



Norwegian University of  
Science and Technology

# Measurement of temperature conditions in grate zone of a 1 MW wood-pellets boiler fired with high ash content wood-pellets

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Master of Science in Energy and Environment

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# Problem Description

Wood pellets with an ash content above 0.5 weight% usually cause problems because of low melting temperatures of the ash depending on the ash composition. Melted ash on the grate causes problems with grate self-cleaning, air distribution, temperature levels and should be avoided. Since the raw material content of the ash is stochastic and not removable, control regimes should be developed to avoid maintenance problems. Two potential solutions without consideration of new boiler construction, are to

- i) control the temperature level in grate zone of the boiler or
- ii) to improve the ash melting properties by the use of fuel additives

The object of this work is to achieve measurement data of these temperature levels from an existing boiler in ordinary running mode. The boiler is located in Sykkylven.

This work is a part of a larger project work within this topic. The student shall cooperate with the ongoing project.

The following questions should be considered in the Master thesis work:

1. Make a literature survey of ash melting problems using wood pellet.
2. Make a proposal for temperature measurements and location on the grate of the boiler.
3. Make a plan and an experimental matrix including a selection of equipment to use.
4. Perform, analyze and report the measurements as a part of the main project.

Assignment given: 15. January 2009

Supervisor: Johan Einar Hustad, EPT



# Preface

This thesis about additives in problematic biomass fuels concludes my master degree at NTNU.

As normally with practical experiments, something goes wrong. This was neither an exception for the work during this thesis and the focus of this project is therefore slightly changed compared to the original object given in the thesis description.

First of all I want to thank my supervisor and friend PhD -student Liang Wang for help and good answers for numerous questions. I hope our collaboration has been fruitful for the both of us, and that my questions have helped you to discover some problems you didn't knew existed.

I would also like to thank Geir Skjevraak for good help, and entertainment during the work in Sykkylven.

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# Abstract

The combustion of biomass could in some cases lead to ash problems induced by high temperatures such as ash sintering, agglomeration and melting. The degrees of these problems depend on the fuel feedstock and are highly dependent on the amount of potassium, sodium and chlorine in the biomass. Straw, grass, bark, branches and wood residues are typical examples of biomass fuels that are connected to the mentioned ash problems.

Addition of additives in the problematic fuels is a possible measure in order to reduce the ash problems. This project studies the effect of some additives in a problematic wood pellet fuel and wheat straw. The wood pellet consist of residues from the furniture industry in the Møre area in Norway, and is causing ash problems in several boilers using this fuel. The additives, clay, sewage sludge, marble sludge and paper sludge, are added in 3 to 10 percent addition in the problematic fuels. The melting temperatures of the resulting ash, as well as the sintering tendency of the different fuel and additive mixtures, are analyzed.

Melting experiments showed that the melting temperature of wood and straw ash was drastically increased by adding sewage and marble sludge. Clay was more effective for wheat straw than wood pellet. Paper sludge increased the melting temperature to some extent for straw ash, but not for wood pellet.

The sintering test revealed an increased sintering for wood pellet with sewage sludge, and a much higher slagging tendency for clay. Marble sludge effectively decreased the sintering of wood pellet ash, even at 1200 °C. Paper sludge did neither reduce the sintering. All additives showed a positive effect on the wheat straw ash sintering, with marble sludge as the indisputable best additive.

The wood pellet, and pellet together with 4 and 8 percent addition of sewage sludge, is combusted in a 1.2 MW boiler to investigate if the sewage are able to reduce the sintering and agglomeration of the ash. The combustion rounds showed that addition of sewage sludge drastically increased the amount of sintered and agglomerated ash. The form of the ash changed from hard slag to more porous ash, but the formed ash was still too hard to not cause problems with the ash removal system.





# Sammendrag

Forbrenning av biomasse kan i noen tilfeller føre til problemer med at aska smelter, sintrer og klumper seg sammen. Dette er forårsaket av høye temperaturer og er avhengig av hvilket brensel som blir benyttet. Brensel som inneholder store mengder med natrium, kalium og klor er ofte forbundet med lave askesmeltetemperaturer og eksempler på slikt brensel er gress, halm, bark, grener og resttrevirke.

Tilsetning av additiver i brenselet er en av flere løsninger for å øke askesmeltetemperaturen og redusere askesintreproblemene. Denne oppgava vil studere effekten av noen additiver i et problematisk trebrensel og halm fra hvete. Trebrenselet er pellets laget av resttrevirke fra møbelindustrien i Møre-området på vestlandet, og forårsaker store askesmelteproblemer i flere forbrenningskjeler som benytter dette brenselet. Additivene som blir testet er leire, kloakkslam, marmorslam og papirslam, og er tilsatt i mengder fra 3 til 10 prosent i trepelleten og halmen. Den resulterende smeltetemperaturen til aska og sintretendensen for ulike brensel og tilsetninger med additiver er analysert.

Smeltetestene viste at askesmeltetemperaturen til trepellet og halm økte betydelig ved tilsetning av marmor- og kloakkslam. Leire var mer effektivt for halm enn trepellet. Papirslam økte askesmeltetemperaturen noe for halm, men hadde liten eller ingen effekt på trepellet.

Askesintretesten viste en økende sintretendens for aska til trepellet blandet med kloakkslam, og en mye høyere tendens for leire. Marmorslam viste seg å være veldig effektiv til å redusere, og nesten eliminere, sintretendensen til trepellet selv ved 1200 °C. Papirslam reduserte ikke sintretendensen. Alle additivene maktet i stor grad å redusere sintretendensen til hvete halm, med marmorslam som det klart beste alternativet.

Trepelleten og pellet med 4 og 8 prosent innblanding av kloakkslam er forbrent i en riskjel på 1.2 MW for å undersøke om denne innblandinga kan redusere sintretendensen til aska som har vært et stort problem for denne kjelen. Forbrenningsrundene viste at innblandinga av kloakkslam økte mengden sintra aske i betydelig grad. Den sintra aska etter forbrenning med kloakk forandret riktignok form og ble mer porøs, men den resulterende aska var allikevel så hard at den vil forårsake store problemer med askefjerningssystemet.



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# Nomenclature

## Chemical substances and compounds

Ca - Calcium  
Cd - Cadmium  
Cl - Chlorine  
Cu - Copper  
Fe - Iron  
HCl - Hydrochloric acid  
K - Potassium  
KCl - Potassium chloride  
Mg - Magnesium  
Na - Sodium  
NaCl - Sodium chloride  
NO<sub>x</sub> - Nitrous oxides  
P - Phosphorous  
S - Sulphur  
Zn - Zink

## Abbreviations

ASTM - American Society for Testing and Materials

HHV - Higher heating value  
LHV - Lower heating value  
EHV - Effective heating value

w.b. - Wet basis  
d.b. - Dry basis  
wt. % - Weight percentage  
mp - Melting point  
AC - ash content  
FC - fixed carbon

XRD - X-ray powder diffraction  
XRF - X-ray fluorescence

DT - Deformation temperature  
ST - softening temperature  
HT - Hemisphere temperature  
FT - Flow temperature

BFB - Bubbling fluidized bed  
FBC - Fluidized bed combustion  
CFB - circulating fluidized bed

# 1 Introduction

Due to its low contribution to global warming, combustion of biomass is a promising method for generating heat and power. Pellet made from different biomass fuels has advantages because of the possibility to combust in an automatic process, to make pellet from several different feedstocks and to increase the energy density of these. An increasing demand for wood pellet are pushing the production towards more problematic feedstocks, as the availability for clean sawdust and other stemwood raw materials are limited. Examples of such new and problematic raw materials are logging residues, some bark, contaminated waste wood and different straw fuels [1]. These raw materials contain high ash content and different substances that will lead to a low ash melting temperature, formation of sticky ash, aerosol emissions and corrosion in boiler tubes.

A low ash melting temperature and the formation of sticky ash is problematic because it will cause sintering and agglomeration of ash that results in ash lumps bigger than a fist (see Appendix L). Melted ash might also fasten to the grate, which disturbs the normal air distribution and leads to incomplete combustion, higher emissions and unburned fuel. With long term combustion processes, the automatic ash removal system is not able to remove the melted and agglomerated ash in the boiler and the boiler has to be shut down and cleaned manually.

When the feedstock is rather virgin the ash melting temperature is high and usually above 1300 °C. But waste wood from the furniture and floor industry is often contaminated by residues from glue, sanding paper and concrete. Experience shows that this lowers the ash melting temperature, and cause problems when using the pellet on regular boilers. However, because the feedstock availability is good and the cost is low, it is interesting to utilize these residues.

Some of the different methods of solving ash related problems are: controlling and lower the temperature on the grate or in the combustion zone, change the composition of the fuel, leaching the fuel or by the use of fuel additives.

A boiler located at Sykkylven in Sunnmøre is combusting pellet from the furniture industry in the Møre area on the western coast of Norway. The plant is struggling with ash problems caused by low ash melting temperatures, which are responsible for frequent shutdowns and the need for manual cleaning of sintered ash blocks and the primary air distribution holes. This thesis will try to identify some possible solutions for the ash sintering problem, and performing the solutions at the plant.

The first part of the thesis is literature review and theory about biomass, ash sintering and additives. The second part is to screen possible additives, make ash samples and melt the samples in the laboratory to register any improvements in the ash melting temperature. The third

part is to use the most promising additives in a large scale at the boiler in Sykkylven and try to eliminate the ash sintering and agglomeration with additives.

Because of some unforeseen episodes during the work in Sykkylven, the focus of this thesis is somewhat altered from the original object; measurement of the temperature conditions in the Sykkylven boiler, to screening and analyzing of possible additives, in agreement with supervisors.

As the work in Sykkylven was reduced, sintering tests of the additives are performed in addition to the melting experiments.

The wood pellet investigated in this thesis is a very special fuel which is not so relevant for other places than Sunnmøre. Wheat straw from Denmark is therefore also included in this study to broaden the evaluation of the investigated additives, as this is a problematic but interesting fuel to utilize worldwide. The root of the problems regarding ash sintering and melting is explained in the ash chemistry, but will be only briefly discussed because of the scope of the thesis.

This master thesis is performed in collaboration with the Ph.D. thesis “Effect of additives in reducing fouling and corrosion in combustion and gasification applications” written by Liang Wang, and “Improvements of utilizations of wood-pellets through small- and medium scale combustion units” by Geir Skjevraak at the Department of Energy and Process Technology, NTNU.

## 2 Biomass

Biomass is a term for all organic material that stems from trees, plants and crops. Organic waste and agricultural and forest residues are considered as biomass. Biomass is a raw material that can be used for the production of e.g. heat, electricity and liquid fuels. The total use of biomass for energy purposes today is about 45 ( $\pm$  10) EJ, which is almost as much as the energy from nuclear and hydropower combined. Most of this use is connected to cooking and small scale heating purposes in developing countries. The total potential for energy from biomass is estimated to between 200 and 400 EJ annually [2].

Biomass can be converted into energy or as energy carriers by thermochemical or biochemical methods. The thermochemical methods include gasification, pyrolysis or combustion, where combustion is by far the most common. Gasification and pyrolysis involves heating of the biomass with limited or no oxygen, creating an energy rich gas that can be utilized for different purposes. Although high costs on the technology has limited the commercial use of gasification and pyrolysis. Biochemical conversion methods lead to either alcohol based liquid or methane gas.

The total biomass use for energy purposes in the Norwegian residential sector is about 6 TWh. The use of wood pellet is limited in Norway, and corresponds to about 0.3 TWh a year in the residential sector and 0.15 TWh in the industry [3].

### 2.1 Biomass combustion technologies

The technologies most widely used for medium and big scale combustion of biomass, are grate combustion and fluidized bed combustion. A third technology, pulverized fuel combustion, has the advantage of very good combustion efficiencies but is usually only used for combustion of coal, possibly co-combustion with biomass, as it is energy intensive to cut or crush woody biomass into small particles. Principal sketches of the different combustion techniques are shown in Figure 2-1.

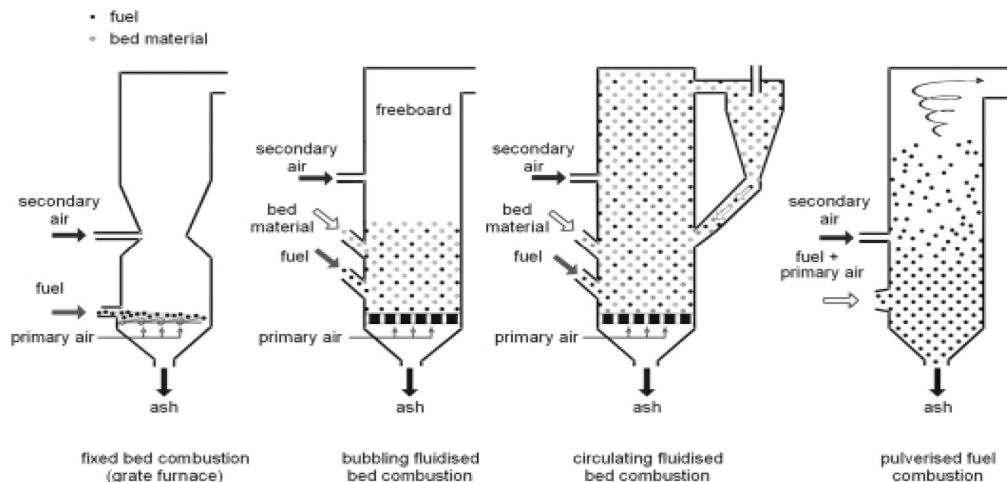


Figure 2-1 Principal combustion technologies for biomass [4].

## 2.1.1 Grate combustion

Combustion using a grid is the easiest and most commonly used technology for small scale heat utilization of biomass. Traveling, fixed, vibrating, rotating and moving grates are all examples of different grate technologies that are being used. All of these technologies have different advantages and disadvantages depending on the fuel properties such as moisture content, particle size and ash content, as well as ash properties.

A well-designed grate has the aim of guaranteeing a homogenous distribution of the fuel and good mixing between the fuel on the grate and the air supply to ensure complete combustion. Inhomogenous air supply might cause slagging, higher aerosol emissions and may increase the excess oxygen amount needed for complete combustion. This excess oxygen supply will cause unnecessary cooling of the combustion chamber and represent a heat loss. Furthermore it is important with a smooth and homogenous transport of the fuel over the grate, and infrared sensors along the grate might be helpful to determine the height, and with that the burnout of the fuel before it is transported out of the combustion chamber [5].

The primary air supply should be divided in subsections and controlled by frequency regulated air fans in order to adjust the air supply needed in the different zones of the furnace. This enables the furnace to run with good conditions even in part load operation. In order to achieve good temperature control in the furnace, water cooled grate and walls and recirculation of the flue gas are possible. Water cooling has the advantage of reducing ash slagging on the grate and increase the lifetime of the grate and insulation bricks in the boiler. Flue gas recirculation is a way to lower the reactivity of air to a lower O<sub>2</sub> content when the static construction elements like grate fans does not allow to regulate. However, it has the disadvantage of increasing the flue gas volume from the combustion [4].

### 2.1.1.1 Traveling grates

There are many ways to design a traveling grate, but they usually consist of several grate bars forming a band that is moving through the combustion chamber. Fuel is supplied at the beginning of the grate and is transported while combusting and the ash are released at the other

end. The speed is constantly adjusted in order to avoid incomplete burnout of the fuel. The advantages of this technology are low dust emissions and good distribution of the fuel. However as the fuel is not stirred in the combustion phase, a longer burning time and a higher primary air supply is needed for complete combustion.

#### *2.1.1.2 Moving grates*

Moving grates is usually inclined, consisting of different grate bars which are moving back and forth such a way that the fuel and ash is transported along the grate. Usually, the whole grate is subdivided into different sections, which can be moved with different speed according to the different stages in the combustion process. The grate bars are made of heat-resistant steel alloys and are often equipped with small channels for primary air supply. This technology often assures a good burnout of the char as the fuel is stirred during the grate transport.

#### *2.1.1.3 Vibrating grates*

This type of furnace consists of an inclined grate connected to vibrators shaking the grate, making the fuel bed move downwards on the grate. With the grate vibration, the tendency of ash agglomeration and sintering is lower, making this type of furnace popular on fuels connected to slagging and sintering problems such as straw and waste wood. Disadvantages connected to the vibrating grates are durability of the higher fly-ash emissions and larger amount of unburned char in the ash as the transportation speed is more difficult to control [6].

#### *2.1.1.4 Fixed grates*

Fixed grates utilize the gravity or scrapers to transport the fuel along the grate. An inclined grate is capable of moving the fuel downwards on the grate because of gravity, but is difficult to control and is rarely used. A fixed grate system utilizes scrapers to push the fuel along the grate, this makes it easier to control the burnout of the char, but, depending on the grate design, the formation of hot-spots on the grate might occur.

### **2.1.2 Fluidized bed combustion**

A fluidized bed combustor (FBC) consist of a cylindrical vessel bottomed by a perforated plate and filled with a suspension of hot, inert and granular material, often sand, silica or dolomite, constituting the bed material. The fuel is fed into the bed material while primary air is blown through special nozzles in the bottom which fluidizes the bed so that it becomes a boiling mass of particles and bubbles. The bed material constitutes 90-98 percent of the resulting mixture of fuel and inert material. Intense heat transfer and good mixing provides good conditions for complete combustion with low excess air amount [4].

A FBC boiler is flexible in terms of fuel mixtures but is limited when it comes to fuel particle and impurities contained in the fuel. Fuel pretreatment, with cutting and removal of metals is therefore crucial. Burning of biomass with high alkali content is often connected with problems such as sintering and agglomeration because of the low melting temperature on these fuels, although this problem can be reduced by lowering the temperature in the bed material.

Two different types of fluidized bed combustors exist, bubbling (BFB) and circulating (CFB) fluidized bed combustion. The CFB furnace is operated with larger velocity on the primary air and the bed material consist of smaller particles than in a BFB furnace, making the bed material flow in a cycle, as shown in Figure 2-1. CFB combustion has better heat transfer properties resulting in better combustion and higher efficiency, but the boiler is more expensive than the BFB boiler. A BFB boiler is also more flexible regarding fuel particle size and moisture content.

Fluidized bed combustion is relevant for boiler capacities above 20 MW, while CFB combustors are usually larger than 30 MW because of the higher costs.

## 2.2 Biomass combustion stages

Combustion of biomass could be divided into three stages. When the fuel is heated from room temperature up to 150 °C, there is a small loss of weight due to moisture vaporization. Between 200 and 400 °C there is a rapid decrease in weight due to vaporization of the volatile components (devolatilization) [7]. The released volatile components will oxidize and burn when the components reacts with air above the grate. At this stage, gasification and/or pyrolyzation of the fuel will take place depending on the air supply. A separation of this process could be utilized to improve the combustion properties and/or reduce NO<sub>x</sub> emissions [8]. After devolatilization, oxidation of the char completes the combustion process. As Figure 2-2 shows, this is a relatively slow process, and sufficient residence time of the fuel in the combustion chamber is important.

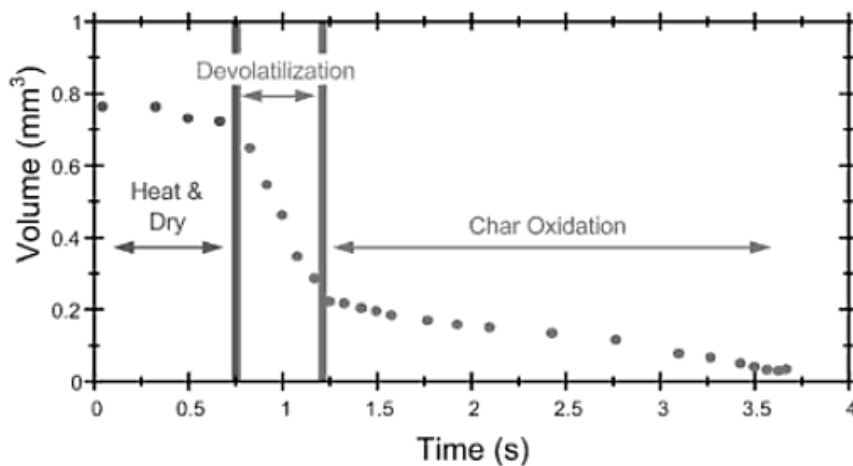


Figure 2-2 The volume decrease during combustion of small biomass particles in different combustion stages [4].

The fractional heat contribution from devolatilization when combusting biomass is approximately 70 percent, compared with 30 - 40 percent for coal because of lower content of volatile matter (biomass as a fuel for co-combustion).



## 2.3 Biomass components

The main components of biomass are cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars, starches, water and ash. The concentration of each compound depends on specie, stage of growth and growing conditions [7]. The hemicelluloses and cellulose consist of various sugars and builds the fibre walls in the wood. Lignin is a complex non-sugar polymer that gives strength to the wood fiber. Biomass rich in sugars are attractive feedstock for fermentation and production of liquid fuels. Lignin is not considered fermentable today and is often thermochemically converted. Combustion is applicable for the whole biomass as long as the moisture content is below 60 percent.

The three biggest, organic components in biomass are oxygen, carbon and hydrogen. Biomass is highly oxygenated compared to fossil fuels and the oxygen content in biomass is typically between 35 and 45 wt. percent (d.b.) [4]. The principal constituent of biomass is carbon, making up from 45 to 55 percent of the weight on dry basis. The hydrogen content is typically 5 to 6 percent. Higher carbon to oxygen ratio increases the heating value.

Volatile matter in biomass refers to the components in the fuel, except for moisture, which are liberated at high temperature in the absence of air. This is usually a mixture of short and long chain hydrocarbons, aromatic hydrocarbons and some sulphur. The volatile matter is thus not a component itself, but consists of some of the biomass components.

Table 2-1 shows some guiding values for the content of nitrogen sulphur and chlorine in biomass fuels.

	Nitrogen	Sulphur	Chlorine
(wt % d.b)			
Birch	0.1 - 0.5	0.03 - 0.1	-
Spruce	0.09 - 1.7	<0.01 - 0.1	<0.01
Bark (spruce)	0.1 - 0.5	0.01 - 0.2	0.01 - 0.37
Straw (wheat)	0.3 - 0.5	0.05 - 0.11	0.01 - 0.7
Grass	0.4 - 3.6	0.08 - 0.7	0.26 - 2.0
Coal	0.8 - 1.5	0.75 - 3.0	0.16 - 0.3

Table 2-1 Typical N, S and Cl concentrations (wt. % d.b.) in some important biomass fuels [4] & and coal [7, 9].

The content of these substances have different implications when combusting biomass. Nitrogen and sulphur leads to the formation of  $\text{NO}_x$  and  $\text{SO}_x$ , who again contributes to acid rain, smog and particles. Although sulphur is more important in the corrosion process, described in section 3.4. Chlorine is a very problematic component that plays an important role in corrosion and ash melting processes, which are thoroughly described in sections 3.4 and 3.3.

For these reasons, grass and straw are problematic combustion fuels, and special considerations needs to be implicated when combusting these fuels. This involves flue gas cleaning, and different measurements in order to reduce corrosion and slagging. Some possible measures will be described later.

In addition to the components mentioned, ash is represented in a varying degree. The ash consists mainly of Si, Al, K, Ca and Mg, depending on the feedstock. Ash content and combustion related implications will be further described in chapter 3.

## 2.4 Biomass properties

When considering utilizing biomass for energy purposes, the moisture and ash content, heating value, density and size of the fuel are of great importance.

The heating value, or calorific value, is the standard measure for the energy content of the fuel. Three different heating values could be used when referring to biomass combustion, that is; higher heating value (HHV), lower heating value (LHV) and effective heating value (EHV). The higher heating value is defined as the heat released during combustion per mass unit fuel under the constraints that the water formed during combustion is in *liquid* phase and that the water and the flue gas have the same temperatures as the temperature of the fuel prior to combustion (ÖNORM C 1138). While the effective heating value is defined as the heat released during combustion under the constraints that the water formed during combustion is in a *gaseous* phase. Lower heating value is defined in the same way as EHV, but assumes a moisture free fuel.

In other words, the HHV includes the heat release from condensation of vaporized and formed water from the fuel, whereas the effective heating value does not take this heat into account. Hence the effective heating value will always be lower, depending on the moisture and hydrogen content in the fuel. If the fuel does not contain any moisture, which is the case for oil and gas, the effective heating value will correspond to the lower heating value.

The higher heating value is given by the formula (MJ/kg d.b.) [4]:

$$HHV = 0.3491 \cdot X_c + 1.1783 \cdot X_H + 0.1005 \cdot X_S - 0.0151 \cdot X_N - 0.1034 \cdot X_O - 0.0211 \cdot X_{ash} \quad (2.1)$$

As can be seen from the formula, carbon, hydrogen and sulphur contributes positively to the heating value, while the content of oxygen, nitrogen and ash will decrease it. Calculation of the HHV is also possible if the amount of fixed carbon is known, and is done by the formula [10]:

$$HHV = 0.196 \cdot X_{FC} + 14.119 \quad (2.2)$$

When calculating the effective heating value, the moisture and hydrogen content of the fuel is taken into account by the formula (MJ/kg w.b.):

$$EHV = HHV \left(1 - \frac{w}{100}\right) - 2.444 \cdot \frac{w}{100} - 2.444 \cdot \frac{h}{100} \cdot 8.936 \left(1 - \frac{w}{100}\right) \quad (2.3)$$

Where 2,444 is the enthalpy difference between gaseous and liquid water at 25°C and 8,936 is equal to  $M_{H_2O}$  divided by  $M_{H_2}$ , and is the molecular mass ratio between water and hydrogen. W and h is the concentration of water and hydrogen in the fuel.

High heating value and density is usually preferred as this reduces the amount of needed fuel. This has implications for the transportation and storage costs which will be reduced.

The moisture content is an important and limiting factor in biomass combustion due to its effect on the heating value. Vaporization of water in the fuel is highly endothermic and the moisture in the fuel must be vaporized before combustion takes place. The self-supporting limit of the moisture content in the fuel is 65 percent and supplemental fuel is needed if the water content exceeds 50 - 55 percent [7]. As the moisture content in the biomass after logging could be high, up to 65 percent of the weight, drying before thermal utilization is almost always necessary.

Although this is both time consuming, space intensive and expensive. Quick drying of the biomass before pelletizing is energy intensive and the heat needed is equal to about 20 percent of the EHV in the fuel [4].

The size of the fuel will influence the combustion, as smaller particles leads to an increased surface area. This means that more fuel is combusted at the same time and a shorter residence time in the combustion chamber is needed.

	Moisture wt. % (w.b.)	HHV, MJ/kg (d.b.)	EHV, MJ/kg (w.b.)	Energy density, MJ/m <sup>3</sup> (w.b)	Volatiles wt.% (d.b)	C wt.% (d.b)	H wt.% (d.b)	O wt.% (d.b)
Wood pellets <sup>1</sup>	10 %	20.0	16.4	9920	-	-	-	-
Bark <sup>1</sup>	~ 50 %	20.2	8.2	2620	-	-	-	-
Woodchips, hardwood, pre-dried <sup>3</sup>	30 %	20.0	8.0	3940	76 - 86	47-51.6	6.1 - 6.3	38- 45.2
Spruce <sup>4</sup>	-	20.9	-	7266 (d.b)	80.2	51.8	6.1	41.2
Birch <sup>2,4</sup>	-	19.2	-	9555 (d.b)	78.7	48.7	6.4	44.8
Straw, high pressure bales <sup>1</sup>	15 %	18.7	14.4	1740	70 - 81	44.90	5.50	41,80
Coal <sup>5</sup>	6 - 10 %	-	25- 28	30 - 36 000	17 - 20	76 - 87	3.5 - 5	2.8 - 11

Figure 2-3 Approximate values for some important properties for biomass and coal [5]<sup>1</sup>, [11]<sup>2</sup>, [4]<sup>3</sup>, [12]<sup>4</sup> and [9]<sup>5</sup>

Other combustion properties like air preheating and excess ratio, combustion temperature, fuel distribution and heat exchange, are all important regarding efficiency and emissions. These properties will mostly depend on the combustion system design.



## 3 Biomass ash and associated problems

Ash is present in all forms of biomass, either bound as salts in the carbon structure, or as mineral particles from dirt or clay introduced to the biomass during harvest or transport. The ash content in different biomass varies and is shown in Figure 3-1.

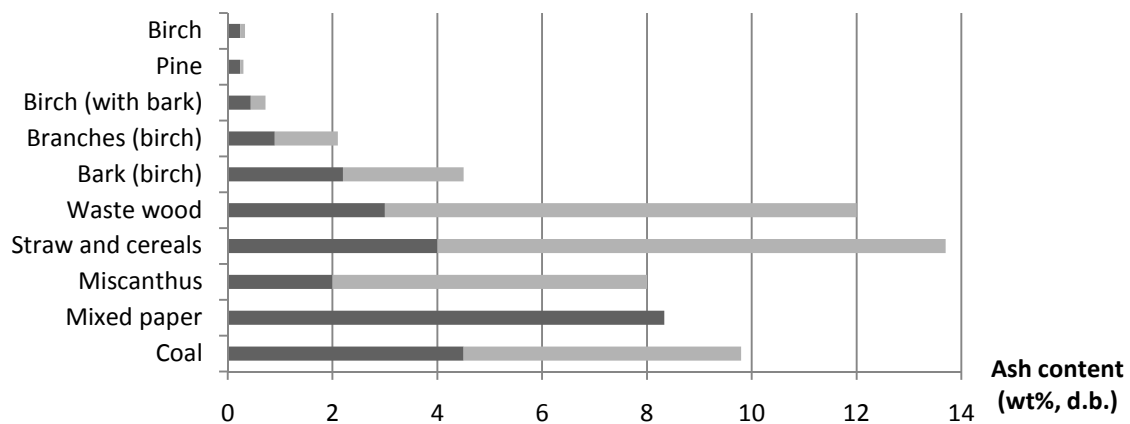


Figure 3-1 Typical ash content in different biomass feedstock [4, 13], paper and coal [7, 9].

Fuels with low ash content are better suited for thermal utilization than fuels with high ash content. A lower amount of ash simplifies the ash removal system as well as ash disposal. Higher amounts of ash will also lead to increased dust emissions, possibly more slagging and the need for a more specialized boiler system [4].

### 3.1 Ash formation and ash behavior on grate combustion

In grate-fired systems, the fuel are distributed over a moving or static grate to form a fuel bed, with the primary air being supplied from underneath. The normal intention is to retrain most of the ash on the grate to be removed to an ash pit, either manually or mechanically. Although a significant proportion of the ash will be released from the bed as fly ash particles entrained in the combustion gases or in the form of vapors and fine fumes.

During combustion, volatile elements and compounds like alkali metals, S, Cl and easily volatile heavy metals (such as Zn and Cd) are released from the fuel to the gaseous phase and subsequently undergo gas phase reactions. These new compounds have a high vapor pressure, and as soon as the vapor pressure exceeds the saturation pressure, particles are formed by

nucleation or they condense on surfaces of existing particles [14]. This happens when there is a high rate of formation of these compounds or when the flue gas enters the cooling stage. Nucleation and condensation are always competing processes, and if there are enough available surfaces for condensation, nucleation will partly or even totally be suppressed. Figure 3-2 provides an informative overview of the principal ash and aerosol formation processes.

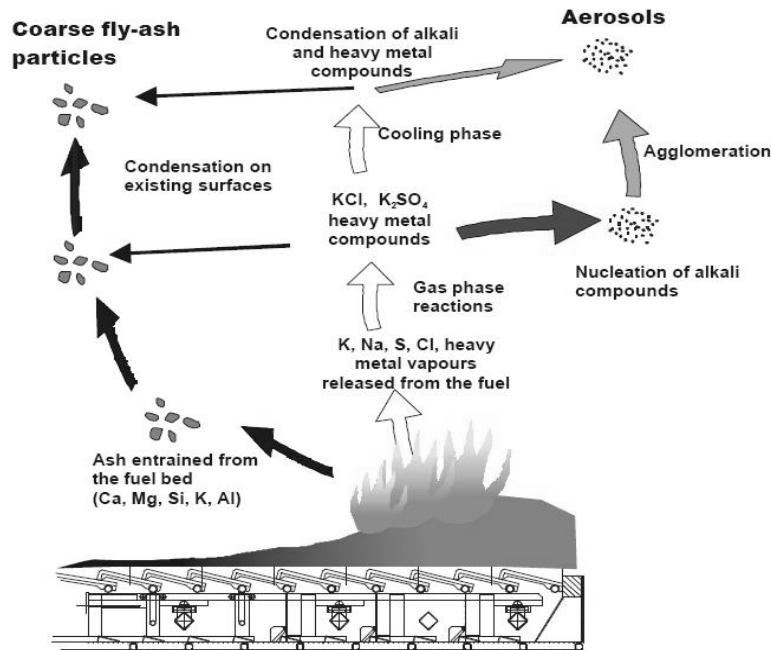


Figure 3-2 Key processes for the formation of fly-ash particles and aerosols from grate combustion of untreated wood chips [14].

Normally the ash is divided into two different ash fractions; bottom ash and fly ash. The bottom ash contains between 60 and 90 wt. percent of the ash fraction, and consists mainly of mineral impurities in the ash [4]. The fly ash is normally distinguished further as coarse fly ash and aerosols.

The coarse fly ash consists of ash retrained from the fuel bed with the flue gas. The particle size can vary between 5 and 200  $\mu\text{m}$ . This ash is also called cyclone fly-ash, as a cyclone is often used to clean these particles from the flue gas. The fine particles are generated by the condensation of the volatile inorganic species from vapor phase, as described above. These particles have typically a diameter below 1  $\mu\text{m}$  and are called aerosols.

## 3.2 Ash composition

The major ash-forming elements in biomass fuels are Si, Ca, Mg, K, Na, and P [4]. The alkali metals K (potassium) and Na (sodium) are highly reactive and play a central role in ash related problems like corrosion and ash melting [15].

	Birch <sup>1</sup>	Spruce <sup>2</sup>	Pine <sup>1</sup>	Wheat straw <sup>3,5,6</sup>	Switch grass <sup>3</sup>	Mixed paper <sup>3</sup>	Coal <sup>3,4,6</sup>
SiO <sub>2</sub>	2.8	8.6- 23.5	39.0	48.0- 57.5	65.2	28.1	37.2 - 59.7
CaO	45.0	36.4- 53.2	25.5	2.8 - 6.1	5.6	7.5	2.1 - 7.5
MgO	10.8	3.7- 6.0	6.5	1.1 - 1.8	3.0	2.4	0.4 - 2.4
Na <sub>2</sub> O	1.3	0.4- 0.7	1.3	0.8 - 14.5	0.6	0.5	0.5 - 1.4
K <sub>2</sub> O	11.4	5.9- 7.6	6.0	16.6 - 25.6	11.6	0.2	0.5 - 5.8
Al <sub>2</sub> O <sub>3</sub>	1.4	-	-	0.8 - 3.5	4.5	55.6	19.8 - 33.9
Fe <sub>2</sub> O <sub>3</sub>	0.7	-	-	0.4 - 0.7	2.0	0.8	3.5 - 17.0
P <sub>2</sub> O <sub>5</sub>	-	-	-	1.1 - 1.3	4.5	0.2	0.1

Table 3-1 Content of the major ash forming elements and chloride formed at 525-550 °C. [16]<sup>1</sup>, [5]<sup>2</sup> [7]<sup>3</sup>, [17]<sup>4</sup>, [18]<sup>5</sup>, [9]<sup>6</sup>.

Table 3-1 show the amount of important ash-forming components in some relevant fuels. Straw generally contains much more potassium, sodium and chlorine than wood, hence cause higher ash-related problems. The concentration of the ash forming elements in the ash, does not give complete information of the content of these problematic elements, as some is released during ashing before the analysis. At 525 °C ashing temperature Thy et.al concluded with a 26 percent potassium loss for wood and 20 percent loss of chloride in wheat straw as the relevant losses, and the losses increased with increasing temperature [18].

In addition to the elements listed in Table 3-1, about 12 other elements are normally represented in the biomass, referred to as minor ash forming elements [4]. These include e.g. the heavy metals Zn, Cd and Cu, and are of especial environmental importance. The concentration of these elements influences both the emissions from combustion and the possibility to reuse the ash for fertilizing purposes. High concentration might lead to cleaning requirements for the flue gas, and the ash needs to be treated as special waste.

### 3.3 Ash melting and sintering

The maximum fuel bed temperature in fixed bed combustion without water cooling on the grate is normally in the order of 1000 - 1200 °C. This rarely involves any problems when burning biomass such as pure wood pellet, unless the grate is badly designed and the temperature increases above this level. Some fuels containing high amounts of ash and/or high amount of potassium, sodium and chloride might involve problems induced by sintering and agglomeration of the ash.

When the combustion temperature reaches a certain level, sintering of the biomass ash will occur and the surface of the ash becomes sticky. This is partly because of the vaporization and release of alkali metals, which will cover the ash particles and form sticky layers that will contribute to sintering and agglomeration [19]. There are also interactions between these alkali metals and quartz or silica that will form alkali metal silicates with a lower melting temperature. The melted or partial melted alkali silicates lead to sintering and agglomerated ash. This is a more frequent phenomenon in CFB than grate boilers.

Depending on the combustion technology, the ash sintering will lead to agglomeration and formation of big particles. Severe sintering and agglomeration of the ash leads to the formation of big ash particles at the size bigger than a fist, and are too big for the automatically ash removal system.

At higher temperatures the ash will melt and stick to the combustion grate and might cover the primary air distribution holes. This causes problem with the air distribution, which again leads to incomplete combustion, higher emissions and unburned fuel.

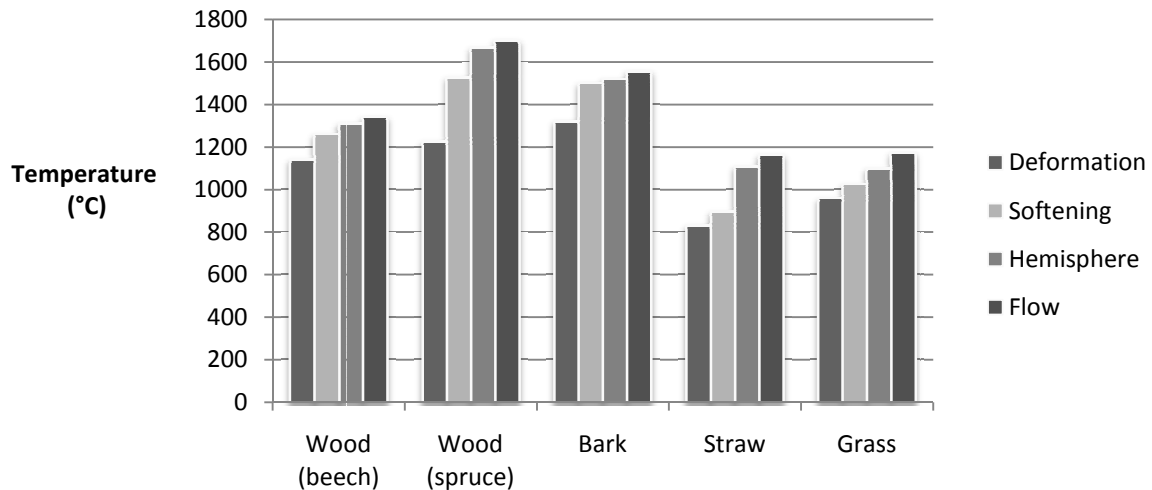


Figure 3-3 Average ash melting temperatures for some relevant biomass feedstock [4].

Different biomass fuels have varying ash deformation and melting temperatures, as shown in Figure 3-3. At softening temperature the ash gets sticky and agglomeration could occur. The melting increases at softening and hemisphere temperature and at flow temperature the ash is liquid. Biomass from regular wood feedstock has generally high ash melting temperatures, while fuel from straw, bark, logging residues and wood with mineral impurities have problematically low melting temperatures, [4]. Although according to the figure, beech wood has lower ash melting temperatures than bark. The low melting temperatures of straw together with high ash content makes straw a problematic fuel to utilize, but high availability of straw has lead to widespread research related to the ash melting problems.

As stated earlier, ash sintering and melting problems are closely related to the amount of ash, alkali metals and chlorine in the fuel. During combustion, the ash forms several different crystalline phases depending on the fuel composition. Fuel rich in potassium and sodium tend to form crystalline phases with a low melting point. Examples of these are sylvite (KCl), fairchildite ( $K_2Ca(CO_3)_2$ ) and arkanite ( $K_2SO_4$ ) with melting points (mp) at 776 °C, 815 °C and 1069 °C respectively<sup>1</sup>, and contributes to a low melting point of the ash [20]. The sodium

<sup>1</sup>The literature regarding this topic often gives one temperature as “the” melting temperature, without informing whether this is deformation, softening, hemisphere or flow temperature. This thesis will also use this term when referring to melting temperatures found in the literature, as it is assumed they use the same definition for the melting temperature.



concentration in biomass is normally much less than potassium, and is to a much lesser extent contributing to the formation of low melting crystalline phases.

Not only the amount of alkaline metals is important, but also the concentration of other substances in the ash.  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{K}_2\text{O}$  might form the silicate  $\text{K}_4\text{CaSi}_3\text{O}_9$  with a melting temperature of  $1150\text{ }^\circ\text{C}$ , although small changes in the composition between these could form compounds with melting points as low as  $850\text{ }^\circ\text{C}$  [20]. The concentration ratio of the different substances does not only affect the melting temperature on the crystalline phases formed, but also the resulting properties of the melted ash. Figure 3-4 show the composition of rice straw ash, which is remarkably similar to the composition of ordinary glass, which helps to explain the rapid sintering, slagging and fouling observed when burning rice straw in wood boilers [7].

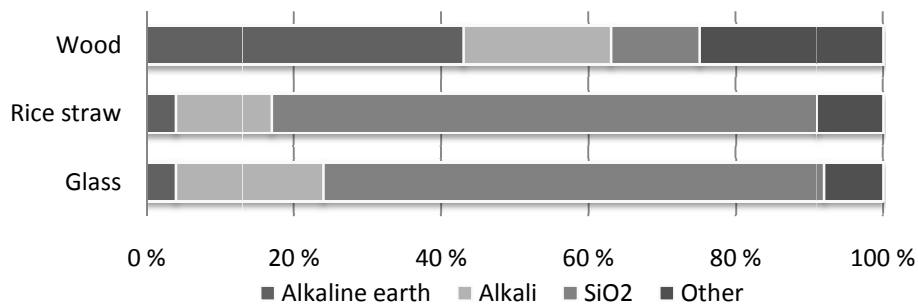


Figure 3-4 Ash composition of wood, rice straw and glass [7].

High silica content in the fuel might also increase the ash slagging, with 20-25 wt. percent ( $\text{SiO}_2$ ) reported as the critical level that will cause ash slagging in residential wood pellet burners [21].

Waste wood from the construction and furniture industry has often a lower ash sintering and melting temperature than virgin wood, most likely caused by contamination of mineral impurities from concrete, glue, sanding paper etc. As the feedstock and impurities varies, the melting temperature will also vary. Melting temperatures for a certain feedstock in the Møre-area in Norway are given later in this thesis.

In addition to the composition of the biomass ash, the design of the combustion chamber will have a significant effect on the ash sintering and melting. Inadequate design of the combustion chamber in relation to the fuel being burned can worsen the ash melting problems, and vice-versa. The factors that have to be considered when designing a boiler are mainly thermal levels in the boiler, size of the boiler and heat transfer surfaces, combustion conditions and soot blowing strategies [22].

### 3.4 Corrosion

The content of alkali metals, potassium and sodium, combined with chlorine, is the root of the problems regarding corrosion on heat-exchanging surfaces in the boiler.

Gaseous HCl and Cl<sub>2</sub> might cause a corrosion often referred to as active oxidation. Chlorides cause the breakdown of the normally protective layer of oxide scales on superheater alloys. This happens through a reaction between chloride and metal, which leads to the formation of metal chloride, FeCl<sub>2</sub>. When exposed to oxygen, metal chloride and oxygen leads to the formation of metal oxide, FeO<sub>3</sub>, often referred to as rust. By this reaction, chloride gas is released and might, react with new metal, thus a *cyclical reaction* is formed [23]. The overall process is shown in Figure 3-5.

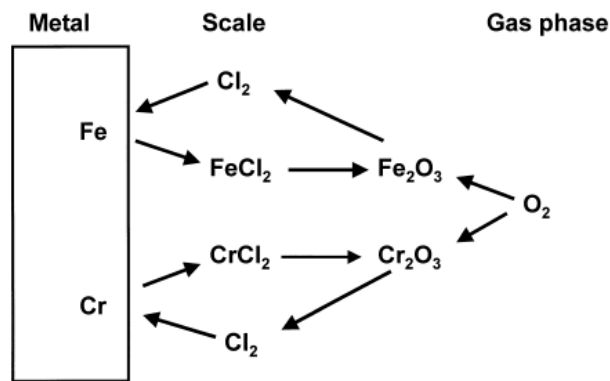


Figure 3-5 Schematic drawing of corrosion caused by gaseous chlorine [23].

This process is normally a minor problem as long as the surfaces in the boiler are clean and oxygen rich, although depending on the chlorine concentration in the flue gas and the temperature. The released volatile components like alkali metals from combustion, reacts with chlorine to gaseous KCl and NaCl. When entering the heat exchanging zone, condensation of these substances on surfaces leads to the deposition of KCl(s) and NaCl(s). This forms a sticky layer that further enhances the deposition of alkali metals. Sulfation of deposited alkali chlorides are probably a source for enhanced corrosion, as gaseous SO<sub>2</sub> and/or SO<sub>3</sub> will react with KCl or NaCl and form gaseous HCl and Cl<sub>2</sub>, which will diffuse to the surface of the metal layer and contribute to the reactions showed in Figure 3-5. Figure 3-6 shows the various corrosion mechanisms taking place in a deposit layer. Potassium chloride behaves as sodium chloride.

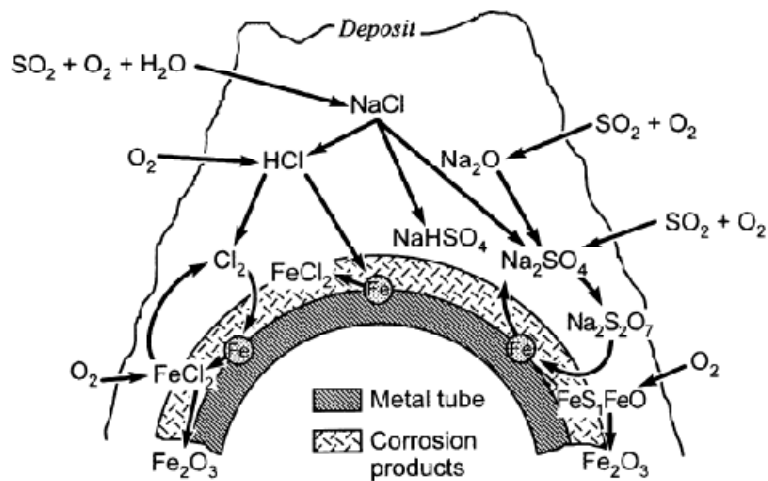


Figure 3-6 Sequence of different reactions happening in biomass combustion deposits [23].

The temperature plays an important role in these mechanisms and 500-550 °C is often a critical temperature for some of the main corrosion reactions [23]. Hence the corrosion described here is often referred to as high temperature corrosion. A high electrical efficiency on biomass fueled power plants are often restricted by high temperature corrosion, as a high temperature on the superheated vapor is needed in order to increase the efficiency. Special metal alloys are used to come to grips with the corrosion problems, although this increases the cost of operation. It is then possible to add additives to the fuel or combustion chamber to reduce the formation of alkali compounds in the flue gas.



## 4 Additives

A possible solution to reduce the ash problems is by adding additives to the fuel or during the combustion process. This will reduce the sintering of the ash by either dilution or reactions.

### 4.1 Additive dilution

The increase in melting temperature from dilution happens because the particles of the additives and the biomass ash are stuck together when the alkaline content of biomass ash starts melting. Meanwhile, an important proportion of the alkaline compounds are volatilized with the increase in temperature and captured by the additives. Additives with high porosity are wanted as this means a larger surface area that is able to adsorb more liquid or gas phase alkali containing species. This adsorption will decrease the tendency of other particles being covered by a sticky layer that will make the ash sinter or agglomerate together. The additives will also form pores in the melted ash which will make the sintered and agglomerated ash crisp and more fragile [20].

### 4.2 Additive reactions

The other effect of additives in biomass fuel is by reactions between the alkaline metals in the fuel and the additives. The additives, called alkali getters, incorporate the potassium and sodium into higher melting compounds [24].

Examples of commercial additives are kaolin, bentonite, dolomite, lime, limestone, ammonia sulphate and sulphur. All relevant additives could be placed in four/three groups according to their chemical composition of interest:

1. Al and Si containing additives
2. P and Ca containing additives
3. S containing additives

Common for these substances are their ability to react with both potassium and sodium chloride, which have melting temperatures at 801 °C and 772 °C respectively [4], and create high melting crystalline phases. The reactions presented with potassium chloride are valid also for sodium chloride.

### 4.2.1 Al and Si containing additives

Silica has the ability to raise the ash melting temperature by reacting with e.g. potassium oxide ( $K_2O$ ), which has a melting temperature at  $740\text{ }^\circ\text{C}$  alone. A reaction could create  $K_2O(SiO_2)_2$  that has a melting temperature at  $1045\text{ }^\circ\text{C}$ , but some potassium silicates like  $K_2O(SiO_2)_4$  has a lower melting temperature (mp=  $770\text{ }^\circ\text{C}$ ), hence the mixing ratio of silicon and potassium is very important but also difficult to control [25]. This also imply that only a small amount of potassium will have a major impact on the ash melting temperature, as silicon alone has an ash melting temperature above  $1400\text{ }^\circ\text{C}$ . With presence of aluminum, higher melting crystalline phases like  $KAlSiO_4$  (mp= $1600^\circ\text{C}$ ) are possibly formed, and the mixture sensitivity is not as severe anymore. Potassium aluminum silicates also generally has much higher melting temperatures than potassium silicates [26]. Aluminum will also increase the reactivity of the reactions between silica and the alkali components, as silica is not very reactive.

Additives containing both aluminum and silica such as kaolin ( $> 99\%$   $Al_2Si_2O_5(OH)_4$ ) and bentonite  $Al_2O_3(SiO_2)_2H_2O$  is preferred. The formula for the reaction of potassium chloride with kaolin is [27]:



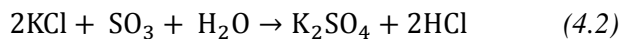
### 4.2.2 P and Ca containing additives

Sufficient amounts of calcium will efficiently increase the melting temperature, as  $(K_2O)_4CaO(SiO_2)_{10}$  melts at around  $940\text{ }^\circ\text{C}$  while  $K_2OCaOSiO_2$  has a melting temperature at  $1540\text{ }^\circ\text{C}$  [25]. Generally, increased addition of calcium will increase the melting temperature of the ash. The purpose of adding phosphorous in addition to calcium is obviously to result in crystalline phases with a high melting temperature. A higher Ca to P ratio is better as the production of  $CaKPO_4$  (mp =  $1560^\circ\text{C}$ ) instead of  $CaK_2P_2O_7$  (mp= $1143\text{ }^\circ\text{C}$ ) and  $K_4P_2O_7$  (mp= $1105\text{ }^\circ\text{C}$ ) is desirable [28]. Typical fuels contain a certain amount of calcium, but further addition of reactive calcium will contribute to a higher melting temperature.

Typical additives containing calcium and/or phosphate includes calcite/lime ( $CaCO_3$ ), limestone (86 % CaO) and calcium phosphate ( $CaHPO_4$ ).

### 4.2.3 S containing additives

Additives containing sulphur, like ammonium sulfate ( $(NH_4)_2SO_4$ ) and pure sulphur, could also be used to raise the melting temperature, as e.g. the reaction with potassium chloride:



But as  $K_2SO_4$  only has a melting point at  $1069^\circ\text{C}$ , the addition of kaolin will lead to the formation of kalsilite with a melting point at  $1600^\circ\text{C}$ :



Magnesium will also increase the melting temperature of the ash [4], but the availability of this in large and cheap amounts is limited and thus not widely used. Mg could be introduced through other additives like dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) and ophite (a kind of magnesiohornblende) [20]. Magnesium in combination with phosphorus will lead to the formation of  $\text{MgKPO}_4$  (mp =  $1520^\circ\text{C}$ ).

The use of heterogeneous additives containing relevant elements from different groups, such as magnesium or aluminum in addition to phosphorous, could drastically reduce the amount of additives needed [25].

Table 4-1 shows the chemical composition of some relevant additives that is widely used.

	Ash composition wt. % (d.b)				
	Limestone	Lime	Dolomite	Kaolin	Ophite
$\text{Al}_2\text{O}_3$	0.22	0.41	0.4	30	13
$\text{P}_2\text{O}_5$	<0.02	<0.02	-	<0.02	<0.02
$\text{SiO}_2$	2.4	2.5	3.4	51	45
$\text{CaO}$	51.0	86	31.0	0.1	8.0
$\text{SO}_3$	1.0	2.2	-	<0.02	0.13
$\text{Fe}_2\text{O}_3$	0.11	0.11	0.6	0.41	9.6
$\text{MgO}$	0.65	0.37	19.7	0.08	11
$\text{K}_2\text{O}$	0.07	0.05	-	0.43	0.18
$\text{Na}_2\text{O}$	<0.02	<0.02	-	0.038	3.0
Cl	<0.01	<0.01	-	<0.01	0.07
$\text{CO}_2$	43.0	1.8	-	<0.3	<0.03

Table 4-1 Concentration of elements and compounds found in some relevant additives [20, 29].

Additivation will also reduce the problem of fouling and corrosion in the boiler, as far more Cl is released as gaseous HCl instead of KCl. The formation of higher melting temperature phases leads to deposit condensation further upstream in the boiler instead of on the heating tubes.

#### 4.2.4 Ash additive literature

There are a handful of projects describing the effect of additives in problematic fuels to reduce the sintering and agglomeration of ash during combustion. The bulk of articles about additives in biomass combustion are related to fluidized bed combustion or the additive effect on corrosion in heat exchanging tubes. They also describe the additive effect on yearly cropped biomass fuels, such as straw, grass or residues, as these fuels are often connected to ash sintering problems.

S. Xiong et al. have performed melting analysis on corn residues mixed with 1, 2 and 3 percent addition of kaolin (99,9 %  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) and calcite (99,9 %  $\text{CaCO}_3$ ) using the ASTM D1857-68 standard [30]. The initial deformation temperature for the corn residue ash was raised from  $1170$  to  $1370^\circ\text{C}$  for an addition of 3 percent kaolin and to  $1290^\circ\text{C}$  for 3 percent calcite. One percent addition of kaolin raised the temperature with  $100^\circ\text{C}$ , while the same amount with calcite did not affect the DT. For all temperatures and additive percentages, kaolin was more effective in raising the ash melting temperatures. Xiong et al. discovered that both calcite and kaolin was effective to reduce ash sintering and agglomeration tendency of corn residues. An

interesting observation was that calcite was more effective than kaolin, despite the lower ash melting temperatures.

M. Öhman et al. studied the effect of both kaolin and limestone in a problematic wood fuel, containing higher amounts of silica and potassium compared to regular stemwood [31]. An additive amount of 0.5 percent limestone decreased the slagging drastically for this fuel at 1000-1100 °C burning temperature. Öhman et al. experienced a higher degree of slagging when kaolin was used as an additive. This was both the case when kaolin was added to the problematic wood fuel, and also when it was added to an originally unproblematic wood fuel [31]. The Öhman study is one of very few studies about additives in wood fuels.

M.J Fernández Llorente et al. performed sintering tests at 1000 °C in an oven, with different problematic fuels that formed hard slag at this temperature and mixtures with potential additives [20]. Some of the fuels were barley straw, thistle and almond shell. Calcium based additives, such as lime (86 % CaO) and to some extent limestone (99 % CaCO<sub>3</sub>), showed good results in terms of reduced sintering and agglomeration. The Al-Si based additive kaolin was the most effective additive, slightly ahead of lime. Limestone and ophite were about equally effective in reducing the sintering, but for these two additives a higher concentration was needed in order to reduce the sintering (>0.5-1.0 g additive/g ash). Pure silica and pure alumina was also tested but had almost no effect on the ash slagging, which underlines the importance of having an additive containing both Si and Al.

### 4.3 Additive amounts

From the reactions in the previous subchapters it follows that the molar ratio is one or two K to one Al, P or S. Ideally, one wants to add a sufficient, but not excessively, amount of additives as they often are more expensive than the fuel and decrease the fuel value. An  $(Al + Si)/(K + Na)$ ,  $(Ca + P)/(K + Na)$  or  $(2S)/(K + Na)$  ratio below one, will in theory give excess amount of K and Na and indicates the need for more additive. A 100 percent utilization of the additives is rarely obtainable, and normally the additive needs to be supplied in stoichiometric excess [24].

It is also possible to add additives on the basis of ash amount in the fuel and additive. Llorente et al. tested eight different additives on five problematic fuels with an additive concentration of 0.125 to 2 g additive/g ash. All additives had an ash content of almost 100 percent. Higher amount of additives reduced the sintering, and for six of the additives, a concentration of 1 to 2 g/g ash eliminated the sintering problems for almost all fuels [20].

Big scale experiments with combustion of straw performed by Dong Energy and Vattenfall, suggest an additive addition of 3- 5 wt. percent to the fuel [32]. This corresponds to a mixing ratio of around 1:1 of additive and fuel ash, which seems to be the general minimum amount of additives that should be added.

Rensen et al. have made a patented description regarding the additive amount of P- and Ca-based additives [25]. The amount is based on calculations of the different chemicals in the additive and fuel after:



$$P_{added} = q1 \times \left( \frac{31}{39} K_w + \frac{31}{23} Na_w - P_w - \frac{31}{35.4} Cl_w \right) \quad (4.4)$$

Where  $P_w$ ,  $Na_w$ ,  $Cl_w$  and  $K_w$  is the amount of phosphorous, sodium, chlorine and potassium in weight percent of the inorganic portion of the fuel material treatment before the mixture with additive, and  $P_{added}$  is the amount of phosphorous that needs to be added by the additive.  $Q1$  is a number between 0.33 to 5, preferably 1.

For the addition of calcium, the following formula is used:

$$Ca_{added} = q2 \times \left( \frac{40}{31} \times (P_{added} + P_w) - Ca_w \right) \quad (4.5)$$

Where  $Ca_w$  is the amount of calcium presented in the fuel before the addition, and  $q2$  is a number between 0.1 and 3, preferably 0.5.

According to Rensen et al., the needed addition of P and Ca could be reduced 10 times by adding small amounts of Mg-containing substances.

## 4.4 Alternative additives

The additives mentioned are commercially available additives that could be used in large scale at power plants. Kaolin, limestone, calcite and ophite, amongst, others have all been identified as additives that will reduce ash sintering [20, 30, 31]. Although the high cost for these and other additives makes them unattractive for large scale usage. A typical commercial additive costs about four to six times the fuel and has little or no heating value [24]. As there is a need for around 5 percent of additives in the fuel, the total fuel price will increase with about 20 percent. Because of this, the options of using waste products containing the demanded substances have been investigated in different research projects. Even though these products are substantially cheaper, problems like varying content of the wanted chemicals and content of heavy metals complicates the use. A project from Dong energy in Denmark tested clay sludge, de-gassed manure and bleaching earth waste as additives to reduce straw slagging and corrosion, and encountered problems like the ones described [24].

In the search for waste products to be used as additives, some guiding rules could be used. The waste product should of course be suspected to contain a great amount of the wanted chemicals Al, Si, P, Ca, S and Mg. They should also be cheap, available in a sufficient amount and possibly easy mixed with the fuel.



## 5 Description of fuels and additives

Two problematic fuels, wood pellet and straw, are used in this project. The wood pellet is made by Møre Biovarme and originates from residues from the furniture industry in the Møre area and consists therefore of a very heterogeneous feedstock. This wood pellet has a problematically low melting temperature most likely induced by contamination of residues from glue, sanding paper and concrete. Some grate boilers combusting this pellet experience severe levels of ash slagging and agglomeration which leads to the need of frequent manual cleaning. The addition of additives to the wood pellet has been proposed as a possible solution to the ash sintering problems.

In order to further evaluate the different additives, the melting temperatures of straw with additives were also investigated. Primarily it is the problematic wood pellet that is the topic for this thesis, but this wood fuel is a very special case. It is therefore interesting to test the effect of the additives on straw as this is a fuel that is more representative for a fuel that is connected to serious ash related problems and is interesting to utilize worldwide. The straw tested is wheat straw from Denmark with high chlorine content.

Four different products are identified as possible additives to be used in the wood pellet from Møre Biovarme. These additives are paper sludge, clay, sewage sludge and marble sludge.

The paper sludge is a waste product from paper production at Skogn in Nord Trøndelag. The paper production involves a lot of kaolin, and the paper sludge contains most likely a lot of aluminum and silica [33]. Hustadmarmor is a marble factory that is extracting marble close to Brønnøysund, and produces marble sludge in great amounts as a waste product. Marble is produced from the mineral calcite which has been proven to reduce ash sintering [20, 30]. The clay selected is from a gravel pit south of Trondheim and can be obtained at a very low cost. The clay is expected to be of similar composition as kaolin which contains around 50 percent silica and 30 percent aluminum [20]. Sewage sludge is expected to contain a lot of aluminum, silica and phosphorus [34, 35], and does in addition contain a calorific value which makes it interesting to utilize this as an additive. Sewage from a treatment plant named Saulekilen in Arendal is chosen as this plant dewateres the sewage down to 10 percent water content, which is needed in order to incorporate this in the wood pellet.

The ash of sewage sludge, paper sludge, clay, pellet and straw are analyzed with XRF and the results are shown in Table 5-1.

	Ash composition wt. % (d.b)				
	Wood pellet	Wheat straw	Sewage sludge	Clay	Paper sludge
Al <sub>2</sub> O <sub>3</sub>	6.1	0.9	55.0	15.1	16.7
P <sub>2</sub> O <sub>5</sub>	2.3	6.0	14.5	0.2	4.4
SiO <sub>2</sub>	12.3	39.2	14.5	59.1	32.1
CaO	34.8	6.1	7.2	4.3	19.5
SO <sub>3</sub>	2.4	5.0	1.1	0.04	5.0
Fe <sub>2</sub> O <sub>3</sub>	4.4	0.4	4.5	10.4	14.0
MgO	5.6	1.9	1.1	4.3	4.3
K <sub>2</sub> O	14.2	29.9	0.7	3.3	1.1
Na <sub>2</sub> O	11.1	1.1	0.5	1.5	0.8
Cl	0.2	9.2	0.1	0.01	0.1

Table 5-1 Ash composition of the fuels and additives at 550 °C ashing temperature.

The table shows surprisingly high sodium content for the wood pellet. Regular wood ash, as shown in Table 3-1, has a Na<sub>2</sub>O concentration at around one percent. The Potassium and chlorine content is only slightly higher compared to the wood ash in Table 3-1, and the high sodium content might be the explanation for the severe ash problems connected to this fuel. The reason for this high amount of potassium is not clear. However it should be noted that the fuel feedstock is constantly varying, and with that the composition of the ash. This sample of fuel is from November '08.

The straw has a quite high potassium and chlorine content compared to the wheat straw in Table 3-1, which helps explaining the low ash melting temperature reported.

The clay has a high amount of silica and aluminum, which makes this an interesting additive. Comparing this to Table 4-1 shows that the clay is very similar to ophite, and also to some extent kaolin, which has been investigated in several different studies [19, 30, 31]. Clay has however a fairly large amount of potassium and sodium, which is two of the unwanted components.

The marble sludge is informed from Hustadmarmor to contain 98 wt. percent (d.b.) CaCO<sub>3</sub> and is therefore not sent for XRF analysis. The elemental composition is probably very similar to the limestone shown in Table 4-1.

Sewage sludge is the most interesting additive in this project, as it is cheap, available in large amounts, has lower ash content than many other additives and contains burnable elements. However the chemical composition will vary, depending on the geographical location of the sewage, and could make it difficult to duplicate the results obtained in one project to another. The sewage sludge in Table 5-1 contains considerably larger amounts of aluminum and less silica, compared to other sewage sludge used for combustion or co-combustion [35, 36]. The amount of phosphorous is fairly high and makes the sewage sludge an interesting additive as most other additives are either Al-Si- or Ca-based. Sewage sludge has previously not been tested as an additive to reduce sintering in biomass combustion, but has performed well as an additive to reduce fouling and corrosion in wood pellet and waste wood combustion [35].

The paper sludge is a very interesting additive as it contains both Si, P, Ca and some Mg and S. The ash content in this paper sludge is expected to be much lower than the other additives. As

with sewage sludge, paper sludge has not been used as an additive to reduce ash sintering and agglomeration. However Aho & Silvennoinen have co-combusted pulp sludge together with bark and showed that the pulp was able to considerably reduce fouling and corrosion compared to combustion with pure bark [33]. The study suggests that the aluminum and silica concentrations should be much higher than the other inorganic elements.

## 5.1 Additive amounts

The ratio of fuel and additives will be based on the Danish patent from Rensen et al. and sewage sludge as this is the most interesting additive. The formulas used in this patent give an additive amount of 5 percent of sewage sludge in wood pellet. This is considerably higher than what is obtained when the molar ratios of  $(Al + Si)/(K+Na)$  and  $(Ca+P)/(K+Na)$  between the wood pellet and sewage is considered. A ratio of 1:1 of these elements gives 0.6 percent and actually - 0.95 percent addition of sewage sludge, based on the Al-Si and Ca-P content of the additive respectively. The negative result of Ca is probably because of a high Ca- content in the wood pellet.

In order to validate whether or not 5 percent sewage is an optimum amount, the melting temperatures of the wood fuel ash will be investigated with 3, 5, 7 and 10 percent addition of sewage sludge. To compare the different additives, these concentrations will be used for all blends.

Table 5-2 shows the molar ratio between the wanted and unwanted chemicals in the resulting ash of the fuels and 5 percent addition of each additive. The ratio setup is taken partly from L.-E. Åmand et al. [35].

		$(Si+Al)/$ $(K+Na)$	$(Ca+P)/$ $(K+Na)$	$(Ca)/$ $(K+Na)$	$2S/$ $(K+Na)$	$S/Cl$	$(Al+Si)/$ $Cl$	$(Al+Si+Ca+P+S)/$ $(K+Na+Cl)$
Wood + 5%	Sewage sludge	4.99	2.59	1.73	0.17	-	-	7.68
	Clay	5.50	1.01	0.98	0.04	-	-	6.53
	Marble sludge		15.5	15.5	-	-	-	15.9
	Paper sludge	0.98	1.61	1.52	0.16	-	-	2.73
Straw + 5%	Sewage sludge	1.13	0.40	0.23	0.28	0.79	3.20	1.23
	Clay	1.55	0.32	0.23	0.24	0.74	4.80	1.51
	Marble sludge	-	1.38	1.28	-	-	-	1.65
	Paper sludge	0.77	0.30	0.19	0.28	0.77	2.16	0.89

Table 5-2 The molar ratios of the given chemicals in the resulting ash from the fuels and mixtures.

The ratios for wood pellet show that an additive amount of 5 percent is probably in the upper limit of what is needed for this fuel, except for paper sludge. For the additives that contains large ash amount (near 100 %), a 5 percent addition corresponds to 6-7 g additives/g fuel ash, which is much higher than the usual 1:1 ratio.

For straw ash it looks like the addition of 5 percent is actually slightly lower than needed, according to the molar ratios, as the ratio should be above one. This does not come as a surprise as the ash content is ten times higher than for wood pellet.

## 5.2 Characterization of fuels and additives

The fuels and additives were exposed for proximate and ultimate analysis. Before the analysis, the pellet, straw and paper sludge was milled into small particles with a diameter of less than 1 mm. The sewage and clay sludge was crushed in a mortar into coarse powder. As the marble sludge contains 98 percent (d.b.) CaCO<sub>3</sub>, only the moisture content was measured.

### 5.2.1 Proximate analysis

A proximate analysis includes measurement of moisture level, volatile matter and ash content. The analysis described below is performed according to the standards ASTM E871, ASTM E872 and ASTM E1755. Each test was performed several times if there were any suspicion that the numbers might be wrong.

Standard test routines include air blowing and heating of lids to 950 °C before use. The weight measurements were performed by an accuracy of 0.01 g during moisture analysis and 0.1 mg when measuring the volatile and ash content.

The content of moisture, volatile matter and ash, are basically measured by heating the samples during different conditions, and weigh the samples before and after heating.

#### 5.2.1.1 Moisture content

The moisture level is measured by weighing the samples before and after several hours in an oven. A sample of additive or fuel, a drying oven and a glass bowl was used for this analysis.

The samples were placed in the glass bowl with a diameter of 6 cm. The bowl was first dried for 30 minutes in the oven at 103 °C. Samples of about 50 g were put in the bowls, weighed and placed in the oven at 103 °C for 16 hours. The samples was then weighed and reinserted in the oven for two more hours. This procedure was repeated until the weight difference was less than 0.2 percent for two consecutive measurements.

The moisture content is given as:

$$\text{Moisture (\%)} = \left[ \frac{W_i - W_f}{W_i - W_c} \right] * 100 \quad (5.1)$$

Where:  $W_i$  = initial weight  
 $W_f$  = final weight  
 $W_c$  = container weight

These characters are used in the calculations of volatile and ash content as well.

#### 5.2.1.2 *Volatile matter*

The volatile matter is determined by exposing the samples for a short time in air poor conditions and an intense heat. A muffle furnace Nabertherm B170 and S27, small crucibles of 35 mm with lids and a sample holder was used for this experiment.

About 1 g of dry fuel or additive were placed in the small crucibles and covered with lids. Three identical samples were made for each test. The crucibles were quickly placed in the muffle furnace at 950 °C for seven minutes. After cooling, the crucibles were weighed and the difference recorded. As the samples did not contain any moisture, the weight difference equals the volatile matter.

#### 5.2.1.3 *Ash content*

The ash content is determined with the same equipment as the volatile matter, but the heat is lower and the duration longer.

As with determination of volatile matter, about 1 g of fuel were placed in small crucibles and covered with lids. The samples was placed in the furnace and heated gradually to 250 °C, and the temperature remained there for 30 minutes. This is necessary to pyrolyze the samples and protect them against explosive combustion. The lids were then removed, and the temperature escalated to 550 °C and remained there for 4 hours. After cooling, the crucibles with the ash were weighed, and the weight difference recorded as the ash content.

#### 5.2.1.4 *Fixed carbon*

The proximate analysis is completed by determination of fixed carbon, which is given as:

$$FC = 100\% - \text{Ash content (\%)} - \text{Volatile matter (\%)} \quad (5.2)$$

The fixed carbon content is the carbon found in the material which is left after the volatile materials are released. This differs from the ultimate carbon content of the biomass because some carbon is lost in hydrocarbons with the volatiles. Fixed carbon is used as an estimate of the amount of coke that will be yielded from a sample of biomass or coal.

### 5.2.1.5 Results

All the results and measurements are shown in Appendix A. The summary from the proximate analysis is shown in Table 5-3.

		Moisture content wt % (w.b)	Volatile matter wt % (d.b)	Ash content wt % (d.b)	Fixed carbon wt % (d.b)
Fuels	Pellet	6.3	84.3	0.7	15.1
	Straw	5.9	75.4	6.3	18.3
Additives	Paper sludge	68.0	73.4	9.1	17.5
	Clay	0.5	3.2	98.1	0*
	Sewage sludge	8.8	53.6	41.7	4.7
	Marble sludge	28.2	-	-	-

Table 5-3 Results from proximate analysis of fuels and additives as received. (\*Assumed zero as V.M + A.C > 100%).

The moisture content clearly shows that paper and marble sludge needs to be dried before it is used as an additive. Paper sludge contains a very low ash content in comparison to other additives, and a higher amount of this needs to be added.

### 5.2.2 Ultimate analysis

The ultimate analysis involves detection of the carbon, nitrogen, sulphur and hydrogen content in the fuel and additives. This is performed by the elemental analyzer vario MACRO CHNS, which is a fully automatically measuring instrument.

The elemental analyzer works after the principle of catalytic tube combustion under high temperature and oxygen supply, using helium as a carrier gas. The samples are destroyed under these conditions and through subsequent catalytic reactions were the analyzed components are formed into CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub>. All other volatile gases (e.g. oxygen, halogens, etc.) are removed from the gas stream by condensation and absorption. The formed gases are separated from each others in adsorption and desorption columns and the amount of each gas is determined with a thermal conductivity detector, as shown in Figure 5-1.



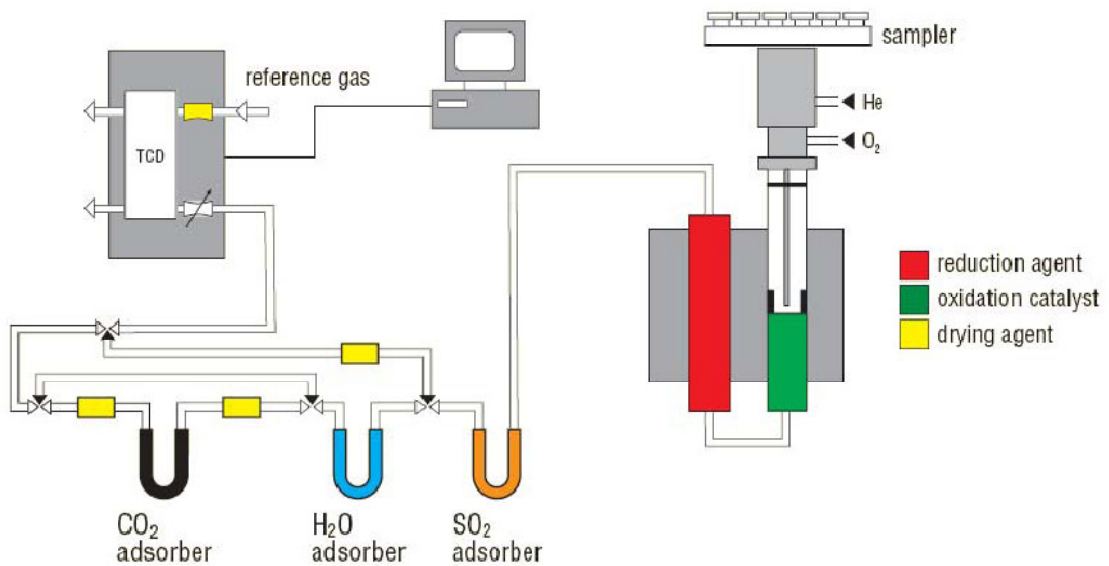


Figure 5-1 Principal sketch of the vario MACRO internal setup [37]

For each of the fuels and additives that were to be analyzed, three samples of about 40 mg were prepared. The samples were packed into thin aluminum foils and pressed together to remove any air inside the foil. In order to give correct values, the samples were completely moisture free. These samples were then placed into the sample holders of the analyzer and the measurement procedure was started.

### 5.2.2.1 Results

The results from the vario MACRO CHNS analyzer are shown in Appendix B, and the average values are given in Table 5-4.

wt % (d.b)	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen*
Wood pellet	49.9	6.4	0.8	0.1	42.1
Wheat straw	46.4	6.2	1.0	0.3	39.8
Sewage sludge	26.4	4.4	3.1	0.8	23.6
Paper sludge	47.9	6.0	1.8	0.5	34.6
Clay	0.5	0.3	0.04	0.05	1.1

Table 5-4 Analyzed and calculated\* elemental composition of fuels and additives.

The oxygen content is not measured by the analyzer, but calculated as the remainder between 100 % and the sum of the ash-, C-, N-, H- and S- content.

### 5.2.3 Heating value

The heating value of the fuels and additives were determined by combusting the samples in a calorimeter, IKA Laboratoriertechnik C5000.

The calorimeter system consists, among others, of a steel bomb with a sample holder as shown in Figure 5-2.

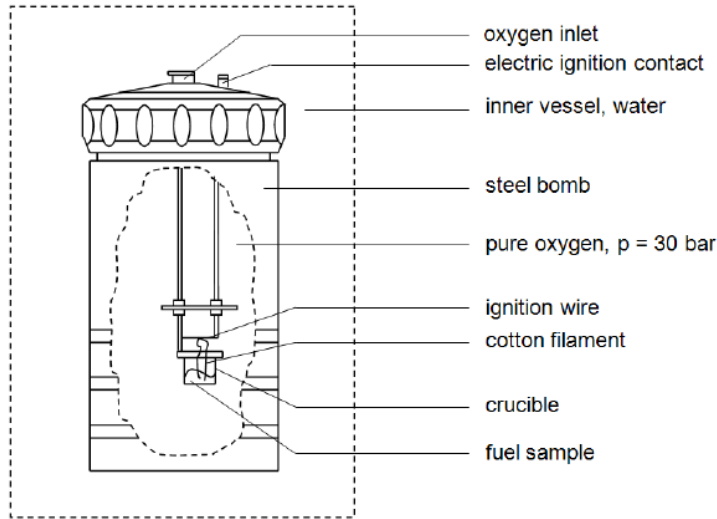


Figure 5-2 The steel bomb in the calorimetric system [37]

About 1 gram of dried fuel or additive, or as much as the crucible size allows, is weighed and placed in a crucible. A cotton filament is working as a fuse between an electric ignition wire and the crucible with the sample. When the measuring procedure starts, the steel bomb is filled with pressurized oxygen at 30 bars to optimize the combustion process, and the sample is ignited. The heating value is determined by measuring the heat increase in the water surrounding the steel bomb, and calculated with the equation:

$$HHV = \frac{c_{H_2O} \cdot \Delta T - Q_e}{m} \quad (5.3)$$

Where  $Q_e$  is the heat contribution from the cotton filament and  $c_{H_2O}$  is the heat capacity of the water.

The sample needs to be completely dry in order to measure the higher heating value. The lower heating value is possible to calculate from the formula:

$$LHV = HHV - \Delta h_{v, H_2O} \cdot r(H_2O) \quad (5.4)$$

#### 5.2.3.1 Results

For every fuel and additive, two or three measurements were performed depending on the difference between the first two samples. The heating value was not measured for clay as Uwe Dunkel already has determined this to zero [37]. The average value is shown in Table 5-5 and all the results in Appendix C. Equation 1.1 is used to calculate a theoretical HHV, based on the results from the ultimate analysis.

Fuel/additive	HHV (MJ/kg d.b.)	
	Measured	Calculated
Pellet	19.9	20.6
Straw	18.5	19.2
Sewage sludge	11.6	11.2
Paper sludge	20.7	20.1

**Table 5-5 Results from measuring and calculation of HHV.**

Sewage sludge has a good heating value, while the paper sludge has a very good heating value, actually higher than both fuels. However the paper sludge has a high moisture content which is decreasing the heating value.



# 6 Laboratory melting and sintering experiments

The purpose of the laboratory experiment is to evaluate the effects on the ash melting temperature from the different additives. Full scale testing is necessary to conclude whether or not an additive is usable, but laboratory work is much less time consuming and work intensive, and will probably give a good indication on whether or not the additive is worth testing in a full scale experiment.

## 6.1 Ash melting

### 6.1.1 Preparation of ash with additives

Ash samples of pellet and straw with different additives were made. Samples consisted of wood pellet or straw with either sewage sludge, pure calcium carbonate, marble sludge, paper sludge or clay.

The straw used was already cut in pieces of about 2 mm and the calcium carbonate is in a form of fine powder. The wood pellet, clay, paper, sewage and marble sludge was either crushed in a mortar or milled before blending, as before the proximate analysis. The samples consisted of 5 g of fuel and either 3, 5, 7 or 10 percent of additives (0.15, 0.25, 0.35 or 0.5 grams). The addition was based on weight percent at wet basis, except for marble and paper, which was first dried as the initial moisture content was so high. As it was difficult to obtain the exact amount of desired additive amount, the blending was between 0.01 percent lower or 0.03 percent higher than the exact amounts. The fuel and additives were thoroughly mixed to obtain a homogeneous mixture. Two identical samples were made for each fuel, additive and additive amount. A sample identifier code was made in order to keep a system of the different samples. The identifier description is shown in Appendix D.

The mixtures were then burned in the oven at 550 °C, after the same procedure as described in section 5.2.1.3. After cooling, the ash was stored in small, sealable plastic bags.

## 6.1.2 Experimental method

The ash was melted in a Carbolite Coal Ash Fusibility Furnace according to the ISO 540:1995(E) standard. This was used to identify the melting temperatures for the different ash samples.

The ash was packed into small cubes of about  $9 \text{ mm}^3$ , placed on a holder and inserted into the fusibility furnace. A picture of the inserted ash cubes are shown in Figure 6-2. The temperature was gradually increased with about  $6 \text{ }^\circ\text{C}/\text{minute}$  until it reached 1550 degrees. The melting behavior was recorded by a camera taking pictures through an inspection hole for every second degree increase. The pictures was manually viewed later to determine the different melting temperatures. Four different temperatures are registered: deformation (DT), softening (ST), hemisphere (HT) and flow temperature (FT). Figure 6-1 show the definition of the shapes at the different temperatures.

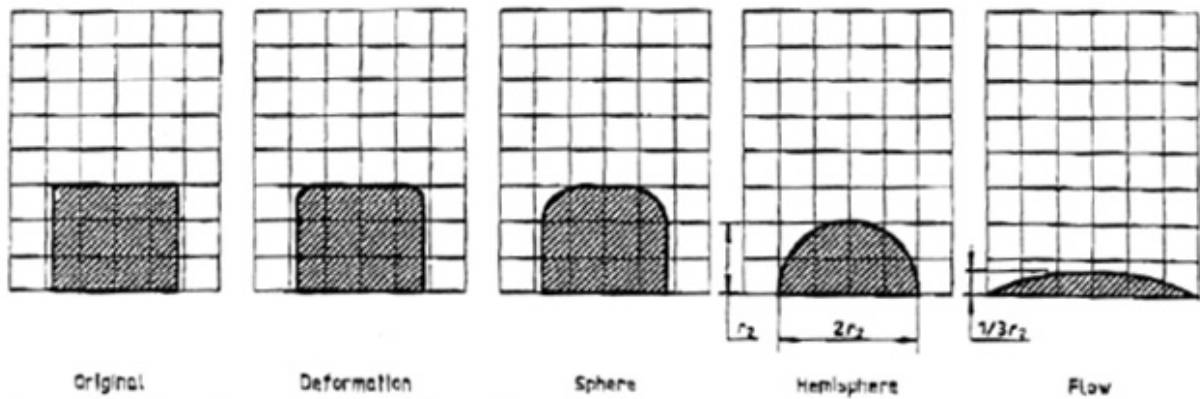


Figure 6-1 Characteristical shapes of the melting ash cubes according to ISO 540:1995(E).

Figure 6-2 show pictures of an ash sample recorded of the digital camera at 1000, 1150, 1300 and 1500  $^\circ\text{C}$ . The samples consist of pure wood pellet from Sykkylven, and the same pellet with 3, 5, 7 and 10 percent addition of sewage sludge. From the pictures it is obvious that the sewage sludge is able to increase the melting temperature.

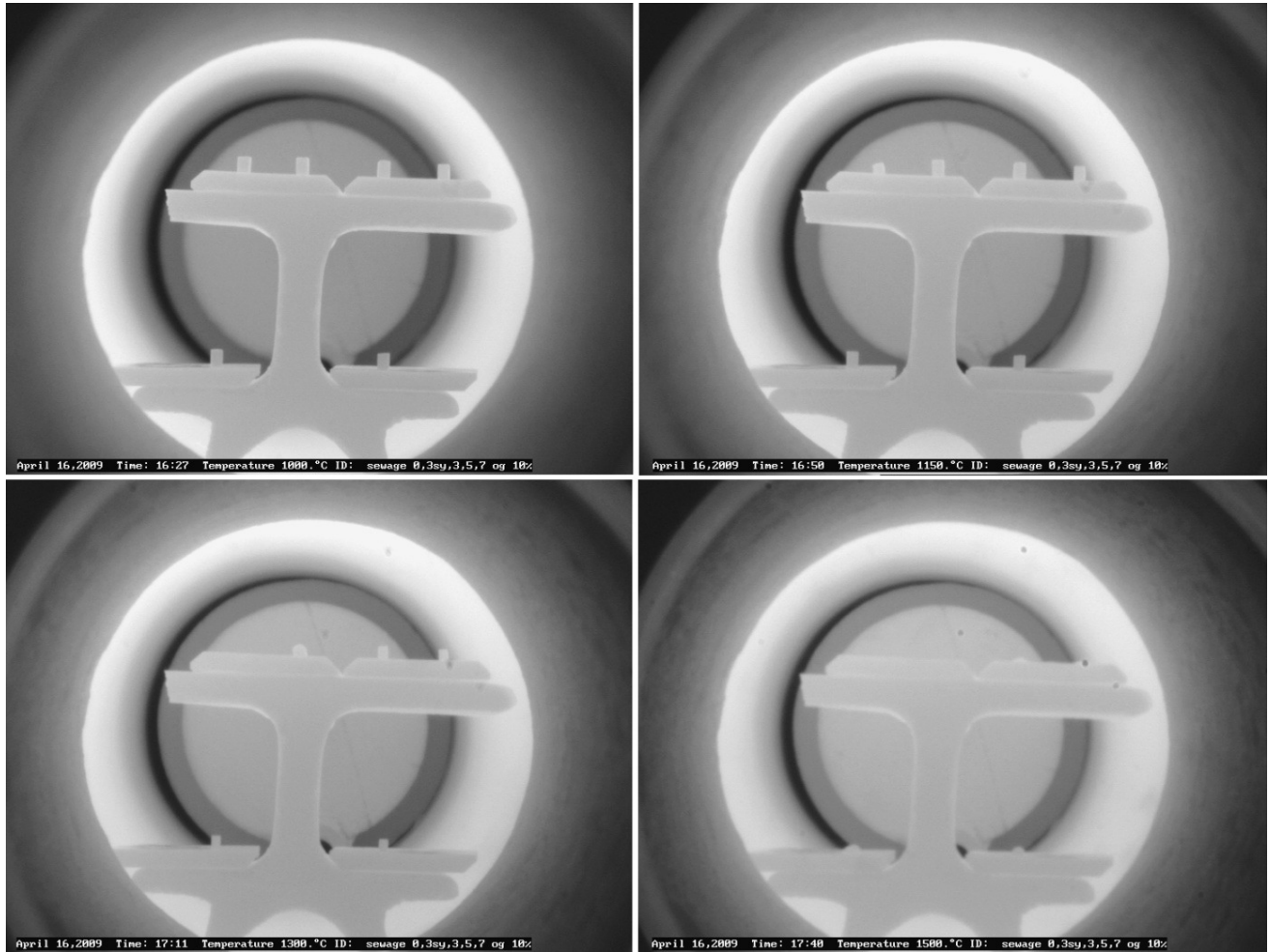


Figure 6-2 Pictures at different temperatures of pellet ash with 0, 3, 5, 7 and 10 percent addition of sewage sludge from the ash fusibility furnace camera.

### 6.1.2.1 Uncertainties

This method of deciding the melting temperatures are connected to some uncertainties. When the temperature increases, the samples rarely behave like the sample in Figure 6-1. They often shrink before the edges are rounded, while according to the definition, the edges are rounded before the sample shrinks. Some samples shrink to ½ of the height while still maintaining sharp corners. The resolution of the camera is low and it is difficult to obtain a good focus on the samples as the heat radiation affects the focus. In addition, a bad attachment of the camera makes the camera holder to slide when the temperature reaches 800 - 900 °C.

The consequence of all this is that it is difficult to make a good registration of the initial deformation temperature, mostly because the difference of the ash deformation at this stage is so small. Nevertheless, these uncertainties apply to all tests and as all the samples are exposed for two independent tests, the results have to be considered as good and usable.

Another method of deciding the melting temperatures is by Mapping Area Fraction (MAF). A small sample is placed at a transparent plate and slowly heated at a constant rate. A light source is placed at one side of the plate, and due to the fact that melted ash becomes transparent, a

sensor at the other side will register the amount of melted ash at any time [27]. This method is better as it does not imply the uncertainty of manual observation.

A drawback of both these methods, compared to real life boilers, is a slow melting rate. The effect of kinetics is an important factor of the ash sintering behavior, and will not be included in these methods. The melting of ash cubic samples will neither give realistic melting temperatures as the cubes are formed by mechanical forces that will influence the heat conductivity and interaction with different particles. This imply that ash fusion test in the laboratory normally gives higher melting temperatures than the real melting temperatures. Ash fusion tests in an Entrained Flow Reactor (EFR) will give a more realistic melting behavior as the fuel is burned in a more similar way compared to real boilers. The EFR is however a big and expensive reactor and the closest one available is in Denmark.

### 6.1.3 Results

Each ash sample were used to produce one cube, which results in two ash melting results for each fuel, additive and additive amount. These results were used to produce the following graphs, showing the upper and lower melting temperature for each sample. All results are possible to contemplate numerically in Appendix F.

#### *6.1.3.1 Pellet with additives*

Figure 6-3 shows influence of type and amount of different additives on wood pellet ash melting behavior.



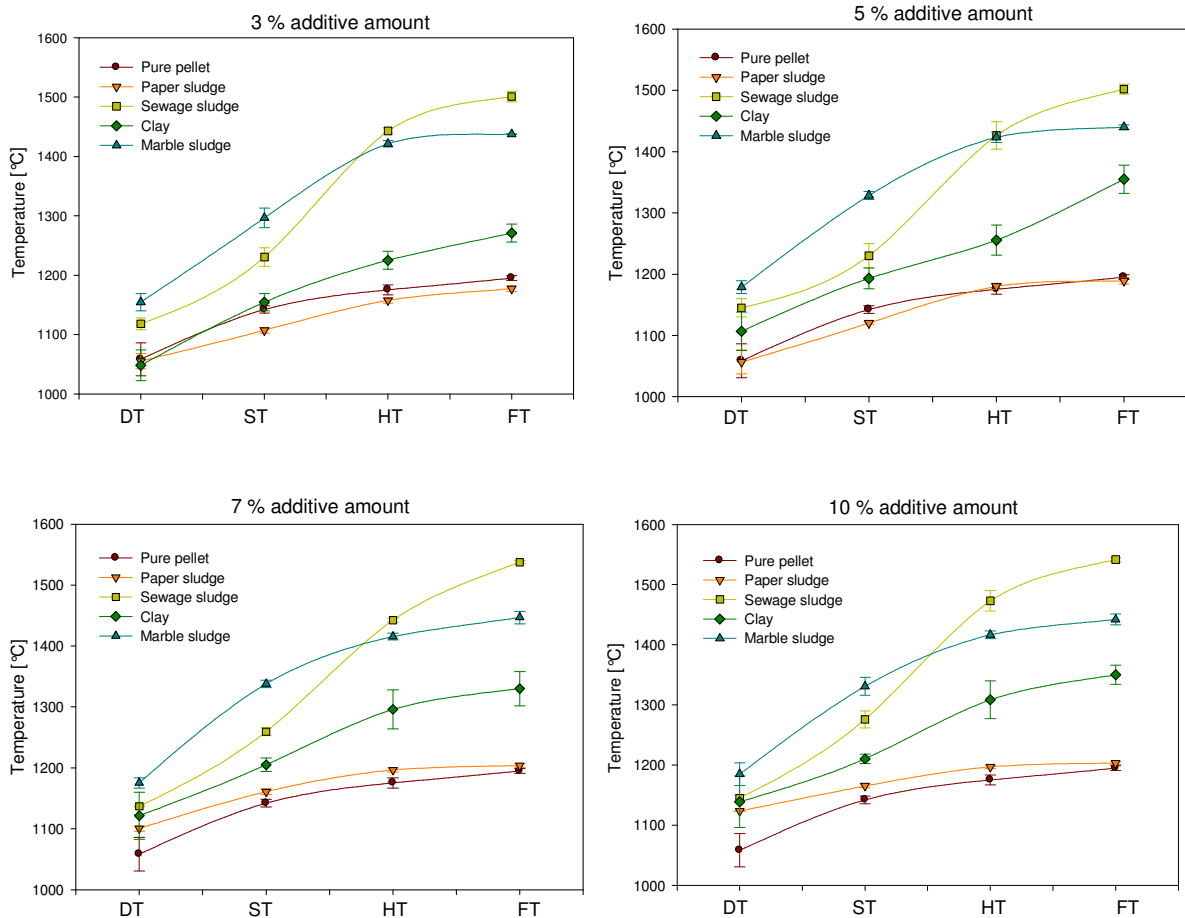


Figure 6-3 Influence on ash melting behavior of different additive amounts, on pure wood pellet and wood pellet mixed with different additives.

The pellet from Sykkylven has relatively low melting temperatures, starting at around 1050°C for the initial deformation temperature and ending at a flow temperature below 1200°C. Compared to pure spruce wood, which has a DT between 1110 to 1340°C and FT above 1700°C [4], these temperatures are low. According to the results, marble and sewage sludge is the most effective additives in order to increase melting temperatures. Clay is helping to some extent, while paper sludge will for mixtures of 3 and 5 percent reduce the melting temperature.

For practical utilization the deformation and softening temperature are the most important temperatures, as the problems with ash sintering and agglomeration arise at this point. The temperature of the ash rarely reaches the temperatures needed to obtain the hemisphere and flow temperature, although if it does it will cause big problems involving grate cleaning.

The influence of the different additives becomes clearer as the temperature rise. The substantially high hemisphere and flow temperatures for marble and sewage sludge, gives an indication for their effectiveness for making high melting compounds, even though the difference from other additives are not that great for the deformation temperature. The effect of this in real life grate combustion is difficult to predict and has to be tested in order to make a conclusion.

Most of test results shown in Figure 6-3 indicate that additives can increase wood pellet ash melting temperature, but the effect of increasing additive amount are shown more clearly in Figure 6-4.

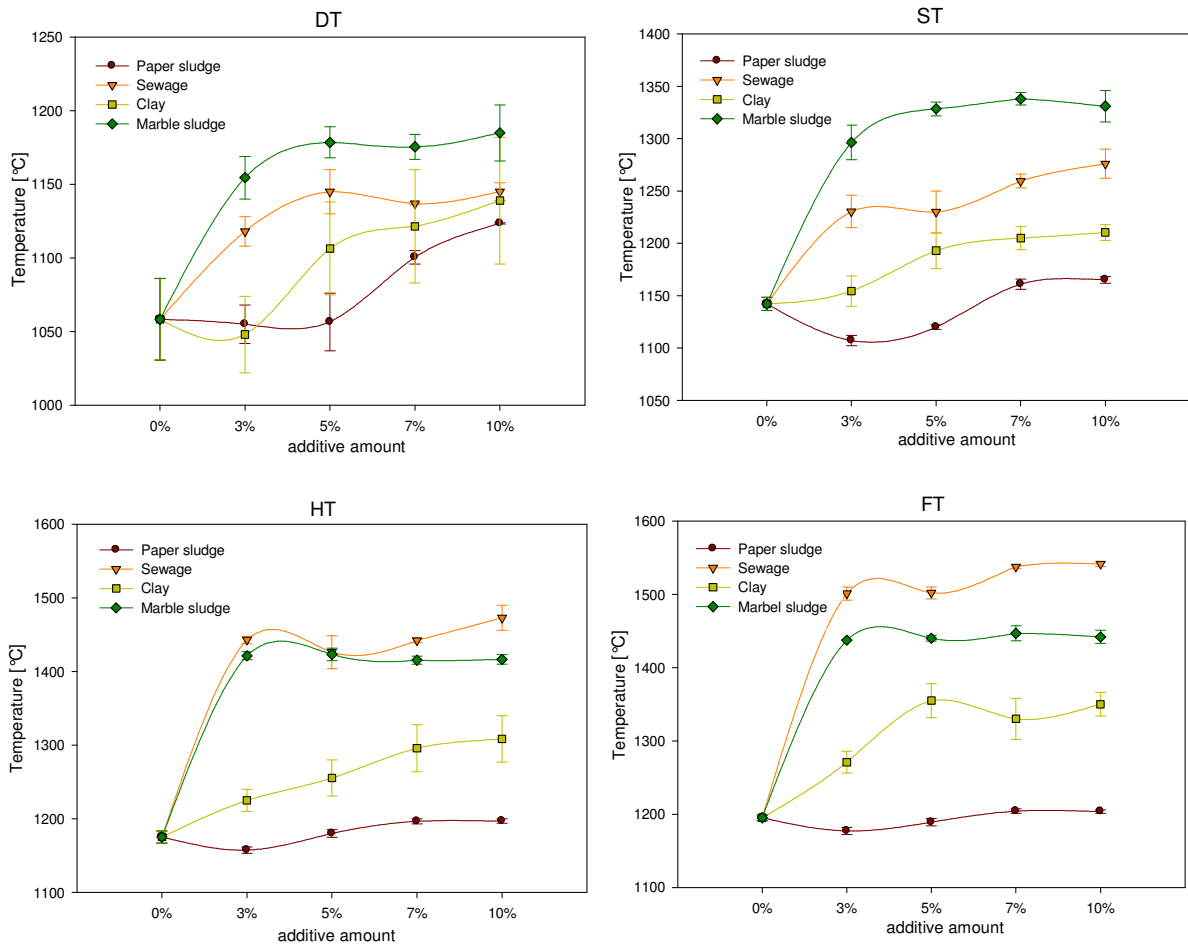


Figure 6-4 The effect of additive amount on deformation, softening, hemisphere and flow temperatures on wood pellet.

Higher additive amount will lead to higher melting temperature, however the increase is considerably lower than one could expect. This is probably because the additive concentration in the ash is already very high at 3 percent addition. The effect of a higher additive amount is most obvious at deformation temperature for clay and paper sludge.

Even though the graph shows a slightly lower DT for 7 percent sewage sludge compared to 5 percent, these results are probably not representative. The same argument is probably valid for the results with marble and clay for HT and FT as well.

These results are interesting because the effect of melting temperature increase is substantial already at 3 percent addition. A low amount of additives is desired as the additives will reduce the heating value of the fuel and are more expensive. The graphs show that the additive concentration is probably much higher than needed as the difference between 3 and 10 percent is very small.

In order to test the influence of addition amount of additives on the pellet ash behavior in an industrial boiler, an additive amount of 3 and 7 percent will be included in the full scale test.

### 6.1.3.2 Straw with additives

Figure 6-5 shows the effect on the characteristic melting temperatures for different amount of additives added in what straw.

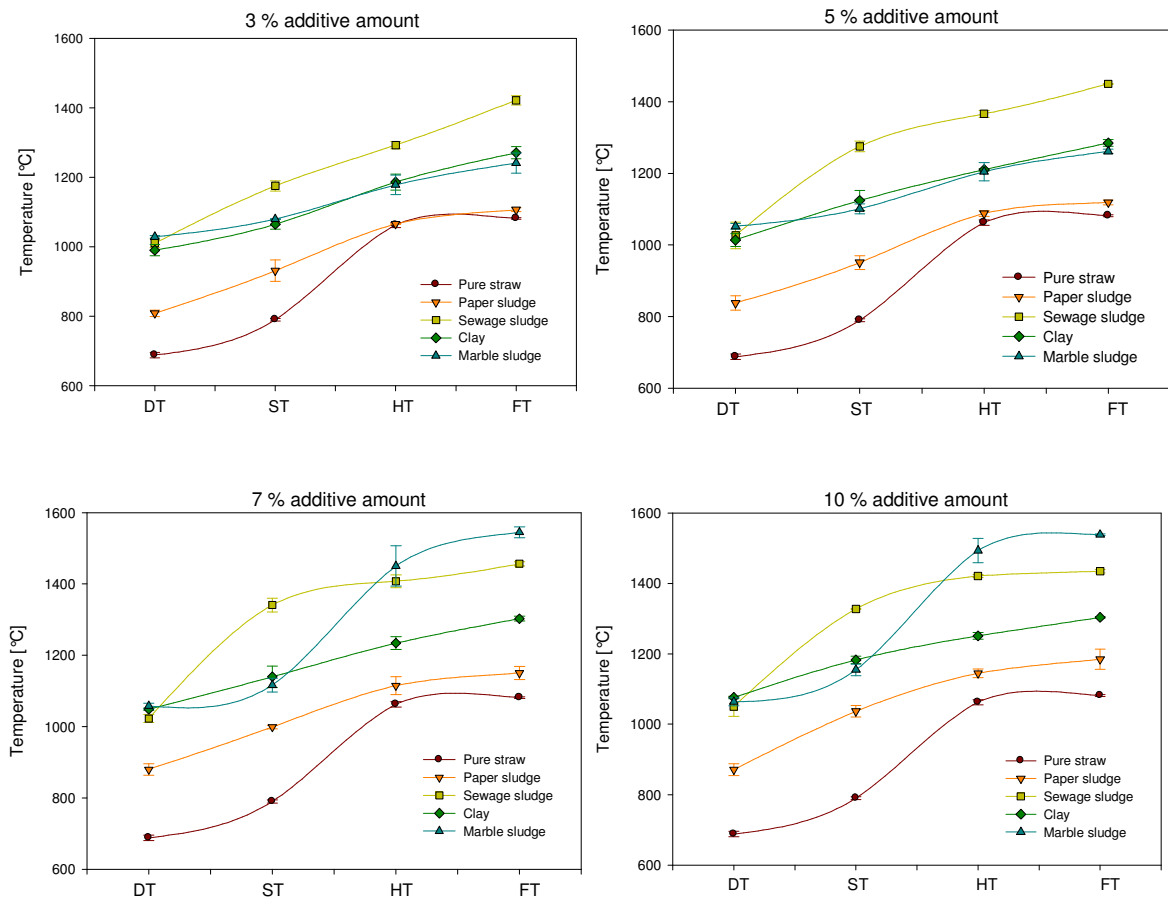


Figure 6-5 Influence on ash melting behavior of different additive amounts, on pure wheat straw and wheat straw mixed with different additives.

The tested straw has a deformation temperature at around 690°C and a flow temperature at 1080 °C, and is thus a very problematic fuel to utilize for combustion purposes. The melting temperatures are slightly lower than a tested wheat straw from Austria, which has a DT above 800°C and a FT around 1100°C [4].

Sewage and marble sludge are probably the most effective additives according to these results. Clay could be as effective as marble because of a similar increase in DT and ST. Addition of paper sludge shows an interesting increase in DT and ST, and could have a positive effect as an additive, in comparison with paper sludge in wood pellet.

The most interesting effect is the clear increase in the deformation and softening temperatures, which are probably the most important temperatures for combustion purposes.

The straw ash FT are almost as low as the HT, as the ash started boiling just after reaching HT, and the ash was considered flowing when this started.

With addition of marble sludge, melting properties of straw has a large variation. This could be a consequence of an unhomogeneous mixture, as the marble sludge had a tendency to agglomerate even though it was crushed into fine powder. The effect of this was obvious at HT and FT for some experiments, and these results should therefore be considered with some uncertainty.

Figure 6-6 shows the effect on the characteristic melting temperatures of straw ash from the different amount of additives added.

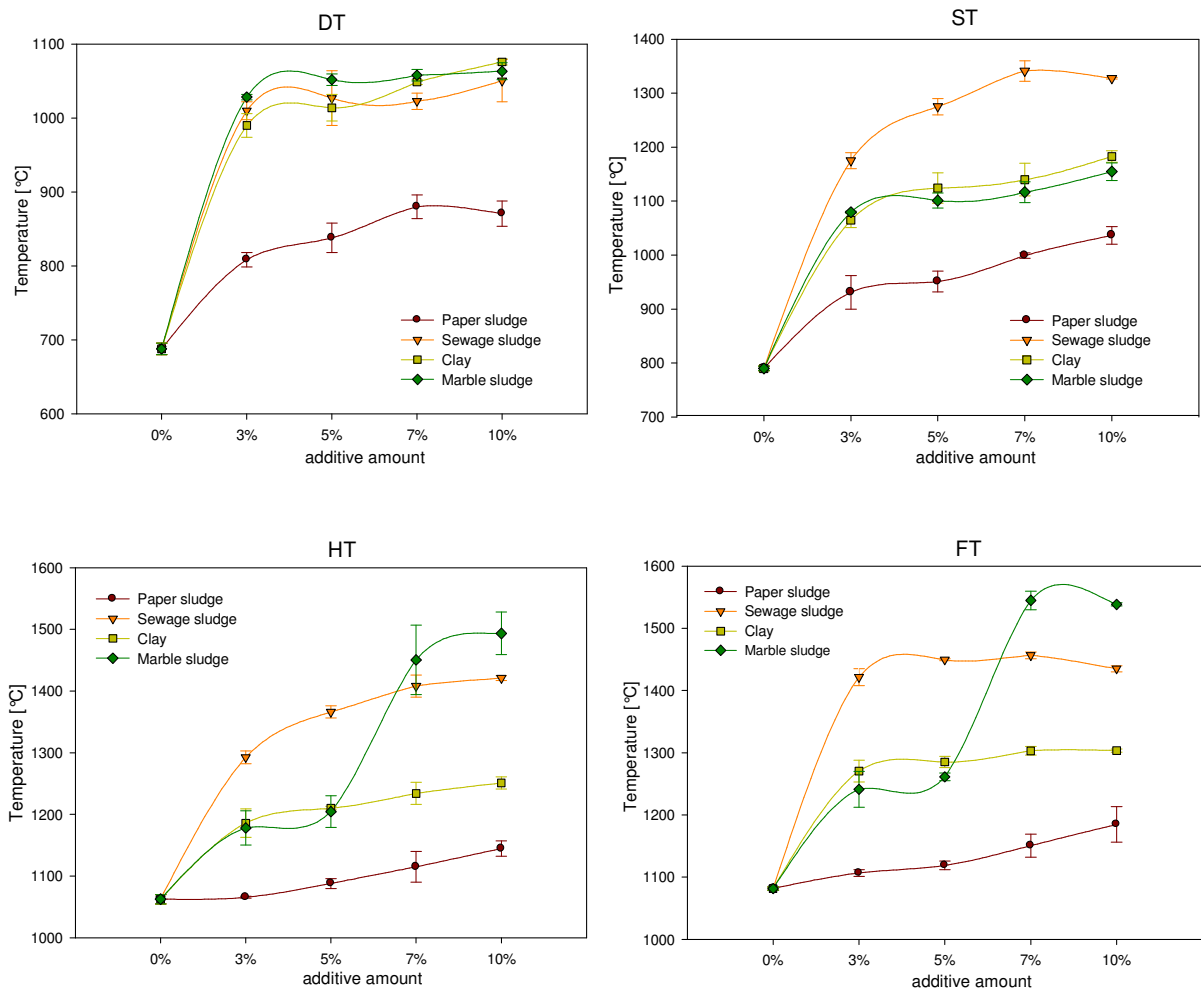


Figure 6-6 The effect of additive amount on deformation, softening, hemisphere and flow temperatures on straw ash.

The melting temperatures are slightly increasing with increasing amount of additives, but not as much as one could expect. As the straw contains about 6 percent of ash, the additive to fuel ash ratio is drastically reduced compared to wood pellet.

The high concentration and high melting temperature results for marble sludge are, as noted earlier, probably affected by bad mixing and should be considered with some uncertainty.

Although the pure calcium carbonate, which was easier to mix, also increased the melting temperature drastically at HT and FT.

### 6.1.3.3 Pure additives

In order to investigate the influence of the different additives on the fuels, the melting temperatures were identified. Figure 6-7 show a highly interesting melting profile for the additives used in the experiment.

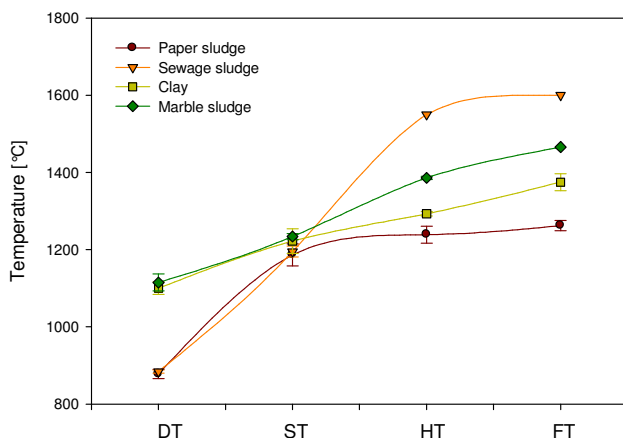


Figure 6-7 The different ash melting temperatures of the four additives in for testing.

The melting temperatures are more or less in coherence with those obtained in the fuel and additive mixtures. The exception for this is sewage sludge, which has a very low deformation temperature. The complex composition of sewage sludge is probably the explanation for the low DT and high HT/FT. Compared to homogeneous substances as marble sludge, sewage sludge obviously contains low melting as well as high melting components. However it is kind of suspicious that the sewage sludge are able to raise the DT for wood pellet as much as Figure 6-3 shows. The flow temperature for sewage sludge, in Figure 6-7 marked at 1600°C, is assumed as the ash barely reached the HT-shape at 1550°C which is the maximum temperature for the oven.

The HT and FT of paper sludge are low, helping to explain the low increase in these temperatures for mixtures with wheat straw.

### 6.1.3.4 Behavior of marble compared to $\text{CaCO}_3$

The calcium carbonate was included to compare how this additive behaves compared to marble sludge. As marble sludge contains 98 percent  $\text{CaCO}_3$ , marble sludge and pure  $\text{CaCO}_3$  should behave the same. Limestone and calcite are both popular  $\text{CaCO}_3$ -based additives, and pure  $\text{CaCO}_3$  could therefore be used as a reference to compare marble sludge with these additives.

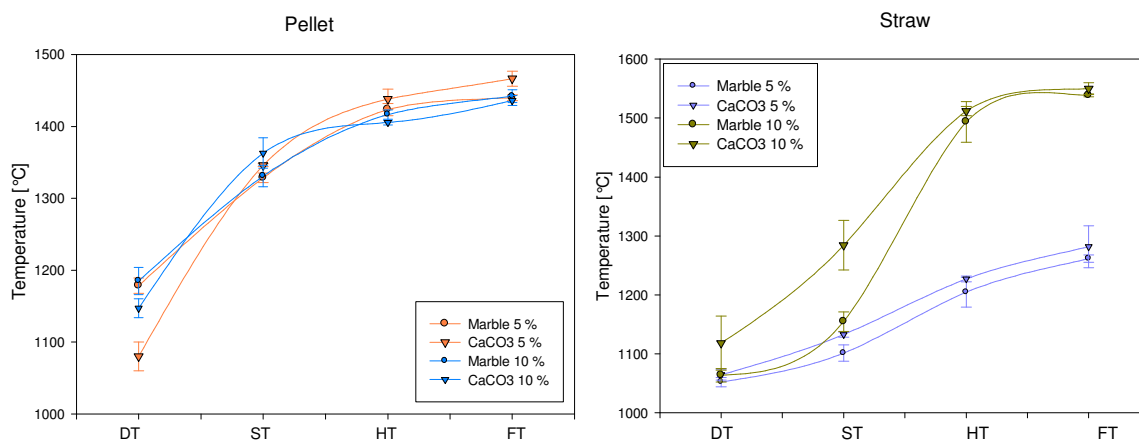


Figure 6-8 Characteristic melting profiles of marble sludge compared to pure  $\text{CaCO}_3$ .

Figure 6-8 show that there is a good correlation between marble sludge and  $\text{CaCO}_3$  in terms of melting profile. The figures show melting temperatures for 5 and 10 percent addition of additives, although all concentrations have a good correlation. An interesting observation is that marble sludge seems to have a better effect of raising the DT for pellet than pure  $\text{CaCO}_3$ . This observation is valid for all four concentrations of marble and  $\text{CaCO}_3$ , but could be an experimental error.

## 6.2 Sintering test

The initial deformation temperature observed from the ash melting will give an indication of the sintering tendency of the ash. However it is not possible to evaluate the stickiness and hence the agglomeration tendency by this method. Sintering tests in a muffle furnace was therefore performed, as it is then possible to combust the biomass at a given temperature, and then physically evaluate the resulting ash.

Mixtures of fuels and additives were burned in a muffle furnace, with same procedures as described in subchapter 5.2.1.3, to investigate the ash sintering tendency. The combustion temperature was set to 750 and 1000 °C for straw and 1100 and 1200 °C for wood pellet, because this is the temperature range where deformation of the ash occurs according to the melting experiments. 1200 °C is also the highest obtainable temperature at the laboratory ovens. The amount of fuel and additive was about 30 g for each sample with wood pellet and 20 g for straw. For the mixture of wood pellet with sewage and marble sludge, the mixture made at Sykkylven, described in subchapter 7.1, was used. For the other fuels and additives, mixtures with given additive amount was made in the laboratory.

After combustion, the state of the ash and degree of sintering and agglomeration was observed. According to these observations, four different classifications of the ash were made. Loose ash (LA) is used when no sintering of the ash has occurred. Weak sinter (WS), when there is a tendency of the ash sticking together. Medium sinter (MS) is used when the ash has sintered

together but is easily breakable. Hard sinter (HS), referring to the formation of hard slag particles.

### 6.2.1 Results

The results from the sintering tests are shown in Table 6-1 and pictures from some of the mixtures are found in Appendix G.

		Wood pellet		Sewage sludge		Marble sludge		Clay		Paper sludge	
				4 %	8 %	4 %	8 %	4 %	8 %	4 %	8 %
1100 °C	LA	WS	MS	LA	LA	HS	HS	WS	WS		
1200 °C	M	MS	HS	WS	LA	-	-	M	M		
		Straw		5 %	10 %	5 %	10%	5 %	10 %	5 %	10 %
750 °C	MS	WS	WS	LA	LA	WS	LA	WS	WS		
1000 °C	M	HS/MS	MS	MS/LA	LA	HS/MS	MS	M	M		
1100 °C	-	-	-	MS/LA	WS	-	-	-	-		

Table 6-1 Results from sintering tests of wood pellet and straw with additives. LA = loose ash, WS = weak sinter, MS = medium sinter, HS = hard sinter, M = melted.

All additives had an effect on the sintering tendency on the wood pellet, with marble sludge being the only one that reduced the sintering. Sewage sludge slightly increased the sintering, while clay sludge formed hard slag at 1100 °C and was therefore not tested at 1200 °C. Pure wood pellet melted at 1200 °C, while the mixture with sewage sludge combusted at 1200 °C formed medium or hard sintered ash, and could in theory reduce the ash problems as melted ash on the grate is more problematic than sintered.

From these results it is obvious that the additives have a better effect on the sintering of straw. At 750 °C ashing temperature, all additives had a clear positive effect with marble sludge being the best, and clay second best. For an ashing temperature at 1000 °C, the pure straw had melted and even evaporated, judging from the form and weight of the ash. This was also the case for straw with paper sludge. Some of the straw ash with additives was of a heterogeneous form, consisting of either hard and medium sintered ash, or medium sintered and loose ash. This might be caused by an uneven distribution of the additives and/or varying temperature conditions in the lids. Because of the good results from marble sludge, this additive was also tested at 1100 °C.

These results can be compared to the study of M.J Fernández Llorente et al. who performed similar tests with different problematic fuels such as thistle, barley straw and almond shell, and potential additives [20]. The study and results are presented in chapter 4.

## 6.3 Elemental and compositional analysis of the ash

### 6.3.1 XRF analysis

X-ray fluorescence (XRF) is a method for identifying elements in the ash. Ash of pure pellet and straw, and these fuels mixed with sewage and clay is analyzed. The results can be viewed in Appendix I.

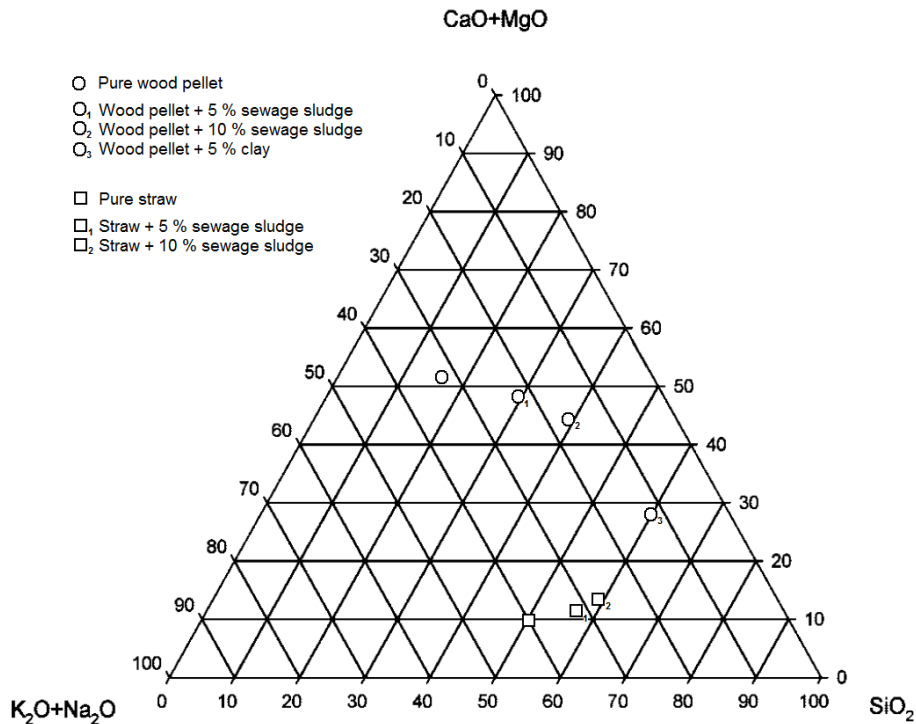


Figure 6-9 Elemental distribution of the formed ash, from pure fuel and fuel mixed with additives with 550 °C ashing temperature.

An XRF analysis of pellet and straw ash with additives show a substantial reduction in the potassium and sodium content of the pellet ash when this is blended with sewage sludge and clay. This is illustrated graphically with Figure 6-9. The potassium content in the straw ash is reduced, but obviously the initial amount is large and 5 percent addition of sewage sludge is not sufficient.

### 6.3.2 XRD analysis

X-ray powder diffraction (XRD) is an analysis method of deciding the crystalline phases formed in the ash. While an XRF analysis mainly gives information about the dilution of the ash because of the additives, an XRD analysis shows the result from any reactions between the fuel and the additives. This is interesting because, as explained in chapter 4, the crystalline phases formed in the ash determine the melting temperature of the ash. Because of a lack in time at the end of this project, only wood pellet with sewage and marble sludge and straw was sent for



XRD analysis as these were the most interesting and the most effective additive respectively. This is neither an important part of the analysis as it includes difficult inorganic chemistry.

The XRD patterns are viewable in Appendix J.

The XRD analysis of pure wood pellet and straw ash reveal why straw has much lower melting temperatures than wood pellet. Sylvite and arcanite melt at 772 and 1069 °C respectively, and are present in great amount in the straw ash. The XRD patterns of pure wood pellet ash reveals little information about the melting of this ash below 1200 °C for neither 550 nor 1000 °C. The presence of potassium aluminum silicate  $\text{KAlSi}_3\text{O}_8$  which has a melting point at 1600 °C is clear but can hardly be blamed for causing the ash melting problems. The ash made at 550 °C show some trace of albite ( $\text{NaAlSi}_3\text{O}_8$ ) and microcline ( $\text{KAlSi}_3\text{O}_8$ ), but interestingly these are not shown in the ash made at 1000 °C.

The analysis of wood pellet with 5 percent sewage sludge also show a nice amount of  $\text{Ca}_9\text{MgNa}(\text{PO}_4)_7$  with an unknown but probably high melting temperature. The creation of  $\text{Al}_2\text{O}_3$  is also quite obvious, although the melting temperature of this is 2054 °C [38]. Albite and microcline has returned in this pattern, and are probably the cause of the high melting temperatures.

Wood pellet ash with 5 percent addition of marble sludge is dominated by lime, CaO, and is probably causing the high melting temperatures for this ash. The only phases containing sodium or potassium is “sodium magnesium aluminum silicate” and muscovite. Microcline and albite are no longer present in the ash.

## 6.4 Laboratory discussion

The results from the laboratory experiments could be compared to the studies of Xiong et al., Llorente et al. and Öhman et al. described in chapter 4. A brief comparison between the additives in this project and those used in the three studies, shown in Table 4-1, is already discussed in chapter 5. Marble sludge should behave more or less the same as lime, and to some extent limestone. Clay is expected to be comparable with kaolin, and especially ophite. Sewage and paper sludge has a composition that is probably not very comparable of any of the additives presented.

Regarding the melting experiment, the results from Xiong et al. stay in contrast to those obtained in the experiments in this thesis, assuming that clay is somewhat similar to kaolin and marble is the same as calcite. Xiong experienced higher melting temperatures with kaolin than calcite, while marble was more effective than clay in terms of raising the ash melting temperature for wood pellet in this thesis. For wheat straw ash, marble and clay was about equally effective.

It is obvious that the experiment with the melting furnace has some shortcomings when it comes to ash sintering and agglomeration. While both sewage sludge and clay sludge increased the initial deformation temperature, these additives increased the sintering and agglomeration

tendency. The sintering test showed that marble sludge has significant improvements in terms of reducing the sintering tendency of the wood pellet, in accordance to the melting experiments. It is highly possible that there is a deformation of the ash at lower temperatures than registered in the melting furnace for wood pellet with sewage and clay, considering the uncertainties in this method.

While Llorente et al. experienced less sintering with adding kaolin than limestone, Xiong et al. showed that calcite is more effective than kaolin. Öhman et al. discovered increased sintering problems when using kaolin rather than limestone. The results from the last two studies are more in accordance with those obtained in this thesis, where the Ca-based additive (marble sludge) is more effective than the Al-Si- based additive (clay). Clay was also an effective additive when added to wheat straw, while mixed with wood pellet it increased the sintering problem. There is no doubt that the fuel used is affecting which additives that is effective. Small changes in the composition of the different additives will possibly also affect the effectiveness of the different additives, which is obviously the case for the Al-Si based additives kaolin, ophite and clay.

Sewage sludge has previously not been used as an additive to increase the melting temperatures of ash, thus it is difficult to compare the obtained results. Nevertheless it is clear that the sewage sludge did not show as good results as expected for wood pellet sintering. The performance of sewage sludge was better, and about equal to clay, when it was used as an additive in wheat straw. The bad results for the sintering test of sewage and wood pellet might have a correlation with the low ash DT for pure sewage sludge. The relatively high DT for sewage and wood pellet ash is suspicious and it is highly possible that a deformation at a lower temperature than registered has occurred.

Despite potentially good additive properties, according to the elemental composition, paper sludge did not increase the melting temperature for wood pellet, except for 7 and 10 percent addition of paper. This is probably explained in the low amount of ash in paper sludge which increases the amount of additives needed. 10 percent addition of paper sludge corresponds more or less to 1:1 in terms of additive and fuel ash, which is often the minimum amount of additives needed. A paper sludge amount of around 15-20 percent is probably needed in order to evaluate the effect of this as an additive in the wood pellet. However paper sludge as an additive performed well together with wheat straw, except for little effect for HT and FT. Nevertheless, the increase in DT and ST might show that this is an effective additive together with wheat straw as long as the temperature is kept below 800 - 900 °C.

XRD analysis of the ash gave little information about the low melting temperature for wood pellet. It is possible that an XRD analysis of the ash made at 1100 °C is necessary. The reason for the high melting temperature wood pellet and sewage sludge ash is probably found in the potassium aluminum silicates formed. It was not possible to find any low melting compounds causing the discovered sintering problems with sewage sludge ash.

Laboratory experiments of the melting temperature and the effect of additives are interesting, but does not give a holistic picture of the additive affect when combusting in real boilers. Most of the literature dealing with these problems usually contains ash samples from boilers, in addition to laboratory melting experiments [30, 31]. To conclude whether or not the tested

additives will have a sufficient effect on the ash sintering problems, full scale testing of pellet with additives are needed.

Full scale experiments will be performed with sewage and marble sludge as additives, as these additives show the best results in the laboratory melting experiments. Sewage sludge has also a good heating value and has therefore a double utilization effect when it is combusted.

The idea with sintering test of the fuels and additives was not realized until after the full scale experiment in Sykkylven, and was not included in the appreciation about which additives to use here. Because of a lack of time the sintering test also became somehow incomplete, and it would have been very interesting to expand this test with more additive ratios and temperatures.



## 7 Sykkylven experiment

The specific wood pellet investigated in this thesis is utilized in several boilers in the area around Sykkylven. Some of these boilers are experimenting ash related problems, depending on the grate technology in the boiler. Boilers with moving and water-cooled grate elements does not experience problems with the wood pellet ash, while boilers with a fixed grate and elements pushing the fuel forward is experiencing severe ash sintering and agglomeration, causing the need for manual maintenance almost every week. With water-cooled grates it is possible to control the temperature level and reduce the formation of hot-spots which will induce sintering. There is no deviation in the problems if the boiler is running in part load operation or the primary air supply is increased.

The experiments were performed together with Geri Skjevraak and Liang Wang from NTNU.

### 7.1 Experiment preparation

Based on the results from the laboratory work, it was decided to add additives to the problematic wood pellet and burn this in a boiler experimenting problems with ash sintering. The boiler is located at the Ekornes furniture factory in Sykkylven, which produces hot water to the local heat distribution system at the factory. The boiler is a 1200 kW TPS Stepfire with a fixed grate and moving scrapes, distributing the fuel and pushing the fuel bed along the grate.

The experiments were decided to last for six hours, to be able to obtain stable conditions in the boiler and possibly produce enough sintered ash to be able to compare the fuel with and without additives. A total of five rounds were intended: one round of pure wood pellet as a reference round, and four rounds of wood pellet with the addition of sewage and marble sludge each containing two different concentrations of the additives. The additives were added between the milling of the fuel and the pellet production, in order to obtain a good mixture of the additives in the pellet. The primary goal was to mix pellet with 3 and 7 percent additives, but as the dosage controlling was difficult, the result was about 4 and 8 percent of additive mixture. An evaluation of the additive mixture is found in Appendix H. Nevertheless this is also highly interesting mixtures. The marble sludge was pre-dried to around 10 percent moisture level, while drying of the sewage sludge was not needed as the moisture level is as low as 9 percent. Two tones of pellet for each round were made in order to secure sufficient fuel to the experiments. The pellet and additive mixturing was performed by Liang and Geir.

Day/ round	Fuel	Boiler load
1	Pure wood pellet	100 %
2	Wood pellet + 4 % sewage	100 %
3	Wood pellet + 8 % sewage	100 %
4	Wood pellet + 4 % marble	100 %
5	Wood pellet + 8 % marble	100 %

Table 7-1 Matrix showing the intended plan for experimental test rounds in Sykkylven

Initially it was intended to also run the boiler in part load operation and increase the primary air supply to see if this would reduce the sintering. Considering the time needed for running, cooling and cleaning the boiler after each experiment, it was not possible to do this during the five days available for experiments. However, according to the operator of the boiler, the ash slagging is just as severe when the boiler is running in part load operation or when the primary air inlet is increased.

The temperature profile on the grate is quite interesting in order to evaluate both the relationship between temperature and sintering, and the effect on the temperature from the additive addition. As the heating value of marble and sewage sludge is 0 and 11.6 MJ/kg (d.b.) respectively, the temperature is expected to decrease. A lance with eight thermoelements was installed 20 cm above the grate to record the temperature profile. Four of the thermoelements was of type K, and four others of type S. Type S thermoelements contains platinum and is much more expensive, but can also tolerate higher temperatures and was therefore used in the grate section where the highest temperatures was expected. The distance between each thermoelement was 25 cm, and none of them were placed over the primary air nozzles as this would disturb the temperature measurements. The lance was inserted through a hole for the ignition mechanism, welded on the other side of the boiler and supported in the middle with a bar. Ideally it would be best to measure the temperature at the grate, but this was found not possible with the available equipment. The temperature recorded 20 cm above the grate is assumed to be the same as at the grate, but this could off course be wrong. Four other thermocouples were installed around the boiler, just above the grate and before, during and after the heat exchanging system. The temperature was logged with a logger unit, computer and the program LabView. An illustration of the placement of the lance and other thermoelements in the boiler can be seen from the figure in Appendix K.

A flue gas analyzer, Testo 350 XL, was used to measure the CO, O<sub>2</sub>, SO<sub>2</sub>, NO and NO<sub>2</sub> levels in the flue gas, in order to evaluate the influence of the additives on the burning conditions. The probe was inserted between the heat exchanger and the cyclone. As these additives might have the ability to reduce corrosion, it would be interesting to measure the emissions of HCl, KCl and NaCl as well, but the measurement equipment for this was not available. Neither was equipment to measure the heavy metals in the flue gas, even though the emissions of these will probably increase because of high heavy metal content in the sewage sludge.

## 7.2 Experimental runs

Before each experiment, the boiler was thoroughly cleaned, even with a vacuum cleaner, to ensure that no ash was left from the previous round, and to obtain a good comparison of the ash between the rounds. A picture of the clean boiler can be enjoyed in Appendix L.

The first experiment was run with pure wood pellet and stopped five hours after stable conditions occurred in full load mode. After the boiler had cooled down, the ash was inspected, removed from the boiler and systemized. There was some excitement regarding whether five hours was enough to produce a sufficient amount of agglomerated slag, but luckily quite some slag was produced and definitively enough to be able to compare the impact of additives.

The next tests were intended to be performed with 4 and 8 percent sewage sludge and 4 and 8 percent marble sludge, in that order. It was attempted to obtain as similar conditions for all experiments as possible, in order to obtain comparable test rounds.

After the third round, pellet with 8 percent sewage sludge, the lance with the thermocouples was broken, probably because of the stress caused by rapid heating and cooling. It was not possible to repair the lance at the spot and the rest of the experiments had to be delayed, and unfortunately not included in this thesis.

## 7.3 Results

Because of the accident during the experiments, the results are also somehow incomplete compared to the initial intention, but a description of the results as extensive as possible is included in this subchapter.

### 7.3.1 Ash sintering and agglomeration

The first experiment with pure pellet produced a relatively high amount of slagging in the boiler. A couple of fist sized ash lumps hard as stone was produced, and also quite a lot of sintered ash with a length/width between 1 and 4 centimeters. The slagging was most severe in the beginning of the boiler where the heat was most intense. Sintering of the ash was also most severe around the primary air distribution inlets. Even though one could believe that the primary air has a cooling effect, this could indicate a higher temperature around these holes. Nevertheless, the extensive sintering around the primary air distribution holes will reduce the inlet air and lead to bad combustion.

Combustion of pellet with 4 percent addition of sewage sludge did not reduce the ash sintering. Actually the amount of sintered, agglomerated and slagged ash increased in this round. However an interesting change of the ash property occurred. Where the pellet with no additives formed slag hard as stone, the ash from pellet with addition of sewage was more porous and a large amount of the sintered ash was possible to break with a strong hand.

Pellet with addition of 8 percent sewage severely increased the amount of sintered ash, but also the porosity of this ash. The resulting ash lumps was larger than those created earlier, and the largest one was about 30 cm in length.

Figure 7-1 shows some representative ash samples taken from the grate after the three combustion rounds, and shows clearly the already explained ash characteristics.



Figure 7-1 Pictures of sintered ash after combustion of pure wood pellet (left) and mixed with 4 (middle) and 8 percent sewage sludge (right).

Cutting of the ash shown in Figure 7-1 revealed another interesting change to the ash, which was the formation of pores in the ash, helping to explain the porosity described earlier. Figure 7-2 shows the cross sectional area of the sintered ash, clearly showing increased formation of pores in line with the increased amount of sewage sludge. The formation of pores is one of the wanted effects from addition of additives, as explained in chapter 4.



Figure 7-2 Sectional area of the sintered ash from combustion of wood pellet (left) and mixed with 4 (middle) and 8 percent sewage sludge (right).



### 7.3.2 Flue gas measurements

The burning conditions in the boiler are obviously very good, considering the low CO levels in the flue gas during steady state operations, shown in Table 7-2.

	O <sub>2</sub> [%]	CO [ppm]	SO <sub>2</sub> [ppm]	NO [ppm]	NO <sub>2</sub> [ppm]	NO <sub>x</sub> [ppm]
Wood pellet	9,53	30,99	-1,23	188,03	1,95	190,01
+ 4 % sewage s	8,55	10,81	-1,71	196,87	1,67	198,54
+ 8 % sewage s	8,27	13,91	29,68	217,36	0,26	217,62

Table 7-2 Emissions from combustion of wood pellets, and wood pellets with additives.

In terms of CO- levels the combustion conditions are actually better when combusting pellet with sewage sludge than without. The change in flue gas emissions has to be analyzed together with the elemental composition of the pellet and sewage, and the lower carbon and oxygen content in the sewage is probably the reason for lower emissions of oxygen and carbon monoxide. It is more difficult to explain why the CO-emissions increase when going from 4 to 8 percent addition of sewage sludge, but could be a result of incomplete combustion.

SO<sub>2</sub>- emissions are solely fuel bound and is normally not a problem when combusting biomass. Combustion with the addition of 8 percent sewage sludge causes a drastically increase in the emissions. However these measurements are dubious as there is no difference between pure pellet and wood pellet with 4 percent sewage, and the negative measurements are probably wrong.

The NO-emissions from burning pure wood pellet is fairly high, and is probably caused by large amounts of urea-based glue residues in the wood. As for the combustion with sewage, the nitrogen content in the sewage sludge is about three times larger than the one in the wood pellet, probably explaining the increased NO- emissions.

### 7.3.3 Temperature measurements

The average temperature measured during steady state in the boiler during the three rounds of combustion is shown in Table 7-3.

(in °C)	A1	A2	B3	B4	B5	B6	A7	A8	A11	A12	A13	A14
Wood pellet	397	405	891	993	1062	985	941	820	112	691	1051	219
+4 % ss	349	362	740	975	1063	986	919	x	125	696	1024	227
+8 % ss	338	268	1007	1128	1056	983	1077	x	106	628	1102	186

Table 7-3 Average temperatures (in °C) in the boiler during steady stage combustion for the three rounds of combustion.

The different symbols, A1, A2, B3 etc., represent the different thermoelements placed around in the boiler. The placement of those can be shown in Appendix L. Thermoelements with A is of type K elements while B is of type S. The first eight thermoelements is those placed on the lance, with A1 being closest to the fuel inlet and A8 closest to the ash outlet. A11-A14 is placed before the cyclone, at the outlet of the combustion chamber, between B3 and B4 and in the

middle of the heat exchanging area respectively. Thermoelement A8 was broken after the first round of combustion.

The temperatures are more or less constant during the first two rounds, but with a good increase in the grate temperature during combustion of wood pellet with addition of 8 percent sewage sludge. The reason for this temperature increase is unknown as all the rounds were performed with the same parameters.

Both the melting experiments and the sintering test showed a deformation temperature for wood pellet at around 1150 °C and a flow temperature below 1200 °C. According to Table 7-3 it is clear that the temperature on the grate is higher than 20 cm above, as the maximum temperature here is 1060 °C, well below deformation temperature. It is also possible that there are creations of hot spots on the grate that will induce the sintering and even melting, as the difference between DT and FT for wood pellet is below 50 °C. The temperature on a grate that is not water cooled is difficult to control and temperature variations around the grate is highly possible.

This, together with the flue gas measurements, show that addition of sewage sludge has little influence on the combustion conditions, not considering the increased sintering.

## 7.4 Sykkylven experiment discussion

The effect of adding sewage sludge in the wood pellet was much worse than expected. In despite the increased porosity of the ash, sewage sludge as an additive will not reduce the problems with ash sintering and agglomeration. Too much sintered ash is formed when pellet with sewage is burned, and the resulting slagging is still so hard that it will probably cause problems with the automatically ash removal system.

The probable explanation of the increased degree of slagging is the high amount of aluminum in the sewage sludge. In an additive point of view it is important to have some aluminum in combination with silica, in order to make the silica react with the alkali metals. But the ratio between these two compounds should probably be in favor of silica.

A possible explanation for the increased sintering and agglomeration during combustion with 8 percent sewage is the higher temperatures in this round.

## 8 Conclusion

The melting experiments in the fusibility furnace showed that all additives, except for paper sludge, were able to raise the ash melting temperatures of the wood pellet, with sewage and marble sludge as the two most promising. The effect of additives in wood pellet was more evident at the higher melting temperatures hemisphere and flow temperature. The increase in melting temperatures was higher for wheat straw ash, especially for the initial deformation temperature, and sewage, clay and marble sludge was observed to be the most effective additives. Paper sludge showed an interesting increase in DT and ST for wheat straw ash.

The sintering test in the lab revealed a higher/worsened sintering effect on the wood pellet ash from all additives, except marble sludge which showed very good anti-sintering properties. A combustion temperature of 1200 °C made the pure wood pellet melt, while the mixture with clay and sewage sludge formed medium or hard sintered ash. The additive effect on wheat straw was considerably better. Marble sludge was the best additive and was able to create loose straw ash even at 1100 °C. Paper sludge had a minor improving effect, while clay and sewage sludge are probably able to prevent severe ash sintering for temperatures below 1000 °C, but more sintering tests are needed to verify this. Marble sludge was for both fuels a very effective additive and was able to almost eliminate the ash sintering.

From the sintering test results, it is obvious that the melting of ash in an ash fusibility furnace with manual registration of the melting temperatures does not give a good indication of the sintering effect from additives on biomass ash.

Big scale combustion experiments with wood pellet and additives at a boiler in Sykkylven was not completed and only pure wood pellet and wood pellet with addition of 4 and 8 percent sewage sludge was combusted. The addition of sewage sludge changed the form of the ash, from hard slag to more porous, sintered ash with a high concentration of pores. However the amount of sintered ash increased with addition of sewage sludge, and the sintered ash was still too hard to not cause problems with the ash removal system.

One possible explanation of the increased degree of slagging is the high amount of aluminum in the tested sewage sludge, but low melting crystalline phases was not detected in the XRD analysis.

Flue gas measurements showed a decrease in the CO- and a slight increase in the NO- emissions when burning wood pellet with sewage sludge under stable, full load conditions. The sulphur emissions was zero when pure wood pellet and the mixture with 4 percent sewage sludge, but when burning the 8 percent sewage sludge mixture the emissions increased to a surprisingly

high level at 30 ppm. The emissions of heavy metals are probably increased by the introduction of sewage sludge in the pellet, although it was not possible to measure these emissions.

The temperature in the Sykkylven boiler was recorded and showed a maximum temperature at 1060 °C when burning pure wood pellet and wood pellet with addition of 4 percent sewage sludge. When burning the fuel with 8 percent addition of sewage sludge, the temperature was considerably increased over the whole grate and a maximum temperature of 1130 °C was obtained. This increased temperature might also be an explanation of the increased ash sintering.

A brief analysis of the XRD results was not able to identify the compounds that are causing the low melting temperature for wood pellet. High amount of sylvite and arcanite are obviously causing the low melting temperatures for wheat straw ash.

Based on the results in this project, neither clay, sewage or paper sludge are able to reduce the problems of ash sintering and agglomeration for the problematic wood fuel. However both clay and sewage sludge, and possibly paper sludge, are able to reduce the sintering problems in wheat straw ash.

All experiments show that marble sludge is a very effective additive for both wood pellet and wheat straw ash.

## 9 Recommendations for further work

The sintering test is probably a more effective way to determine the additive effect on problematic biomass fuels than the fusibility furnace. An extended study that includes more temperatures and additive concentrations is recommended. The marble concentration was probably too high and an analysis on how little marble that is needed to reduce ash sintering would be interesting.

The experiments at Sykkylven should off course be completed with 4 and 8 percent marble sludge addition to the pellet. According to the lab results, these rounds of combustion should contain much less sintered ash.

Sewage sludge is a very interesting additive and it would be advantageous to test a different sludge containing less aluminum. The search for cheap and efficient additives is always needed and could go on for years.

A more extensive analysis regarding XRD patterns from the different ash compositions at more temperatures are needed, as this is the key to understand the melting behavior of ash.



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# Appendix A, Proximate analysis

## A.1 Proximate analysis, fuels

			Crucible + fuel		
Fuel	Date	Crucible weight ( $w_c$ )	Initial weight ( $w_i$ )	Final weight ( $w_f$ )	
<i>Moisture content</i>					Moisture (%)
Wood pellet	29.jan	86,15	137,49	134,55	5,73 %
Wood pellet	30.jan	86,17	137,58	134,21	6,56 %
Wood pellet	02.feb	86,19	127,31	124,57	6,66 %
Straw	02.feb	42,26	62,64	61,43	5,94 %
Straw	03.feb	42,45	62,52	61,33	5,92 %
<i>Volatile matter</i>					Volatiles (%)
Wood pellet	03.feb	10,6821	11,6723	10,822	85,9 %
Wood pellet	03.feb	10,8926	11,9717	11,0563	84,8 %
Wood pellet	03.feb	10,9547	12,0751	11,1406	83,4 %
Wood pellet	06.feb	15,1413	16,126	15,2986	84,0 %
Wood pellet	06.feb	10,8401	11,8292	10,9912	84,7 %
Wood pellet	06.feb	14,6977	15,7143	14,8631	83,7 %
Straw	03.feb	11,5281	12,763	11,822	76,2 %
Straw	03.feb	11,4017	12,4178	11,6707	73,5 %
Straw	03.feb	10,6733	11,8827	10,9581	76,5 %
<i>Ash content</i>					Ash (%)
Wood pellet	05.feb	11,4766	12,4459	11,4822	0,578 %
Wood pellet	05.feb	11,5264	12,5213	11,5331	0,673 %
Wood pellet	05.feb	10,9553	11,9773	10,9626	0,714 %
Straw	05.feb	11,0434	12,0134	11,105	6,35 %
Straw	05.feb	11,3961	12,4317	11,461	6,27 %
Straw	05.feb	10,6754	11,6839	10,7387	6,28 %

## A.2 Proximate analysis, additives

			Crucible + fuel		
Additive	Date	Crucible weight ( $w_c$ )	Initial weight ( $w_i$ )	Final weight ( $w_f$ )	
<i>Moisture content</i>					Moisture (%)
Paper	17.feb	86,03	137,12	102,36	68,04 %
Clay	29.jan	40,49	55,02	54,95	0,48 %
Sewage	02.feb	41,03	60,04	58,36	8,84 %
<i>Volatile matter</i>					Volatiles (%)
Paper sludge	20.feb	11,5237	12,4674	11,7759	73,3 %
Paper sludge	20.feb	10,6812	11,6764	10,9463	73,4 %
Paper sludge	20.feb	11,074	12,0903	11,3438	73,5 %
Clay sludge	17.mar	10,829	11,7389	11,7078	3,42 %
Clay sludge	17.mar	11,1864	12,1411	12,108	3,47 %
Clay sludge	17.mar	11,1435	12,1254	12,0912	3,48 %
Sewage sludge	03.feb	11,086	12,0905	11,5392	54,9 %
Sewage sludge	03.feb	11,3975	12,3556	11,8516	52,6 %
Sewage sludge	03.feb	11,4777	12,4211	11,9178	53,3 %
<i>Ash content</i>					Ash (%)
Paper sludge	05.mar	11,476	12,1414	11,5373	9,21 %
Paper sludge	05.mar	11,044	11,7175	11,1051	9,07 %
Paper sludge	05.mar	11,3972	12,3226	11,4817	9,13 %
Clay sludge	05.mar	11,5178	12,4692	12,4447	97,42 %
Clay sludge	17.mar	10,8918	11,8088	11,7846	97,36 %
Sewage sludge	05.feb	10,8931	11,9132	11,3174	41,59 %
Sewage sludge	05.feb	10,6825	11,6541	11,0879	41,72 %
Sewage sludge	05.feb	11,0798	12,163	11,5324	41,78 %

## Appendix B, Ultimate analyzis

Fuel/additive	Date	Sample weight [g]	N	C	S	H	O (calculated)
Wt. % d.b.							
Wood pellet	21.may	39,95	0,89 %	49,81 %	0,19 %	6,36 %	42,75 %
Wood pellet	21.may	39,92	0,75 %	49,98 %	0,12 %	6,44 %	42,72 %
Wood pellet	21.may	40,50	0,75 %	49,84 %	0,12 %	6,48 %	42,81 %
Straw	21.may	39,11	1,10 %	46,41 %	0,28 %	6,21 %	46,00 %
Straw	21.may	39,04	1,00 %	46,26 %	0,26 %	6,14 %	46,35 %
Straw	21.may	41,53	1,03 %	46,49 %	0,24 %	6,17 %	46,06 %
Sewage sludge	21.may	38,96	3,08 %	26,43 %	0,79 %	4,23 %	65,48 %
Sewage sludge	21.may	42,25	3,08 %	26,33 %	0,78 %	4,56 %	65,25 %
Sewage sludge	21.may	39,45	3,08 %	26,38 %	0,80 %	4,54 %	65,21 %
Paper sludge	21.may	38,07	1,90 %	48,26 %	0,47 %	5,90 %	43,46 %
Paper sludge	21.may	37,84	1,85 %	47,50 %	0,45 %	6,05 %	44,15 %
Paper sludge	21.may	37,26	1,76 %	48,06 %	0,43 %	6,16 %	43,58 %
Clay	21.may	40,21	0,04 %	0,49 %	0,05 %	0,28 %	1,09 %
Clay	21.may	37,82	0,03 %	0,50 %	0,04 %	0,28 %	1,06 %
Clay	21.may	39,02	0,04 %	0,48 %	0,04 %	0,27 %	1,08 %



## Appendix C, Higher Heating value

Fuel/additive	Date	C-value [J/K]	Sample mass [g]	Heating value [MJ/kg]
Wood pellet	02.apr	10844	0,7862	19,740
Wood pellet	02.apr	10844	0,4099	19,552
Wood pellet	15.apr	10844	0,8132	20,341
Wheat straw	02.apr	10844	0,9669	18,522
Wheat straw	02.apr	10845	0,7993	18,388
Wheat straw	15.apr	10845	0,9471	18,474
Sewage sludge	02.apr	10845	1,0182	11,927
Sewage sludge	16.apr	10845	0,9905	11,322
Sewage sludge	15.apr	10845	0,9892	11,567
Paper sludge	02.apr	10845	0,5277	20,801
Paper sludge	16.apr	10845	0,6738	20,675



# Appendix D, Sample identifier

Sample identifier: xyz					
Fuel (x)		Additive (y)		Additive amount (z)	
1	Pellet	1	Paper sludge	1	3 %
2	Straw	2	Sewage sludge	2	5 %
		3	Calcium carbonate	3	7%
		4	Clay	4	10 %
		5	Marble sludge		

Identifier	Abrevia tion	Fuel		Additive					Additive amount			
		Wood pellet	Straw	Paper sludge	Sewage sludge	Calcium carbonate	Clay sludge	Marble sludge	3 %	5 %	7 %	10 %
100	P0	x										
111	PP3	x		x					x			
112	PP5	x		x						x		
113	PP7	x		x							x	
114	PP10	x		x								x
121	PS3	x			x				x			
122	PS5	x			x					x		
123	PS7	x			x						x	
124	PS10	x			x							x
131	PCa3	x				x			x			
132	PCa5	x				x				x		
133	PCa7	x				x					x	
134	PCa10	x				x						x
141	PCI3	x					x		x			
142	PCI5	x					x			x		
143	PCI7	x					x				x	
144	PCI10	x					x					x
151	PM3	x						x	x			
152	PM5	x							x		x	
153	PM7	x							x			x
154	PM10	x							x			x
200	S0		x									
211	SP3		x	x					x			
212	SP5		x	x						x		
213	SP7		x	x							x	
214	SP10		x	x								x
221	SS3		x		x				x			
222	SS5		x		x					x		
223	SS7		x		x						x	
224	SS10		x		x							x
231	SCa3		x			x			x			
232	SCa5		x			x				x		
233	SCa7		x			x					x	
234	SCa10		x			x						x
241	SCI3		x				x		x			
242	SCI5		x				x			x		
243	SCI7		x				x				x	
244	SCI10		x				x					x
151	PM3		x					x	x			
152	PM5		x						x		x	
153	PM7		x						x			x
154	PM10		x						x			x





# Appendix E, Ash samples

## E.1 Wood pellet with additives

	Identifier	Date	Crucible (g)	Fuel (g)	Additive (g)	Additive (%)	Total (g)	Ash (g)	Ash (%)
Paper sludge	111	20.feb	47,7869	5,0002	0,1501	3,00 %	47,8408	0,0539	1,05 %
	111	20.feb	44,5428	5,0003	0,1514	3,03 %	44,5976	0,0548	1,06 %
	112	20.feb	45,1766	5,0006	0,2510	5,02 %	45,2411	0,0645	1,23 %
	112	20.feb	45,2785	4,9998	0,2501	5,00 %	45,3441	0,0656	1,25 %
	113	20.feb	46,304	4,9997	0,3512	7,02 %	46,3742	0,0702	1,31 %
	113	20.feb	47,8798	5,0007	0,3503	7,01 %	47,9496	0,0698	1,30 %
	114	20.feb	46,8807	5,0000	0,5010	10,02 %	46,9674	0,0867	1,58 %
	115	20.feb	47,8523	5,001	0,5001	10,00 %	47,9402	0,0879	1,60 %
Sewage sludge	121	03.feb		5,0014	0,1499	3,00 %		0	0,00 %
	121	03.feb		5,0016	0,1494	2,99 %		0	0,00 %
	122	05.feb	47,7965	5,0003	0,2503	5,01 %	47,9362	0,1397	2,66 %
	122	05.feb	47,8383	5,0001	0,2506	5,01 %	47,9779	0,1396	2,66 %
	123	17.feb	48,629	5,0001	0,3509	7,02 %	48,8069	0,1779	3,32 %
	123	17.feb	47,7865	5,0008	0,3509	7,02 %	47,9658	0,1793	3,35 %
	124	05.feb	44,5403	5,0000	0,5004	10,01 %	44,7756	0,2353	4,28 %
	124	05.feb	47,8571	5,0004	0,5001	10,00 %	48,0943	0,2372	4,31 %
Calcium-carbonate	131	02.feb		5,0015	0,1522	3,04 %		0	0,00 %
	131	02.feb		5,0048	0,1504	3,01 %		0	0,00 %
	132	11.feb	45,2607	5,0002	0,2501	5,00 %	45,5477	0,287	5,47 %
	132	11.feb	45,9446	5,0002	0,2505	5,01 %	46,2309	0,2863	5,45 %
	133	17.feb	44,1043	5,001	0,3503	7,00 %	44,5005	0,3962	7,40 %
	133	17.feb	44,5425	4,9998	0,3506	7,01 %	44,9401	0,3976	7,43 %
	134	11.feb	45,4784	5,0025	0,4998	9,99 %	46,0182	0,5398	9,81 %
	134	11.feb	45,1608	5,0000	0,5008	10,02 %	45,7015	0,5407	9,83 %
Clay	141	17.feb	45,4955	4,9999	0,1500	3,00 %	45,6823	0,1868	3,63 %
	141	17.feb	45,1776	4,9998	0,1502	3,00 %	45,3646	0,187	3,63 %
	142	10.feb	48,6154	5,0029	0,2518	5,03 %	48,9055	0,2901	5,52 %
	142	10.feb	47,861	5,0004	0,2501	5,00 %	48,1473	0,2863	5,45 %
	143	17.feb	45,9671	5,0015	0,3505	7,01 %	46,3509	0,3838	7,17 %
	143	17.feb	45,2781	5,0006	0,3499	7,00 %	45,6654	0,3873	7,24 %
	144	10.feb	46,868	5,0034	0,5010	10,01 %	47,3995	0,5315	9,66 %
	144	10.feb	47,8404	5,0017	0,5012	10,02 %	48,3714	0,531	9,65 %
Marble sludge	151	23.feb	45,9697	5,0016	0,1513	3,03 %	46,1535	0,1838	3,57 %
	152	23.feb	45,4949	5,0005	0,2506	5,01 %	45,7808	0,2859	5,44 %
	153	23.feb	48,627	5,0003	0,3515	7,03 %	49,0154	0,3884	7,26 %
	154	23.feb	44,1057	5,0016	0,5015	10,03 %	44,6429	0,5372	9,76 %

## E.2 Wheat straw with additives

	Identifier	Date	Crucible	Fuel	Additive	Additive (%)	Total	Ash	Ash (%)
Paper sludge	211	05.mar	46,3014	5,0014	0,1511	3,02 %	46,6005	0,2991	5,80 %
	212	05.mar	45,2821	5,0013	0,2505	5,01 %	45,5906	0,3085	5,87 %
	213	05.mar	45,181	5,001	0,3516	7,03 %	45,4945	0,3135	5,86 %
	214	05.mar	44,1093	5,0004	0,5010	10,02 %	44,4474	0,3381	6,15 %
Sewage sludge	221	13.feb	46,293	4,9978	0,1512	3,03 %	46,6573	0,3643	7,08 %
	221	13.feb	46,8744	5,0018	0,1496	2,99 %	47,2408	0,3664	7,11 %
	222	06.feb	44,096	5,0028	0,2496	4,99 %	44,4872	0,3912	7,45 %
	222	06.feb	46,8661	5,0046	0,2492	4,98 %	47,2502	0,3841	7,31 %
	223	13.feb	47,8746	5,0012	0,3498	6,99 %	48,3139	0,4393	8,21 %
	223	13.feb	47,8492	5,0003	0,3501	7,00 %	48,2866	0,4374	8,18 %
	224	06.feb	46,2775	5,0015	0,5004	10,00 %	46,7582	0,4807	8,74 %
	224	06.feb	48,614	5,0032	0,5009	10,01 %	49,0969	0,4829	8,77 %
Calcium-carbonate	231	05.mar	48,6338	5,0004	0,1501	3,00 %	49,0869	0,4531	8,80 %
	232	13.feb	45,2756	5,0021	0,1511	3,02 %	45,7236	0,448	8,69 %
	232	05.mar	45,9716	5,0012	0,2518	5,03 %	46,5221	0,5505	10,48 %
	232	11.feb	46,8681	5,0042	0,2512	5,02 %	47,4163	0,5482	10,43 %
	233	05.mar	46,8824	5,0013	0,3502	7,00 %	47,5347	0,6523	12,19 %
	233	13.feb	45,4918	5,0009	0,3498	6,99 %	46,1443	0,6525	12,19 %
	234	05.mar	45,5019	5,009	0,5010	10,00 %	46,3063	0,8044	14,60 %
	234	11.feb	48,6159	4,9995	0,5021	10,02 %	49,426	0,8101	14,73 %
Clay	241	13.feb	46,2995	5,0005	0,1520	3,04 %	46,756	0,4565	8,86 %
	241	13.feb	46,877	5,0013	0,1512	3,02 %	47,3305	0,4535	8,80 %
	242	10.feb	46,2782	4,9999	0,2511	5,02 %	46,819	0,5408	10,30 %
	242	10.feb	47,7971	5,0005	0,2497	4,99 %	48,3382	0,5411	10,31 %
	243	13.feb	47,876	5,0025	0,3501	7,00 %	48,5276	0,6516	12,17 %
	243	13.feb	47,8498	5,0024	0,3500	7,00 %	48,4994	0,6496	12,14 %
	244	10.feb	44,0951	4,9992	0,5016	10,03 %	44,8842	0,7891	14,35 %
	244	10.feb	44,5331	5,0007	0,5001	10,00 %	45,3194	0,7863	14,29 %
Marble sludge	151	04.mar	48,6341	5,0003	0,1517	3,03 %	49,0798	0,4457	8,65 %
	152	04.mar	45,9697	5,0019	0,2504	5,01 %	46,5059	0,5362	10,21 %
	153	04.mar	46,883	5,0011	0,3513	7,02 %	47,5177	0,6347	11,86 %
	154	04.mar	45,5012	5,0019	0,5005	10,01 %	46,2832	0,782	14,21 %

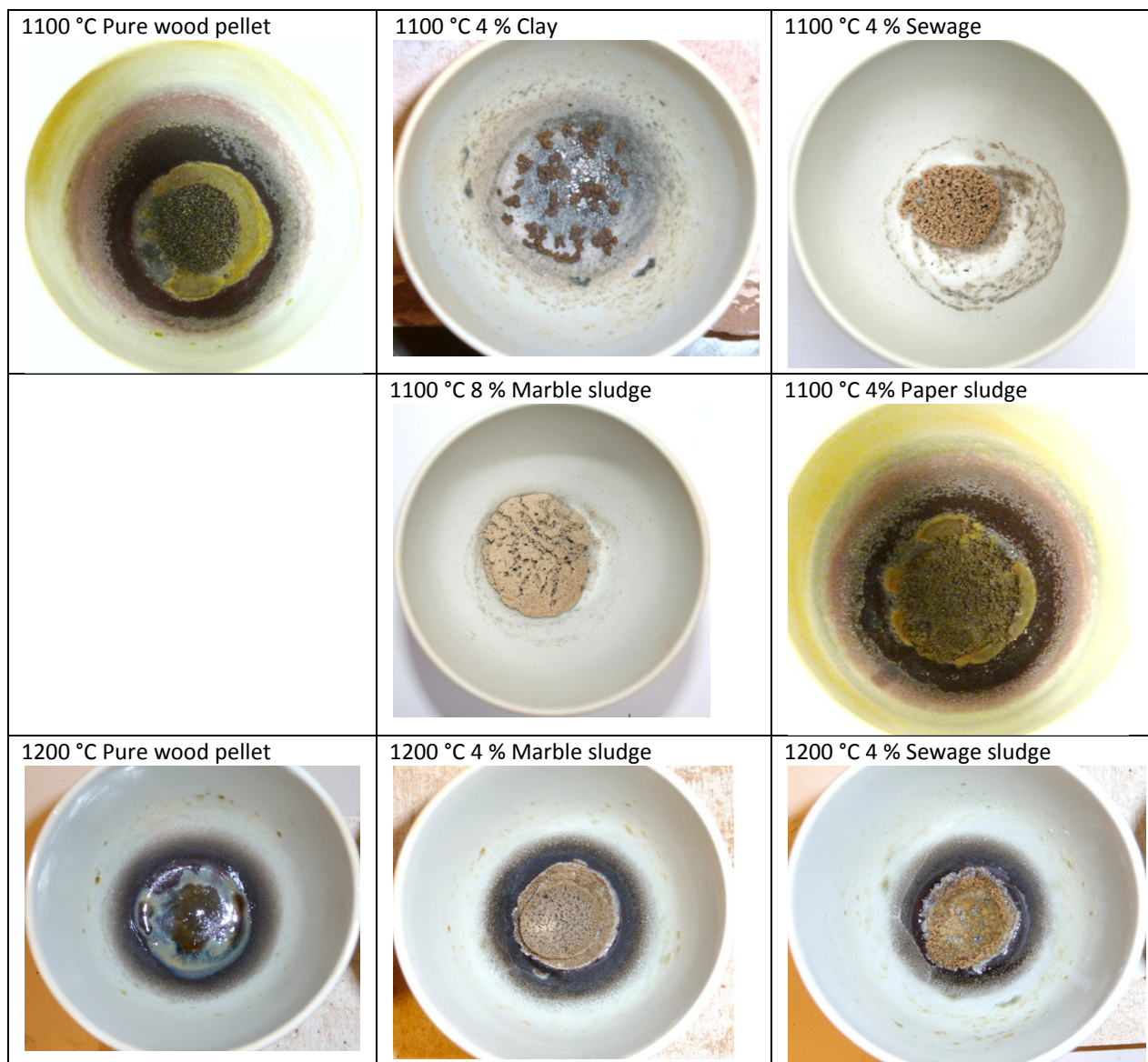
# Appendix F, Ash melting temperatures

WOOD PELLET		Temperature (Average)				Temperature (Max)				Temperature (Min)				Temperature (Difference)			
Identififier	Abbreviation	DT	ST	HT	FT	DT	ST	HT	FT	DT	ST	HT	FT	DT	ST	HT	FT
100	P0	1058	1142	1175	1195	1086	1148	1184	1199	1031	1136	1167	1191	55	12	17	8
111	PP3	1055	1107	1158	1177	1068	1112	1162	1182	1042	1103	1153	1172	26	10	9	10
112	PP5	1057	1120	1180	1189	1076	1122	1185	1194	1037	1118	1175	1184	39	4	10	10
113	PP7	1101	1161	1197	1204	1105	1166	1200	1207	1096	1156	1193	1201	9	10	7	6
114	PP10	1124	1165	1197	1204	1124	1169	1200	1206	1123	1162	1194	1201	1	7	6	5
121	PS3	1118	1231	1443	1501	1128	1246	1448	1510	1108	1215	1438	1492	20	31	10	18
122	PS5	1145	1230	1427	1502	1160	1250	1449	1510	1130	1210	1404	1494	30	40	45	16
123	PS7	1137	1260	1443	1538	1138	1266	1446	1540	1136	1253	1439	1535	2	13	7	5
124	PS10	1145	1276	1473	1542	1151	1290	1490	1545	1139	1262	1456	1538	12	28	34	7
131	PCa3	1089	1332	1463	1475	1120	1340	1476	1485	1058	1324	1450	1465	62	16	26	20
132	PCa5	1080	1346	1438	1467	1100	1348	1452	1477	1060	1344	1424	1456	40	4	28	21
133	PCa7	1122	1353	1427	1473	1147	1366	1433	1480	1097	1340	1420	1466	50	26	13	14
134	PCa10	1147	1363	1406	1436	1160	1384	1409	1443	1134	1342	1402	1429	26	42	7	14
141	PCI3	1048	1155	1225	1271	1074	1169	1240	1286	1022	1140	1210	1256	52	29	30	30
142	PCI5	1107	1193	1256	1355	1138	1210	1280	1378	1075	1176	1231	1332	63	34	49	46
143	PCI7	1122	1205	1296	1330	1160	1216	1328	1358	1083	1194	1264	1302	77	22	64	56
144	PCI10	1139	1211	1309	1350	1182	1218	1340	1366	1096	1203	1277	1334	86	15	63	32
151	PM3	1155	1297	1422	1438	1169	1313	1427	1438	1140	1280	1416	1437	29	33	11	1
152	PM5	1179	1329	1424	1440	1189	1335	1432	1444	1168	1322	1415	1436	21	13	17	8
153	PM7	1176	1338	1416	1447	1184	1344	1421	1457	1167	1332	1410	1437	17	12	11	21
154	PM10	1185	1331	1417	1442	1204	1346	1423	1451	1166	1316	1410	1433	38	30	13	18

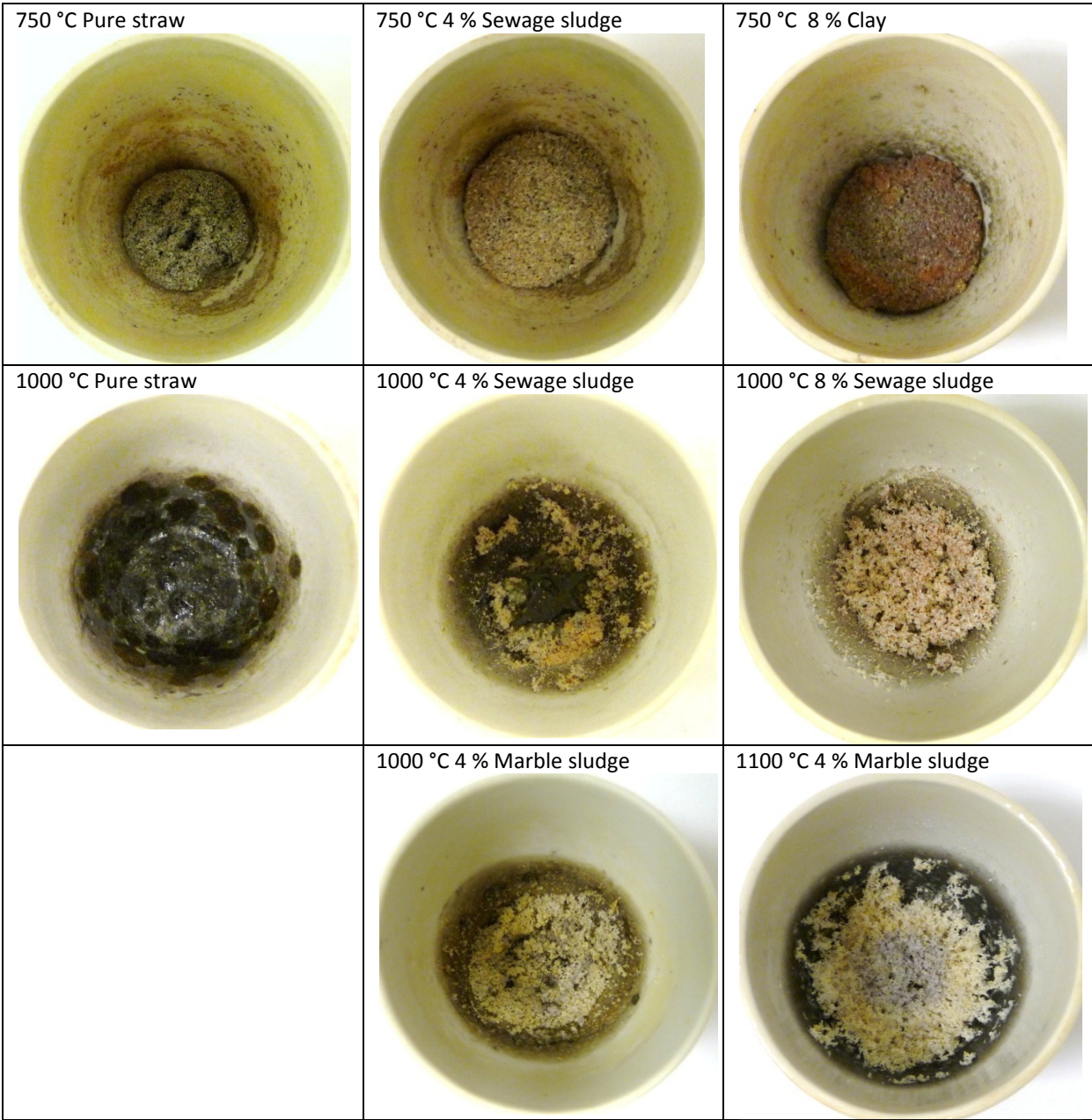
WHEAT STRAW		Temperature (Average)				Temperature (Max)				Temperature (Min)				Temperature (Diff)			
Identifier	Abbreviation	DT	ST	HT	FT	DT	ST	HT	FT	DT	ST	HT	FT	DT	ST	HT	FT
200	S0	688	790	1063	1082	696	794	1070	1084	680	786	1055	1079	16	8	15	5
211	SP3	809	931	1066	1107	818	962	1067	1112	799	900	1064	1101	19	62	3	11
212	SP5	838	951	1088	1119	858	970	1096	1126	818	932	1080	1112	40	38	16	14
213	SP7	880	999	1115	1151	896	1004	1140	1169	864	994	1090	1132	32	10	50	37
214	SP10	871	1037	1145	1185	888	1053	1157	1213	854	1020	1132	1156	34	33	25	57
221	SS3	1010	1175	1293	1422	1022	1190	1303	1435	998	1160	1282	1408	24	30	21	27
222	SS5	1027	1275	1366	1450	1064	1290	1376	1451	990	1260	1356	1448	74	30	20	3
223	SS7	1023	1341	1408	1457	1034	1360	1426	1462	1012	1322	1390	1451	22	38	36	11
224	SS10	1051	1328	1421	1435	1079	1329	1425	1440	1022	1326	1417	1430	57	3	8	10
231	SCa3	1068	1137	1195	1220	1092	1146	1213	1232	1044	1128	1177	1207	48	18	36	25
232	SCa5	1065	1133	1227	1282	1074	1137	1232	1317	1055	1128	1222	1246	19	9	10	71
233	SCa7	1063	1170	1319	1391	1086	1200	1406	1524	1040	1140	1231	1258	46	60	175	266
234	SCa10	1118	1284	1512	1550	1164	1326	1520	1560	1072	1242	1504	1540	92	84	16	20
241	SCI3	990	1065	1186	1271	1006	1078	1209	1288	974	1051	1163	1253	32	27	46	35
242	SCI5	1014	1124	1210	1285	1032	1152	1213	1294	996	1096	1207	1276	36	56	6	18
243	SCI7	1049	1140	1234	1303	1052	1170	1252	1310	1046	1110	1216	1296	7	61	36	14
244	SCI10	1076	1183	1251	1304	1080	1193	1261	1306	1072	1172	1241	1301	8	21	20	5
251	SM3	1029	1080	1178	1241	1032	1081	1206	1270	1025	1078	1150	1212	7	3	56	58
252	SM5	1052	1101	1205	1261	1060	1115	1230	1268	1044	1087	1179	1255	16	28	51	13
253	SM7	1058	1117	1451	1545	1066	1136	1507	1560	1050	1097	1394	1530	16	39	113	30
254	SM10	1064	1155	1494	1539	1075	1171	1528	1541	1052	1138	1459	1536	23	33	69	5

# Appendix G, sintering test pictures

## G.1 Wood pellet with additives



G.2 Wheat straw with additives



# Appendix H, Sykkylven wood pellet mix

The wood pellet with additives made for the big scale experiments in Sykkylven, described under section 7.1, were brought to the laboratory for analysis.

Ash was made at 550 °C in order to see the weight reduction and the corresponding mixture ratio. The results from the ash analysis can be seen from the table.

	Additive amount	Ash content		Possible real additive amount
		Sykkylven mix	Ideal mix	
Sewage	4 %	1,9 %	2,3 %	3,0 %
	8 %	3,2 %	4,0 %	6,2 %
Marble	4 %	3,7 %	4,7 %	3,1 %
	8 %	7,2 %	8,7 %	6,5 %

Table 0-1 Evaluation of the additive mixture made in big scale at Sykkylven.

The table shows the resulting additive amount from the additive to fuel ratio in the mixing process, the ash content of the mixture and the calculated ash content of mixtures containing exactly 4 and 8 percent sewage and marble sludge, after the numbers given in Table 5-3. From these numbers it is possible to calculate the real additive amount in the mixtures, based on the ash content.

It is clear that the samples used here contain a lower amount of additives than wanted. The additive amounts are closer to 3 and 6 percent rather than 4 and 8 percent. As two tones of pellet was made for each mixture, it is clear that some of the pellet will contain more and some less than the resulting total. This is probably the reason for the deviation in concentration, although it is suspicious that all numbers were lower than the indicated concentration. Because it is difficult to measure the flow of fuel in the pellet machine, it is also possible that this amount is underestimated, and the actual additive amount is more close to 3 and 6.5 percent.

The ash made at 550 °C was melted as described in the beginning of this chapter, to see whether the mixing process had any influence on the melting profile of the ash.

Additive		DT	ST	HT	FT
Sewage sludge	3 %	1118	1231	1443	1501
	4 %	1142	1238	1386	1418
	7 %	1137	1260	1443	1538
	8 %	1148	1240	1408	1486
Marble sludge	3 %	1155	1297	1422	1438
	4 %	1206	1312	1422	1446
	7 %	1176	1338	1416	1447
	8 %	1212	1324	1436	1454

Table 0-2 Melting temperatures (°C) of the ash made at 550 °C from Sykkylven (4 and 8 %) and in the lab (3 and 7 %).

The melting temperatures of the pellet made at Sykkylven has some deviation from the one made in the lab. This is especially for sewage sludge, where the Sykkylven mixture has higher DT but lower HT and FT. The mixtures with marble sludge only deviate significantly at DT.





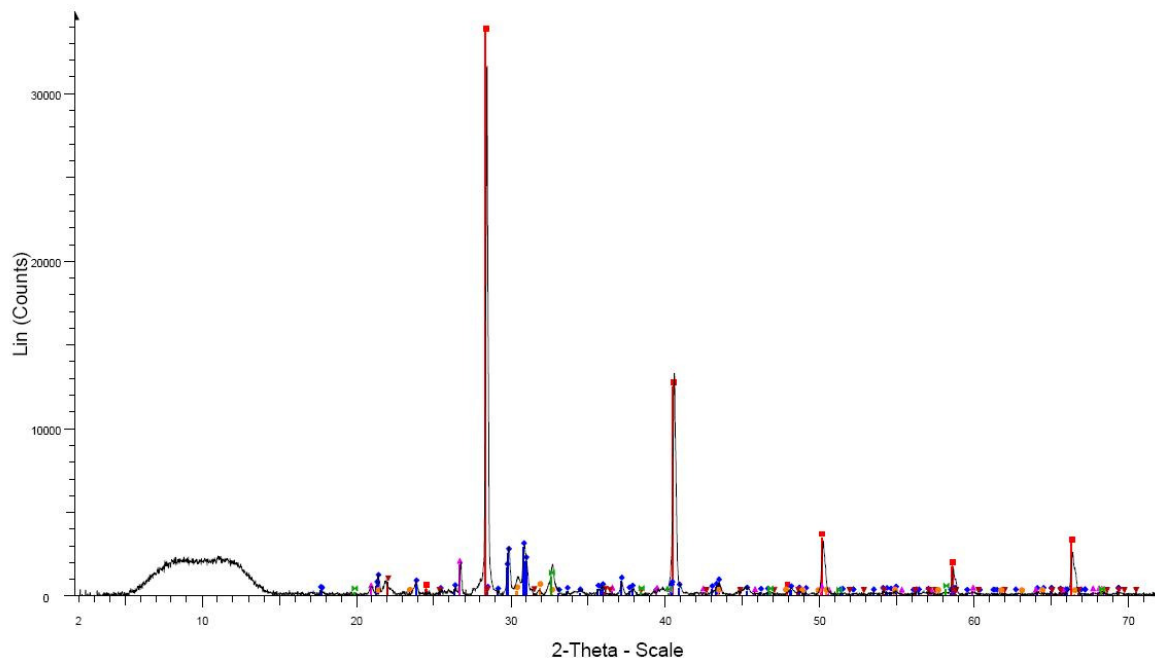
# Appendix I, XRF analysis of fuel and additive mixtures

	Wood pellet				Wheat straw		
	Pure	+5 % sewage	+ 10 % sewage	+5 % Clay	Pure	+5% sewage	+ 10% sewage
Al <sub>2</sub> O <sub>3</sub>	6,12	30,83	39,59	12,96	0,87	4,73	11,25
CaO	34,84	18,98	15,08	18,03	6,13	6,53	6,48
SiO <sub>2</sub>	12,29	14,42	14,48	47,35	39,18	42,45	41,14
K <sub>2</sub> O	14,15	5,54	3,49	5,19	29,95	23,79	19,74
P <sub>2</sub> O <sub>5</sub>	2,28	8,46	10,05	0,91	5,96	6,89	7,55
Na <sub>2</sub> O	11,12	4,75	3,18	4,02	1,14	1,04	0,88
Cl	0,17	0,1	0,21	0,22	9,2	8,73	7,16
Fe <sub>2</sub> O <sub>3</sub>	4,36	5,13	4,86	9,9	0,35	0,97	1,54
SO <sub>3</sub>	2,42	4,88	3,54	0,49	5,03	2,63	2,57



# Appendix J, XRD analysis

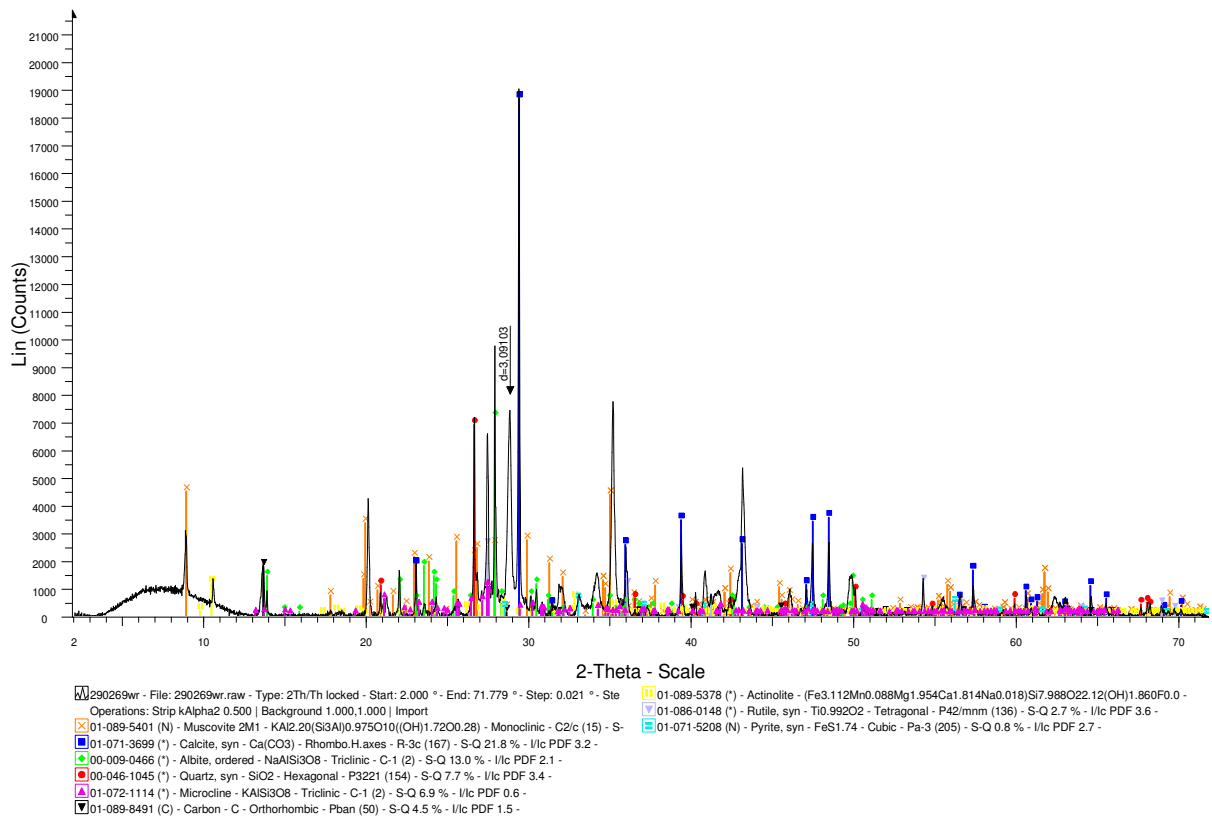
Straw ash 550 °C



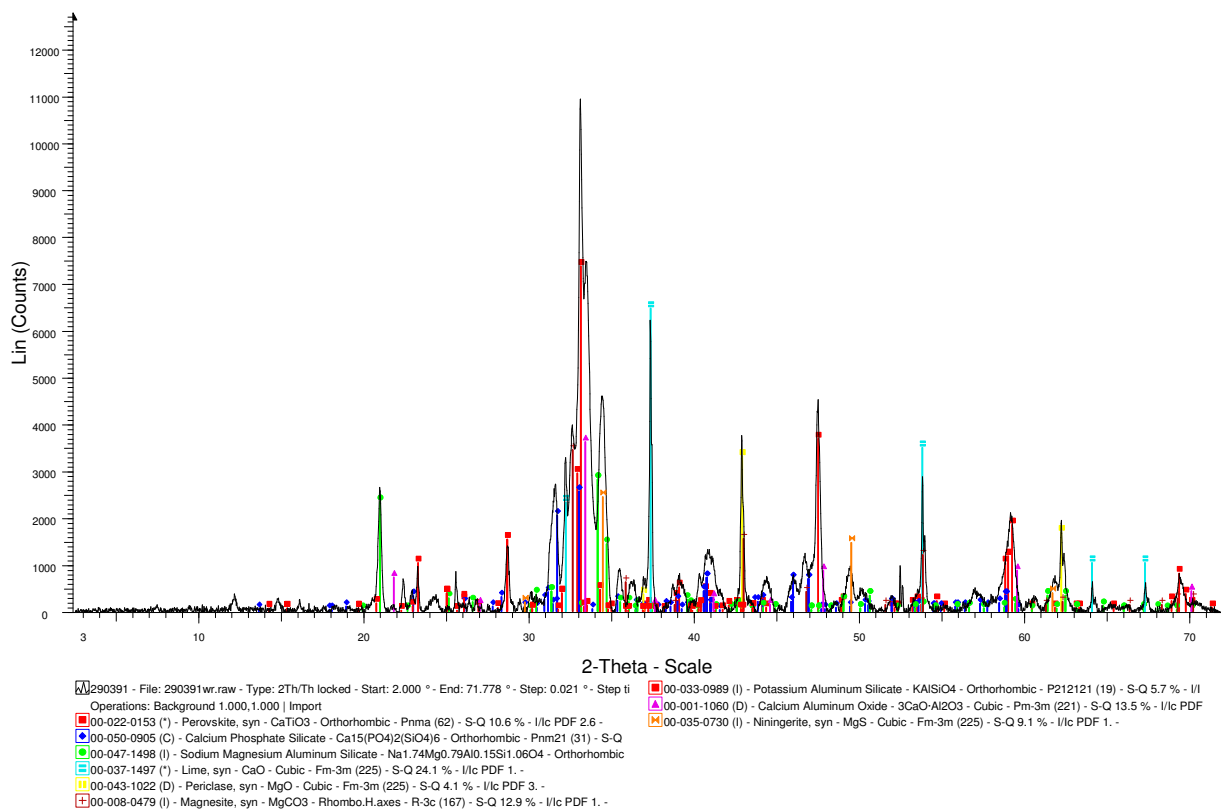
290059 - File: 290059wr.raw - Type: 2Th/Th locked - Start: 2.000 ° - End: 71.779 ° - Step: 0.021 ° - Step time: 261. s - Temp.: 25 °C (Room) - Time Started: 3606 s - 2-Theta: 2.000 ° - Theta: 1.000 ° - Chi  
Operations: Background 0.813,1.000 | Import

- 00-041-1476 (\*) - Sylvite, syn - KCl - Cubic - Fm-3m (225) -
- 00-044-1414 (D) - Arcanite, syn - K<sub>2</sub>SO<sub>4</sub> - Orthorhombic - Pmcn (62) - I/c PDF 1.7
- 00-046-1045 (\*) - Quartz, syn - SiO<sub>2</sub> - Hexagonal - P321 (154) - I/c PDF 3.4
- 00-039-1425 (\*) - Cristobalite, syn - SiO<sub>2</sub> - Tetragonal - P41212 (92) -
- 00-039-1426 (\*) - Potassium Magnesium Silicate - K<sub>2</sub>MgSiO<sub>4</sub> - Cubic - F13\* (0) -
- 00-039-0691 (\*) - Ammonium Cyanide - NH<sub>4</sub>CN - Tetragonal - P42/mcm (132) -

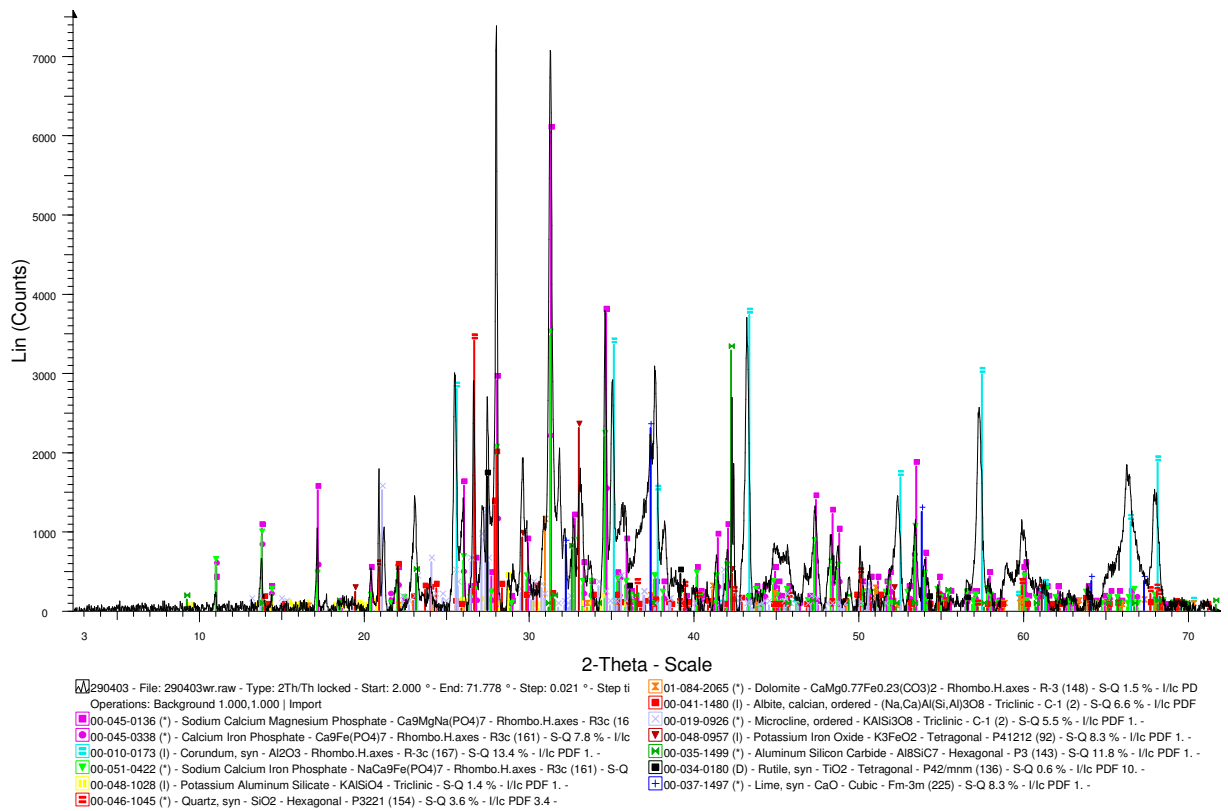
### Wood pellet ash 550 °C



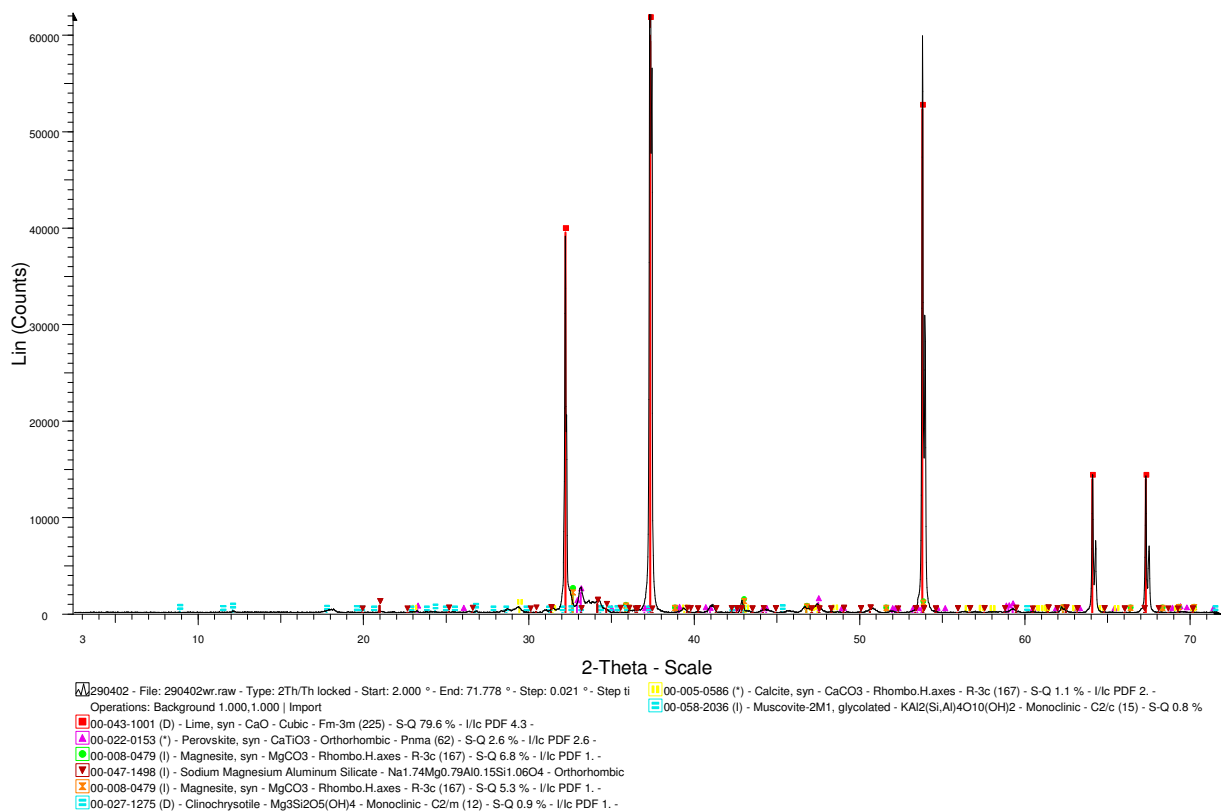
### Wood pellet ash 1000 °C



### Wood pellet + 5 % sewage sludge 1000 °C



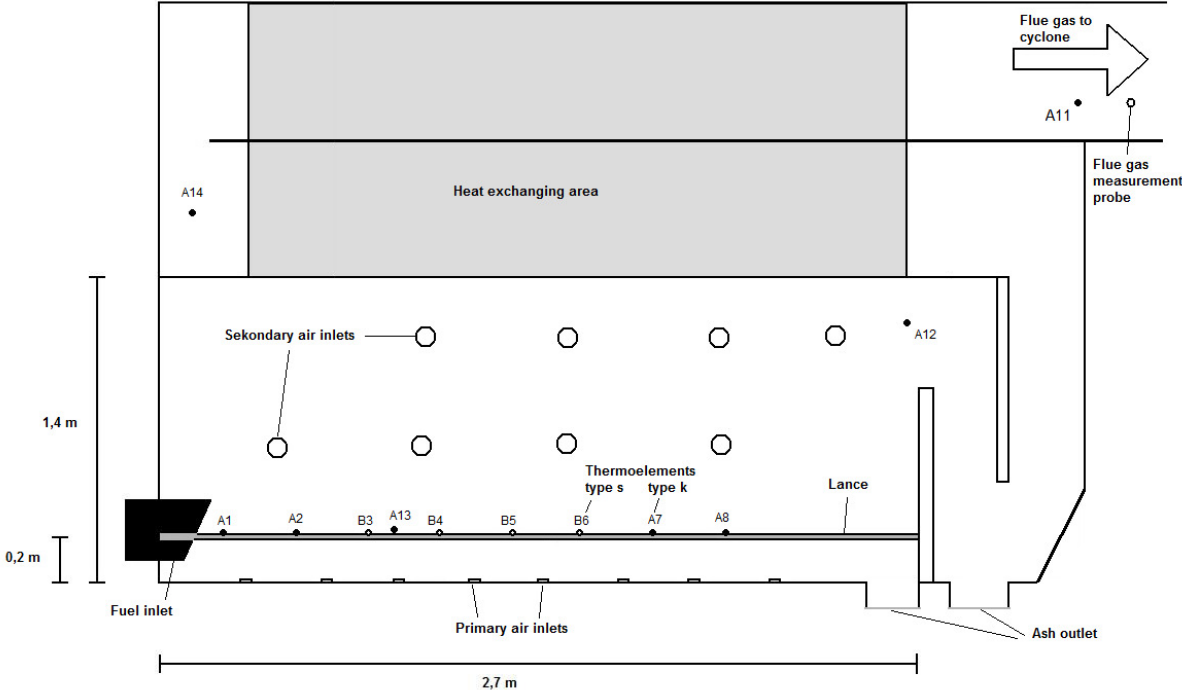
### Wood pellet + 5 % marble sludge 1000 °C



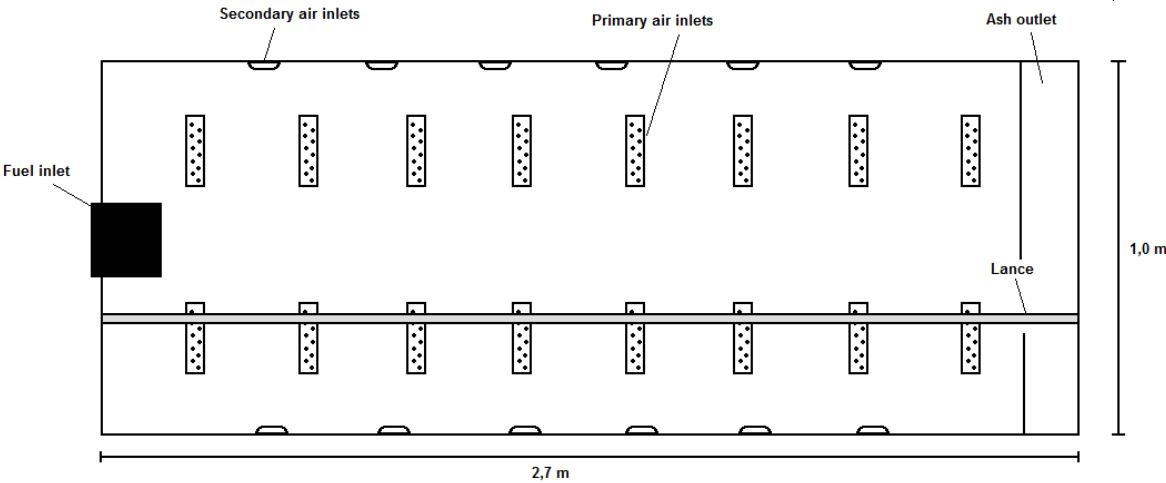


# Appendix K, Boiler illustration

## K.1 From the side



## K.2 From above







# Appendix L, Pictures from Sykkylven boiler

L.1 Sintered and agglomerated ash lump

(Clean wood pellet ash from previous combustion)



L.2 Clean boiler before the experiments



L.3 Ash after combustion with 4 percent sewage sludge

(notice the severe sintering around the primary air inlets)



L.4 Ash after combustion with 8 percent sewage sludge

