in Futtergerste, Maispflanzenfasern und Stroh

Figure 4.6-6: Chlorine distribution in char after corn pyrolysis in muffle furnace (Soukup, 2005)

As can be seen from figures 4.6-5 and 4.6-6 about 15 w-% of origin chlorine were found in corn char using fluidized bed pyrolysis reactor at 400°C and the same amount was found also

after corn pyrolysis at temperature of 450°C using muffle furnace. At higher temperatures the results are different.

Alkali metals (K, Na) are devolatilized in two steps. During the first one (at temperature till $500 - 600^{\circ}$ C) the devolatilization from the organic bonds takes place. With rising temperature, above 600°C, alkali metals release from mineral matrix of the char residue. During this second step, the presence of Cl strongly influences alkali metals behaviour. **Potassium** is mostly bond to chlorine as KCl if chlorine is available in biomass. The most possible potassium compounds released from biofuels are KCl, K₂SO₄ and KOH. Results from the measurements showed that even at 800°C about 70 w-% of K remained in wood char, in case of corn and hemp 89 w-% and 82 w-% respectively of origin potassium were detected in char. Potassium distribution in biomass char is shown in figure 4.6-7.

Behaviour of Na in the biomass is similar as behaviour of K, but the content of Na in biomass is more than 10-times lower.



Figure 4.6-7: Amount of origin potassium in biomass char after pyrolysis at different temperatures

The possibility of results comparison offers figure 4.6-8.

K in Futtergerste, Maispflanzenfasern und Stroh



Figure 4.6-8: Potassium distribution in char after corn pyrolysis in muffle furnace (Soukup, 2005)

In figures 4.6-7 and 4.6-8 potassium distribution in char is shown. As can be seen at temperature of 400°C 100 w-% of origin potassium were found in corn char using fluidized bed reactor and 80 w-% were detected at the temperature of 450°C using muffle furnace. At the temperature of 550°C 75 w-% of potassium were detected in corn char and at temperature of 600°C about 80 w-% were detected in corn char after pyrolysis in fluidized bed reactor.

Based on data from literature and analysis results it is possible to say, that the most volatile metals are **Hg**, **Cd**, **Pb**. These metals are present in the volatiles in the gaseous form. The moot point can be the behaviour of **Zn** and **As**. The behaviour of **Zn** and **As** is very dependent on the presence of chlorine and sulphur.

Metals such as Cr, Cu, Mg and Mn remained mostly in char. Content of Al, Ni, Fe and Li in the biomass is very low, that is why, it was impossible to define their behaviour based on the results from analysis. But from literature is known, that they mostly remain in the char.

The overview of elements distribution after the biomass pyrolysis at temperature of 400, 600 and 800°C is shown in figures 4.6-9, 4.6-10 and 4.6-11.



Figure 4.6-9: Elements distribution in char after pyrolysis process at temperature of 400°C



Figure 4.6-10: Elements distribution in char after pyrolysis process at temperature of 600°C



Figure 4.6-11: Elements distribution in char after pyrolysis process at temperature of 800°C

Figure 4.6-12 shows the amount of selected elements after the same corn pyrolysis in muffle furnace.



Figure 4.6-12: Volatiles, char and elements distribution in corn char after pyrolysis in muffle furnace (Soukup, 2005)

Figures 4.6-9, 4.6-10 and 4.6-12 offer the possibility of results comparison. As can be seen higher amount of carbon was found in corn char after pyrolysis process in muffle furnace. At temperature of 450 °C 58 w-% was detected in char. But using fluidized bed reactor, at temperature of 400°C 40 w-% were detected in corn char.

Also amount of hydrogen which was detected after pyrolysis in muffle furnace was higher than in case of pyrolysis in fluidized bed reactor. At 400°C 13 w-% were detected in corn char using fluidized bed reactor and at 450°C about 20 w-% were detected in corn char after pyrolysis in muffle furnace.

After pyrolysis at 400°C in fluidized bed reactor 60 w-% of origin nitrogen were found in corn char and at 450°C 71 w-% were detected in corn char after pyrolysis in muffle furnace.

Sulphur amounts detected in corn char after pyrolysis in fluidized bed reactor were slightly higher that the sulphur amounts found in char after pyrolysis in muffle furnace.

At temperature of 400°C 14 w-% of origin chlorine were found in corn char using fluidized bed reactor and 21 w-% were detected using muffle furnace.

5 Gasification

In this chapter air gasification of the biomass (milled wood pellets) under ambient pressure using a small scale stationary fluidized bed reactor will be described.

5.1 Characteristics of used biomass

During the gasification process milled wood pellets (granulometry 2-5 mm) were used. Characteristics of the pellets can be seen in the following table.

		Wood pellets (as	Wood pellets (dm)
		used)	
С	[w-%]	45.71	49.00
Н	[w-%]	6.08	6.52
Ν	[w-%]	0.11	0.12
S	[w-%]	< 0.05	< 0.05
Cl	[mg/kg]	121.26	130
Na	[mg/kg]	12.13	13
К	[mg/kg]	329.28	353
Mg	[mg/kg]	121.26	130
Mn	[mg/kg]	88.61	95
Zn	[mg/kg]	8.76	9.4
Hg	[mg/kg]	< 100	< 100
Cd	[mg/kg]	< 1	< 1
Pb	[mg/kg]	< 50	< 50
As	[mg/kg]	< 50	< 50
Moisture	[w-%]	6.72	-
Ash	[w-%]	0.24	0.26
Upper heating value	[kJ/kg]	18620	19962
Lower heating value	[kJ/kg]	17120	18530

Table 5.1-1: Analysis of the wood pellets

Analyses of the wood pellets were performed based on these standards:

- DIN 51701 (preparation of the sample)
- DIN 51718 (moisture)
- DIN 51719 (ash content)
- DIN 51900 T3 (heating value)
In figure 5.1-1 a sample of milled wood pellets that were used for the investigation can be seen.



Figure 5.1-1: Photo of the milled wood pellets

5.2 Characteristics of used bed materials

Three different bed materials were used during the gasification process: quartz sand, olivine and calcite and their influence on NH₃ content, tar content and the gas composition was investigated. Quartz sand is very often used as a bed material during the industrial biomass thermoconversion processes (gasification or combustion in fluidized bed reactors) because of its good mechanical properties. Olivine and calcite are known to lower the tar content in the product gas but there is a lack of knowledge about the influence of these bed materials on NH₃ content in the product gas.

5.2.1 Quartz sand

Austrian quartz sand was used as a bed material during the biomass gasification process. The sample of the sand can be seen in figure 5.2.1-1.



Figure 5.2.1-1: Photo of Austrian quartz sand

- Chemistry: SiO₂, Silicon dioxide
- Class: Silicates
- Group: Quartz
- Hardness: 7
- Mean diameter: 250 µm
- Density: 2600 kg/m^3

Compositionally, quartz is usually quite pure, with only traces of other elements like aluminium, sodium, potassium and lithium. Quartz is found as large crystals that are often beautifully colored by impurities. These impurities cause that quartz form varieties such as agate, amethyst, blood stone, blue quartz, cat's eye, chalcedony, geodes, jasper, opal, rock crystal, rose quartz, smoky quartz etc.

5.2.2 Olivine

Austrian olivine was used during the experimental work. The sample of the olivine is shown is figure 5.2.2-1.



Figure 5.2.2-1: Photo of the olivine

- Chemistry: (Mg, Fe)₂SiO₄, Magnesium Iron Silicate
- Class: Silicates
- Subclass: Nesosilicates
- Group: Olivine
- Hardness: 7
- Mean diameter: 250 µm
- Density: 2900 kg/m³

Table 5.2.2-1 shows the results of chemical analysis of olivine used during gasification and physical properties of the olivine are shown in table 5.2.2-2.

MgO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Cr_2O_3	Mn ₃ O ₄	CaO
W-%						
48.0-50.0	39.0-42.0	8.0-10.5		0.8		0.4

Table 5.2.2-1: Chemical analysis of olivine used during the gasification

Specific weight	Bulk density	Total porosity	Apparent porosity	Water absorption	Bulk weight
g/cm ³		%			kg/dm ³
3.25-3.30	2.80-2.90	13.00-14.00	8.50-9.50	29.0-3.50	1.45-1.70

5.2.3 Calcite

Austrian calcite was used during the biomass gasification. Figure 5.2.3-1 shows the calcite sample.



Figure 5.2.3-1: Photo of the Austrian calcite

- Chemistry: CaCO₃, Calcium Carbonate
- Class: Carbonates
- Group: Calcite
- Hardness: 3
- Mean diameter: 250 µm
- Density: 2710 kg/m³

Calcite contains usually also trace amounts of magnesium, iron, manganese and other elements.

One of the calcite properties is the acid test. Calcite will always effervesce (bubble) when even cold weak acids are placed on specimens. The reason for the bubbling is in the reaction below:

$$CaCO_3 + 2H(+1) \rightarrow Ca(2+) + H_2O + CO_2(g)$$
 [eq. 5.2.3-1]

Based on this reaction it is easy to recognize calcite and dolomite.

Calcite used during the biomass gasification process in the fluidized bed reactor showed a good ability to decrease the tar content in the product gas, what is described in the further work. On the other hand it is a very soft material what causes problems during the fluidized bed gasification process. During the fluidization process the abrasion of the bed material particles takes place and very small calcite particles are not able any more to stay in the reactor and come with the product gas, through the cyclone to the filter, where they are accumulated and rising local pressure in the filter area.

5.3 Characteristics of used additive

The dried saturation sludge from the sugar industry was used as an additive during the biomass gasification process in a ratio sludge/wood of 1/7. The sludge was used during the combustion tests (Szeliga et al., 2004) and based on the results of measurement during the combustion process; the influence of the sludge on the tar content in the product gas was evident. The effect of the lowering tar content in the product gas also during the gasification was expected and experimentally verified.

The saturation sludge is a by-product during the sugar production process from sugar beet. The burnt limestone and carbon dioxide are used for the treatment of sugar juice at sugar factories. Chemical and physical characteristics of the sludge can be seen in the following tables and figures.

SiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	CaO	Na ₂ O		
W-%							
3.24	1.14	0.14	0.31	51.37	0.003		

Table 5.3-1: Chemical analysis of the additive

Mn	Cu	Cd	Zn	Pb	Со	Ni	Cr	Sr
mg/kg								
161	26	0,5	70	22	6	19	< 10	52

Table 5.3-2: Heavy metals in the used saturation sludge



Figure 5.3-1: Granulometry of the used additive



Figure 5.3-2: Photo of the saturation sludge (on the photo mixture with the quartz sand)

As can be seen in the figure 5.3-2, the dried sludge is a very fine material and has a big specific surface. This can be the reason, why the problematic compounds produced during the gasification (tars) can be fixed on this material.

The disadvantage of this material is its very small granulometry. That is why it was expected that this material is too fine to residence for a longer time in the gasification zone and it will leave the reactor with the gas stream. The experiments performed using the gasification unit described in this work and the combustion tests performed in the Czech Republic showed that the residence time of the sludge in the reactor is not only few minutes but several hours. (Szeliga et al., 2004)

5.4 Gasification unit

Gasification tests were performed using a small scale stationary fluidized bed unit (inner diameter 66 mm, height 2.20 m), which was made of high temperature steel (1.48.41). The conversion unit consisted of two stationary fluidized beds, a two-screws feeding system, a cyclone and a filter.

The lower fluidized bed was used for the preheating of incoming fluidization agent (air) and it was formed by the quartz sand, with a mean diameter of $350 \ \mu\text{m}$. The upper one was used for the gasification of the biomass and it was formed by quartz sand, olivine or calcite. Mean diameter of the bed materials in the gasification zone was $250 \ \mu\text{m}$ and the amount $500 \ \text{g}$. The conversion unit was electrically heated using 3 couples of the heating shells and covered with insulation material. The filter and the cyclone were also electrically heated using heating belts.

The gas produced during the gasification was transported through the cyclone, where the coarse particles were separated. The fine particles, which remained in the gas stream, were caught on the filter. The externally heating of the cyclone and the filter was necessary because of the tar condensation, which occurred at a temperature of 350°C and lower. The temperature of the gas after the cyclone was about 410°C. The scheme of the unit can be seen in figure 5.4-1. In figure 5.4-2 a photo of the test rig for the gasification experiments is shown.



Figure 5.4-1: Scheme of the fluidized bed gasification unit

During the gasification process the temperature was measured at three points in the unit and on the wall of the unit:

- in the preheating fluidized bed
- in the gasification fluidized bed
- in the freeboard.

The temperature was measured each 5 seconds and recorded using software "Notebook Pro". The temperature of the preheating fluidized bed was set to 500°C during all gasification experiments. The temperature of the fluidized bed was varying between 750 and 850°C. The freeboard was not electrically heated, it was only isolated with the insulation fibre material ALSITRA made by the firm RATH. The temperature of the freeboard was always about 80°C lower than the temperature in the gasification fluidized bed.

Air was used as the fluidization agent, ER was varying between 0.3 - 0.4. During the gasification process nitrogen flow (100 Nl/h) was used to cool the feeding system.



Figure 5.4-2: Photo of the test rig

5.4.1 Feeding system

A new feeding system was designed and constructed specially for the purpose of this experimental work. Milled wood pellets (granulometry 2-5 mm) were fed into the unit continuously using a system of two screw feeders which were powered by two electromotors coupled with the gear box. The motors and gear boxes were made by Getriebebau NORD GmbH. Using a rotation transformer which was connected with the upper screw feeder it was possible to set the rotation rate and to calibrate the feeding system for the amount of 750 g of



the wood per hour coming continuously to the unit. The lower screw feeder was intended for the fast transportation of the biomass into the unit.

Figure 5.4.1-1: Photo of the feeding system

The biomass was fed into the gasification reactor during all gasification experiments using this feeding system. Further details concerning the feeding system can be found in appendix.

5.4.2 Cyclone and filter

The cyclone diameter was 120 mm and the height 220 mm. The cyclone was necessary to separate the coarse particles from the gas stream. The separation efficiency of the cyclone was very small in the case of particles < 10 μ m. That is why the cyclone was coupled with the filter.

The filter was formed by two flanges and a filter paper fixed between them. The filter paper (diameter 110 mm) consisted of the glass fibres and was suitable for the separation of the fine particles $(0.3 - 1 \ \mu m)$ at temperatures up to 500°C. Before each experiment the new filter paper was installed because of the formation of the filter cake.

Filter and cyclone are shown is figure 5.4.2-1.



Figure 5.4.2-1: Photo of the cyclone and the filter

5.5 Gas sampling and analysis

During the biomass gasification the product gas quality was measured. The gas composition $(C_2H_4, C_2H_6, 1\text{-buten}, N_2, CH_4, hydrocarbons C_3 and C_4, CO and CO_2)$ was measured each 20 minutes using on-line gas chromatograph (GC). CO, CO₂ and O₂ were measured each 2 seconds using NGA 2000 and data recorded using the software program "Notebook Pro".

Device	Туре	Measured gas	Measuring principle	Range	Gas	Sampling
GC		all	Gas chromatography	0-100%	Product	each 20 min
				0.100.0/	Sub	
NGA 2000 Ro		CO	IR-Gas analyser	0-100 %		
		CO_2	IR-Ous analyser	0-100 %	Product	
	RosemountParamagneO2behaviourof oxyger	Paramagnetic		riouuci	Online	
		O_2	behaviour	0-100 %	gas	
			of oxygen			

	Table 5.5-1:	Measurement	devices for	r on-line	measurements
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5.5.1 Gas chromatography

Chromatography is a technique for separating chemical substances that relies on differences in partitioning behavior between a flowing mobile phase and a stationary phase to separate the components in a mixture. The sample is carried by a moving gas stream through a tube packed with a finely divided solid or may be coated with a film of a liquid. Because of its simplicity, sensitivity, and effectiveness in separating components of mixtures, gas chromatography is one of the most important tools in chemistry. It is widely used for quantitative and qualitative analysis of mixtures, for the purification of compounds, and for the determination of such thermochemical constants as heats of solution and vaporization, vapour pressure and activity coefficients.

5.5.2 Non-dispersive IR measuring system

Non-dispersive IR method is described in chapter "Pyrolysis".

5.5.3 Tar sampling and analysis

The definition which components belong to the tar is mainly dependent on the measurement method. At the Institute of Chemical Engineering (Vienna University of Technology) a measurement method was developed, which is based on the tar protocol "Gravimetric Tars" (Neeft et al., 1999). The tar measurement was done by taking isokinetically a side-stream of the product gas for a certain period of time. The gas was led through 6 wash bottles filled with toluene, which was cooled down to -20°C. There the low boiling tars ($T_B < 200^{\circ}$ C) were condensed.

The liquid phases in the washing flasks were unified and the aqueous phase was separated from the toluene phase. The amount of toluene was also marked down and a small sample was taken to characterise the tar composition in a gas-phase chromatograph coupled with a mass spectrometer (GC-MS). Then the main part of the toluene was evaporated from the sample in a rotovapor. The residual was transferred to a Petri dish and dried for a defined period of time in a drying oven. To obtain the amount of the light boiling tars the Petri dish was weighed before and after the analysis.

To determine the quantity of tar and the tar composition in the product gas a gas-phase chromatograph (Perkin Elmer, Autosystem XL) coupled with a quadrupole mass spectrometer (Perkin Elmer, Turbo Mass) was used. The internal standard of the GC-MS covers more components than displayed to ensure that no component is missed.

5.5.4 Ammonia sampling and analysis

For the ammonia sampling the same probe as for tar sampling was used. The sample system consisted of a ball valve, a heated probe and a series of four cooled washing flasks, containing

a sulphuric acid solution to catch the ammonia. The cooling temperature was 2°C, so the temperature near the freezing to ensure a nearly water free product gas. The dry gas flow was monitored with a gas meter. Usually a sampling run lasted for 30 minutes at a flow rate of 0.08 Nm^3 /h. The solvent of four wash flasks was unified for the further analysis. The total amount of ammonia in the sulphuric acid solution was determined by ion chromatography in a Dionex DX-120. Because the samples were introduced in an acid solution, NH₃ was quantitatively detected as NH₄⁺.

5.5.5 H₂S sampling and analysis

Dräger tubes were used for this purpose (range of the measurements 0.5-15 ppm). The gas samples were taken after the filter.

5.6 Experimental part

The biomass gasification was performed under ambient pressure and air was used as the fluidizing agent. Several factors such as temperature, ER, the moisture of the biomass and bed material were varied. During the biomass gasification also an additive (saturation sludge from sugar industry) was used.

Temperature [°C]	750°C	850°C		
ER	0.3	0.4		
Bed material		Quartz	Olivine	Calcite
		sand		
Biomass		6.7	15.2	21.5
moisture [w-%]				
Fuel		Wood	Wood with additive	

Table 5.6-1 shows experimental conditions during biomass gasification.

Table 5.6-1: Conditions which were varied during the gasification of biomass (grey field – standard conditions)

Gasification process

At the beginning of each experiment new filter paper in filter was installed and the biomass fuel was filled into the hopper. The test rig was taken into the operation by switching on the fluidization and setting a required air mass flow. Then the heating shells were also switched on. When the temperature in the fluidized bed reactor nearly reached the desired process temperature, nitrogen for cooling the feeding system and the heating belts for cyclone and filter were switched on. When the temperature in the gasification reactor reached required process temperature the fuel from hopper was fed into the unit and measuring of CO, CO₂ and O₂ started. After approximately 10-15 minutes, when the amounts of CO and CO₂ produced during the gasification were constant the sampling of the gas started.

5.6.1 Results and discussion

5.6.1.1 Influence of temperature and ER

Temperature [°C]	750°C	850°C
ER	0.3	0.4
Bed material		Quartz
		sand
Biomass		6.7
moisture [w-%]		
Fuel		Wood

Table 5.6.1-1: Gasification conditions during experiments

NH₃ content in the product gas

Figure 5.6.1-1 shows that the NH₃ content in the gas phase is strongly dependent on the ER. With higher ER the content of NH₃ measured in the gas phase was significantly lower. As can be seen in the figure, at a temperature of 750 °C and an ER of 0.3, the NH₃ content measured in the gas phase was 338 ppm and at the same temperature and ER of 0.4 it was 266 ppm. At a temperature of 850°C and ER of 0.3 it was 382 ppm, at the same temperature and ER of 0.4, it was only 254 ppm. The influence of the rising temperature of 750°C and 850°C it was 338 ppm and a temperature of 750°C and 850°C it was 338 ppm and a temperature of 750°C and 850°C it was 266 ppm and 382 ppm respectively. At an ER of 0.4 and temperature 750°C and 850°C it was 266 ppm and 254 ppm respectively.





H₂S content in the gas phase

 H_2S content in the gas phase was measured at a temperature of 850°C and an ER of 0.4. 4-7 ppm of H_2S were detected in the gas phase. The content of H_2S in the gas phase is dependent on the sulphur content in the biomass. It is well known that the sulphur content in the wood is very low. In the case of the wood pellets it was less than 0.05 w-% of sulphur. Because of the very low content of H_2S in the gas phase, this was not more measured during the next experiments.

Tar content in the gas phase

The results of the tar measurements are shown in the following figure. As it can be seen, the tar content was dependent on the ER and also on the temperature.

As expected, with higher ER the amount of tars slightly decreased. On the other hand with higher temperature lower amount of tars in the gas phase was expected. But as can be seen in figure 5.6.1-2, the tar content at a higher temperature was also higher. This could be influenced by the different residence time of biomass particles in the reactor at temperatures of 750 and 850°C and by a catalytical effect due to higher char content in the reactor at 700°C.



Figure 5.6.1-2: Tar content in the gas at different temperatures and ER

The composition of the tar was analysed by GC-MS measurements.

The major tar components were: phenol, indene, styrene, naphthalene, acenaphtylene, fluorene, phenanthrene, anthracene and pyrene. Details characteristics of the tar compounds can be found in appendix.

Gas composition and heating value

The composition of the product gas was measured using on-line gas chromatograph (C_2H_4 , 1buten, C_2H_6 , O_2 , N_2 , CH_4 , hydrocarbons – C_3 and C_4) and IR-spectrometer (O_2 ,CO, CO_2).



Figure 5.6.1-3: Gas composition at different temperatures and different ER



Figure 5.6.1-4: Heating value of the product gas

As expected at an ER of 0.3 the heating value of the gas was higher as at an ER of 0.4. In figure 5.6.1-3 it can be seen that at an ER of 0.4 the content of the CO, CH_4 and C_2H_4 in the gas was significantly lower as at an ER of 0.3. On the other hand CO_2 and N_2 at an ER of 0.4 are higher because of the higher amount of oxygen coming into the reactor. The effect of the temperature was not as evident as at varying ER.

5.6.1.2 Influence of bed material

Temperature [°C]	850°C		
ER	0.4		
Bed material	Quartz	Olivine	Calcite
	sand		
Biomass	6.7		
moisture [w-%]			
Fuel	Wood		

Table 5.6.1-2: Gasification conditions during experiments

NH₃ content in the product gas

Figure 5.6.1-5 shows that the NH₃ content in the gas phase during the gasification with the bed material quartz sand and olivine was fairly the same. But in the case of the calcite, the NH₃ content was about 17 % higher. During the gasification nitrogen from biomass is mostly conversed into NH₃, HCN, NO_x, N₂ or heavy aromatic compounds, while a smaller part of nitrogen remains in a solid char. Independent of the type of the feedstock, more NH₃ is formed than other nitrogen containing compounds in most gasifiers. The amount of NH₃ in the gas phase during the gasification is dependent on the nitrogen content in the biomass. The most important requirement for the formation of NH₃ from the reaction in the solid char is the presence of H radicals to hydrogenate the char-N for form NH₃. The hydrogenation process proceeds relatively slowly.



Figure 5.6.1-5: NH₃ content in the product gas using three different bed materials

The calcite is a soft material, which is during the fluidization crumbled and the material with higher specific surface is formed. It is possible, that besides the catalytic effect of the calcite, also the higher specific surface of the calcite was responsible for the higher amount of the NH₃ content in the gas phase.

During the gasification the CaCO₃ decomposes to CaO and CO₂. It is also possible that CaO produced influences the formation of the NH_{3} . A similar effect was observed using the additive, which contains more than 50 w-% of the CaO.

Olivine and dolomite as additives to the bed materials during biomass gasification were compared by Corella et al. (2004). NH_3 content in the gasification gas was higher with dolomite than with olivine.

Tar content in the gas phase

It is well known from literature that using olivine as bed material during biomass gasification the tar content in the product gas can be lower than using quartz sand. In the case of the calcite, a significant reduction of the tar content in the gas phase was measured. The reason could be a catalytic effect of the calcite and also a fixation of tars on the filter cake, which was formed not only by char particles but also by the calcite particles escaped from reactor.



Figure 5.6.1-6: Tars content in the gas phase





Figure 5.6.1-7: The composition of the product gas using three different bed materials

As can be seen in figure 5.6.1-7 lower amount of CH_4 was detected in gas using olivine and calcite what influenced also the heating value of product gas.



Figure 5.6.1-8: Heating value of the product gas

5.6.1.3 Influence of the fuel

Temperature [°C]	850°C	
ER	0.4	
Bed material	Quartz	
	sand	
Biomass	6.7	
moisture [w-%]		
Fuel	Wood	Wood with additive

Table 5.6.1-3: Gasification conditions during experiments

Clean wood and mixture of wood with the sludge (weight ratio - saturation sludge/clean wood = 1/7) were used during these experiments.

NH₃ content in the gas phase

The results showed that the amount of NH_3 produced during the gasification of clean wood was lower than in the case of a mixture of wood with the sludge. The saturation sludge from sugar industry contains about 1.23 w-% of nitrogen. It is evident that the nitrogen from the sludge caused the higher content of the NH_3 .



Figure 5.6.1-9: NH₃ content in the gas phase during the gasification of the wood and the mixture of wood with sludge

Tar content in the gas phase

The catalytic effect of the sludge on the tar formation is given in figure 5.6.1-10. As can be seen, the tar content was about 32 % lower if the mixture of the wood and the sludge was used. The catalytic effect of several sludges on the tar formation is well described by Szeliga et al. (2005).



Figure 5.6.1-10: Tars content in the gas phase

Gas composition and heating value

The product gas composition and heating value are shown in figures 5.6.1-11 and 5.6.1-12. As can be seen in the figure, higher CO_2 , N_2 and H_2 contents were found in the gas using the sludge as an additive.



Figure 5.6.1-11: Gas composition



Figure 5.6.1-12: Heating value of the gas produced during biomass gasification

The heating value of the product gas was lower when the sludge as an additive was used, because of the lower content of the CH_4 and CO in the product gas.

5.6.1.4 Influence of the moisture content of biomass

Temperature [°C]	850°C		
ER	0.4		
Bed material	Quartz		
	sand		
Biomass	6.7	15.2	21.5
moisture [w-%]			
Fuel	Wood		

Table 5.6-4: Gasification conditions during experiments

The moisture of the milled wood pellets used during the gasification is originally of 6.7 w-%. The wood with higher moisture was prepared manually using a distilled water of a high purity, which was sprayed on it. The milled wood pellets were well mixed before they entered the reactor. During the experiments when the wood with moisture of 6.7 and 15.8 w-% was

used, no problems with the feeding were achieved but using the wood with moisture of 21.5 w-% caused problems during the feeding process because of the fuel bridges building.

With higher moisture of the wood rose also ER, because of oxygen which was fixed in additional water and slightly lower amount of wood entering the gasification reactor. Higher ER caused lower tar, CH_4 , hydrocarbons (KW) and NH_3 content in gas what can be seen well at following figures. The amount of N_2 was higher because of rising ER.

NH₃ content in the gas phase

A significant lower content of NH_3 and tars with higher moisture of the wood was found in the gas phase. On the other hand the results of the gas composition, measured using on-line chromatograph, showed higher amounts of CO_2 and N_2 and lower amount of CO and CH_4 in the gas. All these results demonstrate the higher ER.



Figure 5.6.1-13: NH₃ content in the product gas using the wood of different moisture

Tar content in the gas phase

The tar content in the gas phase was lower when the wood with higher moisture was used. This was caused by the steam formed from the fuel moisture and higher ER during the gasification process.



Figure 5.6.1-14: Tar content in the gas phase

Gas composition and heating value

The heating value was lower when the wood with higher moisture was used. As can be seen in the figure 5.6.1-15 also the CH₄ and CO contents were lower because of higher ER.



Figure 5.6.1-15: Gas composition



Figure 5.6.1-16: Heating value of the product gas

With higher moisture of wood (higher ER) lower heating values of the gas were calculated. This was caused by lower amounts of CH₄, hydrocarbons and CO in the gas.

5.6.2 Biomass gasification - Conclusions

The gasification process was performed under the different temperatures and ER. Three types of the bed materials and wood of different moisture with or without additive was used. NH_3 , H_2S , tar content and the gas composition were measured during the gasification. The effect of the temperature was not as significant as in the case of ER. With higher ER lower tar and NH_3 concentrations were detected. Higher ER caused also lower heating value of the product gas because of lower concentrations of CH_4 and CO and higher N_2 and CO_2 amounts.

Quartz sand, olivine and calcite were used as bed materials during the gasification process. The NH₃ content using the quartz sand and the olivine was nearly the same, 254 and 242 ppm respectively. Using the calcite, 296 ppm of the NH₃ was detected in the gas. The amount of tars in the case of quartz sand was 7.2 g/Nm³. Lower amounts (6.3 g/Nm³) were measured using olivine and only 1.5 g/Nm³ of tar was detected using calcite as a bed material. The calcite has a good ability to lower the tar content in the product gas; on the other hand it is a very soft material and in the fluidized bed reactor it is crushed into the very small particles, which leave the reactor with the product gas stream.

The gas heating value of 9.27 MJ/Nm³ was calculated when the quartz sand was used as bed material. The lower values 7.14 and 7.47 MJ/Nm³ were calculated in the case of olivine and calcite respectively.

Wood with different moisture was used. 6.7, 15.8 and 21.5 w-% was the water content of the wood during the investigations. With higher moisture of wood, a lower NH₃ content in the gas phase was measured. (254, 82.67 and 50 ppm). But the higher contents of N₂ were measured in the product gas with rising moisture. The tar content in the gas phase decreased with the rising moisture. 7.2, 4.9 and 3.3 g/Nm³ were the values of the tar measured in the gas using the wood with 6.7, 15.8 and 21.5 w-% of the fuel moisture.

With the rising moisture of the wood, the heating value of the product gas decreased. Using wood with moisture of 6.7 w-% a gas with a heating value of 9.27 MJ/Nm³ was produced, but using the wood with moisture of 21.5 w-% it was only 4.51 MJ/Nm³. All these results demonstrate the higher ER.

The saturation sludge from sugar industry was added to the fuel, the ratio of sludge/wood was 1/7. As expected the tar content using this additive was reduced to 68 % of the origin amount using only clean wood. On the other hand the NH₃ content in the gas phase rose from 254 ppm to 391 ppm using the sludge as an additive. It is possible that the sludge supports the formation of NH₃ because of nitrogen content in the sludge.

Influence of ER on N2, NH3 and tar content in gas during biomass gasification

Figure 5.6.2-1 shows influence of ER on N₂ content in gas during biomass gasification.



Figure 5.6.2-1: N₂ content in gas during biomass gasification at different ER

As can be seen in figure 5.6.2-1, with higher ER also higher amount of N_2 in gas can be found. It is caused by higher amount of N_2 which is entering the gasification reactor. By

comparison of figures 5.6.2-1 and 5.6.1-15 ER during gasification of wood with different moisture can be defined approximately.

Figure 5.6.2-2 shows NH_3 content in gas at different ER. Based on figures 5.6.2-1 and 5.6.2-2 it is possible to say that with higher ER higher amount of N_2 and lower amount of NH_3 can be detected in gas.



Figure 5.6.2-2: Influence of ER on NH₃ content in gas during biomass gasification

Tar content in gas during biomass gasification is also influenced by ER, what can be seen in figure 5.6.2-3.



Figure 5.6.2-3: Influence of ER on tar formation during biomass gasification

With higher ER lower tar content in gas can be found. Tars consist of carbon and hydrogen as well as other hydrocarbons and CH_4 that is why at higher ER also lower amounts of CH_4 and hydrocarbons were detected in gas.

It is possible to say that at higher ER higher amounts of N_2 , CO_2 and lower amounts of NH_3 , tar, CO, hydrocarbons and CH_4 can be expected in gas during biomass gasification.

6 Conclusions

Experimental investigations of elements behaviour during the biomass pyrolysis and gasification were performed. Elements behaviour, respectively their distribution into the gas or solid phase during the thermochemical conversion processes of biomass is a very complex process influenced by many factors, such as temperature, pressure, fuel moisture, heating rate and presence of other elements.

6.1 Biomass pyrolysis

During the biomass pyrolysis three biomass types were used: wood, corn and hemp pellets. The effect of temperature on the elements behaviour was investigated. The pyrolysis tests were performed using a laboratory scale stationary fluidized bed reactor at temperature range of $300 - 850^{\circ}$ C. Nitrogen was used as a fluidizing agent and quartz sand as a bed material.

The amount of the volatile matter and the distribution of elements such as Cl, N, S, alkali and heavy metals into the gas or solid phase were in the focus of interest.

Chlorine content in the biomass strongly influences the behaviour of other elements (especially metals) during the thermochemical conversion processes. Chlorine can cause corrosion problems in conversion units because of the formation of HCl.

Distribution of chlorine into the char and volatiles after the pyrolysis was very different in the case of wood, corn and hemp. This difference can be caused by the content of potassium in the biomass. At 800°C 72 w-% chlorine from the wood released into the volatiles, in the case of corn it was 95 w-% and by the hemp about 50 w-% of origin chlorine released into the volatiles.

Nitrogen is mainly fixed in biomass in organic form as biopolymers, proteins, alkaloids, etc. During the biomass pyrolysis can be nitrogen found in the gas in form HCN and NH_3 . These are two important precursors of NO_x which is formed during the combustion. At 800°C only 23 w-% of origin nitrogen were found in the wood char, 20 w-% in the corn char and only 3.5 w-% were detected in the hemp char.

Sulphur is fixed in proteins and enzymes. During the pyrolysis process sulphur is present mainly as H_2S (g). Elementary analysis of the biomass samples before and after pyrolysis process showed that sulphur in the fresh biomass and the char was present in form of SO_4^{2-} or S^{2-} . After the pyrolysis at 800°C 47 w-% of the origin sulphur was found in the wood char, 40 w-% was still left in the hemp char, but only 3 w-% in the corn char.

Alkali metals in the biomass are fixed in the form of dissolved salts in the moisture or as a cation attached to carboxylic and other functional groups, which is high mobile. It is mostly

bond to chlorine as KCl if chlorine is available in biomass. The most possible potassium compounds released from biofuels are KCl, K_2SO_4 and KOH. Alkali metals (K, Na) are devolatilized in two steps. During the first one (at temperature till 500 – 600°C) the devolatilization from the organic bonds takes place. With rising temperature, above 600°C, alkali metals release from mineral matrix of the char residue. During this second step, the presence of Cl strongly influences alkali metals behaviour. Results from the measurements showed that even at 800°C about 70 w-% of origin potassium remained in wood char and about 80 w-% were detected in the corn and hemp chars. Behaviour of Na in the biomass is similar as behaviour of K, but the content of Na in biomass is more than 10-times lower.

Based on data from literature and analysis results it is possible to say, that the most volatile metals are Hg, Cd, Pb. These metals are present in the flue gas in the gaseous form. The moot point can be the behaviour of Zn and As. The behaviour of Zn and As is very dependent on the presence of chlorine and sulphur. Elements such as Cu, Rc, Mg, Mn, Al, Fe, Li, Ni and Sn remain mostly in char after the biomass conversion processes.

6.2 Biomass gasification

The gasification process was performed using a small scale stationary fluidized bed unit under the different temperatures and ER. Three types of the bed materials and the wood of different moisture with or without additive was used. NH₃, H₂S, tar content and the gas composition were measured during the gasification.

The effect of the temperature on the NH_3 and tars amounts was not as significant as in the case of ER. With higher ER the lower tar and NH_3 concentrations were detected. Higher ER caused also lower heating value of the product gas because of lower concentrations of CH_4 and CO.

The quartz sand, olivine and calcite were used as bed materials during the gasification process. The NH₃ content using the quartz sand and the olivine was nearly the same, 254 and 242 ppm respectively. Using the calcite, 296 ppm of the NH₃ was detected in the gas.

The amount of tars in the case of quartz sand was 7.2 g/Nm³. Lower amount, 6.3 g/Nm³ was measured using olivine and only 1.5 g/Nm³ of tars was detected using calcite as a bed material. The calcite has a good ability to lower the tar content in the product gas; on the other hand it is a very soft material and in the fluidized bed reactor it is crushed into the very small particles, which leave the reactor with the product gas.

The gas heating value of 9.27 MJ/Nm³ was measured when the quartz sand was used as the bed material. The lower values 7.14 and 7.47 MJ/Nm³ was measured in the case of the olivine and the calcite respectively.

The wood with different moisture was used. 6.7, 15.8 and 21.5 w-% was the water content of the wood. With higher moisture of the wood, the lower NH₃ content in the gas phase was

measured. It was 254, 82.67 and 50 ppm. But the higher contents of N_2 were measured in the product gas with rising moisture. It is possible to say, that with the rising moisture of the wood the nitrogen from the fuel is transformed rather to N_2 than to NH_3 . The tar content in the gas phase decreased with the rising moisture. 7.2, 4.9 and 3.3 g/Nm³ were the values of the tars measured in the gas using the wood with 6.7, 15.8 and 21.5 w-% of the fuel moisture. With the rising moisture of the wood, the heating value of the product gas decreased. Using the wood with moisture of 6.7 w-% the gas with heating value of 9.27 MJ/Nm³ was produced, but using the wood with moisture of 21.5 w-% it was only 4.51 MJ/Nm³.

The saturation sludge from sugar industry was added to the fuel, ratio sludge/wood =1/7. As expected the tar content using this additive was reduced to 68 % of the origin amount using only clean wood.

On the other hand the NH₃ content in the gas phase rose from 254 ppm to 391 ppm using the sludge as an additive. It is possible that the sludge supports the formation of NH₃. NH₃ is produced by the hydrogenation of the stable N-containing structures. The necessary is the availability of the hydrogen. As can be seen in the figure 5.6.1-11, during the gasification of the wood with the additive, the higher amount of the hydrogen was found in the product gas. It can be one of the reasons, why the NH₃ content was higher using the additive. The second reason for the higher NH₃ can be the nitrogen content in the saturation sludge.

7 Nomenclature

MSW	Municipal solid waste	$\mathbf{U}_{\mathbf{L}}$	Minimal fluidization velocity	[m/s]
dm	Dry mass	μ	Dynamic viscosity	[kg/ms]
v. high	Very high	ρ _g	Density of gas	[kg/m ³]
v. low	Very low	Pp	Particle density	[kg/m ³]
FBN	Fuel-bound nitrogen	ER	Equivalent ratio	[-]
EU	European Union	HCV	Higher calorific value	[MJ/Nm ³]
RDF	Refuse derived fuel	LCV	Lower calorific value	[MJ/Nm ³]
cr	Condensed solid phase	Α	Cross section of fluidized bed	[m ²]
ICP- AES	Inductively coupled plasma- atom emission spectroscopy	$\mathbf{H}_{\mathbf{L}}$	High of the layer at minimum fluidization velocity	[m]
KW	Kohlenwasserstoffe (C ₃ and C ₄)	$\epsilon_{ m L}$	Porosity at minimum fluidization velocity	[-]
g	Gravitation parameter			
GC	Gas chromatograph			
IR	Infrared			

8 Appendix

8.1 List of publications

Hrbek, J., Hrbek, M., Hofbauer, H., (2004): Nitrogen, sulphur, chlorine and heavy metal behaviour during biomass pyrolysis and gasification, Proc. of Science in Thermal and Chemical Biomass Conversion, Victoria, Canada, 30. August – 2. September 2004

Hrbek, J., Winter, F., Hofbauer, H., (2005): Quality and amount of volatiles and char from pyrolysis of corn and hemp, Proc. of the 14th European Biomass Conference, Paris, France, 17.-21. October 2005

8.2 Heavy metals

Species	Temperature	Species	Temperatur
As (g)	2000	Cr(OH) ₅ (g)	3000
AsCl ₃ (g)	2000	$CrO_2(OH)_2$ (g)	3000
AsH ₃ (g)	2000	CrO(OH) ₄ (g)	3000
AsO (g)	2000	$Cr(OH)_6$ (g)	3000
AsS (g)	1500	CrS (g)	2000
$As_2(g)$	2000	Cr (cr)	2000
$As_3(g)$	2000	CrCl ₂ (cr.l)	1500
$As_4(g)$	2000	$CrCl_3$ (cr)	1000
$As_4O_6(g)$	2000	Cr_2O_3 (cr)	2000
$As_2O_3(cr.l)$	700	CrS (cr)	2000
$As_2O_5(cr)$	1000	$Cr_2(SO_4)_2$ (cr)	780/1000
$Ca_2(AsO_4)_2(cr)$	1700	$[Cr(H_2O)_{\delta}]_2$	540
043(11004)2(01)	1,00	$(SO_4)_{x}^{2}H_2O_1(cr)$	0.0
		$[Cr(H_2O)_{cl_2}]$	540
		$(SO_4)_{r}^{2}^{2} H_2O_1(cr)$	0.0
Cd (g)	2000	$[Cr(H_2O)_{cl_2}]_{cl_2}$	540
cu (g)	2000	$(SO_4)_r 4H_2O_1(cr)$	540
CdCl. (g)	2000	$[Cr(H_{2}O)_{2}]_{2}$	540
cuci ₂ (g)	2000	$(SO_{1})_{a} = 5H_{a}O_{1}(cr)$	540
CdO(a)	2000	$(50_4)_3 511_2 O(CT)$	540
CuO (g)	2000	$(SO_1) 12HO(cr)$	540
CdS(a)	2000	$(30_4)_3 J^2 I I_2 O(CI)$	1900
$Cd_{(arl)}$	1000	$CaO(CI_2O_3(CI))$	1900
$CdCl_{(c1,1)}$	1200	$\mathbf{C}\mathbf{u}$ (a)	2000
CdO(ar)	1200	Cu (g)	2000
CdO(cr)	1200	CuCl (g)	2000
$CdO Al_2O_3 (Cr)$	1200	Curi (g)	2000
$C_1(OI)$ (cr)	1700/1200		2000
$Cd(OH)_2$ (cr)	1200	CuS (g)	2000
CdSO (cr)	1200/1200	$\operatorname{Cu}_2(\mathbf{g})$	2000
$CaSO_4$ (cr)	1300/1200	$(CuCl)_3$ (g)	2000
\mathbf{C}	2000	CuCl (cr,l)	1400
Cr (g)	2000		1300
$\operatorname{CrCl}_2(\mathbf{g})$	2000	$CuO Al_2O_3$ (cr)	1400
$CrCl_2O_2(g)$	2000	$CuO \cdot Fe_2O_3$ (cr)	1300
$\operatorname{CrCl}_3(\mathbf{g})$	2000	Custes (cr)	1200
$\operatorname{CrCl}_4(\mathbf{g})$	2000	$CuSO_4$ (cr)	1000
CrO (g)	2000	$Cu_2O \cdot Al_2O_3$ (cr)	1200
Cr(OH) (g)	3000	$Cu_2O \cdot Fe_2O_3$ (cr)	1600
CrO_2 (g)	2000	Cu_2S (cr,l)	2000
$Cr(OH)_2$ (g)	3000	Cu_5FeS_4 (cr)	1200
CrOOH (g)	3000		
CrO_3 (g)	2000		
$Cr(OH)_3$ (g)	3000		
$CrO(OH)_2$ (g)	3000		
Cr(OH) ₄ (g)	3000		
CrO ₂ OH (g)	3000		
CrO(OH) ₃ (g)	3000		
Hg (g)	2000	Pb (g)	2000
HgCl (g)	2000	PbCl (g)	2000
HgCl ₂ (g)	2000	PbCl ₂ (g)	2000
HgH (g)	2000	PbO (g)	2000
HgO (g)	2000	PbS (g)	2000
HgS (g)	2000	Pb ₂ (g)	2000
HoCl. (cr.l)	1500	Pb (1)	2000
		DI CI (D	2000
HgO(cr)	1000	PbCl ₂ (cr,l)	2000
HgO(cr) $Hg2Cl_2(cr)$	1000 1500	PbCl ₂ (cr,l) PbO (cr,l)	2000
HgO (cr) Hg2Cl ₂ (cr)	1000 1500	PbCl ₂ (cr,l) PbO (cr,l) PbO·SiO ₂ (cr)	2000 2000 1800
$H_{gO}(cr)$ $Hg_{2}Cl_{2}(cr)$ Ni (g)	1000 1500 2000	PbCl ₂ (cr,l) PbO (cr,l) PbO·SiO ₂ (cr) 2PbO·SiO ₂ (cr)	2000 2000 1800 1800
HgO($_2$ (cr,i) HgO($_cr$) Hg ₂ Cl ₂ (cr) Ni (g) Ni(CO) ₄ (g)	1000 1500 2000 2000	PbCl ₂ (cr,l) PbO (cr,l) PbO·SiO ₂ (cr) 2PbO·SiO ₂ (cr) PbS (cr)	2000 2000 1800 1800 1800

Table 8.2-1: Heavy metals species used in calculation of Sørum et al. (2003). The temperature indicates the maximum temperature for which the thermodynamic data are valid

Species	Temperature	Species	Temperature
NiCl ₂ (g)	2000	Pb ₃ O ₄ (cr)	1500
NiO (g)	2000		
Ni (cr,l)	2000	Zn (g)	2000
NiCl ₂ (cr,l)	1400	$ZnCl_2(g)$	2000
NiO (cr)	2000	ZnS (g)	2000
NiO·Al ₂ O ₃ (cr)	2000	Zn (cr,l)	1100
NiS (cr,l)	2000	$ZnCl_2(cr,l)$	900
NiS_2 (cr,l)	2000	ZnO (cr)	2000
NiSO ₄ (cr)	1200	ZnO·SiO ₂ (cr)	2000
NiO·Fe ₂ O ₃ (cr)	1500	ZnS (cr,S)	1300
2NiO·SiO ₂ (cr)	1800	ZnSO ₄ (cr)	1500
Ni_3S_2 (cr,l)	2000	2ZnO·SiO ₂ (cr)	2000
		ZnO·2ZnSO ₄ (cr)	1200

Bold: Species used for both reducing and oxidising conditions; Normal: Species used only for reducing conditions; *Italic*: species used only for oxidising conditions.
8.3 CO and CO₂ amounts produced during the wood pyrolysis



Figure 8.3-1: Wood pyrolysis at 300°C – amount of CO₂ produced during the process



Figure 8.3-2: Wood pyrolysis at 300°C – amount of CO produced during the process



Figure 8.3-3: Wood pyrolysis at 400°C – amount of CO₂ produced during the process



Figure 8.3-4: Wood pyrolysis at 400°C – amount of CO produced during the process



Figure 8.3-5: Wood pyrolysis at 500°C – amount of CO₂ produced during the process



Figure 8.3-6: Wood pyrolysis at 500°C – amount of CO produced during the process



Figure 8.3-7: Wood pyrolysis at 600°C – amount of CO₂ produced during the process



Figure 8.3-8: Wood pyrolysis at 600°C – amount of CO produced during the process



Figure 8.3-9: Wood pyrolysis at 700°C – amount of CO₂ produced during the process



Figure 8.3-10: Wood pyrolysis at 700°C – amount of CO produced during the process



Figure 8.3-11: Wood pyrolysis at 800°C – amount of CO₂ produced during the process



Figure 8.3-12: Wood pyrolysis at 800°C – amount of CO produced during the process

8.4 Feeding system

	Mounting	Output shaft	Ratio	Rpm
		Ø x Lg.	1:x	1/min
Upper screw	H1	HW16H7	26,00	51
Lower screw	H1	HW16H7	5,40	245

Table 8.4-1: Gear box characteristics used for feeding system in gasification process

	Output	Rpm	Supply	Hz.
	kW	1/min		
Upper screw	0,18	1360	230/400 V	50
Lower screw	0,18	1360	230/400 V	50

Table 8.4-2: Motor characteristics used for feeding system in gasification process

The motors and gear boxes were made by Getriebebau NORD GmbH. The scheme of the screw feeders and the feeding system can be see in the following figure

Name	Structure	Empirical formula	Molar mass	Melting	Boiling
		Iormula	(g/mor)	Joint (C)	point(C)
Phenol	Су ^{он}	$\mathrm{C_6H_6O}$	94,11	4 3° C	182°C
Styrene		$\rm C_8H_8$	$104,\!15$	-30,63°C	$145,2^{\circ}\mathrm{C}$
2–Methylphenol	СТ он	$\rm C_7H_8O$	108,18	31°C	$191^{\circ}\mathrm{C}$
4–Methylphenol	С) Он	$\rm C_7H_8O$	108,18	$35^{\circ}\mathrm{C}$	$202^{\circ}\mathrm{C}$
2,4–Dimethylphenol		$\mathrm{C_8H_{10}O}$	$122,\!17$	$26^{\circ}\mathrm{C}$	$211,5^{\circ}\mathrm{C}$
1H–Indene	$\hat{\mathcal{O}}$	C_9H_8	116,16	-1,8°C	182,6°C
Naphthalene	$\tilde{\mathbf{Q}}$	$\mathrm{C_{10}H_8}$	128,17	$80,2^{\circ}\mathrm{C}$	218°C
Acenaphthylene		$\mathrm{C}_{12}\mathrm{H}_8$	152,20	92°C	$265^{\circ}\mathrm{C}$
Acenaphthene		$\mathrm{C}_{12}\mathrm{H}_{10}$	$154,\!21$	$96,2^{\circ}\mathrm{C}$	$279^{\circ}\mathrm{C}$
Fluorene	\widetilde{OO}	$\mathrm{C_{13}H_{10}}$	166,22	115°C	298°C
Phenanthrene		$\mathrm{C}_{14}\mathrm{H}_{10}$	178,23	101°C	$340^{\circ}\mathrm{C}$
Anthracene	UU)	$\mathrm{C}_{14}\mathrm{H}_{10}$	178,23	$218^{\circ}\mathrm{C}$	$340^{\circ}\mathrm{C}$
Pyrene	(\mathcal{D})	$\mathrm{C_{16}H_{10}}$	202,26	150°C	393°C

8.5 Tars in the product gas during the biomass gasification

Table 8.5-1: Structure of the tars in the product gas

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