

Gasification of Non-woody Biomass

Economic and Technical Perspectives of Chlorine and Sulphur Removal from Product Gas

(Non-confidential version)

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Acknowledgement/Preface

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Abstract

This project has the objective to investigate the economic and technical perspectives for the replacement of woody biomass with non-woody biomass in a biomass gasification process. Non-woody biomass fuels like straw, manure and sludge are cheap fuels with an increased chlorine, sulphur and ash content. A representative biomass composition for non-woody biomass is 13 wt% ash, 0.3 wt% chlorine and 0.6 wt% of sulphur. The replacement of expensive woody biomass fuels with non-woody biomass has a high economic potential, due to the low price of non-woody biomass. However, in a biomass gasifier the chlorine and sulphur is partly released as gas phase compounds or bounded in the ash. In order to fulfil the emission limits the chlorine and sulphur compounds should be partly removed. Consequently additional gas cleaning equipment is necessary for the removal of the chlorine and sulphur containing compounds. These additional measures in the gas cleaning increase the operational and investment costs of the gas cleaning. In this report the economic and technical perspectives for the use of non-woody biomass in a biomass gasification process for the production of electricity and/or heat with a boiler, gas engine and fuel cell were discussed. The project focussed on the additional measures needed in the gas cleaning for the removal of chlorine and sulphur containing compounds.

The economic perspectives are positive for the use of non-woody biomass in a gasifier for the application of the product gas in a boiler, gas engine or fuel cell. The total additional gas cleaning costs for the removal of chlorine and sulphur compounds are approximately **26** euro/tonne biomass for the boiler application, **23** euro/tonne biomass for the gas engine application and **19** euro/tonne biomass for the fuel cell application. Therefore with a woody biomass price of 50 euro/tonne biomass the application of non-woody biomass in a gasifier becomes attractive when the price of the non-woody biomass becomes below 15 to 20 euro/tonne on the condition that the ash disposal costs are lower than 60 euro/tonne biomass.

Keywords

Biomass, waste, gasification, gas engine, boiler, fuel cell, technical perspective, economic perspective, chlorine release, sulphur release, gas cleaning, dioxins, HCl, H₂S, COS, fluidized bed gasification, direct gasifier, indirect gasifier.

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Summary

This project has the objective to investigate the economic and technical perspectives for the replacement of woody biomass with non-woody biomass in a biomass gasification process. Non-woody biomass fuels like straw, manure and sludge are cheap fuels characterized by an increased chlorine, sulphur and ash content¹. The replacement of expensive woody biomass fuels with non-woody biomass has a high economic potential, due to the low price of the non-woody biomass. The chlorine and sulphur in the biomass is in a fluidized bed gasifier partly released as gas phase compounds or bounded in the ash. In order to fulfil the emission limits the chlorine and sulphur compounds should be removed. Consequently, additional gas cleaning equipment is necessary for the removal of the chlorine and sulphur containing compounds. These additional measures in the gas cleaning increase the operational and investment costs of the gas cleaning. In this report the economic and technical perspectives for the use of non-woody biomass in a biomass gasification process for the production of electricity and/or heat with a boiler, gas engine and fuel cell are discussed. The project focuses on the additional measures needed in the gas cleaning for the removal of chlorine and sulphur containing compounds.

The composition of product gas from the gasification of non-woody biomass was determined based on experimental results and the in-house ECN gasifier model. An experimental program was defined to investigate the release of chlorine and sulphur compounds in a fluidized bed gasifier. grass, RDF and sewage sludge were the selected fuels for the experiments. Grass and RDF are fuels with a high chlorine content and sewage sludge has a high sulphur content. The experiments with grass were stopped at an early stage due to bed agglomeration. The chlorine in the other fuels was for a substantial part, 50% to 90%, bounded to the ash and removed with the solids in the gas. The remaining chlorine was mainly released as HCl. The dioxin concentration was relatively high (0.4-75 ng I-TEQ) and clearly related to the chlorine content of the fuel. The dioxin concentration strongly reduced with increasing gasifier temperature (from 750°C to 850°C). The sulphur in the biomass was mainly, for 70% to 90%, converted into H₂S and COS. At a low gasifier temperature of 750°C also other organic sulphur compounds, such as mercaptane and CS₂, are present in the product gas at low concentration. Only a small amount of sulphur was bounded to the ash. For the conversion of woody biomass a high gasification temperature was selected, because at a high temperature the composition of chlorine and sulphur compounds becomes simpler and the organic sulphur and chlorine concentration is significantly reduced.

The boundaries for the gas cleaning are determined by the raw gas composition at the inlet and the emission limits and prime mover requirements for the outlet of the gas cleaning. For the boiler and gas engine application the gas cleaning should be able to fulfil the emission limits. The emission limit is more stringent than the boiler and gas engine requirements. For a fuel cell application the chlorine and sulphur removal is determined by the fuel cell requirements. The emission limits in the Netherlands are divided in white list fuels and yellow list fuels. Some of the non-woody biomass fuels have to meet the white list limits other has to meet the yellow list requirements. Since the yellow list limits are most stringent, the gas cleaning was designed to fulfil the yellow list emissions.

Three different 10 MW_{th} gas cleaning designs were made for the three product gas applications boiler, gas engine and fuel cell when non-woody biomass is applied in the gasifier at 850°C. The boiler and gas engine have a direct gasifier installed upstream, and the fuel cell an indirect gasifier. The sulphur in the gas cleaning is removed in process with two different solid sorbents. In the first stage the bulk of the sulphur is removed with a cheap sorbent. A second stage with

¹ A representative biomass for non-woody biomass contains 13 wt% ash, 0.3 wt% chlorine and 0.6 wt% of sulphur.

another sorbent (ZnO) is used to remove the last amount of sulphur to fulfil the emission limits or the fuel cell requirements. The spent sorbent of both stages must be disposed and cannot be regenerated. HCl was removed with a sorbent. This sorbent can be recycled by the supplier. For the gas engine application the HCl was removed downstream OLGA. Dioxins are removed together with tars in OLGA for the fuel cell and gas engine application. For the boiler, additional measures (catalytic, active carbon) should be taken to remove dioxins in the flue gas of the boiler, if necessary. The gas cleaning was theoretically able to fulfil the emission limits and fuel cell requirements.

The technical perspective of the gas cleaning for the boiler, gas engine and fuel cell application is positive. The gas cleaning technologies are simple and theoretically able to reduce the Cl and S concentration sufficiently to fulfil the emission limits or the fuel cell requirements. However the three systems for the removal of H₂S, COS and HCl are not fully developed yet. Future development of the three systems should focus on the sorbent use and the reliability of the moving bed.

The economic perspectives are positive for the proposed gas cleaning systems. The total additional gas cleaning costs for the removal of chlorine and sulphur compounds are approximately **30** euro/tonne biomass (dry and ash free) for the boiler application, **28** euro/tonne biomass for the gas engine application and **20** euro/tonne biomass for the fuel cell application. The total capital investment costs and the sorbent costs (purchase and disposal) have a similar contribution to the total additional gas cleaning cost. With a woody biomass price of 50 euro/tonne biomass the application of non-woody biomass in a gasifier becomes attractive when the price of the non-woody biomass becomes below 15 to 20 euro/tonne on the condition that the ash disposal costs is lower than 60 euro/tonne ash. The disposal costs for ash is to a large extent determined by the ash quality, which should be investigated case by case. The ash disposal costs are relevant to take into account in the cost calculations and can determine the profitability of a project. The disposal costs can range between 0 (application in road pavement) and 150 Euro/tonne ash (landfill costs).

1. Introduction

1.1 Background

Gasification of untreated wood for the generation of electricity and heat is relatively expensive. The untreated wood price accounts for approximately 30% of the electricity production costs [1]. The electricity costs can potentially be decreased by the application of cheap biomass fuels like manure, sludge, and straw. However these cheap non-woody biomass fuels often contain a considerable amount of ash, chlorine and sulphur. In the gasifier the sulphur and chlorine is converted into HCl, H₂S, COS and other Cl and S containing compounds. These compounds must be removed in the gas cleaning from the product gas. The benefits of the low price of non-woody fuel must outweigh the extra gas cleaning costs.

1.2 Problem definition

The application of non-woody cheap biomass fuels like straw, manure and sludge in a gasifier for the production of electricity and heat seems to be economically attractive. However, extra investment is necessary in the gas cleaning for the removal of the chlorine and sulphur containing compounds. It is unknown whether the additional gas cleaning is technically and economically beneficial.

1.3 Objective

The aim of this project is to evaluate the **technical** and **economic** perspectives for the application of non-woody cheap biomass fuels in a gasification process for the production of electricity and heat with a gas engine, fuel cell or boiler. The project will focus on the additional measures to be taken in the gas cleaning for the removal of chlorine (Cl) and sulphur (S) compounds.

The technical perspectives will be determined based on the technical consequences by switching from woody to non-woody biomass. The technical consequences are the need for additional gas cleaning measures to fulfil the Cl and S emission legislations and the specification of the gas engine, fuel cell or boiler. The technical perspectives will be judged based on the increase in complexity of the gas cleaning and the expected change in reliability of the process when woody biomass is replaced by non woody biomass.

The economical perspectives will be determined based on the economical consequences by switching from wood fuel to non-woody fuel. The economic consequences can be categorised in:

- Additional investment and operational costs;
- Benefits of a lower fuel price.

The sum of the additional investment and operational costs, and the benefits due to a lower biomass price will give the economic perspectives. The additional gas cleaning costs will be compared with the price of woody biomass, and the maximum non-woody biomass price for breakeven will be given.

1.4 Method

A four-step procedure has been followed to come to a judgement of the economic and technical perspectives for the application of non-woody biomass in a biomass gasification process:

1. Design basis

The design basis gives the boundaries (input and output) for the process design. A representative biomass composition was determined based on an evaluation of the biomass composition of several non-woody biomass samples. Furthermore the emission and prime mover specifications are defined in the design basis.

2. Determination of gas composition

For the design of the gas cleaning the inlet gas composition should be predicted when the representative biomass is fed to a gasifier. For the prediction of the gas composition downstream a gasifier, experiments with the ECN laboratory scale fluidized bed gasifier were performed. Three non-woody (biomass, RDF, grass, and sewage sludge) were selected as fuel for the gasifier. The gas composition was determined at high and low gasifier temperature. The experimental results together with the ECN gasifier model were used for the prediction of the gas composition when the representative biomass is applied as fuel in a gasifier.

3. Evaluation of technical perspectives

The technical perspectives were determined for the application of product gas in a

- boiler;
- gas engine;
- fuel cell;

The perspectives were evaluated for a system with a fuel capacity of 10 MW_{th}. A process flow diagram and general mass and heat balance was made for the three systems. Based on the process flow diagram and the mass and energy balance the additional gas cleaning equipment were dimensioned. The technical perspectives were evaluated in terms of complexity and reliability.

4. Evaluation of economic perspectives

The investment and operational costs were determined based on the mass and energy balance and the process flow diagram defined in 3. The total capital investment costs and operational costs are given as Euro per tonne biomass. Comparison of the total additional gas cleaning costs with the price of woody biomass gives the economic perspectives for the application of non-woody biomass.

1.5 Demarcation

In this report a process assessment is made for the production of electricity and heat with a gas engine, fuel cell and boiler from non-woody biomass, using a fluidized bed gasifier for the thermal conversion of the biomass into a product gas. Only additional costs for the application of non-woody biomass streams will be given with woody biomass as reference. The project will focus on additional measures needed in the gas cleaning for the removal of Cl and S containing compounds. The removal of trace elements like Hg is dependent on the type of biomass. Therefore the removal of trace elements is not taken into account in the gas cleaning.

In the gasifier fuels with a high Cl content are prone to cause bed agglomeration. However carefully mixing of different type of non-woody biomass can reduce the risk of bed agglomeration. Also additives can be used to reduce the risk of bed agglomeration. The measures to avoid bed agglomeration cannot be generalised and will be dependent on the ash composition of the feedstock. Therefore the measures needed to avoid agglomeration in the gasifier are not taken into account. Additional information on bed agglomeration can be found in [2].

2. Design basis

The design basis gives the boundary conditions for the gasification process. In this project the technical and economic benefits when switching from woody biomass to non-woody biomass will be evaluated. The extra costs for the application of non-woody biomass are largely dependent on the extra gas cleaning costs. For the selection and dimensioning of gas cleaning equipment the gas composition and concentration at the entrance and outlet of the gas cleaning must be defined. The gas composition at the inlet is to a large extent determined by the biomass composition and conditions in the gasifier. A representative biomass composition will be defined in Paragraph 2.1 based on the composition of several non-woody biomass fuels. The specification for the gas cleaning is determined by the emission limits and specifications for a boiler, gas engine, and fuel cell, which are discussed in Paragraph 2.2 and 2.3.

2.1 Biomass composition (C, S, and ash) of non-woody biomass

A general and widely accepted definition for biomass is²: "Biomass represents the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fractions of industrial and municipal waste". This means that the material from plant and trees as well as the manure of animals and humans can be called biomass. In this report biomass will be separated in woody and non-woody biomass. Woody biomass is wood from trees without the leaves, bark and roots. Non-woody biomass is in this report waste from the industry, agriculture and animals. Examples of non woody biomass are grass, straw, manure, and sludge.

The elemental composition of biomass is dependent on the source. Table 2.1 shows an indicative biomass composition (ultimate) for several woody and non-woody biomass fuels. An important difference between woody and non-woody biomass is the relatively high chlorine, sulphur and ash content in non-woody biomass.

Table 2.1 *Ultimate composition of several biomass type taken from the Phyllis database*³

	C (wt%daf)	H (wt%daf)	O (wt%daf)	N (wt%daf)	S (wt%daf)	Cl (wt%daf)	Ash (wt%db)	H ₂ O (wt%ar)
Untreated wood	48,8	6,0	44,6	0,4	0,03	0,02	1,6	12,8
Treated wood	50,7	6,1	41,7	1,2	0,11	0,08	2,7	17,8
• Demolition	49,4	5,9	43,1	0,9	0,08	0,05	4,3	18,9
• Impregnated	52,5	6,2	40,4	0,6	0,17	0,11	1,5	23,5
• Particle board	50,1	6,2	41,6	2,2	0,08	0,08	2,3	11,1
Gras	49,2	6,0	43,5	0,9	0,16	0,38	3,6	15,4
Straw	50,5	6,1	41,3	1,1	0,15	0,48	10,9	6,1
Manure	51,8	6,4	34,2	4,4	0,85	1,41	32,9	45,7
• Poultry	48,2	5,6	34,8	6,2	0,74	0,73	19,6	30,1
• Cow	53,1	6,8	34,9	2,6	0,95	1,66	43,7	14,9
• Pig	54,1	6,8	33,0	4,3		1,84	35,4	92,1
Sludge	50,2	7,2	39,7	2,9	1,0	0,3	25,3	25,3
• Food industry	52,8	8,1	39,9	1,0	0,77	0,01	9,3	7,8
• Paper	49,2	6,0	43,1	1,1	0,45	0,43	33,3	36,8
• Sewage	48,5	7,5	36,2	6,7	1,87	0,53	33,4	31,2
RDF	51,8	7,2	39,3	1,1	0,40	0,39	15,0	25,0
MSW	56,0	5,1	26,6	1,2	0,50	1,13	39,6	34,8

daf = dry and ash free basis; db = dry basis; ar = as received basis

² 2001/77/EG (RES/Electricity from Renewables Directive)

³ See for the database www.Phyllis.nl

In order to define a reasonable representative biomass composition for this project, a statistical analysis on the sulphur and chlorine content of several type of biomass streams was performed. The result of this analysis is given in Figure 2.1 for sulphur and Figure 2.2 for chlorine. The figures give the total elemental concentration range (100% confident limit) for all the samples and for 95% of the samples (mean +/- standard deviation). The full range is represented by the blue bars and the 95% confident range is given by the yellow part of the bars.

The sulphur in plants can be bounded as inorganic sulphur and as organic sulphur. The roots of the plants assimilate S as SO_4^{2-} . The inorganic sulfate can be converted into amino acids for the production of protein. The sulphur content in biomass can range from 0,05 wt% to more than 3 wt%, depending on the origin of the biomass. A rough distinction between (biologically) processed biomass like manure and sludge and non processed biomass can be made. The relatively high sulphur content could be explained by the relatively high proteine content in manure and sludge.

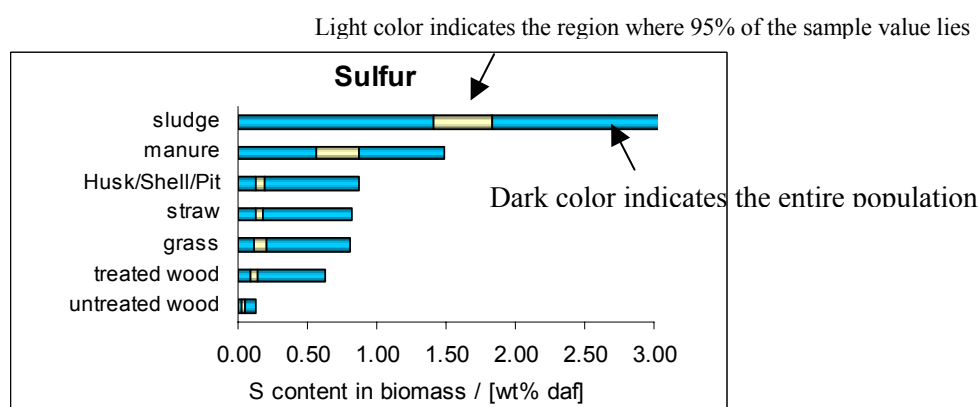


Figure 2.1 Sulphur content of various biomass streams [3]

The chlorine in plants is mainly bounded as inorganic salt in the form of potassium chlorine (KCl) and quaternary ammonium chlorine. Chlorine is important in osmoregulation, the maintenance of electrochemical equilibrium in cells/compartments and in the regulation of enzyme activity. The chlorine content in biomass can range from 0,01 to 2,4 wt% on dry and ash free basis. In general a high chlorine content is observed in fast growing plants like grass and straw (see Figure 2.2). The level is influenced by the location of growth and the period of harvesting⁴ [4].

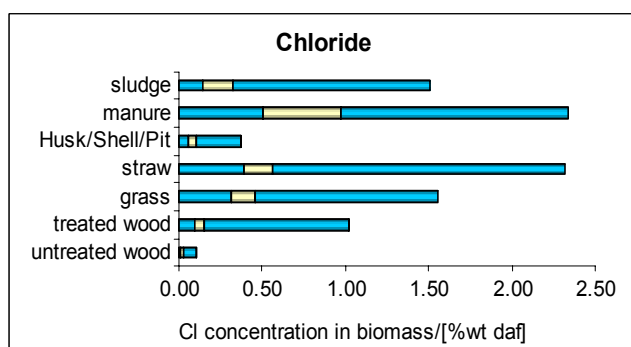


Figure 2.2 Chlorine content of various biomass streams [3]

⁴ The chlorine content of biomass harvested in the winter is normally lower than in the summer because of the low plant activity during the winter. Furthermore the chlorine content in biomass is higher on locations near the sea due to the increased NaCl concentration in the soil.

Table 2.2 gives the representative biomass composition to be used in the design of the gasification process. The composition of the representative biomass was based on a mixture of 50% beech, 25% sludge and 25% grass. The selection of this mixture was firstly based on the high chlorine and sulphur content of the mixture. Secondly the ratio of the fuels was determined by the risk of bed agglomeration. Bed agglomeration forms an important risk in the application of biomass with a high KCl content. Bed agglomeration is not expected with the mixture of the three fuels.

Table 2.2 *Proximate and ultimate composition of the representative biomass (Feed mix) [3]*

		Beech	Sludge	Verge Grass pellet	Representative composition
Source		ECN-C--04-024	ECN-C--04-024	Phyllis	
moisture	wt% wet	9.9	7.2	7	15
ash	wt% dry	1	34	18	13
Volatiles	wt% daf	84	81	79	82
HHV	kJ/kg daf	19,748	19,258	19,961	19,679
LHV	kJ/kg daf	17,491	17,754	18,722	17,865
C	wt% daf	49.2	53	49.9	50.3
H	wt% daf	6.1	7.4	5.7	6.3
O	wt% daf	44.2	41.1	40.9	42.6
N	wt% daf	0.19	7.7	2.47	2.6
S	wt% daf	0.02	2	0.18	0.56
Cl	wt% daf	0.004	0.16	0.86	0.26
Ash composition					
Al	mg/kg dry	48	17,000	0	4274
As	mg/kg dry	0.9	6.8	1	2.4
Ca	mg/kg dry	2,900	27,000	13,000	11,450
Cd	mg/kg dry	0.09	1	1	0.545
Co	mg/kg dry	12	4.8	1.2	7.5
Cr	mg/kg dry	1.5	39	11	13.25
Cu	mg/kg dry	1.6	350	10	90.8
Fe	mg/kg dry	37	33,000	0	8,269
Hg	mg/kg dry	0.01	0	0	0.005
K	mg/kg dry	1,200	4,400	21,000	6,950
Mg	mg/kg dry	370	5,000	1,900	1,910
Mn	mg/kg dry	54	450	150	177
Mo	mg/kg dry	0.8	12	0	3.4
Na	mg/kg dry	11	1,600	1,500	781
Ni	mg/kg dry	2.5	22	16.0	10.8
P	mg/kg dry	89	30,000	2,400	8,145
Pb	mg/kg dry	3.1	120	14	35.05
Sb	mg/kg dry	13	3.4	1	7.6
Se	mg/kg dry	1.4	5	1	2.2
Si	mg/kg dry	170	31,000	38,000	17,335
Sn	mg/kg dry	0.4	20	10	7.7
Sr	mg/kg dry	4.8	270	0	69.9
Zn	mg/kg dry	3.2	830	44	220.1

2.2 Specifications for Cl and S compounds for prime movers

The product gas from the gasifier will be applied in a boiler, gas engine and fuel cell. The requirements for chlorine and sulphur containing compounds are given in Table 2.3.

Table 2.3 *Requirements for a gas engine and fuel cell*

		Boiler	Gas engine	Fuel cell
Total S	mg/m _n ³	72 ¹	80	1
Total Cl	mg/m _n ³	35 ¹	100	1
NH ₃	mg/m _n ³	--	50	fuel
Dust (d _{max} = 10 μm)	mg/m _n ³	1000 ²	50	<0.1
Tar		dewpoint < 400°C	tar dewpoint < 10°C	unknown

¹ Sulphur and chlorine for a direct air blown fluidized bed gasifier with emission limits as requirement.

² It is assumed that dust removal with a cyclone is sufficient to relief the boiler from heavy fouling with dust.

Removal of chlorine and sulphur upstream the boiler can decrease the risk of corrosion in the boiler. However the maximum allowable concentration for the boiler will be dependent on the materials used in the boiler. It can be stated that when the sulphur and chlorine content in the product gas is reduced to such an extent that the emission limits are reached that corrosion in the boiler is also minimised. Therefore the chlorine and sulphur requirements for the boiler are based on the emission limits for SO_x and Cl in the exhaust gas.

The Cl and S requirements for a gas engine are based on corrosion and oil degradation. The concentration of sulphur compounds is for a gas engine not critical, but related to the time between oil exchanges and can attack metal parts. The SO₂ or SO₃ formed on combustion increase the acidity of the oil, until the buffering capacity of the oil is depleted and the corrosion risk becomes unacceptable. The concentration of chlorine is for a gas engine critical, because HCl is very corrosive. It attacks almost all metal parts of the gas engine and destroys the additives of the lubricating oil, and thus decreases the time between oil exchanges.

The S and Cl requirements for a fuel cell are based on the degradation of the electrodes [5]. A solid oxide fuel cell is an electrochemical device that converts H₂ directly into electricity and heat [6]. Hydrocarbons are reformed into CO and H₂, and the CO is shifted to H₂ in the SOFC. The catalytically active electrodes are degraded or the catalytically activity for the reforming and WGS reaction deactivated in the presence of H₂S or HCl in the product gas.

2.3 Emission limits

In the Netherlands the biomass fuels are categorised in white list fuels and yellow list fuels. White list fuels are clean biomass and biomass residues. Anually 2.8 million tons of these white list fuels are available in the Netherlands with main contributions of forestry residues, roadside grass, and clean rest wood. Yellow list fuels are contaminated biomass. Anually 12,4 million tons of contaminated biomass is available and the main contributions come from the food industry, manure, municipal waste, industrial wastes, construction and demolition wastes and waste from enterprises. The white and yellow lists have been used to define emission legislations (see paragraph 2.4).

This project concerns the thermal conversion of non-woody biomass fuels that has an increased chlorine and sulphur content. Some of these fuels like grass and straw are white list fuels and some fuels like manure and sludge are yellow list fuels. There are simple emission limits for "white list" biomass fuels and more demanding limits for "yellow list" biomass fuels. The most recent information can be found at www.infomil.nl.

Table 2.4 presents the emission limits defined in 2002, in preparation of more definite limits to be confirmed in new versions of the regulations (BEES and BVA). For this project the emission limits for the yellow list fuels was used for the design of the gas cleaning in this project.

Table 2.4 *Emission limits in mg/m_n³ for stand-alone biomass installations using clean biomass ("white list") or contaminated biomass ("yellow list")*

	White list at 6% O ₂	Yellow list at 11% O ₂
NO _x	100-200 ¹	70-130 ¹
SO ₂	200	40
Dust	20	5
HCl		10
VOS (volatile organics)		10
CO		50
Cd + Tl		0.05
Hg		0.05
Total heavy metals		0.5
Dioxins and furans (ng TEQ)		0.1

¹ The higher value applies when the installation has an equivalent electrical efficiency above 40%. Equivalent electrical efficiency is the sum of the electrical efficiency and 0.47 times the thermal efficiency (i.e. delivered heat).

3. Experimental determination of the gas composition

As described in previous chapter non-woody biomass is fuel with a relatively high chlorine, sulphur and ash content. In a biomass gasifier the chlorine and sulphur in the fuel can be released in several chemical forms. During the devolatilization of the biomass the sulphur can be released as organic and inorganic sulphur. Inorganic sulphur is mainly present in the form of H_2S and to a minor extent bounded in the ash. Organic sulphur is mainly present in the form of COS and to a minor extent in the form of mercaptane, CS_2 and tar. The chlorine can be released as HCl and can for a substantial part be bounded to the ash, which is depending on the ash composition and temperature of ash removal. The chlorine can react further with organic species to form chlorobenzenes and dioxins in the gas phase. When the gas is cooled down the chlorine can condense in the form of alkali salts (Na, K) or as NH_4Cl in the presence of NH_3 . The vapour pressure for NH_4Cl is given in Figure 3.1.

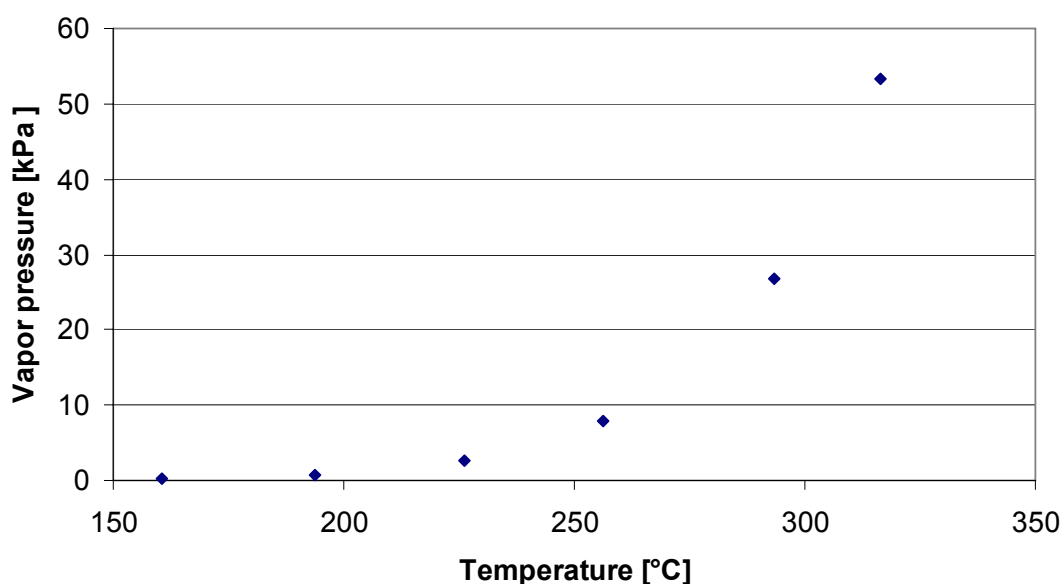


Figure 3.1 *Vapour pressure of NH_4Cl in relation with the temperature [7]*

The experimental program in this report focuses on the formation of chlorine and sulphur containing compounds in a gasifier. Emphasis was put on the conversion of non-woody biomass fuels with a high sulphur and/or chlorine content. The experiments were conducted in a 1 kg/h lab-scale bubbling fluidized bed gasifier. The objective of the experiments was to determine the influence of the gasifier temperature and biomass composition on the gas composition, with the accent on chlorine and sulphur containing compounds.

In Paragraph 3.5 the experimental results were translated for the determination of the gas composition from the representative biomass composition defined in Paragraph 2.1.

3.1 Fuel preparation

Five types of biomass fuel were selected for the experiments: grass pellets, RDF pellets, sewage sludge pellets, beech, and white pellets. Grass was selected for its high chlorine content and is a natural biomass. RDF, a mixture of paper and plastic waste, was selected for its high chlorine content and is a waste stream in the industry. Dried sewage sludge (RWZI) was selected for its high sulphur content and is currently used as fuel in a fluidized bed combustor. Beech was mixed with grass pellets to reduce the risk of agglomeration. The sewage sludge was mixed with

white pellets to decrease the total ash concentration. The biomass streams were fed from separate bunkers and mixed up in the feeding screw. The biomass fuels are industrially available.

Table 3.1 *Composition of grass pellets, RDF, sewage sludge (RWZI), white pellets and beech*

	Grass pellets	RDF	Sewage Sludge (RWZI)	Beech	White pellets
C (daf)	45.6	48.9	49.1	48,8	48.3
H (daf)	6.7	7.0	6.9	6.0	6.4
N (daf)	3.6	0.7	7.1	0.1	0.1
O (daf)	39.1	41.4	38.1	44.4	45.3
S (daf)	0.3	0,04	1.5	0.02	0.01
Cl (daf)	1,7	1,5	0,3	0.01	0.01
Ash (db. 550°C)	12,8	7,4	27,1	1.0	0.3
Moisture (ar)	8,5	4,5	7,4	10.2	6.8

Composition in wt%; daf = dry and ash free basis; db. = on dry basis; ar = as received

For the fuel preparation all the pellets were crushed and sieved to bring the fuel on specification. Particle dimensions ranged from 0.2-2.0 mm. The beech with a particle size of 0.75-2.0 mm was bought from J.Rettenmaier & Sohne (Rauchergold HBK 750/2000) and could be used without further preparation. Table 2.3 gives the ultimate and proximate analysis data of the fuels.

3.2 Experimental set-up

The gasification experiments were conducted in the 1 kg/h bubbling fluidised bed gasifier, WOB⁵, at ECN. The gasifier is electrically heated and has an internal diameter of 74 mm (bottom section), increasing to 108 mm (freeboard) at a height of 500 mm. The total length is 1100 mm from the metal distributor plate to the product gas outlet. Bed temperatures are measured at four points in the bed. The applied bed material is 0.27 mm dia. silica sand. Typically, the total amount of the bed is 1 kg. For each experiment a new sand bed was used to avoid the influence of accumulated ash of previous experiments on the results.

Gas samples were taken on three locations in the installation as schematically shown in Figure 3.2. The first sample point, GA1, was mounted in the middle and on the central axis of the freeboard. Sample point GA1 was used for gas phase alkali and chlorine measurements. The second sample point, GA2, was mounted at the top on the central axis of the freeboard. Sample point GA2 was used for tar and dust measurements. The third sample point, GA3, was mounted downstream the cyclone operated at approximately 500°C. Sample point GA3 was used for the measurement of permanent gas, tar, dust, NH₃, HCl, HCN, H₂S, and COS concentration.

⁵ See <http://www.ecn.nl/biomass/wob/index.html>

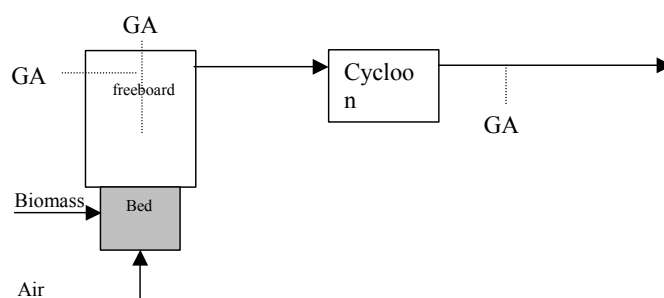


Figure 3.2 Schematic of the 1 kg/h bubbling fluidized bed gasifier(WOB) at ECN. For standard conditions, i.e. a biomass feeding rate of 1 kg/h, an air flow rate of 16 l/min and a gasifier temperature of 850°C, the corresponding gas residence time for the three sample points are: GA1-2 s, GA2-3.6 s, GA3-4s

3.3 Gas analysis

The gas analysis comprises the measurement of permanent gases, tar as well as sulphur and chlorine containing compounds. The concentration of CO, CO₂, CH₄, H₂, C₂H₄, C₂H₆, benzene, toluene, H₂S, and COS is measured on-line every three minutes with gas monitors and/or micro-GC. Gas samples were taken with a sample bag for the analysis of the compounds methyl mercaptane, ethyl mercaptane, and CS₂. The gas samples were off line analysed with a sensitive gas chromatograph. Dioxins were measured as described in Paragraph 3.4.3. The concentration of tar compounds and the gravimetric tar concentration were determined with the Guideline method [8].

The Guideline method is an internationally standardised tar measurement method. It allows for sampling and analysis of tars (and particles) in biomass gasification gases. The tar and particle sampling system consists of a heated probe, a heated particle filter, a condenser and a series of impinger bottles containing isopropanol to dissolve tars. The solvent containing bottles are placed in a cold bath of 20°C and -20°C. The post sampling involves Soxhlet extraction of the tars on the particle filter and the collection of tars in one bulk solution. From this bulk solution the sulphur and chlorine content was determined and the concentration of individual tar compounds was analysed. Also the gravimetric tar concentration in the bulk solution was determined. The full version of the guideline can be found on the dedicated web-site www.tarweb.net.

Table 3.2 gives the location of measurement divided per type of measurement. The procedure of analysis is given in Appendix A.

Table 3.2 Location of sampling

	GA1	GA2	GA3
Gas composition			X
Guideline TAR		X	X
HCl	X		X
Dioxin			X
NH ₃			X
HCN			X
HCL/Alkali	X		
Ash		X	X

3.4 Experimental results

The experimental conditions are given in Table 3.3. The biomass was fed with a feeding rate of 0,6 to 1 kg/h. The amount of air was adjusted to the biomass feeding rate. For each fuel the gasifier was operated at 850°C and 750°C. Gas measurements were performed as discussed in previous paragraph..

Table 3.3 *Experimental conditions*

		1	2	3	4	5	6
Biomass 1		Grass pellets	Grass pellets	Sewage sludge	Sewage sludge	RDF	RDF
Biomass 2		--	Beech	White pellets	White pellets	--	--
Feeding rate biomass 1	g/h	1249	87	487	487	705	691/800 ⁶
Feeding rate biomass 2	g/h	--	935	521	560	--	--
Air flow	m _n ³ /h	0,96	0,96	0,90	0,93	0,63	0,72
Gasification temperature	°C	750	850	750	850	725	820

Table 3.4 gives the average concentration of the main gas compounds and impurities measured on location GA3. The gas composition for experiments 1 and 2 with grass pellets is not given due to agglomeration of the gasifier bed in the early stage of the experiments. In the second experiment, grass was mixed with beech (1:10) to avoid bed agglomeration. The ratio of the mixture was determined based on the concentration and ratios of different group of elements in the mixture (see ref [4]), in such a way that the risk on agglomeration was minimized. In spite of the ten times dilution of grass with beech, the bed agglomerated within a few hours. Therefore no gas composition data is available of these experiments.

Table 3.4 *Gasifier conditions and average gas composition measured on location GA3*

		3	4	5	6
Date		2-3-2005	3-3-2005	14-3-2005	10-3-2005
Biomass 1		Sewage sludge	Sewage sludge	RDF	RDF
Biomass 2		White pellets	White pellets	--	--
T gasifier	°C	750	850	725	820
ER	--	0.22	0.23	0.21	0.21
Product Gas flow	m _n ³ /h wb.	1.8	1.9	1.2	1.3
H ₂ O calculated	vol% wb.	14.8	11.5	16.3	12.5
Permanent gases					
CO (db.)	vol% db.	14.4	16.8	10.3	12.1
H ₂	vol% db.	11.4	14.9	5.1	7.1
CO ₂	vol% db.	15.1	13.5	15.5	13.7
CH ₄	vol% db.	4.1	4.1	5.7	6.4
N ₂	vol% db.	51	47	52	53
Acetylene (C ₂ H ₂)	vol% db.	0.04	0.07	0.1	0.2
Ethylene (C ₂ H ₄)	vol% db.	1.5	1.6	4.2	4.6
Ethane (C ₂ H ₆)	vol% db.	0.3	0.1	0.7	0.3
Benzene (C ₆ H ₆)	ppmv db.	1999	3094	6743	9309
Toluene (C ₇ H ₈)	ppmv db.	1078	655	2378	1490
LHV excl. tar	MJ/m _n ³ db.	6.3	7.0	8.4	9.3
Total GC Tar	g/m _n ³ db.	15.3	11.6	26.9	26.4
Gravimetric Tar	g/m _n ³ db.	28.3	10.0	12.4	15.9
Sulphur					
H ₂ S	ppmv db.	2305	1725	89	28

⁶ From the mass and energy balance the total feed rate must have been 800 g/h instead of the measured 691 g/h.

		3	4	5	6
COS	ppmv db.	158	185	10.5	19
(H ₂ S+COS)/Fuel-S	%	110	94	58	28
S in cyclone ash	mg/kg	6043	6471	1448	1248
Chlorine					
HCl	mg/m _n ³	36	54	1559	5123
HCl/Fuel-Cl	%	7%	9%	14%	48%
Dioxines	ng I-TEQ/m _n ³	1.98	0.38	74.22	4.50
Cl in tar solution ³	mg/m _n ³	8	56	3344	4124
Cl in cyclone ash	mg/kg	1164	842	61964	60848
Nitrogen					
NH ₃	ppmv db.	10281	4150	130	584
HCN	ppmv db.	NA ⁷	1247	96	207
Ash					
Ash	g/m _n ³	6.3	5.8	3.9	5.2
Cyclone ash	g/h	44	54	2.5	12
FB expansion ⁸	g/h	75	131	30	--

3.4.1 Permanent gases

The permanent gases are the most important compounds that can be used as fuel for the boiler and gas engine. The permanent gases are the following compounds: CO, H₂, CO₂, CH₄, N₂, C₂H₄, benzene, toluene. The concentration of the permanent gases are given Table 3.4.

RDF produces a product gas with a relatively high concentration of hydrocarbons. The concentration of methane, ethylene, benzene, toluene, and tar is considerably higher than in product gas from the gasification of sewage sludge, resulting in a lower H₂ and CO concentration. The high amount of hydrocarbons in the product gas increased the lower heating value of the product gas substantially. Also the gasifier temperature increased the hydrocarbon concentration leading to a further improvement of the Lower Heating Value. A similar relation with the temperature can be seen with sewage sludge.

The type of fuel and gasifier temperature have both a large impact on the CO, CH₄, CO₂, and H₂ concentration in the product gas, as can be seen in Figure 3.4. Product gas from RDF has typically a lower CO and H₂ concentration and a higher CH₄ concentration than product gas from sewage sludge. Furthermore, for both fuels the H₂ and CO concentration increased with increasing gasifier temperature, the CH₄ concentration remained the same and the CO₂ concentration decreased with increasing gasifier temperature.

Figure 3.4 gives the changes of the CO, H₂, CH₄, and CO₂ concentration in the time. The concentrations were stable during the day. Only in experiment 3 the H₂ concentration increased in time and did not reach steady state. The increase in H₂ concentration can be a result of the Water Gas Shift (WGS) reaction that reaches equilibrium.



The WGS reaction in experiment 3 almost equilibrated at the end of the day. The equilibrium constant, K_p, for the WGS reaction was calculated with the CO, CO₂, H₂O and H₂ concentration. Subsequently, the temperature of equilibrium was calculated from the temperature-K_p relation, which is available in the literature. In experiment 3 the equilibrium temperature decreased from 1150°C at 9:00 to 802°C at 16:30. The WGS equilibrium could have been accelerated during the day due to the accumulation of catalytically active elements in

⁷ NA = Not Analysed

⁸ FB = Fluidized Bed

the ash. The ash accumulation was significant with a rate of 75 g/h in a bed of 1000 g of starting material (silica sand). In theory the CO_2 concentration should increase and the H_2O and CO concentration should decrease when H_2 concentration increases due to the WGS reaction. In Figure 3.4 the concentration of CO , and CO_2 remain the same. That means that beside the WGS reaction CO and CO_2 must have been produced in for example (hydro)carbon gasification reactions.

The WGS reaction in experiment 4 did reach equilibrium all day but the WGS reaction in product gas from RDF, experiment 5 and 6, was not at equilibrium.

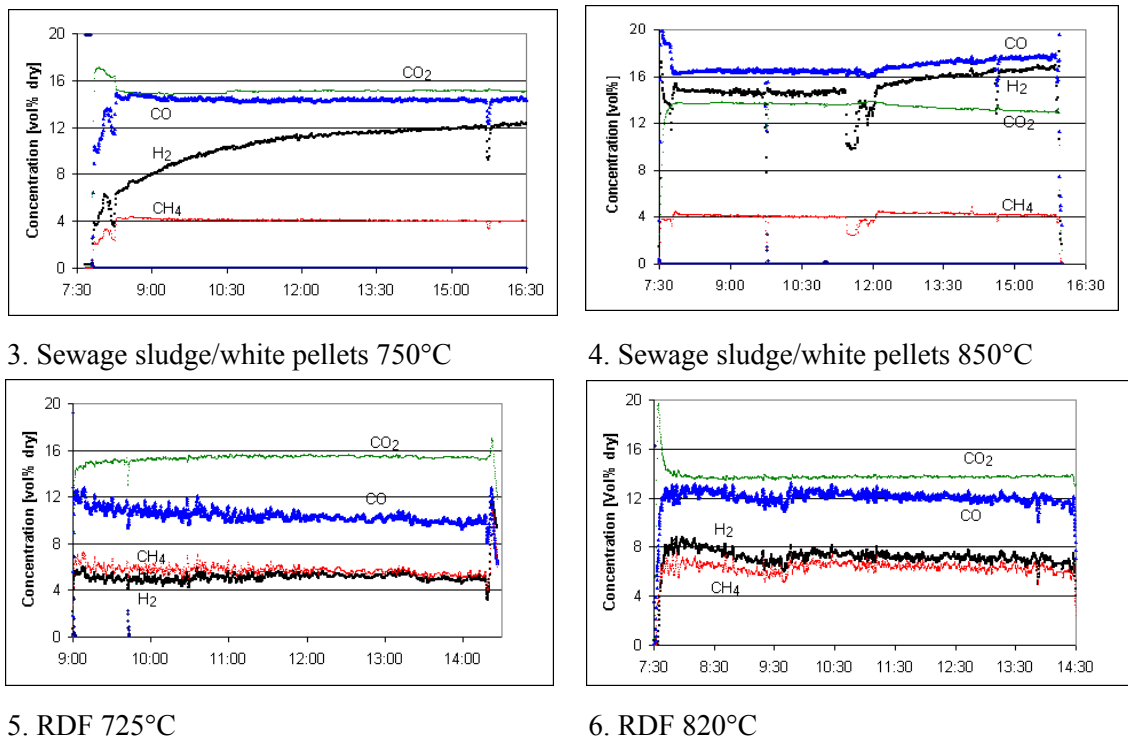


Figure 3.3 Dynamic concentration of CO , H_2 , CH_4 , CO_2 for experiments 3-6

3.4.2 Sulphur in gas phase compounds

The sulphur in the biomass is mainly released as H_2S and COS . Also low concentrations of mercaptane and CS_2 are formed. The contribution of sulphur bounded in the ash is low. The sulphur content in the biomass as well as the gasifier temperature has an influence on the distribution of the sulphur in the product gas. Table 3.5 gives results for two different locations in the installation, which were measured with two different methods:

- GA3: The first method (M1) is used for the determination of H_2S and COS in product gas on sample point GA3. This method uses a micro GC on line. The gas conditioning upstream the micro GC removes dust, water and tar from the gas by cooling. Every 3 minutes a gas sample is analysed and reported. Table 3.5 gives an average of several measurements.
- GA1: The second method (M2) is used for the combined determination of low concentrations (<100 ppmv) of H_2S , COS , mercaptanes, and CS_2 in the gas phase. Sample bags were taken on sample point GA1. The gas in the bags was off-line analysed with a Gas chromatograph.

The sulphur in RDF is for approximately 50% to 60% converted into gas phase compounds and for 10% to 30% bounded in the ash. The remaining 10% to 20% is unknown. The gas phase sulphur compounds were mainly present as H_2S and COS . The concentration of mercaptane and CS_2 was very low. The sulphur balance for RDF is with 60 to 70% relatively low. The balance

is improved to 70% to 90% when the sulphur in the accumulated ash, different from bottom or fly ash, is taken into account.

The sulphur in sewage sludge is for almost 95% converted into gas phase compounds. The contribution of the sulphur in the ash can be neglected on the total sulphur balance. The sulphur is to a large extent converted into H₂S and COS. Also mercaptane and CS₂ is produced at low gasifier temperature. The concentration is a bit higher compared to the RDF experiments.

Table 3.5 Concentration of sulphur in gas phase compounds in ppmv db. and in ash in mg/kg

	3		4		5		6	
Biomass 1	Sewage sludge		Sewage sludge		RDF		RDF	
Biomass 2	White pellets		White pellets		--		--	
Temperature	750°C		850°C		725°C		820°C	
	GA3	GA1	GA3	GA1	GA3	GA1	GA3	GA1
Balance	107%		94%		68%		59%	
M1/M2. H ₂ S	2305		1725		89	75	28	74
M1/M2. COS	158		184		10.5	12	19	10
M2. Mercaptane ⁹		25.4		0.5		7.0		0.1
M2. CS ₂		5.3		5.9		0.3		1.5
S in cyclone ash	6043		6471		1448		1248	
S in ash on probe GA1			2794					720

Beside the sulphur content in the fuel also the gasifier temperature influences the H₂S, COS mercaptane and CS₂ concentration. The concentration of mercaptane decreases significantly with increasing gasifier temperature. Apparently, mercaptanes are unstable compounds at high gasifier temperature. Also the H₂S concentration decreases with increasing gasifier temperature. The COS concentration, at the other hand, increases with increasing gasifier temperature. The relation between the H₂S and COS concentration with the temperature is in agreement with the temperature dependency according to thermodynamic calculations.

3.4.3 Chlorine in gas phase compounds

In general the HCl and dioxin concentration is correlated to the chlorine content in the fuel. RDF, a fuel with high chlorine content, produces a product gas with a high HCl and dioxin concentration. Table 3.6 shows the measured results. The concentration of HCl and dioxins is for sewage sludge considerably lower due to the low chlorine content in the fuel. A substantial fraction (50wt% to 90wt%) of the chlorine is bounded in the ash, depending on the gasifier temperature and fuel composition. The HCl concentration in the product gas increases with increasing gasifier temperature.

⁹ The mercaptane composition was dominated by methyl-mercaptane

Table 3.6 Concentration of chlorine in gas phase in mg/m_n^3 and ash in mg/kg . The chlorine in the gas phase is determined with three different methods

	3		4		5		6	
	Sewage sludge		Sewage sludge		RDF		RDF	
	White pellets		White pellets		--		--	
Temperature	750°C		850°C		725°C		820°C	
	GA3	GA2	GA3	GA2	GA3	GA2	GA3	GA2
Balance	25%		41%		36%		55%	
M1. HCl	36		54		1559		4983	
M2. Tar solvent ¹⁰	8	63	56	58	4124	4746	3344	3006
M3. Alkali solutionGA1	128*		236*		2166*		4363*	
Cl in cyclone ash	1164		842		61964		60848	
Cl in ash on probe GA1			157				30848	

The sulphur content in the gas phase was determined with 3 different methods:

- The first method (M1) is used for the determination of HCl in product gas on GA3. Product gas is drawn with a pump through the impingers for a certain period of time. The chlorine content in the impingers is determined off line with an ion chromatograph.
- The second method (M2) was used for the combined determination of organic chlorine and tar, using the standard tar protocol as described in paragraph 3.3. The chlorine content in the bulk tar solution was determined with an EOX analyser (Coulometric, after combustion). The tar solvent will probably also dissolve some of the HCl and therefore overlap with method M1.
- The third method (M3) was used for the combined determination of HCl and Na, K and Ca on GA1. Gas was drawn with a pump through the impingers for a certain time. The probe was rinsed with a 0,05 HNO₃ solution and mixed with the solution of the two impingers. The Cl content in the bulk solution was determined with an ion chromatograph. This method in principle could give similar results as method M1.

For sewage sludge the third method, M3, gives a consequently higher Cl concentration in the gas phase than method M1. The largest difference in gas sampling between method M1 and M3 is the temperature of ash removal and the location of sampling. The dust filters were operated at a temperature of 750-850°C for M1 and at 350°C for M3. The sampling and analysis procedure of these two methods is further similar. One reason for the difference in the measured Cl concentration between these methods can be the interaction of chlorine with dust. At low temperature the chlorine content in the ash is two times higher than at high temperature, as will be discussed in Paragraph 3.4.6. This can explain the difference in results between GA1 (M1) and GA3 (M3).

With increasing gasifier temperature the Cl concentration measured with method 1 increases and with method 2 decreases. Method 1 measures the HCl concentration and method 2 the concentration of chlorinated tars as well as a part of the HCl. The chlorinated tars might be cracked or the formation suppressed at high gasifier temperature leading to an increase in HCl. This can explain the increasing Cl concentration measured with method 1 and the decreasing Cl concentration measured with method 2. The reduction in the dioxin concentration with increasing gasifier temperature, as will be discussed in section 3.4.5, confirms this mechanism.

The chlorine mass balance was not closed. The main reason for the incomplete chlorine balance is that a considerably amount of Cl is not measured due to the accumulation of ash in the installation. For the RDF experiments only 20% to 30% of the fuel ash was found back as cyclone ash, bottom ash or as fly ash downstream the cyclone. The remaining 70% to 80% of the ash accumulated in the installation and was not measured. When this accumulated ash is taken into account in the chlorine balance than the balance is for 80% to 90% closed. A similar

¹⁰ The chlorine content has been determined with the Ion Chromatography method.

figure was obtained with sewage sludge. Apparently, a test period of 6 to 8 hours is too short to obtain a steady state for a closed ash and, with that, a closed chlorine balance. The strong relation between the ash and chlorine balance means that a large part of the chlorine is bounded in the ash.

3.4.4 Tar composition

Tar is a general name for hydrocarbons with a molecular weight larger than benzene. Tar is present in raw product gas as gas phase hydrocarbon compounds. The formation of tar in the gasifier is very complex due to the huge amount of reaction pathways possible and the continuous changing product gas composition [9]. Inside a fluidized bed gasifier unstable tar compounds are converted into more stable compounds. Sometimes ash can accelerate tar conversion reactions. The tar composition downstream the gasifier is dependent on the gasifier temperature, gas residence time in the gasifier and the biomass composition used. Also the air to fuel ratio, the particle size and the biomass moisture content can have an impact on tar formation. The presence of tar in biomass product gases can be problematic when the gas has to be cooled down. Below a temperature of 400°C tars start to condense resulting in plugging of piping and pollution of condense water. Special attention should be paid for the controlled removal of tar compounds.

Table 3.7 gives the tar composition measured with the tar protocol. The tar compounds are grouped in classes according to the classification system as explained in Appendix B and [10]. RDF fuel produces a product gas with a high tar concentration, considerably higher than sewage sludge product gas. The tars from RDF have both a high concentration of light class 3 and 4 tars as well as heavy class 5 tars. For sewage sludge a part of the class 2 tars could not be analysed due to the presence of unknown tar compounds that overlap with the known class 2 tars. With increasing gasifier temperature the gravimetric, class 2 and class 3 tars are reduced in concentration and the class 4 and 5 tars are increasing in concentration, as expected [10].

Table 3.7 *Tar composition and concentration in mg/m_n³ divided according to the tar classification system. Toluene is left out of the tar spectrum*

	3		4		5		6	
Biomass 1	Sewage sludge		Sewage sludge		RDF		RDF	
Biomass 2	White pellets		White pellets		--		--	
Temperature	750°C		850°C		725°C		820°C	
	GA3	GA2	GA3	GA2	GA3	GA2	GA3	GA2
Phenol								
Naphthalene								
Class 2	194	139	221	325	1275	1355	160	279
Class 3	917	753	498	404	8040	8217	4345	6015
Class 4	1927	1411	3168	1696	7772	6066	14484	15496
Class 5	105	72	247	123	370	226	1603	1506
Total unknowns	12108	15183	7458	4668	8920	9920	6276	8550
Total tar	15250	17559	11592	7217	26378	25784	26868	31846
Total Gravimetric	28283	28720	9987	3643	15918	15839	12359	12732

For sewage sludge the contribution of the unknowns is extremely high. Most of the unknowns are appearing in the light part of the GC tar spectrum, between benzene and phenanthrene. The high concentration of unknowns is most probably caused by the presence of primary tars in the product gas. Primary tars are normally not measured as individual compounds, and are analysed with the GC as unknowns. Primary tars are especially formed at low gasifier temperature. The concentration unknowns decrease with increasing gasifier temperature for sewage sludge.

3.4.5 Dioxins

Next to macro components, such as phenol, benzene etc. present in (raw) product gas at g/m_n^3 levels, tars include also a whole variety of trace compounds, some of which are highly toxic. One of such examples is the family of chlorinated organics: polychloro-dibenzo-*para*-dioxins and dibenzofurans (PCDD/Fs), commonly known as *dioxins*. Chemically, these are chlorinated derivatives of aromatic ethers, which are highly thermally stable. The whole dioxin family consists of 210 congeners, yet it has been observed that only 18 of them, namely those containing chlorine on the (lateral) 2,3,7,8 positions, are highly toxic. Their toxicity, however varies with substitution degree (i.e. 2,3,7,8 tetrachloro-dibenzo-*para*-dioxin (2,3,7,8- T_4CDD) is 10 000 times more toxic than the perchlorinated compound octa chloro dibenzod-*para*-dioxin (O_8CDD)). In order to express the toxicity of a mixture containing a whole range of the said compounds, it is necessary to relate it to the toxicity of the most toxic dioxin, the above-mentioned 2,3,7,8- T_4CDD . This is done by multiplying the concentrations of each of the 18 toxic isomers with their Toxicity Equivalence Factors (TEF), which ranges from 0.1 to 0.0001 (for O_8CDD). Summing up the obtained Toxicity Equivalence (TEQ), yields a number indicating the toxicity of the mixture.

Dioxins are emitted in all thermal processes, where the combination of an inadequate process temperature ($<850^\circ\text{C}$), the presence of chlorine as well as insufficient concentration of oxygen and residence time ($<2\text{s}$) allows aromatics to form and/or survive. Gasification was long-thought to be dioxin-free, yet even at first glance it can be concluded that at mild temperatures and with the chemical environment of the (fluidised bed) gasification, dioxins are not unlikely to occur. In the series of preliminary tests performed at ECN Biomass a while ago, the presence of PCDD/Fs in (raw) producer gas was indeed confirmed.

In this, more advanced, study, the influence of the process parameters as well as that of the fuel quality on the concentration of dioxins in the raw product gas was investigated. During a fourfold of tests, two fuels, namely sewage sludge and RDF, were gasified in the WOB test rig at two temperatures: 750°C and $820/850^\circ\text{C}$. Results of the measurements, performed on the dedusted product gas by means of the so-called PUF-plugs (quenched to suppress secondary formation in the sampling system) and analysed in accordance with the NEN-EN-1948-2 norm, are given in Figure 3.3 and Table 3.8. Overviews of the isomer patterns are shown in Figure 3.4. and 3.5.

Table 3.8 *Summary of dioxin outputs data*

Fuel		RDF	RDF	Sewage Sludge	Sewage Sludge
Temperature	$^\circ\text{C}$	725	820	750	850
PCDDs	ng/m_n^3	27.6	5.5	2.3	0.7
PCDFs	ng/m_n^3	345.3	28.9	9.4	1.2
Sum PCDD/Fs	ng/m_n^3	373.0	34.4	11.8	1.9
toxicity eq.	$\text{ng I-TEQ}/\text{m}_n^3$	74.2	4.5	2.0	0.4

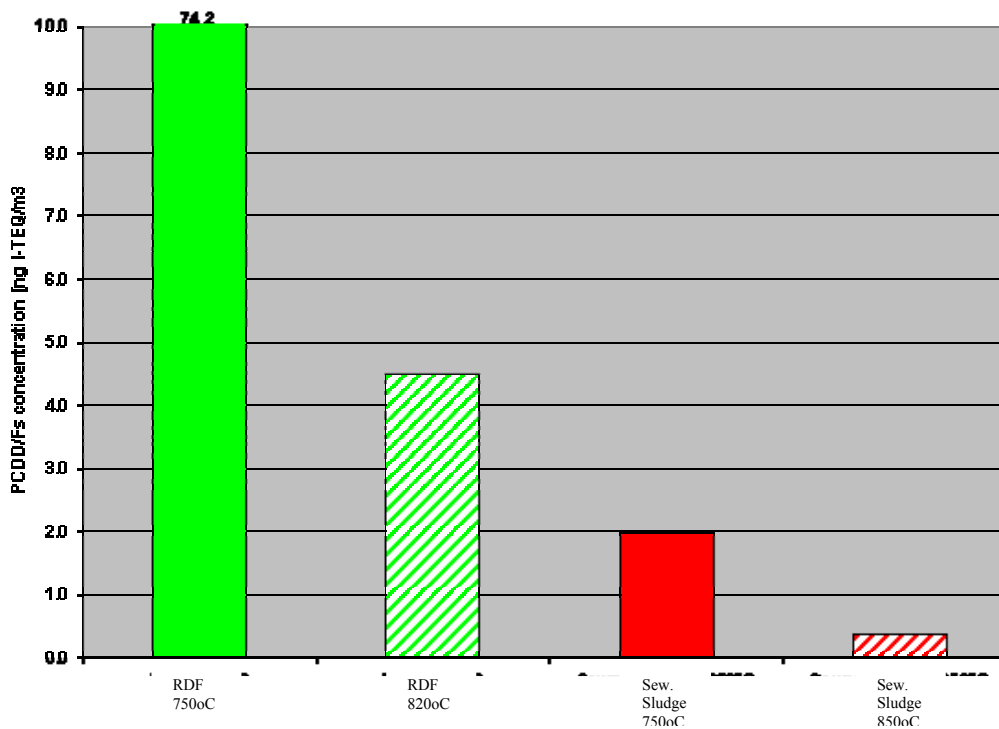


Figure 3.4 *Dioxin levels in raw producer gas as a function of fuel and gasification temperature*

As can be seen in the above table and figure, the concentrations of dioxins in raw product gas vary over a two orders of magnitude broad range, between 1 and 100 ng Toxicity Equivalents per cubic meter. Further it can be concluded that the gasification temperature has a very deep impact on the outputs and the toxicity of the emitted dioxins, as both fuels show a significant reduction (~5-10 times) at higher process temperature. Also the levels of chlorine species in the systems appear to have a great influence on the dioxin yields. Overall, dioxins levels when using sewage sludge are one order of magnitude lower than with RDF. At the same time the measured levels of chlorine species (HCl and – likely- other chlorinated species, both organic and inorganic) were greatly lower when gasifying sludge. This could be traced back to the composition of the tested fuels (0.15 vs. 1.5 % w/w for the sludge (with 50% of white wood pellets) and RDF, respectively). Another important parameter is the level of sulphur in the system. Although the numbers are not completely clear, it is obvious that the sludge leads to a much higher concentration of sulphur in the system, which in turn may affect the free chlorine concentration in the gas. And since Cl₂ is a much more potent chlorinating agent than HCl, a decrease in its concentration would mean a decreased chlorination capacity of the system, decreasing the levels of chlorinated organics, such as i.e. chlorophenols, which may lead to dioxin formation, through a multitude of pathways.

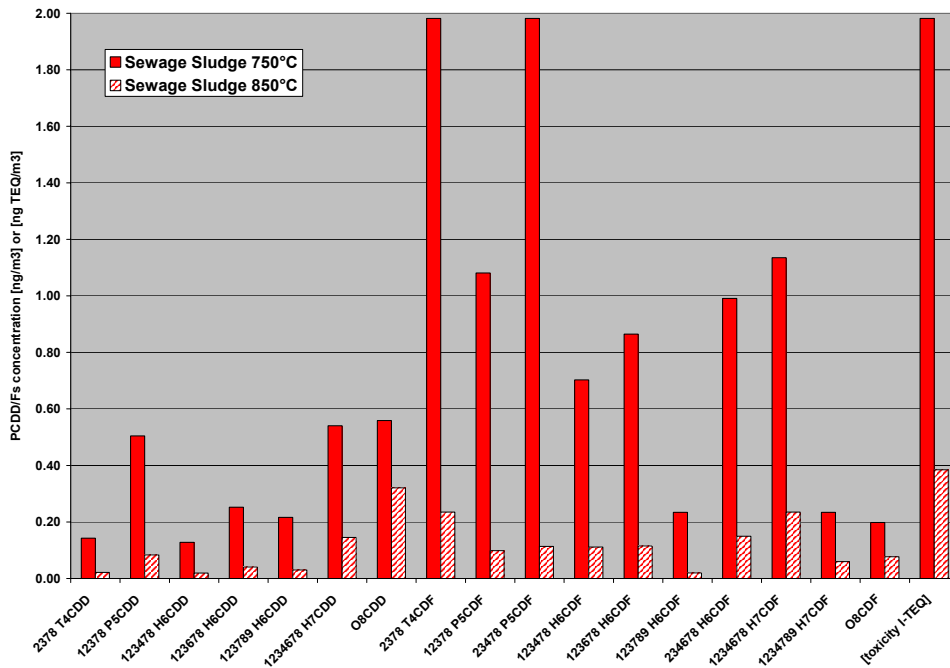


Figure 3.5 PCDD/Fs isomers distribution in tests with sewage sludge

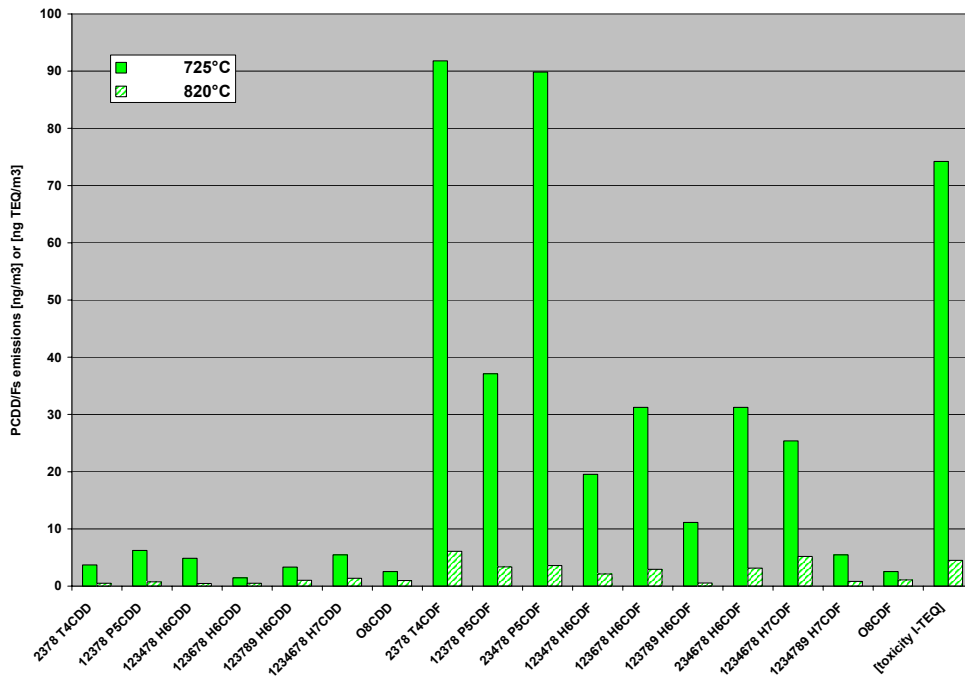


Figure 3.6 PCDD/Fs isomers distribution in tests with RDF

3.4.6 Fate of ash and alkali metals

Ash in biomass can accumulate in the fluidized bed of the gasifier as bottom ash and can entrain with the product gas as fly ash. During the gasification of sewage sludge and RDF, substantially amount of bottom ash was produced resulting in an increase in the amount of fluidized bed material. Part of the inorganics in the fly ash like the Alkali metals can partly vaporise at gasifier temperature. Subsequently the vaporised ash compounds can condense in a typical temperature window of 500°C to 850°C. Table 3.9 gives the measurement results for the ash and the alkali metals.

The concentration of the alkali metals in the freeboard of the gasifier is dependent on the temperature of the freeboard. At high temperature a part of the alkali metals vaporise, among which the earth alkali metal Ca has the highest vapour pressure. The total alkali concentration increases 3 to 8 times with increasing temperature from 735 to 850°C.

The chlorine content in the ash is dependent on the temperature of collection. On sample point GA1 the ash is collected at high temperature, similar to the freeboard temperature. The cyclone ash was collected at the cyclone temperature of approximately 550°C. For both ash samples, from the cyclone and from the freeboard, the chlorine content was analysed. The chlorine content in the ash collected in the gasifier freeboard on sample point GA1 was 2 to 7 times lower than the chlorine content in the cyclone ash. The difference can be a result of condensation of chlorine compounds, like KCl and NaCl on ash particles when the gas is cooled down.

The sulphur content of the ash is also dependent on the temperature of collection. The sulphur content in the ash collected in the gasifier freeboard was two times lower than the sulphur content in the cyclone ash. The difference can be a result of condensation of sulphide compounds, like PbS, ZnS and AsS, on ash particles when the ash is collected at a decreased temperature like in the cyclone.

Table 3.9 *Ash composition and flows*

Biomass 1			Sewage sludge	Sewage sludge	RDF	RDF
Biomass 2			White pellets	White pellets	--	--
T gasifier	°C		750	850	725	820
Ash		g/m _n ³	6.3	5.8	3.9	5.2
Cl in ash	GA3	mg/m _n ³	1164	842	61964	60848
Cl in ash	GA1	mg/m _n ³		157		30848
S in ash	GA3	mg/m _n ³	6043	6471	1448	1248
S in ash	GA1	mg/m _n ³		2794		720
Ca in gas	GA1	mg/m _n ³	5.6	17.5	8.4	41.4
K in gas	GA1	mg/m _n ³	1.2	2.1	0.7	19.2
Na in gas	GA1	mg/m _n ³	0.3	0.2	1.2	17.3
Cyclone ash flow		g/h	44	54	2.5	12
Fluidized bed increase		g/h	75	131	30	--

The ash balance was not completely closed. Only 25% to 40% was measured as bottom or fly ash for sewage sludge and for RDF only 15% to 33% of the fuel ash was measured as bottom or fly ash. The remaining 60% to 85% of the ash accumulated in the installation. Apparently the 8 hours of testing was too short to reach a steady state for the ash.

3.5 Gas composition for gas cleaning design

In Paragraph 2.1 a representative biomass composition was determined for this project. The composition was based on a thorough evaluation of the Cl and S content in several biomass streams. Finally a mixture of grass, sludge and beech was chosen for the determination of the biomass composition. The representative fuel has an ash content of 13wt%, a chlorine content of 0.26wt% and a sulphur content of 0.56wt%.

In this paragraph a product gas composition will be calculated for the application of the representative biomass in an air blown direct (DIR) or indirect (IND) fluidized bed gasifier. The gas composition was determined with the expert gasifier model of ECN. The experimental

results were used to determine the concentration of Cl and S containing compounds in the gas phase. The assumptions for the calculation of the gas composition of the indirect or direct gasifier are given in Table 3.10.

The indirect gasifier is used upstream the fuel cell and the direct gasifier upstream the gas engine and boiler. For a fuel cell an indirect gasifier is not preferred due to the presence of N₂ in the product gas. Appendix C explains the indirect gasifier configuration [11].

Table 3.10 *Assumptions for the determination of the product gas composition*

Biomass input 10 MWth.	IND+DIR	For non-woody biomass a small scale system was selected. Non-woody biomass is normally locally available as industrial, agricultural and forestry waste streams. The small scale fits the local processing of the waste stream in a gasification process.
Gasifier temperature 850°C	IND+DIR	From the experiments it can be concluded that the release of S and Cl compounds simplify when the gasifier temperature is increased from 750°C to 850°C. The mercaptanes disappear and the chlorinated hydrocarbons are significantly reduced in concentration.
25% conversion of fuel Cl into HCl	IND+DIR	Experiments indicate that a fuel with high chlorine content and a relatively low ash content like RDF (1.5wt% Cl and 7 wt% ash) can release a part (50%) of the Cl as HCl. Sewage sludge, a fuel with a low chlorine content and a high ash content produces less HCl. The representative biomass has a high ash content and a low Cl concentration. Therefore the release of Cl as HCl from the representative biomass fuel has been assumed to be relatively low.
75% of the chlorine is bounded in the ash	IND+DIR	Experiments indicate that a large part of the Cl is bounded in the ash, especially for a fuel with a high ash content and a moderate Cl concentration. The ash of the representative biomass contains enough K, Na and Ca to bind the Cl to the ash. The contribution of chlorinated hydrocarbons has been neglected because of the high gasifier temperature.
The chlorine and sulphur is released in the gasification zone	IND	The indirect gasifier produces a flue gas and a product gas. It is assumed that most of the chlorine and sulphur is released in the gasification zone of the gasifier. The flue gas is expected to contain only chlorine and some sulphur bounded in the ash.
100% of the sulphur is released as H ₂ S or COS	IND+DIR	The experiments with the direct air blown gasifier indicate that sulphur in a fuel with a high S content, like sewage sludge, is for 80-90% released as H ₂ S and for 10% as COS. A similar situation is assumed for the indirect gasifier.
0% of the sulphur is bounded in the ash.	IND+DIR	The amount of sulphur in the ash is neglected.

The carbon content in the ash is 19wt%	DIR	The carbon content in fly ash from a direct gasifier is a result of an incomplete carbon conversion in the gasifier. The bottom ash will also contain carbon but the carbon content is expected to be lower due to the long residence time of the bottom ash in the gasifier. The total carbon content is expected to be 19% resulting in a 93% carbon conversion in the gasifier.
The carbon content of the ash is 0wt%	IND	In the indirect gasifier the char is used in the combustor of the gasifier as fuel for the gasifier. The ash from the cyclone in the product gas will be returned to the combustor of the gasifier. Therefore the ash of the indirect gasifier does not contain carbon.

An important difference between the indirect gasifier and the direct gasifier is the amount and calorific value of product gas produced. The indirect gasifier produces two gas streams at similar flow rates, a product gas and flue gas. In this project it is assumed that the sulphur and chlorine compounds are released in the product gas. The ash from an indirect gasifier does not contain carbon. Therefore the ash flow rate is lower than for a direct blown gasifier. The product gas composition is depicted in Table 3.11.

Table 3.11 *Product gas composition on wet basis for the gasification of 10MW_{th} representative biomass in a direct or indirect air blown fluidized bed gasifier. The composition of the representative biomass is given in Table 2.2*

		Indirect	Direct
Feeding rate ar.	kg/h	2500	2500
Air flow rate	m _n ³ /h	2540	2500
Gasifier temperature	°C	850	850
Gas composition			
CO	[vol%]	25.4	12.5
H ₂	[vol%]	15.6	7.9
CO ₂	[vol%]	9.9	13.0
H ₂ O	[vol%]	29.6	17.1
CH ₄	[vol%]	10.8	3.2
N ₂	[vol%]	0.5	42.9
C ₂ H ₄	[vol%]	3.6	1.1
Benzene	[vol%]	0.9	0.3
Toluene	[vol%]	0.0	0.1
H ₂ S	[ppmv]	2997	1344
COS	[ppmv]	331	149
NH ₃	[ppmv]	18282	8254
HCN	[ppmv]	6033	2724
HCl	[ppmv]	351	196
Tar	[mg/m _n ³]	40000	10000
Fly+Bottom ash	kg/h	285	383
Gas flow rate (incl. tar)			
	[m _n ³ /h]	2067	4570
	[kg/h]	2073	5379
	[m ₃ /h]	8500	18793

4. Technical perspectives

This chapter will give the technical consequences for the use of non-woody biomass instead of woody biomass in a gasification process. The consequences for the gas cleaning are summarized in a process flow diagram. For the gas cleaning, technologies were selected that are developed for other applications like for the coal and oil industry. The technologies must be able to fulfil the emission limits and prime mover requirements, as defined in Chapter 2 of this report. The consequences for the gas cleaning of the three product gas applications: boiler, gas engine and fuel cell are discussed separately in Paragraph 5.2-5.4. The first paragraph of this chapter provides a comprehensive review of gas cleaning technologies available for the removal of H₂S, COS, and HCl.

4.1 Review of Cl and S gas cleaning methods

4.1.1 HCl removal

HCl removal processes can be categorized in two groups a dry process and a wet process. In the dry process, product gas is contacted with an adsorbent. For wet process, product gas comes into contact with a chemical solution or water.

Dry removal

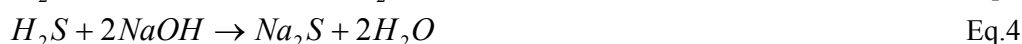
There are two types of adsorbent available for HCl removal, Na-carbonate adsorbent and Ca-oxide adsorbent [12]. For the application in product gases the Ca adsorbent is less suitable for HCl removal, because the adsorbent reacts also with CO₂ in the product gas. The CO₂ is preferentially adsorbed because of the high concentration. Dry scrubbing of HCl with NaHCO₃ at high temperature between 400-500 °C is able to reduce the concentration of HCl to lower than 1 ppmv.

Water scrubber

In principle HCl absorbs well in water. Aspen modelling showed that the product gas from a biomass gasifier produces enough water condensate to remove 500 ppmv of HCl from the gas [13]. To maximise the contact area between the product gas and the water condensate a water scrubber can be used. Water can be used as cooling agency. In some areas the wastewater regulation might not allow disposing chlorine in the surface water. In that case additional wastewater treatment equipment should be installed like an ionic exchanger. Due to the large amount of water condensate in the product gas, water cleaning can become expensive.

Caustic scrubber

A caustic scrubber is very effective for the combined removal of CO₂, HCl, COS and H₂S. The compounds are converted into stable salts like Na₂CO₃, HCl, NaHS and Na₂S. This process is useful for removing a trace amount of impurities from the gas streams. Caustic is usually in excess and recycled back to have a maximum use of the caustic, and add fresh NaOH as required. The reactions are showed below [14]:



Equation 1 is undesirable because of the low solubility of the carbonate salt. This reaction can be prevented by short residence time [14]. Since reaction 2 and 3 is much faster than reaction 1, it is possible to achieve a higher degree of H₂S and HCl removal than CO₂ removal [Picciotti 1978]. The formation of NaHS (eq2) is preferred over Na₂S when less NaOH is used.

4.1.2 H₂S and COS removal

H₂S removal

The removal of H₂S is often coupled to CO₂ removal. Kohl [14] gives general guidelines for a preliminary screening for a H₂S and CO₂ removal process. The H₂S removal processes can be grouped into six types. Table 4.1 gives the list and also suggests the preferred areas of application for each process type.

Table 4.1 *Guideline for H₂S removal process [14]*

Type of process	Plant size	Partial pressure	Sulphur removal capacity
Absorption in alkali solution	H	L	H
Physical absorption	H	H	H
Liquid oxidation	H	L	L
Dry sorption/Reaction	L	L	L
Adsorption	L	L	L
Membrane permeation	L	H	L

Plant size : H = > 20 MMSCFD (23597 m_n³/h)

Partial pressure: H = > 6.9 bara

Sulphur capacity: H = > 10 ton/day

MMSCFD is Million Standard Cubic Feet per Day.

L = low; H = high

Both absorption in an alkaline solution (chemisorption by e. g. aqueous diethanolamine, NaOH solution) and in a physical sorbent (e.g., poly ethylene glycol) are suitable for treating high-volume gas streams containing H₂S and/or CO₂. However, physical absorption processes are not economic competitive when the acid gas partial pressure is low because the capacity of physical solvents is a strong function of partial pressure. According to Christensen and Stupin, physical absorption is generally favoured at acid gas partial pressure above 6.9 bara, while alkaline solution absorption is favoured at lower partial pressures. Tennyson and Schaaf placed the boundary line between physical and chemical solvents at 6.9 bara.

Solid sorption is applicable to low quantities of H₂S, as indicated in Table 4.2. Suitable adsorbent are the oxide of Fe, Mn, Zn, Cu and Ca. Most sorbents cannot be regenerated and must be disposed after being used. Solid sorption processes (zinc-titanate and zinc Ferrite) that use sorbents that can be regenerated are under development [15].

Adsorption with molecular sieves is a viable option when the amount of sulphur is very low and the gas contains heavier S compounds (such as mercaptane and COS) that must also be removed. Also water and CO₂ are removed in large quantity.

Membrane permeation involves the separation of individual compounds on the basis of the difference in their rates of permeation through a thin membrane barrier. In general membranes for H₂S removal are applied for small-scale plants with gases containing a high H₂S concentration. The capacity is accomplished by using proportionately increasing amount of modules. Therefore, the process does not realize the economy of scale and becomes economic less competitive with absorption processes as the plant size is increased.

Table 4.2 Overview of process conditions and performance of various H₂S removal processes

Technology	Final H ₂ S conc. (ppmv)	Operating temperature (°C)	Product	S-product
Physical absorption				
Rectisol	< 1	-60 to 65	H ₂ S	S (via Claus)
Chemical absorption				
Alkanolamine	~1-2	<20* - 150°C	H ₂ S	S (via Claus)
Liquid phase oxidation				
	**	**	S	
Membrane separation				
	<1	20-50	H ₂ S	S (via Claus)
Dry sorption***				
CaCO ₃	50-100	1000 max	CaS	CaSO ₄
MnO	5	1000 max	MnS	S
CuO	<1	360 max	CuS	disposal
ZnO	~0.1	450 max	ZnS	disposal
ZnFe ₂ O ₄	~0.2	450 max	ZnS	S
ZnTiO ₃	~0.3	450 max	ZnS	S
Fe ₂ O ₃	1	500 max	FeS	S
Molecular sieve				
	20 ppb	not available	H ₂ S	S (via Claus)
Biological conversion				
	2 ppmv	40 max		S
THIOPAQ				
	1-2	ambient	S	

* Depends on the boiling point of amines

** Final concentration depends on the process, operating temperature and pressure

*** Final H₂S concentration depends on gas composition. Water has a negative influence

Furthermore RTI international also develops a single step sulphur recovery process (SSRP) by using activated alumina catalyst. The SSRP consists of injecting SO₂ directly into the quenched syngas to oxidize H₂S selectively and recover sulphur in a single step.

Sulphur recovery process

In general H₂S can be recovered as elemental sulphur, S, by using a biological process or by the reaction with SO_x. The standard technology for recovery of a concentrated H₂S gas stream to elemental sulphur is the Claus process. Since the disclosure of the process by Claus in 1883, the process has undergone several modifications. The most significant modification was to replace thermal conversion to a catalytic conversion in 1936. The quality of the recovered S is very high.

Normally a Claus process is operated parallel to a physical or chemical absorption/desorption process like the Rectisol process or alkanol amine process. The Rectisol or alkaline amine process removes the H₂S from a diluted gas stream. The gas from the desorption step is concentrated with H₂S and can be applied in the Claus process for the conversion of H₂S to elemental sulphur.

Alternatively to the Claus process, H₂S can be easily and economically converted to elemental sulphur by a biological process. The THIOPAQ process uses micro-organism to convert S²⁻ to elemental S. The H₂S can be removed in an alkaline scrubber from the gas. The chemically absorbed H₂S can consequently be fed to the biological reactor where the H₂S in the solution is converted into elemental sulphur with the bacteria present in the reactor.

Selection

For a biomass gasification process of 10 MW_{th}, the plant size (5000 m_n³/h), H₂S concentration in product gas (2300 ppmv) as well as the elemental sulphur capacity (0.6 tonne/day) is low, according to the specifications of Table 4.1. Therefore the only suitable technologies for the removal of H₂S are dry sorbents and adsorbents, solids. Due to the high CO₂ and H₂O content in

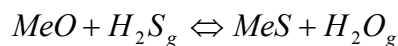
biomass product gases a dry sorbent/reaction should be selected for the removal of H₂S from the product gas.

For the selection of the sorbent the following two parameters should be investigated:

- Thermodynamic equilibrium between the metal oxide sorbent and H₂S;
- Stability of metal oxides under the gas condition

Westermorel and performed an evaluation of candidate solid sorbents for high temperature desulphurization processes in low calorific gases, like biomass product gas. In potential 28 solid metal oxides were subject to thermodynamic and stability analysis. Eleven candidate solids based on metal Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu and W showed to be thermodynamically feasible. More discussion on practical issues in addition to thermodynamic constrains can be found in Slimane and Abbasian (2000) and Newby (2001).

The gas composition strongly influences the adsorption process. The presence of CO and H₂ determine the reducing condition of the gas. Some metal oxide can be reduced to a metal. The lower melting point of metal leads to melting of sorbent and causes the deactivation of sorbent [15]. Moreover, CO can form with some metals and at certain temperature metal carbonyl, Me(CO)_n, which can lead to the evaporation of metal and the deactivation of the sorbent [15]. The presence of water reduces the sorbent capacity over the whole temperature range because water is a product of the adsorption process according to the following reaction:



Therefore, it is important to use the right gas composition for the thermodynamic calculations. In this report the choice was made for a two stage H₂S removal:

- In the first stage the bulk of the H₂S and COS is removed with a cheap sorbent;
- In the second stage an expensive sorbent is used for H₂S removal to reach the specified low H₂S concentration.

The amount of sorbent to be used is determined by the amount of H₂S present in the gas and the degree of conversion for a typical sorbent.

COS removal

Carbonyl sulfide (COS) is an organic sulphur compound. Physical and chemical removal process cannot remove COS efficiently. Thermodynamic calculation of the simulated gas composition shows that the reaction of COS shifts towards the formation of H₂S as the gas is cooled down to a low temperature. At a gas temperature of 200 °C, thermodynamically there is no COS present. This implies that it is possible to convert COS to H₂S. The catalysts to convert COS into H₂S are activated alumina, titania on alumina and Mo/Co catalyst.

The ZnS product from the absorption of H₂S with ZnO also catalyzes the COS conversion via the hydrogenation reaction. So, when the ZnO bed contains ZnS, COS can be converted into H₂S. The H₂S is, subsequently, adsorbed by the ZnO. Than an upstream catalyst is not necessary for the removal of COS. Care should be taken during the start up period when there is no ZnS layer on the surface of ZnO. Fresh ZnO might have to be mixed with a small amount of spend ZnS to rely on the guard bed during start up.

4.2 Gas cleaning for boiler application

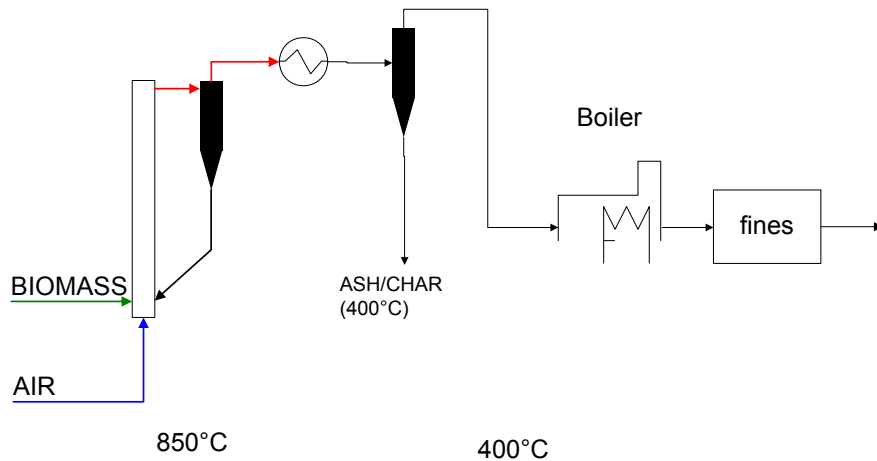


Figure 4.1 *Reference process flow diagram for the application of product gas in a boiler, using woody biomass as fuel for the direct air blown fluidized bed gasifier*

The product gas from a circulating fluidized bed (CFB) gasifier can be used in a boiler for the production of heat or electricity with a steam turbine. This section will discuss the difference in gas cleaning when switching from woody to non-woody biomass. For woody biomass the product gas from the CFB gasifier is cooled down to 400°C. Downstream the cooler the gross ash particles are removed with one to three cyclones to relieve the boiler from high dust loads and, therewith, to reduce the risk of boiler fouling. Downstream the boiler the remaining ash is removed in the flue gas with a bag house filter to fulfil the emission limits. In this application tar removal is not necessary. The process flow diagram is given in Figure 4.1.

When woody biomass is replaced by non-woody biomass the product gas will contain chlorine and sulphur compounds like H₂S, HCl, and COS and an increased amount of ash. The gas composition downstream the gasifier for a representative non-woody biomass is given in Paragraph 3.5. To fulfil the emission limits sulphur and chlorine must be removed for 97% and 86% respectively. The sulphur and sulphur can be removed in the product gas upstream the boiler or in the flue gas downstream the boiler. There are several reasons to choose for product gas cleaning:

1. The risk of boiler corrosion is reduced when the S and Cl is removed from the product gas upstream the boiler.
2. The product gas flow is approximately two times lower than the flue gas flow rate, which means that smaller equipment can be applied for the gas cleaning.
3. The sulphur and chlorine in the product gas do not have to be removed deeply to fulfil the emission limits. In the boiler the gas is diluted due to the addition of combustion air and thus the concentration of S and Cl reduces.

A disadvantage for product gas cleaning is that H₂S and COS is more difficult to remove in product gas at high temperature than SO_x in flue gas at elevated temperature. This project focuses on product gas cleaning.

The gasifier is operated at 850°C. Downstream the gasifier the product gas is cooled down in a double pipe cooler. Then the dust, and the bulk of the sulphur is partly removed. Downstream the gas is cooled down further in a double pipe cooler. The HCl is then removed to fulfil the emission limits of 10 mg/m_n³. In the last step upstream the boiler H₂S and COS is further removed (polishing step) with ZnO to fulfil the emission limits.

The boiler should have a low-NO_x burner, and probably also a dioxin removal system should be installed in the flue gas, in order to fulfil the NO_x and dioxin emission limits. The dioxin can be reduced with a deNO_x catalyst or with activated carbon in the flue gas of the boiler. The activated carbon can be used as fuel for the gasifier where the dioxins are destroyed. In the period of this project the knowledge of dioxin emission in the boiler was not sufficient to take the removal into account and is therefore not included in the process design.

The spend sorbent should be treated, ZnO leaves the system as ZnS and Sodium bicarbonate leaves the system as NaCl. The NaCl can be returned to the supplier for recycling. The total amount of ZnO and sorbent, sodium bicarbonate and spend sorbent is given in Table 4.3.

Table 4.3 *Amount of sorbent necessary for the removal of H₂S, COS and HCl in a 10MW_{th} gasification process for boiler application.*

	Total sorbent amount [kg/h]	Total amount of spend sorbent [kg/h]
ZnO	2.6	2.8
Bulk Sorbent	103	107
NaHCO ₃	7.1	6.3

The technical perspective of the gas cleaning for the boiler is promising. The sulphur and chlorine concentration in the product gas downstream the gas cleaning is easily reduced. The gas cleaning technologies are simple and theoretically able to sufficiently reduce the Cl and S concentration in the product gas to fulfil the emission limits. Therefore, the reliability of the gas cleaning is maximised, but should be validated experimentally.

4.3 Gas cleaning for gas engine application

The product gas from a fluidized bed gasifier can also be used for the production of electricity and heat with a gas engine. This section will discuss the difference in gas cleaning when switching from woody to non-woody biomass. For woody biomass fuels the product gas is normally cooled down to 400°C. Downstream the cooler the ash is partly removed by the cyclone. Downstream the cyclone the tars are removed with OLGA [16]. After OLGA the gas is further cooled down and water is removed in the quench. In the last step of the process NH₃ is removed in an aqueous scrubber [17] to bring the product gas on specification for the gas engine. A deNO_x system is not necessary in the exhaust of the gas engine when a NH₃ system is installed. The process diagram for the application of woody biomass in a gasifier is given in Figure 4.2.

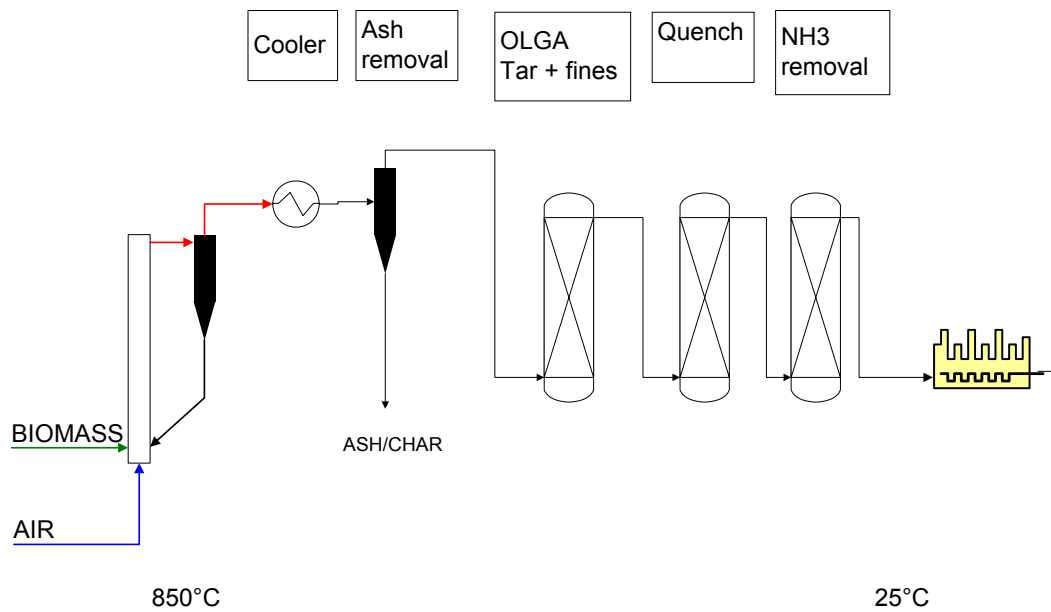


Figure 4.2 Reference process diagram for the application of product gas in a gas engine, using woody biomass as fuel for the direct air blown fluidized bed gasifier

When woody biomass is replaced by non-woody biomass the product gas will contain chlorine and sulphur compounds like H_2S , HCl , and COS and an increased amount of ash. The gas composition downstream the gasifier is given in paragraph 3.5 for a representative non-woody biomass. The ash and the Cl and S compounds are removed from the product gas in order to fulfil the gas engine specification and the emission limits for SO_x and HCl , which are given in Paragraph 2.3 and 2.5. For the gas engine sulphur and chlorine must be removed for 67% and 69%. To fulfil the emission limits the sulphur and chlorine must be removed for 97% and 86%. So when the emission limits are obeyed then also the gas engine requirements are fulfilled.

The gas cleaning is similar to the gas cleaning for the boiler application. The gasifier is operated at $850^\circ C$. Downstream the gasifier the product gas is cooled down in a double pipe cooler to $770^\circ C$. Then the dust, H_2S and COS is partly removed. Downstream the product gas is further cooled down in a double pipe cooler. Subsequently, the H_2S and COS is further removed (polishing step) with ZnO to fulfil the emission limits for SO_x . Downstream the sulphur polishing step the tars and dioxins are removed from the gas with OLGA. In the quench, downstream OLGA, the HCl is dissolved in the water condensate and removed from the product gas to fulfil the HCl emission limits. Finally NH_3 is removed with an aqueous scrubbing system. The exhaust of the engine does not need additional flue gas cleaning.

The ZnO leaves the system as ZnS . The spent sorbents are discharged. The total amount of sorbent and spend sorbent is given in Table 4.4.

Table 4.4 Amount of sorbent and spend sorbent for the removal of H_2S and COS in a $10MW_{th}$ gasification process for gas engine application

	Total sorbent amount [kg/h]	Total amount of spend sorbent [kg/h]
ZnO	2.6	2.8
Bulk sorbent	103	107

The sulphur removal system is similar to the boiler application, but the chlorine removal system is different. The chlorine is removed in a water quench. The water quench is in first instance installed for gas cooling and the removal of water from the product gas. However, the amount of

water condensate is sufficient to dissolve the gas phase chlorine to such an extent that the chlorine emission limits and gas engine requirements are fulfilled. The presence of NH_3 in the product gas will avoid water condensate with a low pH¹¹ and improves the HCl removal. The chlorine removal can therefore be done without additional investment or operational costs. The chlorine containing water condensate will not have a very low pH and cleaning will be dependent on the wastewater requirements defined by local authorities.

For the development of the H_2S and HCl removal systems emphasis must be put on some operational risks:

- The possible formation of ZnCl_2 : due to a reaction of ZnO with HCl the ZnCl_2 can vaporise. The vaporisation will be dependent on the partial pressure of HCl, the residence time of ZnO in the product gas and the temperature of operation.
- The formation of NH_4Cl in OLGA: when the NH_4Cl leads to problems in OLGA, HCl should be removed upstream with sodium bicarbonate.

As a conclusion the technical perspectives of the gas cleaning for the gas engine are very similar to the boiler perspectives, as discussed in previous paragraph. Instead of chlorine removal with sodium bicarbonate, the HCl is removed together with the water condensate in the scrubber. The HCl removal can easily be controlled by the addition of water to the scrubber.

4.4 Gas cleaning for fuel cell application

This section will discuss the difference in gas cleaning downstream an indirect gasifier for the application of the product gas in a SOFC fuel cell when woody biomass is replaced by non-woody biomass. This section will be a bit scientific/theoretical, because the fuel cell has never been applied downstream a biomass gasifier on industrial scale. The fuel cell should be seen as a long-term application. On the short term the 10MW_{th} does not fit the scale of the current fuel cell but it is expected that research will lead to larger scale fuel cells, as soon as the market is ready for fuel cells. Nevertheless, it is interesting to discover the differences between a boiler, gas engine and fuel cell application for the removal of Cl and S compounds.

The requirements for a fuel cell differ significantly from the requirements for a boiler or gas engine. The product gas is preferably not diluted with N_2 . The N_2 dilution decreases the electric potential of the fuel cell, which results in loss of power. To avoid N_2 dilution, a fluidized bed gasifier can be operated with pure oxygen instead of air. However, for an oxygen blown gasifier an expensive oxygen separation unit and additional steam is necessary. In this report the N_2 free product gas is made in an indirect gasifier. A description of an indirect gasifier can be found in Appendix C or in [19]. The absence of N_2 will lead to a more concentrated gas, which means that probably also the concentration of sulphur and sulphur containing compounds will increase.

¹¹ The pH would become 1.2 when only HCl would dissolve in the water condensate without NH_3 absorption.

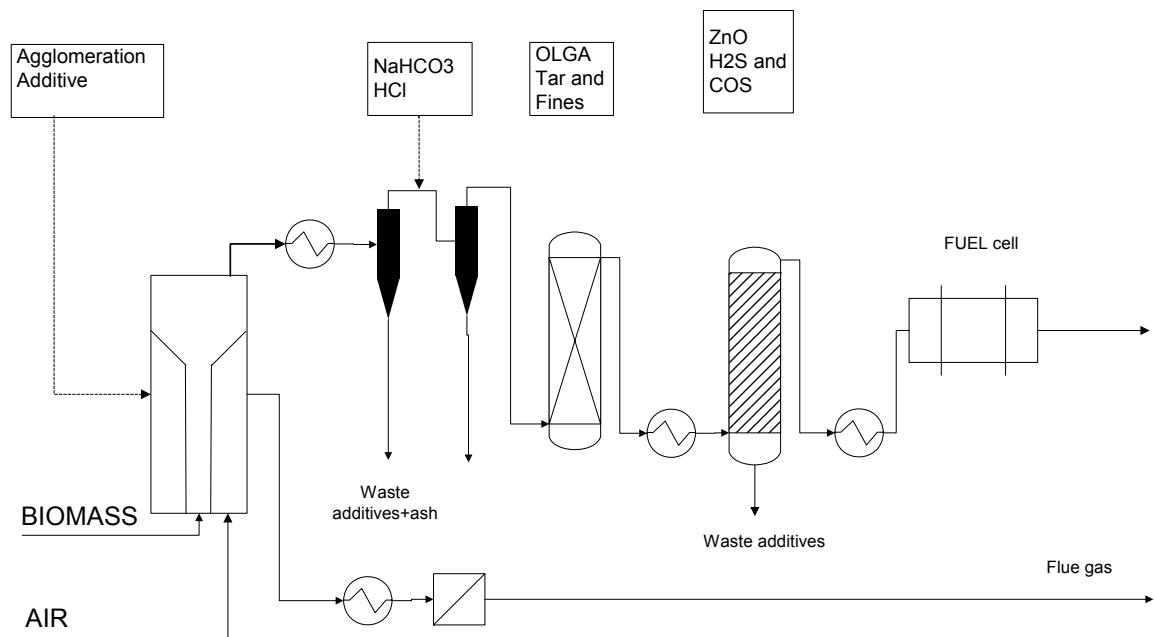


Figure 4.3 Reference process diagram for the application of product gas in a **SOFC fuel cell**, using woody biomass as fuel for the direct air blown fluidized bed gasifier

When woody biomass is used in the indirect gasifier than the gas cleaning as in Figure 4.3 is proposed for fuel cell application. For the gasification of woody biomass the product gas will be cooled. Downstream the cooler the ash is partly removed by the cyclone. Then trace amount of HCl is removed with sodium bicarbonate downstream the cooler. Subsequently, OLGA removes the tars and fines. Downstream OLGA the product gas is heated for the removal of trace amounts of H₂S and COS. Finally the gas will have to be heated to the fuel cell temperature. The removal of NH₃ is not necessary for a SOFC fuel cell, because NH₃ is a fuel for a SOFC and converted into N₂. The ash from the product gas is returned to the combustor. In this way all the ash leaves the system in the flue gas of the gasifier. The flue gas is cooled down and the ash is removed in a bag house filter. The spend sodium bicarbonate and ZnO are discharged as spend sorbent. The sodium bicarbonate can be returned to the supplier for recycling.

The process flow diagram does not change much when woody biomass is replaced with non-woody biomass. The ZnO for H₂S removal and the entrained flow reactor for HCl removal will remain in the process. An extra sulphur removal step is included just downstream the gasifier, to prevent high ZnO sorbent costs, like is proposed for the boiler and gas engine application. The HCl concentration should be reduced with 99.5% and H₂S + COS should be removed for 99.9% to fulfil the fuel cell requirements. The requirements for the fuel cell are given in Paragraph 2.4 and the gas composition of the raw product gas is given in Table 3.11 of Paragraph 3.6.

The indirect gasifier is operated at 850°C. Downstream the gasifier the product gas is cooled down to 770°C. Downstream the cooler the bulk of the sulphur and dust is removed. Then the product gas is further cooled down for the removal of HCl with sodium bicarbonate. Downstream the HCl removal the tars, dioxins, and fines are removed with OLGA. Finally the gas is heated to remove trace amount of H₂S and COS to bring the product gas on specification for the fuel cell. The last heater is installed to bring the product gas to the operation temperature of the fuel cell.

ZnO leaves the system as ZnS and sodium bicarbonate leaves the system as NaCl. The NaCl can be returned to the supplier for recycling. The total amount of ZnO, bulk sorbent, sodium bicarbonate and spend sorbent is given in Table 4.5.

Table 4.5 *Amount of sorbent and spend sorbent necessary for the removal of H₂S, COS and HCl in a 10MW_{th} gasification process for fuel cell application*

	Total sorbent amount	Total amount of spend sorbent
	[kg/h]	[kg/h]
ZnO	1.7	1.9
Bulk sorbent	107.1	110.8
NaHCO ₃	8.1	7.2

The total amount of sorbent and spend sorbent for the fuel cell application is higher than for the boiler and gas engine application. Most important reason is the low sulphur and chlorine limits for the fuel cell, which is lower than the emission limits. The decrease in the amount of ZnO for the fuel cell application is caused by an increase in sulphur removal in the bulk sulphur removal section. The degree of sulphur removal in this section increased because the inlet sulphur concentration increased and the outlet concentration, which is determined by the thermodynamic equilibrium, remained the same.

As a conclusion the technical perspective of the gas cleaning for a fuel cell looks promising. The gas cleaning technologies are simple and theoretically able to reduce the Cl and S concentration sufficiently to fulfil the fuel cell requirements. A guard bed will protect the fuel cell against deactivation with sulphur. Furthermore, the controllability of the chlorine removal system and the advantages of and risks with the sulphur removal section is similar as for the boiler operation.

5. Economic perspectives

As soon as a process is technically feasible the economics will determine whether the process is applied on commercial scale. This project focuses on the feasibility of replacing expensive woody biomass fuels with cheaper non-woody biomass fuels. For the non-woody biomass fuels additional gas cleaning is necessary for the removal of HCl, H₂S, and COS, as discussed in previous chapter. The extra costs for the application of the additional gas cleaning should be lower than the difference in biomass costs. In this chapter a cost estimate will be given for the investment and operational costs of the additional gas cleaning. The additional gas cleaning costs will be expressed in Euro per tonne dry and ash free (daf) biomass so the costs can easily be compared with the biomass price. The sum of the additional gas cleaning costs and the biomass price should be compared with the price of woody biomass, which is approximately 50-100 Euro/tonne of biomass.

5.1 Method

The investment estimate in this chapter is done on conceptual design level and has an accuracy of approximately $\pm 40\%$ and should, therefore, be used as an indicative figure. The total capital investment and operational costs were estimated for the additional gas cleaning, as discussed in Chapter 4 for the boiler, gas engine, and fuel cell application. For the determination of the total capital investment costs a design was made of the most important gas cleaning equipment. Based on the equipment size investment cost (installed) of the equipment was estimated with standard correlations available in the literature. The costs were corrected for inflation. For the determination of the TCI, standard cost factors were used according to a standard breakdown as given in Table 5.1.

Table 5.1 *Breakdown of the total capital investment costs [18]*

Total Capital Investment				
Fixed Capital Investment			Working Capital	Start-up Costs
Direct Costs		Indirect Costs	Working Capital	Start-up Costs
ISBL Costs (onsite)	OSBL Costs (offsite)	Indirect Costs	Working Capital	Start-up Costs
Purchase & Installation of • Process equipment • Piping & appurtenances • Instrumentation & Controls • Electric equipment & materials • Civil & structural • Process Buildings	• Auxiliary buildings • Yard Improvements • Service facilities • Storage • Packaging plant • Land	• Up-front R&D • Up-front license • Engineering • Construction • Contractor's fee • Contingencies	• Inventories • Salaries/wages due • Receivables less payables • Cash	• Modifications • Start-up labour
73-83%			10-20%	6-8%
100%			12-28%	8-10%
70-85%		15-30%		

Furthermore the following economic parameters were used:

- Interest rate = 6%.
- Depreciation time = 15 year.
- Yearly operating time = 8000 hours.

The result of the economic evaluation is expressed in euro/tonne biomass in Paragraph 5.2-5.4 for the boiler, gas engine and fuel cell application respectively. Also the total investment and TCI in kEuro is given.

5.2 Boiler application

The gas cleaning for the removal of HCl, H₂S and COS from product gas consists of three sections:

1. Section 1: Bulk sulphur removal
2. Section 2: HCl removal
3. Section 3: Sulphur polishing

Table 5.2 gives the investment costs for each section separately. The operational costs are given in Table 5.3. The numbers are indicative.

Table 5.2 *Investment (installed) for the application of non-woody biomass in a 10 MW_{th} gasification process for boiler operation*

	Investment (installed equipment)	
	[kEuro]	[Euro/tonne biomass daf]
Bulk sulphur removal	416	2.9
Sulphur polishing	134	0.9
HCl removal	134	0.9
Total	684	4.7

daf = dry and ash free

The total investment costs are to a large extent determined by the costs for the bulk sulphur removal section. The sulphur polishing and HCl removal sections are similar systems and, therefore, the investment costs for these systems are comparable. The low price is determined by the simplicity of equipment in combination with the lower temperature of operation.

The main operational costs for the additional gas cleaning are the sorbent costs and the disposal costs of spend sorbent. The costs for utilities like electricity is negligible. The main operational costs are given in Table 5.3. The operational cost calculations are based on commercial prices, provided by the supplier of the sorbent. The price for spend sorbent is also based on the price for disposal given by the receiver (GP Groot). The disposal costs for the bulk sulphur removal is very dependent on the quality of the spend sorbent. When the quality of the sorbent improves due to the separation of ash and sorbent the disposal costs can decrease significantly (even to zero).

The sorbent costs (purchase and disposal) for sulphur removal are much higher than for chlorine removal. The reason for the high costs are firstly the high concentration of sulphur in the product gas and secondly the high purchase and disposal costs of the sorbent. In order to minimize the sulphur removal costs a relatively cheap sorbent was selected for the bulk sulphur removal. This sorbent is not able to remove sulphur sufficiently and therefore an additional more expensive sorbent was needed to bring the product gas on specification. Remarkable is the similar sorbent costs (purchase and disposal) between the bulk sulphur removal section and the polishing section. The amount of sorbent is for the bulk section significantly higher.

Table 5.3 *Operational costs for the application of non-woody biomass in a gasification process*

	Sorbent	Spend sorbent
	Euro/tonne biomass input daf	Euro/tonne biomass input daf
Bulk sulphur removal	2.5	5.3
Sulphur polishing	4.0	1.3
HCl removal	0.6	0.6
Total	7.1	7.2

daf = dry and ash free

The total additional gas cleaning costs for the boiler application reads as:

Sorbent costs	= 7.1 Euro/tonne
Spend sorbent costs	= 7.2 Euro/tonne
TCI	= 15.6 Euro/tonne
Total	= 29.9 Euro/tonne biomass (daf)

The sorbent costs dominate the price of the additional, Cl and S, gas cleaning. The sorbent costs can possibly be reduced further when an inexpensive sorbent is used in the polishing section. However, most sorbent for the removal of sulphur can not be applied at high temperature or is not able to remove sulphur sufficiently in the presence of water. Therefore, the use of another type of sorbent will need to cool down the product gas, which will lead to the condensation of tar and consequently the need for the installation of a tar removal system, which will increase the TCI.

The disposal costs for ash is an cost item, which was not taken into account in the operational cost calculations. The disposal costs for ash is to a large extent determined by the ash quality, which should be investigated case by case. The ash disposal costs are relevant to take into account in the cost calculations. The disposal costs can range approximately between 0 and 150 Euro/tonne. When the ash can be used for road pavement, than the disposal costs can reach almost 0 euro/tonne ash. The bottom ash is a typical ash stream that can be suitable for road pavement. When the ash can be discharged as raw material for the cement industry than the costs can be 60 euro/tonne ash. Fly ash can be a candidate for the cement industry, depending on the quality of the ashes. When the ash should be dumped than a maximum price of 150 euro/tonne ash should have to be payed. Therefore the ash disposal costs can range from 0 to 23 Euro/tonne biomass¹², depending on the ash quality, which is similar to the total additional gas cleaning costs. Therefore, the profitability for the application of non-woody biomass wil largely depend on the ash quality of the fly and bottom ash and should be investigated at the start of a commercial project.

In general, the economic perspectives for the application of non-woody biomass for boiler application are positive. The total additional gas cleaning costs are approximately 30 euro per tonne biomass (daf) with an ash content of 13wt%, a chlorine content of 0.26wt% and a sulphur content of 0.6wt%. With a biomass price of 50 euro/tonne the application of non-woody biomass can become attractive below a price of 20 euro/tonne biomass depending on the ash disposal costs. Also the chlorine and sulphur content in the biomass is quite important for the total additional gas cleaning costs because an increase in concentration will also increase the use of sorbent and thus increases the operational costs. Special attention should be paid to the dioxin and NOx emissions of the boiler. Measures for the removal of NOx and dioxins in the flue gas of the boiler are not part of the economic evaluation.

¹² The basis for the ash amount is the in Table 2.2 given biomass composition of the representative biomass (ash content = 13wt%).

5.3 Gas engine application

The gas cleaning for the removal of HCl, H₂S and COS from product gas consists of three sections:

1. Section 1: Bulk sulphur removal
2. Section 2: Sulphur polishing
3. Section 3: HCl removal

Table 5.4 gives the investment costs for each section separately. The operational costs are given in Table 5.5. The numbers are indicative.

Table 5.4 *Investment costs (installed) for the application of non-woody biomass in a 10 MW_{th} gasification process for gas engine operation*

	Investment	
	[kEuro]	[Euro/tonne]
Bulk sulphur removal	416	2.9
Sulphur polishing	134	0.9
HCl removal	0	0
Total	550	3.8

The total investment costs are to a large extent determined by the costs for the bulk sulphur removal section. The investment costs of the HCl removal section is set on zero because the HCl is removed in the quench downstream OLGA, which was already present in the reference process.

The main operational costs for the additional gas cleaning are the purchase sorbent costs and the disposal costs of spend sorbent. Additional wastewater treatment costs are not taken into account. These will be dependent on the regulations defined for wastewater by the local authorities. The presence of Cl in water does not automatically lead to an increase in wastewater treatment price. The costs for utilities like electricity is negligible. The main operational costs are given in Table 5.5.

The operational cost calculations are based on commercial prices, provided by the supplier of the sorbent or the receiver of the spend sorbent (GP Groot). The disposal costs for the bulk sulphur removal sorbent is dependent on the quality of the spend sorbent. When the quality of the sorbent improves due to the separation of ash and sorbent the disposal costs can decrease significantly (even to zero).

Table 5.5 *Additional gas cleaning operational costs for the application of non-woody biomass in a 10 MW_{th} gasification process for gas engine operation*

	Sorbent	Spend sorbent
	Euro/tonne biomass input	Euro/tonne biomass input
Bulk sulphur removal	2.5	5.3
Sulphur polishing	4.0	1.3
HCl removal	0	0
Total	6.5	6.6

The total additional gas cleaning costs for the boiler application reads as:

Sorbent costs	= 6.5 Euro/tonne
Spend sorbent costs	= 6.6 Euro/tonne
TCI	= 14.6 Euro/tonne
Total	= 27.7 Euro/tonne biomass (daf)

Also for the gas engine application the sorbent costs dominate the price of the additional gas cleaning. The total additional costs are a bit lower than for the boiler application due to the missing additional costs for the removal of HCl. The sorbent costs can possibly be reduced further by the use of inexpensive sorbent for the sulphur polishing section. In contrast to the boiler application, for the gas engine operation a cheaper sorbent could potentially be used upstream the gas engine, where the water content in and the temperature of the product gas is low.

Like for the boiler application the ash disposal costs were not taken into account in the operational cost calculations. The ash disposal costs can range between 0 and 23 euro/tonne biomass depending on the ash quality of the bottom and fly ash, as explained in previous section. Thus for the application of non-woody biomass with a high ash content, the ash quality and the market price should be investigated at the start of a project.

In general, the economic perspectives for the application of non-woody biomass are positive for a gas engine application. The gas cleaning contain measures for the removal of dioxins and the reduction of NOx. The total additional gas cleaning costs are approximately 28 euro per tonne biomass with an ash content of 13wt%, a chlorine content of 0.26wt% and a sulphur content of 0.56wt%. With a woody biomass price of 50 euro/tonne the application of non-woody biomass can become attractive below a price of 0 to 25 euro/tonne biomass depending on the ash disposal costs. Also the chlorine and sulphur content in the biomass is quite important for the total additional gas cleaning costs, because an increase in concentration will also increase the use of sorbent and thus increases the operational costs.

5.4 Fuel cell application

For the fuel cell application the process flow diagram for the gasification of woody biomass already contains a chlorine and sulphur removal section due to its stringent requirements. The HCl, H₂S and COS is removed in three sections:

- Section 1: Bulk sulphur removal
- Section 2: Sulphur polishing
- Section 3: HCl removal

Table 5.6 gives the additional investment costs (installed) for each section separately when switching from woody to non-woody biomass. The operational costs are given in Table 5.7. The numbers are indicative.

The reference process flow diagram already contains a chlorine and sulphur removal section. Therefore, when switching from woody biomass to non-woody biomass, only the bulk sulphur removal is added to the process. The sulphur polishing and HCl removal section do not change considerably in size and thus the investment costs are for these sections similar and not taken into account for the calculation of the additional costs. The total investment costs of the bulk sulphur removal section is important lower than the bulk removal section of the boiler and gas engine application.

Table 5.6 *The investment and total capital investment (TCI) of the additional gas cleaning by switching from woody to non-woody biomass. The total investment and TCI of each section is given between brackets*

	Investment	
	[kEuro]	[Euro/tonne biomass daf]
Bulk sulphur removal	317	2.2
Sulphur polishing	139	1.0
HCl removal	81	0.6
Total	352	3.8

The main operational costs for the additional gas cleaning are the sorbent purchase costs and the disposal costs of the spent sorbent. The operational cost calculations are based on commercial prices, provided by the supplier of the sorbent or by the receiver (GP Groot) of the spent sorbent. The disposal costs for the bulk sulphur removal is dependent on the quality of the spent sorbent. When the quality of the sorbent improves due to the separation of ash and sorbent the disposal costs can decrease significantly (even to zero). The costs for utilities like electricity is negligible. The main operational costs are given in Table 5.3.

Table 5.7 *Operational costs of the additional gas cleaning for the application of non-woody and woody biomass in a 10 MW_{th} gasification process for fuel cell operation. The number between brackets gives the operational costs for each section*

	Sorbent		Spent sorbent	
	woody biomass	Euro/tonne biomass input	Woody biomass	Euro/tonne biomass input
Bulk sulphur removal	0	2.6	0	5.5
Sulphur polishing	0.9	2.6	0.3	0.9
HCl removal	0.5	0.6	0.5	0.6
Total	1.4	5.8	0.8	7.0

The total additional gas cleaning costs for the boiler application reads as:

Sorbent costs	= 4.4Euro/tonne
Spent sorbent costs	= 6.2 Euro/tonne
<u>TCI</u>	<u>= 9.7 Euro/tonne</u>
Total	= 20.3 Euro/tonne biomass

The TCI and sorbent costs are low due to the presence of chlorine and sulphur removal equipment and use of sorbent in the reference gas cleaning with woody biomass as feedstock for the gasifier. The TCI increases to 12.5 Euro/tonne biomass when the TCI of all three sections is taken into account. The total sorbent costs (12.8) are given in Table 5.7.

Like for the boiler and gas engine application the ash disposal costs were not taken into account in the operational cost calculations. The ash disposal costs can range between 0 and 17 euro/tonne biomass depending on the ash quality of the bottom and fly ash, as explained in the boiler section. The maximum disposal costs are a bit lower than for the gas engine or boiler application, because an indirect gasifier produces less amount of ash due to the reduction in the carbon content of the fly ash. Nevertheless for the application of non-woody biomass with a high ash content, the ash quality and the market price should be investigated at the start of a project because the total ash disposal costs can influence the profitability of the project significantly.

In general, the economic perspectives for the application of non-woody biomass are positive for a fuel cell application. The requirements can be reached for a reasonable price. The total additional gas cleaning costs are approximately 20 euro per tonne biomass with an ash content

of 13wt%, a chlorine content of 0.26wt% and a sulphur content of 0.56wt%. With a woody biomass price of 50 euro/tonne the application of non-woody biomass can become attractive below a price of 13 to 30 euro/tonne biomass depending on the ash disposal costs. Also the chlorine and sulphur content in the biomass is quite important for the total additional gas cleaning costs, because an increase in concentration will also increase the use of sorbent and thus increases the operational costs.

6. Conclusion

The objective of this project was to investigate the economic and technical perspectives for the replacement of woody biomass with non-woody biomass in a biomass gasification process for the operation of a boiler, gas engine and fuel cell. Non-woody biomass is in this report waste from the industry, agriculture and animals. A representative composition for non-woody biomass was given as 13 wt% ash, 0.3 wt% chlorine and 0.6 wt% of sulphur.

Design basis

For the boiler and gas engine application the chlorine and sulphur in the product should be removed to fulfil the emission limits. For a fuel cell application the sulphur and chlorine removal is determined by the fuel cell requirements. For the emission limits some of the non-woody biomass fuels should meet the emission limits for white list fuels and other should meet the yellow list limits. For the gas cleaning design the yellow list emission limits were used as directive, because these are most stringent.

Experimental results

An experimental program was defined to investigate the release of chlorine and sulphur compounds in a fluidized bed gasifier. Grass, RDF and sewage sludge were the selected fuels for the experiments. Grass and RDF are fuels with a high chlorine content and sewage sludge has a high sulphur content. The experiments were performed at a gasifier temperature of 750°C and 850°C respectively. The experiments with grass were stopped at an early stage of the experiments due to bed agglomeration. The most important results are:

- The chlorine in the fuels was for a substantial part, 50% to 90%, bounded to the ash and removed with the solids in the gas. The remaining chlorine is mainly released as HCl. The dioxin concentration was relatively high (2-75 ng TEQ) and the concentration was clearly related to the chlorine content of the fuel. The dioxin concentration strongly reduced when the gasifier temperature was increased from 750°C to 850°C.
- The sulphur in the biomass was mainly, for 70% to 90%, converted into H₂S and COS. At a low gasifier temperature of 750°C also other organic sulphur compounds, such as mercaptane and CS₂, are present in the gas at low concentration. Only a small amount of sulphur was bounded to the ash.
- The sulphur and sulphur in the ash is dependent of the temperature of collection. At high temperature (>750°C) the chlorine and sulphur concentration in the ash is substantially lower than at low temperature (500°C).

For the determination of the gas composition a high gasifier temperature was selected, because at a high temperature the composition of chlorine and sulphur compounds becomes simpler and organic sulphur and chlorine are strongly reduced at high temperature.

Technical perspectives

Three different gas cleaning designs were made for the three product gas applications boiler, gas engine and fuel cell. The designs were made for the application of woody as well as non-woody biomass in the gasifier at 850°C. The boiler and gas engine have a direct gasifier installed upstream, and the fuel cell an indirect gasifier. The gas cleaning should bring the product gas on specification for the application as defined in the design basis. The differences in the process flow diagram between woody and non woody biomass are the presence of HCl and H₂S and COS removal technologies in the gas cleaning for non-woody biomass.

The sulphur in the gas cleaning is removed in a two-staged process with two different solid sorbents. In the first stage the bulk of the sulphur is removed. Since the cheap sorbent can not

remove the sulphur sufficiently, a second stage with another sorbent (ZnO) is used to remove the last amount of sulphur to fulfil the emission limits or the fuel cell requirements.. The spend sorbent of both stages must be disposed and cannot be regenerated.

HCl was removed with a sorbent for the fuel cell and boiler application and in an aqueous scrubber for the gas engine application. The sorbent can be recycled to the supplier. The aqueous quench was installed downstream the tar removal unit OLGA. Dioxins are removed together with tars in OLGA for the fuel cell and gas engine application. For the boiler additional measures should be taken for the dioxin removal in the flue gas of the boiler, when necessary. The gas cleaning was theoretically able to fulfil the emission limits and fuel cell requirements.

The technical perspective of the gas cleaning for the boiler, gas engine and fuel cell application is positive. The sulphur and chlorine concentration in the product gas downstream the gas cleaning are expected to be controlled easily. The gas cleaning technologies are simple and theoretically able to reduce the Cl and S concentration sufficiently to fulfil the emission limits or the fuel cell requirements. Future development of the three systems should focus on the determination of the sorbent use and the reliability of system for the bulk sulphur removal.

Economic perspectives

The economic perspectives are positive for the proposed gas cleaning systems. The total additional gas cleaning costs for the removal of chlorine and sulphur compounds are approximately **30** euro/tonne biomass (dry and ash free) for the boiler application, **28** euro/tonne biomass for the gas engine application and **20** euro/tonne biomass for the fuel cell application. The total capital investment costs and the sorbent costs (purchase and disposal) have a similar contribution to the total additional gas cleaning cost. With a woody biomass price of 50 euro/tonne biomass the application of non-woody biomass in a gasifier becomes attractive when the price of the non-woody biomass becomes below 15 to 20 euro/tonne on the condition that the ash disposal costs is lower than 60 euro/tonne ash. The disposal costs for ash is to a large extent determined by the ash quality, which should be investigated case by case. The ash disposal costs are relevant to take into account in the cost calculations and can determine the profitability of a project. The disposal costs can range between 0 (application in road pavement) and 150 Euro/tonne ash (landfill costs).

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Appendix A Monstername

Guideline: is monstername via standaard teerprotocol

HCl-stof: is monstername via heet (350 C) vlakfilter en daarna door wasflessen (2) met demiwater met 2% H₂O₂, waarna Cl analyse via Ionchromatografie (ic) en de H₂O₂ oxideert de SO₂ en SO₃ door naar SO₄, waarna Sox kan worden geanalyseerd als SO₄ met ionchromatografie (ic).

NH₃: is monstername via heet (350 C) vlakfilter en daarna door wasflessen (2) met 0.05 M HNO₃, waarna NH₄ analyse via AMFIA

HCN: is monstername via heet (350 C) vlakfilter en daarna door wasflessen (2) met 2M NaOH, waarna CN analyse via FIA

HCL-alkali: is monstername via hete probe met frit en daarna door wasflessen (2) met demiwater met 2% H₂O₂ in 0.05 M HNO₃
de probe wordt uitgespoeld met 0.05 M HNO₃ en spoelsel wordt bij wasflesoplossing gevoegd en geanalyseerd op Cl, Na, K, en Ca.

In guideline monsters (IPA) is ook Cl en S gehalte bepaald. Chloor met de EOX analyser (coulometrie, na verbranding). S met ICP na ontsluiting.

Appendix B Classification of tar

In many previous studies, the focus of tar production has mainly been on a total amount of tars, reported in g/m_n^3 or mg/m_n^3 . However, earlier work at ECN has revealed already that often (changes in) the tar composition is the dominant factor, when looking at the impact on downstream equipment. Therefore, in the framework of the project "Primary measures for tar reduction in fluidised-bed biomass gasifiers" funded by the Dutch Agency for Research in Sustainable Energy (SDE), a tar classification system was defined based on the physical tar properties: water solubility of tar and tar condensation. Table B.1 gives a description for the five tar classes in the classification system with the focus on the tar properties. Table B.2 presents the tar compounds that belong to a tar class, and a sampling method for the determination of the different tar classes.

Table B.1 *Description of the tar classes with a focus on the tar properties*

	Description
Class 1	GC undetectable tars. This class includes the heaviest tars that condense at high temperature even at very low concentrations.
Class 2	Heterocyclic components (like phenol, pyridine, cresol). These are components that generally exhibit high water solubility, due to their polarity.
Class 3	Aromatic components. Light hydrocarbons that are not important in condensation and water solubility issues.
Class 4	Light polyaromatic hydrocarbons (2-3 rings PAH's). These components condense at relatively high concentrations and intermediate temperatures.
Class 5	Heavy polyaromatic hydrocarbons (4-5 rings PAH's). These components condense at relatively high temperature at low concentrations.

Table B.2 *Example of tar compounds in each tar class in the classification system and possible sampling methods*

	name	sample methode	tar components
Class 1	GC-undetectable	Guideline	Determination by subtracting GC- detectable tar fraction from total gravimetric tar concentration (not in this project).
Class 2	heterocyclic aromatics	Guideline or SPA	pyridine, phenol, cresol, quinoline
Class 3	aromatics (1 ring)	Guideline or SPA	xylene, styrene, toluene
Class 4	light PAH* (2, 3 ring)	Guideline or SPA	naphtalene; methyl-naphtalene; biphenyl; ethenylnaphtalene; acenaphtylene; acenaphtene; fluorene; phenanthrene; anthracene
Class 5	heavy PAH* (>3-ring)	Guideline or SPA	fluoranthene; pyrene; benzo-anthracene; chrysene; benzo-fluoranthene; benzo-pyrene; perylene; Indeno-pyrene; Dibenzo-anthracene; Benzo-perylene

* PAH = poly-aromatic hydrocarbons

Appendix C Indirect gasifier

Indirect (allothermal) gasification is characterized by the separation of the processes of heat production and heat consumption. It therefore generally consists of two reactors, connected by an energy flow. One important category of allothermal gasification is formed by the processes where biomass is gasified/pyrolysed and the remaining solid residue (char) is combusted to produce the heat for the first process. Examples of this kind are the FERCO/SilvaGas-process developed by Battelle and the FICFB-process developed by the University of Vienna. An overview is given in reference [19].

These types of reactor theoretically are operated at an equilibrium based on the temperature dependence of the char yield in the gasifier: char yield increases with temperature. Since this char is combusted to produce the heat, this leads to an equilibrium where char yield matches the energy demand of the gasification.

Allothermal gasifiers generally produce two gases: a medium calorific gas with little or no nitrogen and a flue gas. The production of a N_2 -free gas without the need of air-separation is one of the advantages over direct gasification processes like a CFB. Another important advantage is the complete conversion. The ashes that remain, contain little or no residual carbon since this is the product of a combustion process. Indirect gasifiers also have the option to deal with residues from e.g. gas cleaning such as tars. These can be added to the combustor and contribute to the overall efficiency rather than impose a waste problem.

Milena is the name of a technology developed by ECN to fulfil the demands of a biomass-to-SNG process with a high efficiency. Milena is an indirect gasifier operating similarly to the FERCO/Silvagas-concept: biomass is heated and gasified in a circulating flow of hot sand and the less reactive remaining solid char is directed to the combustor where the circulating sand is heated. However, Milena is simpler, more compact, and better suited for operation at elevated pressure. The gasification takes place in a riser, whereas a bubbling fluidised bed serves as combustor. The two reactors are integrated as schematically shown Figure C.1

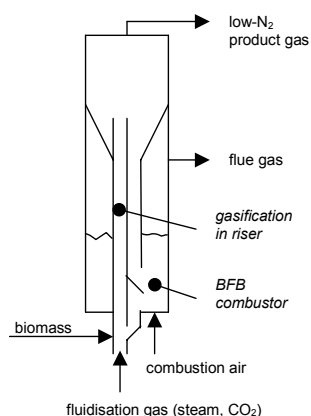


Figure C.1 *Schematic drawing of the Milena indirect gasification technology.*

Table C.1 shows a typically calculated composition of the raw gas directly downstream the gasifier. The resulting cold gas efficiency after gas cleaning is approximately 80%.

Table C.1 *Calculated product gas and flue gas composition in large-scale (100 MW_{th}) Milena gasification plant operated with wood (25% moisture)*

		product gas	flue gas
CO	vol% dry	29	
H ₂	vol% dry	31	
CO ₂	vol% dry	20	18
N ₂ + Ar	vol% dry	0	80
CH ₄	vol% dry	14	
C ₂₋₅	vol% dry	5	
C ₆₋₇	vol% dry	1	
tar (C ₈₊)	g/m _n ³ dry	45	
H ₂ O	vol% wet	35	4
O ₂	vol% dry		2