

**CONVERSION OF BIOMASS,
PREDICTION AND SOLUTION METHODS
FOR ASH AGGLOMERATION AND RELATED
PROBLEMS**

Contract JOR3-95-0079

Final Report

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Preface

This report describes the results obtained in a project financed by the European Commission, (contract number JOR3-95-0079 in the framework of the JOULE III programme), NOVEM (Netherlands agency for energy and the environment, project 355196/1030), ECN and Risø. Originally it has been a project of three partners: ECN (NL), Risø (DK) and Aalborg Boilers. After the amendment of 31 August 1998, only ECN and Risø were left to meet the objectives. In the same amendment, the duration of the project has been extended by 6 months.

The present report has been edited by A. van der Drift and A. Olsen, however many people have been involved. Within ECN, Herman Bodestaff, Joep van Doorn, Frank Ligthart, Rian Visser, John Neeft and many more have contributed. Sønnik Clausen, Torben D. Petersen, Jørgen Bilde-Sørensen, Jesper Vejlø Carstensen have been working on the project for Risø. Also Marcus Øhman and Christoffer Boman from ETC (S), Peder Stoholm from Danish Fluid Bed Technology ApS (DK), Karin Poulsen from ReaTech (DK), B. J. Gerrits from TNO (NL), Susanne Westborg and Henning Munk Jensen from dk-TEKNIK (DK), Jaana Latikainen Luntama and Antero Moilanen from VTT (FIN) and Johnny Helbo Hansen, Peter Binderup Hansen and Kate Wieck-Hansen from I/S MIDTKRAFT have contributed to the result of the project (all, except MIDTKRAFT, acting as subcontractor from Risø).

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Keywords

ash, biomass, agglomeration, sintering, defluidisation

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EXECUTIVE SUMMARY

When biomass is used as fuel for thermal conversion plants, minerals from the fuel can be responsible for major problems. Generally, these problems are associated with the existence and development of low melting compounds or eutectics, which form sticky layers. In a fluidised bed, this can result in bed-agglomeration and defluidisation. This causes local high temperature, which often accelerates the process. It ultimately can lead to a completely sintered bed content with a glassy phase gluing the bed particles together and shut down of the plant.

The main objective of this project is to develop a methodology to predict ash/bed agglomeration and sintering problems, to indicate related problems and, furthermore, to identify solution methods to make different types of biomass streams more viable for energy production.

Within the present study, selected fuels are subjected to different existing methods together with some new ones, in order to determine the agglomeration temperature. The selected fuels are verge grass, Danish wheat straw (both stored dry and partly leached due to rainfall), sewage sludge, cacao shells and willow as a reference. The methods used within the study are chemical analysis of fuel and ashes, determination of standard ash melting temperatures, compression strength measurements of the ash, DTA/TG analysis of the ash, SEM and ESEM (high temperature environmental scanning microscopy), two different lab-scale bubbling fluidised bed combustion facilities, a lab-scale bubbling fluidised bed gasifier and a circulating fluidised bed gasifier. The lab-scale facilities have been used to test potential measures to reduce the problem of agglomeration. These measures are the use of additives (kaolin, magnesite, dolomite, gibbsite and sewage sludge) and non-quartz bed materials (alumina and mullite).

The work performed within the project has led to the following results. Chemical analysis of the fuel can give a first indication of whether there might be an agglomeration problem during thermal conversion. In general a high K-content means an increased risk for agglomeration. However, the K-content alone is not a good indicator. Also chlorine proved to be very important.

From the methods used in the project, laboratory fluid bed agglomeration experiments seem to give the most reliable information about conditions and temperatures where agglomeration takes place. Contrary to methods like DTA, compression strength and ash melting temperatures, all processes that might be relevant for agglomeration actually can occur during fluid bed experiments: fuel-bed material interactions, volatilization and condensation, shear forces, temperature homogeneity and accumulation. Standard tests have been developed where process temperature is gradually increasing until agglomeration. These tests have been applied in the project at three different laboratories: ECN (NL), ETC (S) and VTT (FIN). They have proved to be accurate and reproducible.

It has been shown that the addition of kaolin, magnesite, dolomite and sewage sludge significantly reduce the risk of agglomeration. The agglomeration temperatures increased with at least 60°C in these cases.

During combustion experiments, measured particle temperatures appeared to be up to 100°C higher than the bed temperature. This might have a large influence on agglomeration. Because gasification, contrary to combustion, is a process where peak temperatures are lower or even absent, one might expect that agglomeration during gasification will occur at higher temperatures than during combustion. This however can not be concluded from the experiments,

illustrating the importance of other factors like the design of fluid beds (the gas distribution, the type of nozzles, etc.).

It can be concluded that not only the type of fuel and other chemical “input” is determining the agglomeration temperature, also other factors like gas distribution, size of bed material, type of nozzles, cyclone efficiency in CFB’s, etc. can have an important role. This means that results from lab-scale facilities can be interpreted in a relative way (comparing fuels and evaluate possible solution) but should always be used with great care when trying to draw conclusions for full-scale plants. Nevertheless, standardised lab-scale bubbling fluidized bed experiments, as developed and used in this project, seem to be the most reliable tools for the prediction of agglomeration.

1. OBJECTIVES

The main objective of this project is to develop a methodology to predict ash agglomeration and sintering problems, to indicate related problems and, furthermore, to identify solution methods to make different types of biomass streams more viable for energy production.

2. ACTIVITIES

The activities within the project are divided into a number of tasks:

Task 1: Information and material collection

Task 2: Selection of biomass fuels and other materials

Task 3: Description of the lab-scale apparatus and test procedures

Task 4: Construction and modification of lab-scale fluidised bed

Task 5: Development and description of an agglomeration model

Task 6: Performance of lab-scale and bench-scale tests

Task 7: Description of the total methodology for prediction of ash agglomeration and related problems, and identification of potential solutions

Task 8: Conclusive evaluation

In the following chapters, results obtained within each task will be presented subsequently.

3. RESULTS

In this chapter, the results within each task will be described as separate sub-chapters. Within task number 8 (conclusive evaluation, chapter 3.8) the information obtained within the different tasks will be combined.

3.1 TASK 1: Information and material collection

Evil elements

In the literature there is good agreement as to what is seen as the source of ash agglomeration and related problems. Generally alkali metals (mainly potassium in case of biomass) are considered as the main component causing the agglomeration problems. In biomass, alkali metals concentrate in biomass-parts of most vigorous growth. Likely problematic fuels are therefore residues of agricultural (annual) crops, young energy crops and all other fuels containing high amounts of young organic material. Problems are more severe when a high alkali content is combined with high contents of sulphur (in combustion), chlorine, silica and phosphorus. In annex 1 a review of relevant literature is given.

Apart from chemistry, system design and operational conditions are very important factors determining the time-scale of the process. Temperature is the most important factor. The higher the temperature the more severe the problems are. It's important to realise that local peak temperatures may initiate the problem in cases where only the average temperature is measured. For high-sulphur fuels there appears to be a temperature window where in-bed sulphur retention is less and agglomeration problems are reduced. The use of silica-sand bed material promotes agglomeration due to reaction of alkali compounds with the silica to form low-melting surfaces on the particles. The time-scale of the agglomeration process and maximum allowable temperatures in the bed are furthermore strongly influenced by fluidisation conditions (related to both temperature homogeneity and friction between particles), gas atmosphere, bed and fuel particle size, and ash re-circulation from cyclones (in CFB's).

Mechanism

Mentioned elements (K, Na, Cl, S, Si, P) form low-melting compounds or eutectics which become deposited on the bed particles, coating them with a sticky layer. Another possible mechanism can be distinguished where particles are chemically bonded together by gas-solid reactions.

Prediction

Three possible prediction methods can be distinguished:

- Temperature comparison method: This method is a comparison between the process temperature (during gasification or combustion) and some typical temperature measured in a laboratory. The so-called softening temperature of an ash sample, considered as the temperature where agglomeration starts, can be determined using standardised methods. This temperature can also be estimated using the ash composition. In general this method is considered as very inaccurate. It suffers from the limitation that gas-phase reactions, reactions between gas components and the ash, condensation of alkali vapours, the influence of particle-to-particle collisions in fluidised-beds and partitioning of elements can not be adequately simulated in the laboratory. Furthermore, thermal ashing to prepare a laboratory ash can create artefacts in the ash and, more important, gives a substantial alkali-loss, artificially increasing the ash-fusion temperatures. Also the accumulation of certain components in a real process is not included in laboratory tests. These methods can

therefore not give absolute agglomeration temperatures, but some seem useful for gaining a more fundamental understanding of ash behaviour in thermal conversion

- Agglomeration lab test: This method is a laboratory test with ash and bed material. In this test the temperature is determined at which agglomerates are formed. This method should result in more realistic predictions since volatilisation/condensation and accumulation of components and gas-gas and gas-solid reactions can take place, depending on the specific experimental facility and test procedure.
- Mathematical prediction method: The mathematical prediction method concerns the calculation of possible low-melting mixtures of components available in the system. The chemical composition of the materials used have to be measured. These methods usually are equilibrium calculations and therefore do not include kinetics.

Annex 1 contains a literature review on agglomeration. In annex 2, the prediction tools reported in literature are summarised.

Prevention

Adding inert high-melting minerals (CaO, MgO), sulphur-sorbents (limestone, dolomite) and alkali-sorbents (clay minerals) to the bed is reported to reduce agglomeration problems in fluidised-beds, but mechanisms are not fully understood. In some reported cases, sulphur-sorbents even decreased ash deformation temperatures and increased fouling. Blending of straw with wood and coal is reported to be successful to some extent. In full-scale practice, the bed-material is refreshed regularly before a critical ash-accumulation (alkalis) or agglomeration level is reached.

A commercial combustion facility at Grenaa, Denmark

The Grenaa CFB¹ CHP² plant was commissioned January 1992. The plant, which is based on a conventional steam cycle, is producing electricity, district heat and process steam for nearby industry. It can be fired with coal and coal/straw mixtures. Typical data are shown below.

Owner	I/S Midtkraft		
Location	Grenaa, DK		
Year of commissioning	1992		
Max. coal / straw share	% / %	100 / 60	by energy
Annual straw consumption	ton	70,000	at 50 % straw
Annual coal consumption	ton	38,000	at 50 % straw
Boiler capacity	MW	78	
Steam flow rate	kg/s	29	
Steam pressure	MPa	9.2	
Feed water temperature	°C	170	
Superheating temperature	°C	505	(no re-heating)
Electric output (net at max. heat duty)	MW	17.8	
Process steam export	MW	25	8.3 bar, 210°C
Hot water for district heating (max.)	MW	32	

A typical content of bed material in the system is 24 t. By adding a similar amount of coal fly ash from a nearby grate fired boiler (20 t) and some fresh sand (3 t) every 24 hour, it is possible to keep the concentration of water soluble potassium in the re-circulating bed particles below 2000 ppm. This concentration is believed to be a safe limit for avoiding problems due to agglomeration and deposition in the boiler. However, 4000 ppm has also been achieved without any problems.

Severe bed sintering/agglomeration seems not to be a major part of the history of the plant. The reason is probably the frequent change of bed particles, improved temperature control and other measures (including design modifications), that has been realised in order to deal with other problems. However, bed sintering/agglomeration is occasional seen as a consequence of

¹ CFB: circulating fluidised bed

² CHP: combined heat and power (electricity)

improper plant control. In particular the operator has to be careful when performing a sudden switch from a volatile to a less volatile fuel such as from a high share of straw to coal only. Hence, the control system tends to overshoot in this situation, which may lead to a severe temperature excursion within the first half-hour or so.

3.2 TASK 2: Selection of biomass fuels, bed materials and additives

Criteria

Biomass materials tested within the project were chosen according to several criteria. Firstly the fuel should have potential to cause agglomeration problems during thermal treatment. This potential is related to the chemical composition, especially concerning the list of elements mentioned in the previous chapter known to cause agglomeration problems. Secondly it should be a material that is relevant in a European background. In other words: it should be available for energy conversion in certain quantities either now or in the near future. As a reference willow has been chosen which is a possible energy-crop in Northern Europe and is considered to be non-problematic for agglomeration. Bed materials and bed additives are chosen because of reported potential for reducing agglomeration problems.

Biomass fuels

The fuels chosen are:

1. verge grass,
2. Dutch wheat straw,
3. Danish wheat straw,
4. weathered Danish wheat straw (subjected to rainfall)
5. sewage sludge and straw/sludge-mixtures,
6. cacao shells,
7. willow (as a reference fuel)

Bed materials

The following bed materials were chosen for the lab-scale fluidized bed tests.

1. silica: SiO_2 ,
2. alumina: Al_2O_3 ,
3. mullite: $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$

Silica is the most common bed material. Since silica is considered to play a role in agglomeration, alumina has been chosen as a more inert bed material. Finally mullite is chosen because it's cheaper than pure alumina and might show the inert character of alumina, see also annex 1.

Bed additives

The additives chosen for tests in some fluidized bed experiments are based on literature findings, see annex 1. Chosen additives all represent different (suspected) mechanisms for improving agglomeration:

1. kaolin: $\text{Al}_2\text{SiO}_5(\text{OH})_4$,
2. magnesite: MgO ,
3. gibbsite: $\text{Al}(\text{OH})_3$,
4. dolomite: $\text{MgCO}_3 \cdot \text{CaCO}_3$

Kaolin is considered as a chemical getter of alkali's. It binds the alkali metals into a harmless component. Magnesite probably influences the viscosity of the melt. Battelle reports positive results obtained with MgO . Gibbsite on the other hand decomposes to very porous Al_2O_3 capable of physically getting alkali's. Dolomite, known for its suitability as tar cracker and NH_3 -reduction agent, is proven to reduce agglomeration in straw combustion when used as bed material by VTT. Besides this, dolomite is cheap.

Not all combinations of fuels, additives and bed materials as mentioned above were tested. A selection has been made for each type of experiment. In table 3.1 the combinations of selected materials and experiments are given.

Table 3.1 *Experimental programme with selected biomass materials, marked grey are experiments actually performed within the project. Also indicated are combinations of tests and materials reported in literature [1] but worthwhile for comparison. BFBG: bubbling fluidized bed gasification, BFBC: bubbling fluidized bed combustion, CFBG: circulating fluidized bed gasification, DTA/TGA: differential thermal analysis/thermo-gravimetric analysis, HTM: high temperature microscope*

facility	experiment/analysis	1.	2.	3.	4.	5.	6.	7.
		verge grass	Dutch straw	Danish straw	Danish weathered straw	sewage sludge	cacao shells	willow
a. chemical labs	chemical analysis							
b. BFBG	gasification (5 kW _{th})							
c. BFBC	combustion and controlled aggl. (5 kW _{th})					(*)		
d. CFBG	gasification (500 kW _{th})	[1]					[1]	[1]
e. DTA/TGA	melting temp. of ash and ash/bed							
f. compression strength	compr. strength of sintered ash pellets							
g. standard facilities	standard ash melting temperature							
h. HTM	heating while observing ash/sand							
i. BFBC	combustion and controlled aggl. (5 kW _{th})							

* two different sewage sludges are tested, also in combination with Danish straw (fuel #3)

3.3 TASK 3: Description of the lab-scale apparatus and test procedures

3.3.1 Chemical laboratories at ECN and Risø (DK-TEKNIK) (a)

The selected biomass fuels, see chapter 3.2., were analysed in chemical laboratories of ECN and DK-TEKNIK as a subcontractor of Risø. Fuels number 3, 4 and 7 were ashed at three different temperatures (450, 550 and 650°C) and the ash was subsequently analysed. Some samples were analysed by both laboratories to be able to compare results. For the analyses, standard procedures were used as indicated by [2] for ECN and several, mostly ISO, standards for DK-TEKNIK.

3.3.2 BFBG: bubbling fluidized bed gasification facility (5 kW_{th}) at ECN (b)

The ECN lab-scale bubbling fluidized bed gasification facility (BFBG), called WOB, has been designed and constructed specially for the project. The design fuel rate is about 1 kg/h being about 5 kW_{th}. Figure 3.1 shows a picture and figure 3.2. shows a schematic representation of the facility. It consists of the following parts.

Feeding system

The feeding system consists of a couple of closed vessels of 20 litre equipped with a mechanism to prevent bridging of the fuel. A dosing screw conveyer moves the fuel towards another screw, which takes care of quick transport into the hot gasification reactor. Fuel feeding rate is adjusted according to the calibration of feeding rate with number of revolutions per minute of screw conveyer. The above described test facility has been used to test different bed materials and additives in order to detect possible positive effects. The additives have been added into the system by mixing it with the biomass fuel beforehand.



Figure 3.1 *BFB gasifier at ECN*

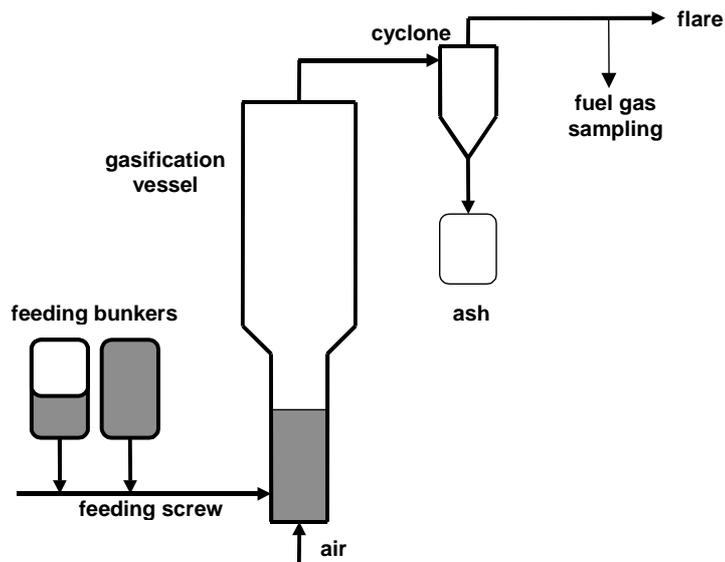


Figure 3.2 *Schematic drawing of the BFB (bubbling fluidized bed) gasification set-up (called WOB) at ECN used to do agglomeration tests*

Gasification vessel

The vessel is an electrically heated metal construction with an internal diameter of 74 mm. The diameter increases to 108 mm at a height of 500 mm. Total length is 1100 mm from air-inlet to fuel gas outlet. The air is supplied via a sintered metal distribution plate. Temperatures are measured at 50, 100, 150, 225 mm height above the distribution plate using 2 mm thermocouples centred in the vessel. At 30 mm height a thermocouple measures the temperature close to the wall opposite to the fuel inlet, which is at the same height. 65 mm underneath the distribution plate, the temperature of the incoming air is measured in the centre of the pipe. The bed material used is either 0.5 mm or 0.27 mm. (the minimum fluidisation velocity is 10 resp. 3 cm/s in case silica sand is used). The air flow used is 16 nl/min (velocity at

800°C is 24 cm/s) for the 0.5 mm sand and 10 nl/min min (velocity at 800°C is 15 cm/s) for the 0.27 mm bed material. The amount of bed material in all cases is 1 kg.

Fuel gas treatment

The fuel gas passes a cyclone to separate particles from the gas. The resulting ash passes a valve system to be able to remove the ashes during operation. The fuel gas is sampled for analysis just after the cyclone. The hot fuel gas passes an electrically heated pipe and is flared.

Test procedure

Two different kind of tests have been defined for the “WOB”:

- Test X: In a so called X-test the biomass material is converted by air-blown gasification at 750° during 4 hours while feeding the material with about 1 kg/h. Fresh bed material is used for every test. The amount of air is fixed to obtain an equivalence ratio between 0.25 and 0.30, being a realistic value for full-scale plants. Subsequently the temperature of the bed is raised stepwise (by adjusting the electrical heating of the gasification vessel) with 25° every 30 minutes until agglomeration occurs, see figure 3.3. Both the fuel feeding rate and air flow remain unchanged. The 4 hours of stationary operation makes up the biggest part of the total duration of the experiment. This ensures a certain ash accumulation in the system which is independent on the agglomeration behaviour of the fuel tested. The result of a X-test is a temperature at which agglomeration is starting to occur. The point where agglomeration starts is characterised by a sudden drop in pressure usually together with a dramatic decrease of temperature homogeneity in the bed.
- Test Y: In a Y-test, a temperature is chosen, lower than the temperature found in the X-test, at which the conversion takes place until agglomeration. The result of a Y-test is a time-to-agglomeration at a certain temperature. Fresh bed material is used for every test.

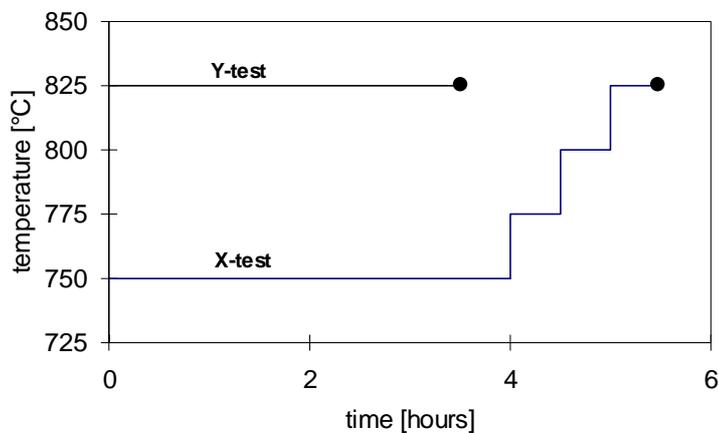


Figure 3.3 *Schematic representation of the two types of standard agglomeration tests in lab-scale fluidized bed gasification facility at ECN*

Measurements

Standard measurements comprise the concentration of gaseous components CO, H₂, CO₂ and CH₄ in the fuel gas, the solid fuel mass flow, the ash mass flow and the incoming air and nitrogen volumetric flow. The concentration of nitrogen in the fuel gas is calculated and is used for determining the total volumetric flow of the fuel gas.

During some tests, bed material was collected, both during the gasification test (after four hours at 750°C) and after actual agglomeration, for further chemical analysis.

3.3.3 BFBC: bubbling fluidized bed combustion facility (5 kW_{th}) by Risø (ETC) (c)

Lab-scale bubbling fluidized bed combustion experiments took place at ETC (Energiteknisk Center in Luleå/Piteå in Sweden), as a subcontractor of Risø. The experiments were performed by Risø staff in co-operation with the local scientists. In figure 3.4 a sketch of the fluidized bed combustion system at ETC is given. Quartz sand (542 gram) has been used with a diameter of 200-250µm, unless stated otherwise. The velocities used were about 4 times the minimum fluidisation velocity, which is 7 cm/s. The fuel was fed as pellets of 5 mm diameter and approx. 7 mm long.

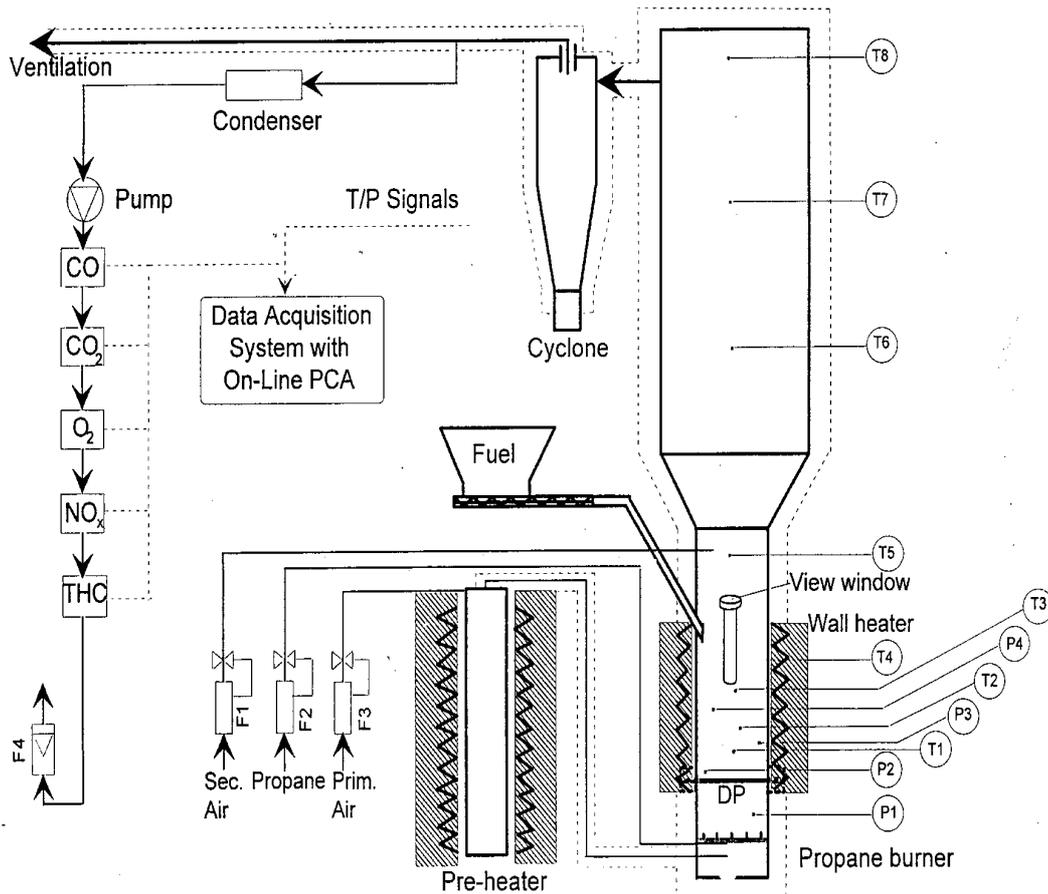


Figure 3.4 Sketch of fluidised bed combustion facility at ETC in Sweden

The bed is normally operated at 5 kW_{th}, but the power may be higher. The inner diameter of the bed section is 100 mm and the reactor height is 1.8 m. The fuel is fed above the bed (upper bed feeding) which requires the fuel to be pelletized. The fuels have been pelletized without the addition of any kind of binder material.

The test procedure is to ash a certain amount of fuel at fixed temperature ("ashing temperature") by combustion and subsequently stop the biomass fuel feeding and raise the bed temperature externally (by supplying propane flue gas with the same [O₂] concentration as the biomass flue gas) with 2-3°C/min until agglomeration occurs. This point can be detected by looking at the temperatures in and pressure drop over the bed. The point where agglomeration starts is characterised by either a sudden drop in pressure or a sudden change in temperature.

During several tests the particle temperature (both sand and biomass/char) is measured using a FTIR pyrometer. An infrared-probe was therefore developed for measuring temperatures of burning particles inside the ETC fluidized-bed reactor. Optical access to the bed is obtained

through a hot sapphire window at the end of a ceramic probe-tip (not cooled). Radiation spectra ($1.4 - 5.7 \mu\text{m}$) from the interior of the fluidized bed reactor are measured at three positions with a Fourier transform infrared spectrometer connected to the probe with a mid-infrared optical fiber. At the relatively long wavelengths, temperature measurements are hardly disturbed by soot radiation. Figure 3.5 shows a drawing of the probe for temperature measurements.

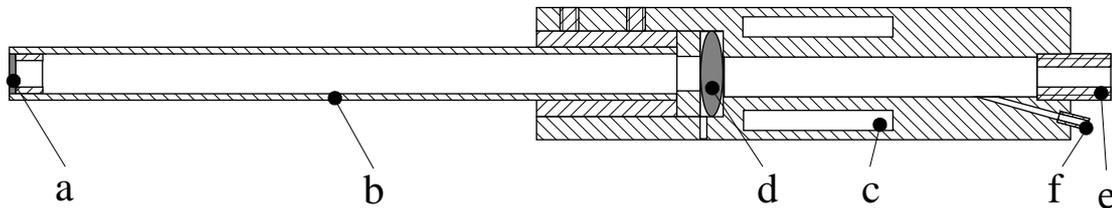


Figure 3.5 *The infrared probe used for measurements of particle temperatures in a fluidized bed. Via an infrared fiber, a FTIR spectrometer is coupled. Letters a: sapphire window; b: ceramic tube; c: water-cooled mount; d: lens (CaF_2); e: connector for the optical fiber and f: purge gas*

3.3.4 CFBG: circulating fluidized bed gasification facility ($500 \text{ kW}_{\text{th}}$) at ECN (d)

The ECN circulating fluidized bed gasification facility, called BIVKIN, is designed to gasify biomass and waste streams and to do research on the conversion itself and the fuel gas characteristics. It is an atmospheric air blown facility of about $500 \text{ kW}_{\text{th}}$. Figure 3.6 shows a schematic of the facility, see also [3].

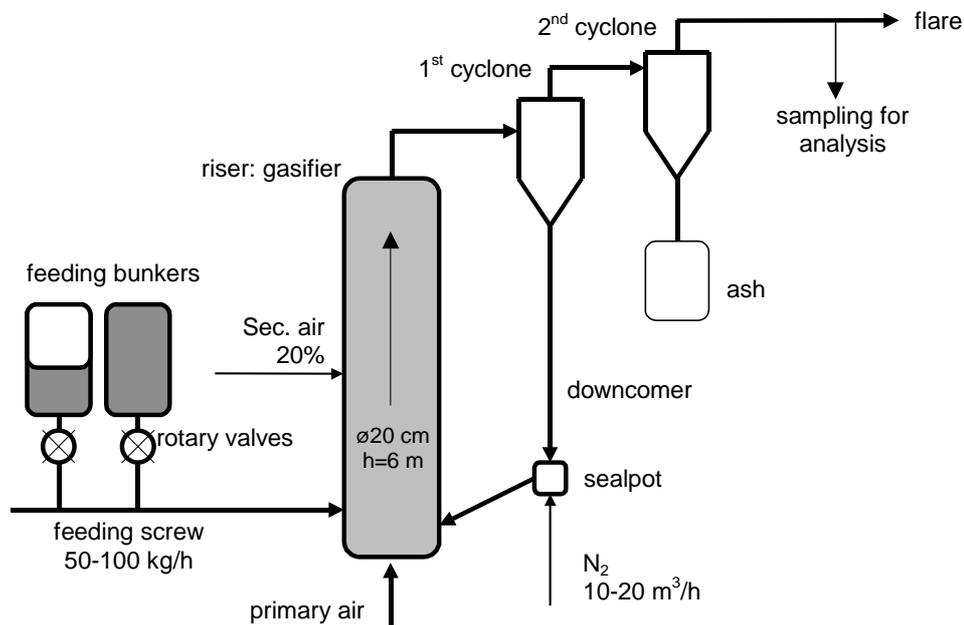


Figure 3.6 *Schematic drawing of CFB (circulating fluidized bed) facility at ECN, called BIVKIN*

Feeding system

It is equipped with various feeding systems of which two can be used simultaneously. The straw used as fuel within this project has been fed using a simple closed bunker and a (non-air tight) rotary valve for the dosing of the fuel. Since the straw was in the form of pellets, no problem

with bridging occurred. The valve dumps the fuel on a screw transporting the material into the bottom of the reactor.

Gasification vessel

The gasification vessel (or reactor or riser) is a 20 cm diameter and 6 meter high refractory lined pipe. Thermocouples and pressure measuring points are present at different location along the length of the reactor.

Circulation system

The gas flow, containing large quantities of sand (and char) passes the first cyclone, which is part of the circulation system. The particles separated from the gas fall down into the downcomer and passes a bubbling fluidized bed seal operated on nitrogen. The total nitrogen flow (feeding system and seal) is 15 Nm³/h in average. The particles are flowing back into the bottom of the reactor.

Fuel gas treatment

The fuel gas passes a second cyclone separating the ash from the gas. The ash passes a valve system for continuous removal. The fuel gas is sampled for analysis just after the second cyclone. The fuel gas is flared.

Measurements

Standard measurements comprise the concentration of components CO, H₂, CO₂, CH₄, ethene, ethane, NH₃, HCl, water, benzene, toluene and xylene in the fuel gas, particles and light tars (molecular weight up to 300 g/mol) in the gas, the solid fuel mass flow, the ash mass flow and the incoming air and nitrogen volumetric flow. The concentration of nitrogen in the fuel gas is calculated and is used for determining the total volumetric flow of the fuel gas. The particles in the fuel gas and the ash from the second cyclone have been analysed for chlorine and sulphur as well as the ash-content (550°C). Samples were taken from the sealpot every hour and subsequently analysed on potassium.

Test procedure

The process temperature has been chosen to be low (750°C) in order to avoid agglomeration. The test took 10 hours. The question was how great the penalty was concerning carbon conversion and tar emission. Since agglomeration wasn't expected to occur within 10 hours at 750°C, the concentration of K in the bed has been monitored during the test in order to measure accumulation. The bed material used is 0.5 mm diameter riversand containing 96.5 wt% SiO₂, 1.6 wt% Al₂O₃, 0.4 wt% Fe₂O₃, 0.7 wt% K₂O and 0.2 wt% Na₂O. The amount of air was adjusted, with constant fuel feeding rate, until a stationary situation was reached at desired temperature. Total heat losses are about 40 kW due to active cooling of feeding screw and convection heat losses of the whole system.

3.3.5 DTA/TGA: differential thermal analysis and thermo-gravimetric analysis at ECN and Risø (e)

In the DTA/TGA apparatus the temperature difference between the ash sample and an inert material is measured during heating, to reveal exothermic and endothermic processes in the ash. Endothermic peaks are associated with decomposition, vaporisation or melting. This information allows location of the initial melting temperatures. The weight loss of the sample is simultaneously measured to reveal (in combination with chemical analysis) e.g. decomposition of carbonates (CO₂ release), vaporisation of alkalis and chemical reactions with the gas phase.

Both ECN and Risø did perform measurements with their DTA/TGA facility. The test apparatus and conditions are seen in table 3.2.

Table 3.2 *Risø and ECN test apparatus and conditions for DTA/TGA-analysis*

	unit	Risø	ECN
apparatus		TA Instruments SDT 2960	Seiko TG/DTA 320U
sample holder		Al ₂ O ₃ (>99.5 %)	Platinum
sample mass	mg	6-16	11
gas flow rate	ml/min	500 or 80	80
temperature range	°C	20-1000/1200	100-1000/1200
heating rate	°C/min	10	10
atmosphere		N ₂ or N ₂ /O ₂ (80% / 20%)	N ₂
sample drying		sample kept dry	In situ, 6 hours at 100 °C

In all of the Risø and ECN tests the temperature was increased to at least 1000°C (1200 °C in some of the tests). In the Risø tests it was emphasised to minimise the uptake of moisture in the time period between ashing and the DTA/TGA test and hence a period for drying at constant temperature in the DTA/TGA was not included. ECN included an approx. 6 hour in situ drying period, and therefore the plots based on ECN data start at approx. 100 °C.

ECN performed in situ cooling and reheating in all of the tests. However, since no thermal reactions could be detected during an extra heat up at ECN, such tests were not performed at Risø.

The tests were carried out using the ash of different fuels, made at different temperatures. Risø also did tests with a mixture of silica sand (0.1 mm) and ash (with different ash/sand ratio's) in order to measure the influence of the sand. In table 3.3 an overview is given of the DTA/TGA tests performed with the different biomass fuels.

Table 3.3 *Experimental programme performed with the DTA/TGA facilities at ECN and Risø. All experiments were carried out both in pure nitrogen and nitrogen/oxygen (80%/20%) atmosphere, except the sand/ash samples*

sample	ashing temperature	fuel #3: unweathered wheat straw	fuel #4: weathered wheat straw	fuel #7: willow
pure ash	450°C	Risø: N ₂ and N ₂ /O ₂ ECN: N ₂	Risø: N ₂ and N ₂ /O ₂ ECN: N ₂	Risø: N ₂ and N ₂ /O ₂ ECN: N ₂
	550°C	Risø: N ₂ and N ₂ /O ₂ ECN: N ₂	Risø: N ₂ and N ₂ /O ₂	Risø: N ₂ and N ₂ /O ₂
	650°C	Risø: N ₂ and N ₂ /O ₂ ECN: N ₂	Risø: N ₂ and N ₂ /O ₂	Risø: N ₂ and N ₂ /O ₂
ash and sand	550°C	Risø: N ₂ (0, 50, 75, 90 and 100% sand)		

3.3.6 Compression strength measurement facility by Risø (TNO) (f)

Compression strength measurements were performed at TNO in the Netherlands as a subcontractor of Risø. TNO is a research institute with some experience with this kind of tests and especially with the preparation of samples for the compression tests.

When a compressive force is applied in an axial direction on a cylindrical pellet, the pellets tend to swell. Depending on the cylinder's elasticity and plasticity, cracks will form in the pellet as the applied force increases. At a certain point, the force reaches a maximum and causing the pellet to break. The measured compression strength will be a function of both the specific

strength of the pellet, the pellet size and the testing device. Both the pellet size and the device is kept constant. The procedure used is according to a standard procedure based on methods used in Abo Academy in Finland:

Low temperature ashing

- milling if necessary to size under 10 mm
- drying at 105 °C till constant weight
- pyrolysis in inert nitrogen atmosphere below 500°C
- ashing of char in nitrogen/air mixture below 500°C to obtain a C content < 1 % (total C according to standard ASTM E 1019)

Sample preparation

- grinding of the ash below < 0.25 mm
- sieving below < 0.125 mm

Pelletising

- compression to pellets in a mould with a pressure of 10 kg/cm²
- pellet dimensions are: length = 1 cm and diameter = 1 cm

Heat treatment

- four hours in air at 600, 700, 750, 800, 850 and 900°C

Compression strength measurement

- in standard equipment: three pellets per temperature

3.3.7 Standard facilities for measuring standard ash melting temperatures by ECN (NMi) and Risø (DK-TEKNIK) (g)

Standard ash melting temperatures are determined both by DK-TEKNIK and NMi in the Netherlands. NMi did the tests in a reducing atmosphere (20% CO in N₂), whereas Risø used dry air as a medium. Using standard procedure ASTM D1857, four typical temperatures were determined:

IDT = initial deformation temperature

ST = softening temperature

HT = hemispherical temperature,

FT = fluid temperature (total fusion)

3.3.8 SEM and HTM (high temperature microscope) at Risø (h)

The SEM spectroscopy measurements were performed with a JSM-840 scanning electron microscope equipped with a NORAN Voyager version 3.5 energy dispersion x-ray spectrometer. In order to obtain a reasonable statistics at least 3 measurements of each type of particles present in the sample were always taken. The measurements included - if possible - also the agglomerated transition bridge between particles. The measurements were performed on bed ash samples before and after agglomeration in the fluidised bed.

ESEM (HTM) investigations were performed using ElectroScan ESEM model E-3 instrument equipped with a high temperature stage and a Kevex energy dispersive x-ray spectrometer. In figure 3.7 the main part of the apparatus is shown. With this facility it's possible to heat a sample in a hot stage while observing it. In order to prevent blowing the powder out from the crucible at a certain temperature (above 400-500°C), probably because of electrostatic forces, it appeared to be necessary to pelletize the sample first. Because this was not desirable, the design of the hot stage was changed and the problem was solved.

The high temperature stage is a specially designed electrically heated unit. As mentioned, this unit was improved during the project. The improved unit was also capable of reaching higher temperatures (1500°C instead of 900°C).

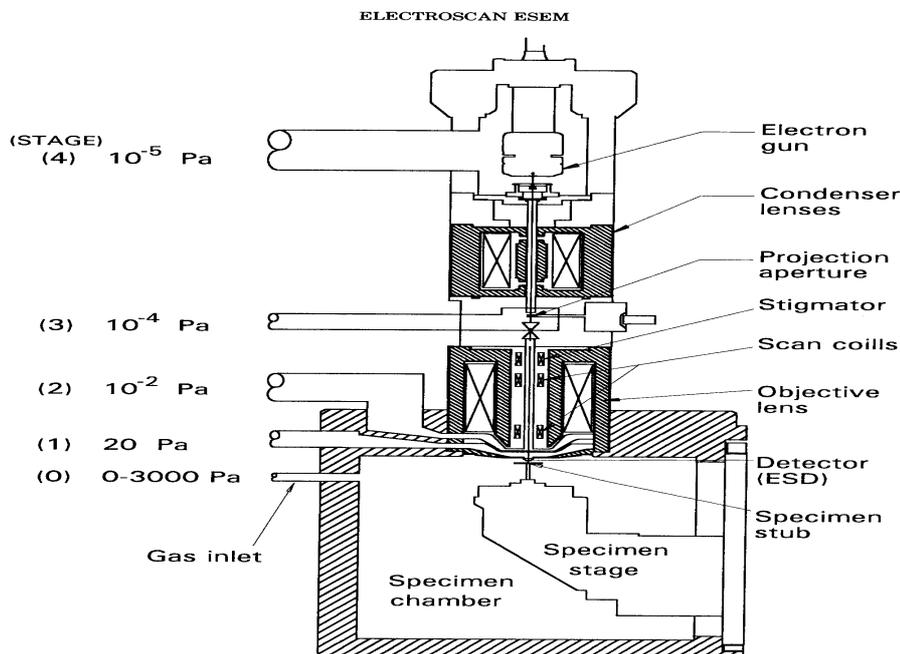


Figure 3.7 *Electroscan ESEM model 20 used to perform the high temperature microscopy (HTM) measurements at Risø*

3.3.9 BFBC: bubbling fluidized bed combustion facility by Risø (VTT) (i)

VTT performed the experiments as a subcontractor of Risø. Both weathered and fresh wheat straw (fuel #3 and 4) was combusted in a small fluidized-bed reactor. The suitable feedstock fraction for the fuel feeding equipment was above 0.56 mm. The fuel is fed with a screw feeder using a small amount of nitrogen (0.5 l/min) as a purging gas. The feeding tube is located 10 cm above the air distributor. A schematic diagram of the lab-scale atmospheric fluidized-bed reactor is shown in Figure 3.8. The diameter of the bed and freeboard is 3.5 cm, and the height from the air distributor to the gas outlet pipe is 53.5 cm. The bed thermocouple is located in the fluid-bed region of the reactor, the height from the air distributor being 6 cm, and the freeboard thermocouple is located 21 cm higher. The bed material used is silica sand (350-560 µm). The fluidization velocity was 0.4 m/s.

3.3.9.1 Test procedure

At a given temperature, a fixed amount of fuel (50 gram) is combusted in the bed containing 65 gram of bed material. The fuel feeding rate is used to control the bed temperature, sometimes together with electric heaters. After the fuel batch is fed, the reactor is emptied and a new experiment starts at a higher temperature (steps of 25°C) until signs of ash sintering are observed. The test series started at the temperature of 700°C.

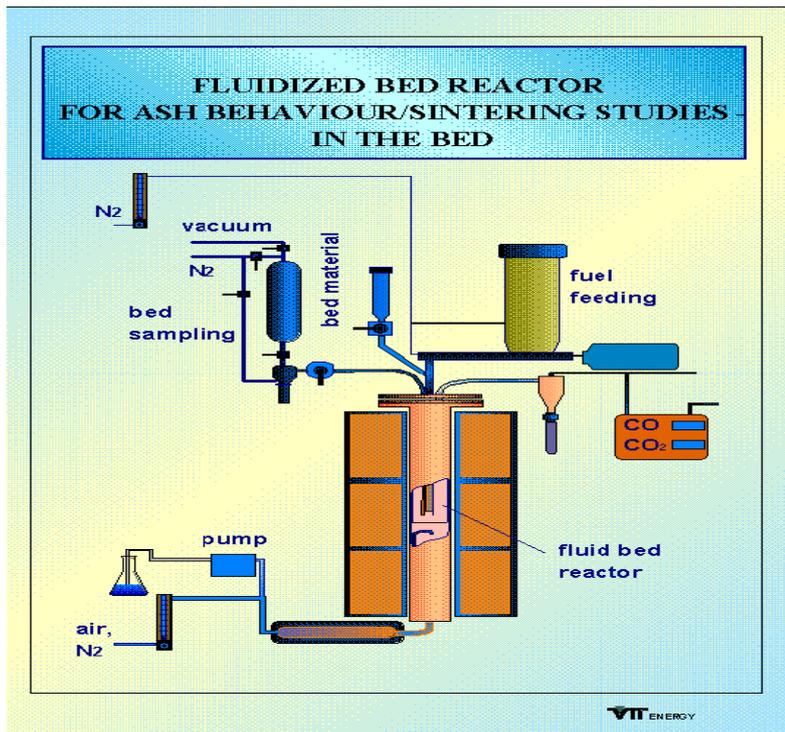


Figure 3.8 Sketch of bubbling fluidized bed combustion facility at VTT in Finland

3.3.10 Other facilities

During the project several facilities have been used with no successful outcome. In this chapter these will be shortly mentioned together with the reason why it was decided to stop using them.

BFBG: bubbling fluidized bed conversion facility at ECN (200 W)

At ECN a 200 W bubbling fluidized bed was constructed. It is designed to operate at a load of about 50 gram/hour and can operate from pyrolysis- to combustion mode. The biomass was fed by a calibrated screw feeder through a cooled tube from the top of the reactor. The quartz reactor had an internal diameter of 40 mm. The whole reactor was placed in a furnace in order to minimise heat loss. During the first tests it appeared that the feeding system failed. The problems were associated with the fact that the feeding-pipe passed through the hot zone which resulted in unwanted hold-up of material and premature pyrolysis, unless the measures taken to prevent early warming up of the material. This meant unstable conditions in the gasification vessel. Fixing the problem seemed hopeless given the small size. It was therefore decided to not continue the experiments with this facility and instead use an existing gasification set-up at the Technical University of Delft in the Netherlands.

BFBG: bubbling fluidized bed gasification facility at Delft Technical University (5 kW_{th})

The gasification facility at TUD is a 1 kg/h bubbling fluidized bed (about 5 kW) with pneumatic feeding system. During the test runs with straw and road side grass, it turned out that the TUD-facility has some major disadvantages. The feeding system often failed feeding the material with constant flow. Because of the feeding system being pneumatic, the air flow is relatively fixed and high. Because of this, and the absence of external heating/cooling, reactor-temperature and air/fuel-ratio are not independently controllable. Another major draw back is the fact that there are no pressure measurements in the bed which can be used to detect agglomeration in an early stage.

All the problems and disadvantages of existing test units have shown us that the specific demands that exist for a test facility to use in the present project are hard to meet. It was decided to build a new facility at ECN. This facility has been used in the project and is described in more detail in chapter 3.3.2.

Sinterdisk

The sinterdisk is a metal plate where ash/sand mixtures can be pressed into pellets and subsequently heat treated up to 900°C. After this it should be possible to press the (sintered) pellet out for further analysis like SEM and compression strength measurement. The test is based on similar tests done in the US to characterise coal. It turned out that the pellets didn't come out in one piece, making further analysis impossible. It was decided to stop the sinterdisk-experiments since also similar tests were performed by TNO (compression strength measurement of ash pellets, see chapter 3.3.6) and Risø (high temperature microscope, see chapter 3.3.8).

3.4 TASK 4: Construction and modification of lab-scale fluidised bed

BFBG: bubbling fluidized bed gasification facility (5 kW_{th}) at ECN (b)

The facility has been designed and constructed for the project. It has been equipped with sampling points, temperature and pressure points etc. in such a way that agglomeration could be determined in an early stage. The design combines the best features of several other facilities around the world.

BFBC: bubbling fluidized bed combustion facility (5 kW_{th}) at ETC (c)

The bubbling fluidized bed combustion unit has been adjusted for the purposes of the project. Since agglomeration is very dependent on temperature, Risø built a fibre-optic IR-probe which can be inserted at various places in the bed or in the free board. Insertion of the probe in the bed required some modification of the fluid bed system. The probe is connected to an Fourier transform infrared (FTIR) spectrometer. This probe measures the temperature of the different particles during the formation of the ash and during the agglomeration process. Furthermore the gas temperature might be extracted from absorption bands of CO₂.

CFBG: circulating fluidized bed gasification facility (500 kW_{th}) at ECN (d)

The circulating fluidized bed gasification facility has been equipped with a facility to take bed material samples for further analyses. This has been done by creating a nitrogen-blown L-valve in the sealpot.

3.5 TASK 5: Development and description of an agglomeration model

Bed samples collected when firing DK straw (fuel #3) and DK weathered straw (fuel #4) show that the overall compositional distributions of the major fraction of the bed particle coatings are mainly limited (>85 % of the material) to the ternary system K₂O-CaO-SiO₂ [4]. Figure 3.9 shows the K₂O-CaO-SiO₂ ternary diagram with some solidus (initial melting) temperatures and the compositions of the bed material coatings from using the two different straws (average value of approximately 20 EDS spot analysis). The chemical compositions of these samples are mainly restricted to the SiO₂ rich corner in figure 3.9, and silicates with these compositions have a first melting temperature of 720°C.

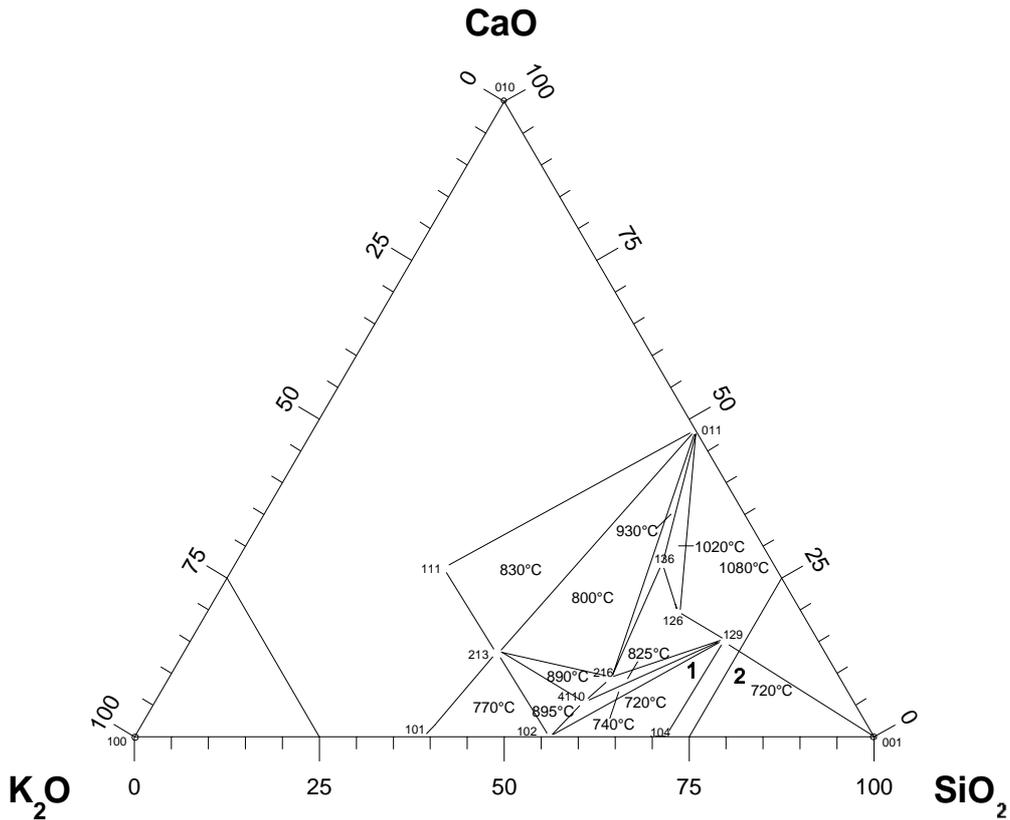


Figure 3.9 K_2O - CaO - SiO_2 ternary diagram with some solidus temperatures (extracted from [4]) and the composition of the different bed particle coatings. Plot marks (abbreviations) for the different bed samples are: 1: wheat straw (fuel #3) and 2: weathered wheat straw (fuel #4)

Previous results [5,6] have indicated that the chemical characteristics, and thereby the melting behaviours of the coatings, are very important for the bed agglomeration process. If the coating has a high enough fraction of molten phase, it will cause bed agglomeration, and, in the most severe cases, defluidization. For silicate melts, the viscosity of the melt has to be taken into consideration to determine the fraction needed for “stickiness”[6]. It was therefore of interest to determine the melting behaviours of bed coatings when burning DK straw (fuel #3) and DK weathered straw (fuel #4), and compare the melting temperatures with the corresponding agglomeration temperatures.

Owing to a lack of thermodynamic data for several intermediate phases in the system K_2O - CaO - SiO_2 , thermodynamic multi-component, multiphase equilibrium calculations could not be used to accurately determine the melting behaviour of the bed particle coatings. Instead, extracting melting behaviour data from the phase diagram K_2O - CaO - SiO_2 performed the evaluation. The average composition (see figure 3.9) of approximately twenty EDS spot analysis from bed sample coatings after agglomeration were included in the comparison.

The resulting fractions of melt (solid lines) versus temperature are shown in figure 3.10 together with the determined initial agglomeration temperature (vertical lines), determined by the controlled fluidized bed agglomeration method.

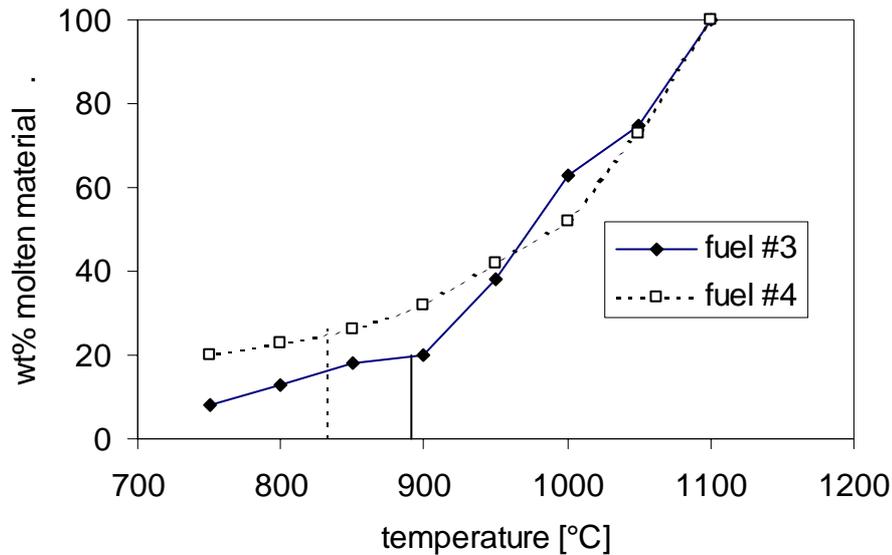


Figure 3.10 *Melting behaviour of different spot characteristics (average values) of bed coatings from bed samples when burning wheat straw (fuel #3) and weathered wheat straw (fuel #4). The initial bed agglomeration temperatures, determined with the controlled bed agglomeration test, are represented by the vertical lines*

Apparently around 20% molten material seems to be enough to initiate agglomeration in the fluidised bed system.

3.6 TASK 6: Performance of lab-scale and bench-scale tests

3.6.1 Chemical laboratories at ECN and Risø (DK-TEKNIK) (a)

Analyses of biomass fuels

The selected biomass fuels, see chapter 3.2, have been analysed for their chemical composition and heating value. Table 3.4 shows the results. The results are stored in a public database, called Phyllis. It is available on the Internet (<http://www.ecn.nl/phyllis>).

Table 3.4 *Chemical composition of the seven selected biomass/waste fuels as used in the project. In the right columns, the average composition is given of several fuels according to the Phyllis database on chemical composition of biomass [7]. HHV: higher heating value, dry: on dry basis, daf: on dry and ash-free basis.*

		1	2	3	4	5	6	7	average values from Phyllis		
		----- wheat straw -----									
		verge grass	Dutch	Danish (dry)	Danish (wet)	sewage sludge	cacao shells	willow	wheat straw	sewage sludge	willow
ash mixed	wt% dry								6.6	39	1.9
ash 450	wt% dry			7.2	3.3			4.0			
ash 550	wt% dry		11.9	7.1	3.3	36.4		2.9			
ash 650	wt% dry		10.1	6.7	2.9			1.6			
ash 815	wt% dry	15.3		4.6			10.2				
volatiles	wt% daf	79.0	78.3	80.7		82.1	75.1	81.2	81.0	87.6	83.1
HHV	kJ/kg daf	19880	18730	19920	20070	24100	20540	19250	19470	21890	19800
C	wt% daf	49.9	49.7	49.4		53.0	52.5	49.2	49.1	52.7	49.7
H	wt% daf	5.68	5.76	6.42		8.20	5.70	5.99	5.87	7.51	6.06
O	wt% daf	40.9	43.0	43.1		29.0	38.2	44.2	43.6	31.0	43.6
N	wt% daf	2.31	0.71	0.48		8.46	3.36	0.51	0.78	6.71	0.63
S	wt% daf	0.17	0.17	0.17		1.11	0.24	0.036	0.15	2.09	0.06
Cl	wt% daf	0.74	0.70	0.43	0.13	0.22	0.02	0.02	0.45	0.23	0.01
F	wt% daf	0.0034	0.0014	0.0011			0.0011	0.010	0.0011	0.025	0.0030
Al	mg/kg dry		940				900	100	940	20300	59.5
As	mg/kg dry	1.0	2.5				1.5	1.2	2.5	5.6	1.3
B	mg/kg dry		5.3				47	9.0	5.3	62	9.8
Ba	mg/kg dry		23				26	4.0	23	400	4.0
Ca	mg/kg dry	13000	3700				2330	4650	2625	39000	5720
Cd	mg/kg dry	1.0	0.6				0.60	2.35	0.2	1.4	2.4
Co	mg/kg dry	1.2	1.5				1.2	0.6	1.5	6.6	0.6
Cr	mg/kg dry	11	3.1				6.1	27	3.1	64	14
Cu	mg/kg dry	10	2.6				39	26	3.3	450	13
Fe	mg/kg dry		580				840	110	290	50800	68
Hg	mg/kg dry	0.04					0.05	0.05	0.02	2.3	0.05
K	mg/kg dry	21000	13200	12400	6100	6000	26550	2550	9133	1675	2894
Mg	mg/kg dry	1900	690				5185	530	863	3700	524
Mn	mg/kg dry	150	17				74	11	8.5	405	9.7
Mo	mg/kg dry		2.3				0.5	0.5	2.3	6.4	0.5
Na	mg/kg dry	1500	320	100	60	1030	59	205	831	895	210
Ni	mg/kg dry	1.6	1.3				11.4	41.5	1.3	170	26
P	mg/kg dry	2400	760	700	600	11100	3725	650	465	21900	708
Pb	mg/kg dry	14	2.9				19	238	0.89	180	238
Sb	mg/kg dry	1.0	3.0				1.0	2.5	3.0	0.3	2.5
Se	mg/kg dry	1.0	2.0				1.0	1.0	2.0	0.4	1.0
Si	mg/kg dry	38000	34000				7050	1280	20250	32600	618
Sn	mg/kg dry	10	2.0				2.8	1.7	2.0	24	1.7
Sr	mg/kg dry		25					14	25	350	14
Te	mg/kg dry	1.0					1.0	1.0			1.0
Ti	mg/kg dry		37					9.0	37	420	4.0
V	mg/kg dry	6.1	1.7				2.0	0.4	1.7	14	0.28
Zn	mg/kg dry	44.0	12				91	64	12	930	97

From the table, some observations can be made. The K- and Cl-content of straw decreases significantly by allowing rain to wash the material. At the same time, the ash content also is reduced by washing. This may be explained by the leaching out of inorganic material. The K-content, generally thought to have a main role in agglomeration, is very high for verge grass and cacao shells (more than 2 wt% of the fuel). Although less in concentration, also the wheat straw (not washed by rain) contains large amounts of K. Sewage sludge however contains much less K but has relatively high amounts of sulphur, calcium and iron. Furthermore, verge grass and Dutch wheat straw contain very much silicon compared to the other fuels, probably due to sand.

In table 3.5 some indices used for predicting problems concerning agglomeration are given. The alkali-index is the ratio of the sum of K_2O and N_2O and the higher heating value. Values higher than 0.17 kg/GJ are considered to cause possibly problems, values exceeding 0.34 kg/GJ almost certainly cause problems concerning slagging and fouling. Another index is the molar ratio between potassium and chlorine. For combustion purposes also sulphur has to be considered. The idea about this ratio is that it gives an indication of how volatile the K is. Chlorine and (for combustion) sulphur are important elements forming volatile components with potassium.

Table 3.5 *Some indices for the fuels used in the project*

		1	2	3	4	5	6	7	average values from Phyllis		
		verge grass	Dutch	wheat straw		sewage sludge	cacao shells	willow	wheat straw	sewage sludge	willow
				Danish (dry)	Danish (wet)						
alkali-index	kg/GJ	1.6	0.98	0.81	0.38	0.56	1.7	0.18	0.7	0.24	0.19
K/(Cl)-ratio	mol/mol	2.6	1.7	2.6	4.1	2.5	98	12	1.9	0.6	19
K/(Cl+2S)-ratio	mol/mol	1.7	1.1	1.4		0.2	4.4	2.4	1.1	0.03	1.8

From the table it can be seen that only willow and sometimes sewage sludge show a low alkali-index. For cacao shells it turns out that it contains high amounts of K but hardly any chlorine to make the K volatile in gasification atmosphere. This might reduce the agglomeration problems for cacao shells considerably.

Analyses of ashes from biomass fuels

The composition of the ashes produced by three fuels, ashed at different temperatures, is given in tables 3.6 to 3.8. Note that the elements are reported as oxides, according to international agreements. This does not mean that the elements are actually present as oxides.

Table 3.6 *Ash composition [wt%] of willow, ashed at different temperatures*

willow						
ashing temp. [°C]:	450	550	650	450	550	650
analysis by:	ECN	ECN	ECN	Risø	Risø	Risø
P_2O_5	7.3	10.2	10.8	10.0	11.0	13.0
SO_3	2.6	3.2	3.6	2.5	2.4	4.1
Na_2O	2.2	2.5	2.57	2.6	2.7	3.1
MgO	4.1	4.8	5.1	4.6	4.8	5.0
Al_2O_3	2.6	0.3	0.3	1.7	1.8	2.0
SiO_2	27	2	2	17	17	20
K_2O	10.1	12.1	12.8	12.0	13.0	13.0
CaO	25	37	38	30	32	36
TiO_2	0.15	0.03	0.02			
Fe_2O_3	1.4	0.3	0.2	1.4	1.4	1.6
CO_2	0.9	2.2	1.8	16	15	7.5
Cl	0.41	0.75	0.67	0.75	0.49	0.16
sum	84	76	77	99	102	105

Table 3.7 *Ash composition [wt%] of wheat straw (dry), ashed at different temperatures*

wheat straw (dry)						
ashing temp. [°C]:	450	550	650	450	550	650
analysis by:	ECN	ECN	ECN	Risø	Risø	Risø
P ₂ O ₅	2.7	2.1	2.4	2.5	2.5	2.3
SO ₃	4.1	4.0	5.2	3.7	3.1	4.1
Na ₂ O	0.22	0.25	0.49	0.16	0.16	0.19
MgO	2.1	1.9	2.1	2.0	2.0	1.8
Al ₂ O ₃	0.2	0.1	0.2	<0.2		<0.2
SiO ₂	59	56	56	51	51	51
K ₂ O	17.4	21.5	22.0	21.0	21.0	22.0
CaO	6	6	6	7	7	7
TiO ₂	0.02	0	0.02			
Fe ₂ O ₃	0.1	0.1	0.1	0.09		0.1
CO ₂	0.3	0.2	0.1	0.85	0.69	0.22
Cl	1.7	3.3	1.3	4	3.7	3.8
sum	94	96	96	92	91	93

Table 3.8 *Ash composition [wt%] of weathered wheat straw (wet), ashed at different temperatures*

weathered wheat straw (wet)						
ashing temp. [°C]:	450	550	650	450	550	650
analysis by:	ECN	ECN	ECN	Risø	Risø	Risø
P ₂ O ₅	3.8	4.2	4.3	4.0	4.1	3.6
SO ₃	5.8	5.6	6.4	4.5	4.4	5.9
Na ₂ O	0.2	0.3	0.4	0.2	0.3	0.3
MgO	2.6	2.8	3.1	2.6	2.4	2.8
Al ₂ O ₃	0.3	0.4	0.4	0.4	0.4	0.5
SiO ₂	39	45	47	37	39	40
K ₂ O	21	19	22	23	24	25
CaO	12	13	14	15	15	16
TiO ₂	0.02	0.02	0.02			
Fe ₂ O ₃	0.2	0.2	0.2	0.33	0.3	0.3
CO ₂	0.8	0.7	0.5	7.37	2.79	0.99
Cl	0.8	0.6	0.9	1.0	0.7	0.4
sum	87	92	99	95	93	96

The following observations can be made. In general ECN and Risø report similar results. The chemical analysis results show some variance for the same fuel, probably due to the heterogeneous nature of biomass and the small size of the analysed samples. The high silicon content in willow ashed at 450 °C is likely to be due to contamination with sand or earth. The sum of all oxides is 70-80% for willow and about 85% for straw. This probably means that certain elements are measured in too low concentrations. This might well be the case for SiO₂ which is difficult to dissolve and is present in relatively large quantities.

The differences between the ashes made by combustion at different temperatures are rather small. Ashing at temperatures going from 450° to 650°C does neither result in a significant loss of alkalis expressed in wt% of the ash nor does it result in a significant decrease of the ash content (see tables 3.6 to 3.8). There is a decrease in carbonate content in some of the ashes with increasing temperature. This however is probably not so important as carbonates decompose before they melt and a loss of carbonate would therefore not influence the melting behaviour determined in DTA/TG or other techniques.

3.6.2 BFBG: bubbling fluidized bed gasification facility (5 kW_{th}) at ECN (b)

Tests have been performed with different fuels. Using Dutch straw, different bed materials and additives are used as well as bed material sizes. Figure 3.11 shows a typical result of a so-called X-test, see chapter 3.3.2. for description of procedure. In figure 3.12 a detail of the last 20 minutes is given.

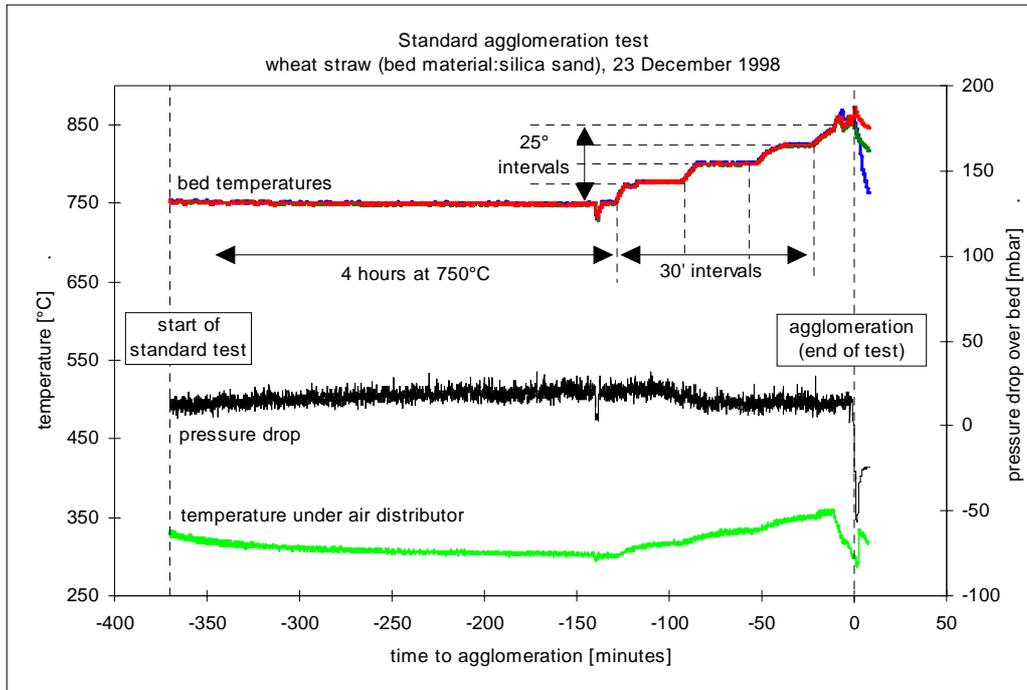


Figure 3.11 Result of X-test with Dutch wheat straw in standard agglomeration test in BFBG at ECN

From the figure it's clear that the temperatures within the bed start to deviate as soon as agglomeration is starting. The differences between the different thermocouples keep increasing when continuing the conversion process. At a certain time also the pressure drop across the bed starts to change suddenly. This usually is considered as the moment agglomeration starts. From the figure however it's clear that about 7 minutes earlier (in this particular case) the temperatures in the bed start to deviate. Even earlier, the temperature just underneath the air distributor plate started to decrease. So, the moment pressures drop over the bed starts to change and agglomeration is considered to be a fact is preceded by changing temperatures.

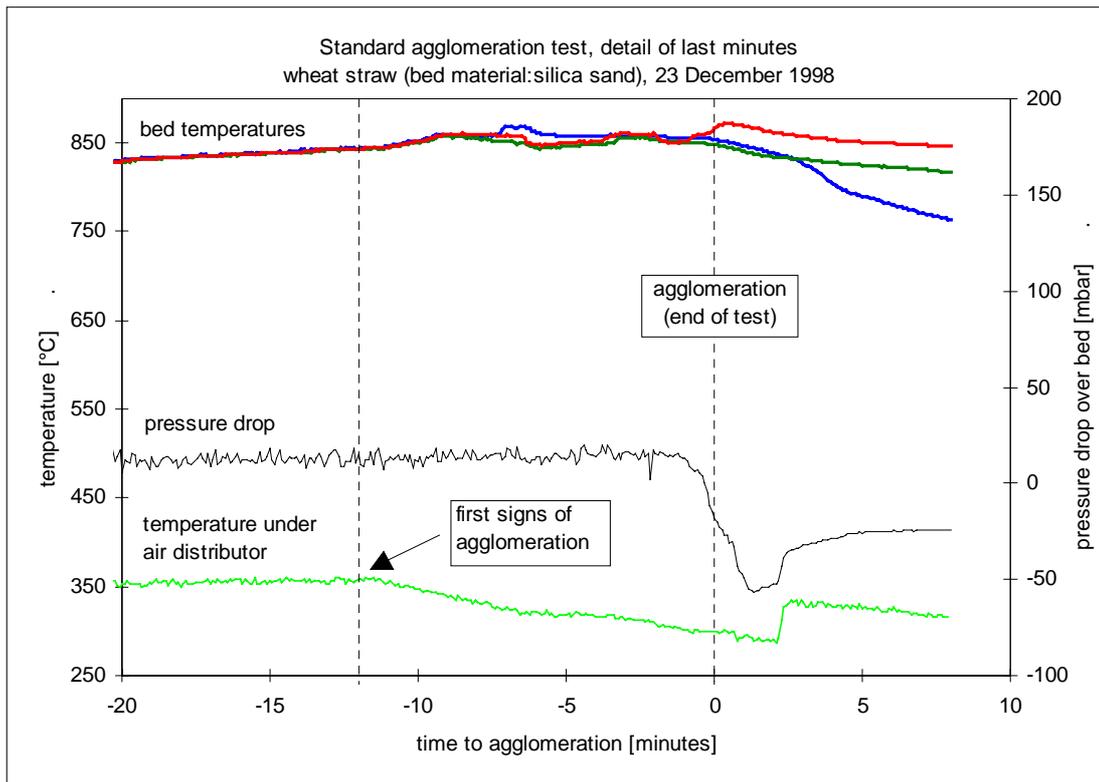


Figure 3.12 Detail of last 20 minutes of X-test with Dutch wheat straw in standard agglomeration test in BFBG at ECN.

Tables 3.9 and 3.10 sum up the bed materials and additives used in the different experiments and the different parameters and data relevant for this project. Table 3.11 shows the agglomeration temperatures for the tests done.

Table 3.9 Bed material data used for tests in BFBG facility at ECN

bed material	main components	particle size [μm]			density [kg/m^3]	total outer surface for 1 kg material [m^2]	min. fluidization velocity for median size particles [m/s]
		D_{10}	D_{50}	D_{90}			
silica (500 μm)	SiO_2 (>96.5%)	480	500	520	2600	4.6	0.11
silica (250 μm)	SiO_2 (>98.5%)	120	250	320	2600	9.2	0.028
alumina	Al_2O_3	120	200	250	4000	7.5	0.027
mullite	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	120	200	250	3200	9.4	0.022

Table 3.10 The additives used in the experiments in the BFBG at ECN. The mass flow of all additives was 2 wt% of the fuel mass flow (approx. 1 kg/h)

additive	formula	way of feeding	density [kg/m^3]	size [μm]	remarks
kaolin	$\text{Al}_2\text{SiO}_5(\text{OH})_4$	mixed with fuel	2600	< 250	Euroclay, extruder dried DB-kote II
magnesite	MgO	mixed with fuel	3600	< 75	M.A.F., MgO no 12, mesh 200
dolomite	$\text{MgCO}_3 \cdot \text{CaCO}_3$	separate feeding	1400	700-1000	Marches les Dames
gibbsite	$\text{Al}(\text{OH})_3$	mixed with fuel	2400	30-150	Pecheney Belgium NV, SH950

When comparing tests 1 with 2 and test 20 with 5 it is striking that the temperatures are (about) the same but the time to agglomeration is very different. The time to agglomeration for an X-test is relatively long. Apparently, in an X-test the temperature reached in the last phase of the test is the most crucial parameter for agglomeration. Even though the amount of ash in the system is much higher for the X-tests than for the Y-tests mentioned, this does not result in significantly quicker agglomeration. This observation leads to the conclusion that the agglomeration temperature as measured in an X-test is the limiting temperature even for short-term experiments.

Table 3.11 *Overview of tests performed (marked grey) with the lab-scale BFBG (WOB) at ECN and the measured agglomeration temperature and, if applicable, the time-to-agglomeration. All fuels were sieved to 700-2000 μm . Bed material is silica (SiO_2), unless stated otherwise*

test no.	type of test	fuel #1 verge grass	fuel #2 Dutch straw	fuel #4 Danish straw (weathered)	fuel #6 cacao shells	fuel #7 willow	bed material or additive (*)	bed material size [μm]
1	X	825°						500
2	Y	825°/20 minutes						500
3	Y	800°/1 hour						500
4	X		810° and 810°					500
5	Y		835°/2 hours					250
6	Y		810°/8.4 hours					250
7	X		840°				bed: alumina	200
8	X		840°				bed: mullite	200
9	X		>930°				add: kaolin	250
10	X		>960°				add: magnesite	250
11	X		840°				add: gibbsite	250
13	X			800°				500
15	X				900°			500
16	X					875°		500
18	X		>900°				add: dolomite	200
20	X		840° and 840°					250

(*) only mentioned if test has not been done using silica as bed material with no additive, when additives were used, 2wt% of fuel input has been added, see tables 3.9 and 3.10.

Figure 3.13 shows the relation between time and agglomeration temperature. It shows that agglomeration occurs at lower temperature if more fuel has been added to the system. In other words, it illustrates that accumulation of elements has the expected effect on agglomeration. For the tests performed, an extension of time (amount of fuel and ash fed to the system) with a factor of 3 decreases the agglomeration temperature with about 25°C.

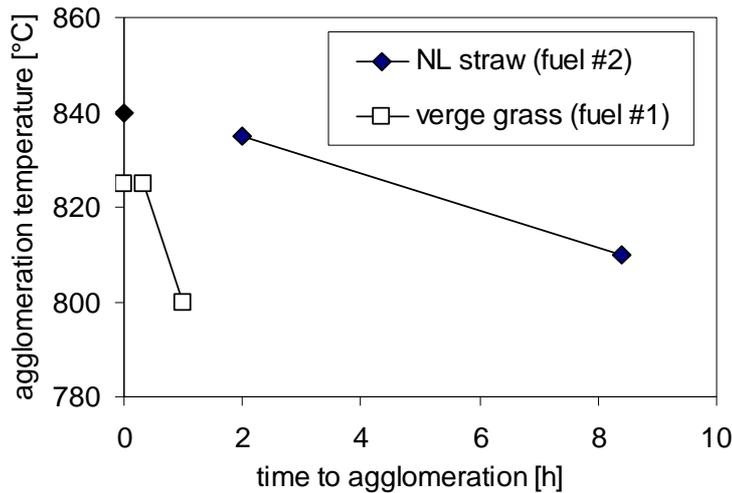


Figure 3.13 *The relation between time to agglomeration and agglomeration temperature for two fuels, the data on the y-axis are the results of a standard X-test (starting at 750°C and gradually increasing)*

Furthermore, smaller bed material increases agglomeration temperature (test 20 compared to test 4) and extends the time to agglomeration at a given temperature (test 6 compared to test 3 and test 5 compared to test 2). This might be the result of two effects: (1) smaller bed material means also more bed material surface available for melting components and thus thinner sticky layers less capable of sticking together particles and (2) more rigorous mixing and more friction between particles because of the larger gap between minimum fluidization velocity and actual velocity.

Cacao shells seem to show low tendency for agglomeration compared to the other fuels. This is not what would be predicted when considering K-content as the most useful prediction tool. Cacao shells have the highest K-content of all fuels tested. However, cacao shells are very low in chlorine. The high K/Cl ratio, also given in table 3.5, indicate that there's little chlorine to make the K mobile. The low chlorine content is a plausible explanation, other reasons should not be excluded.

The use of alumina and mullite (tests 7 and 8) as bed material instead of silica (test 20) does not change the agglomeration temperature. This might mean that either the silicon of the sand does not play a significant role in agglomeration or the silicon already present in the straw is more than the minimum amount necessary for the process of agglomeration. Since the amount of silicon in the straw is rather high (3.4 wt% Si in the dry fuel which is 7.3 wt% if present as SiO₂) the latter possibility seems plausible.

Kaolin, magnesite and dolomite used as additives (tests 9, 10 and 18 versus test 20) turn out to increase the agglomeration temperature by at least 60°C. Gibbsite however does not seem to improve the process. Apparently, gibbsite does either not form the porous particles in the reactor as expected or the extra surface created by the porous particles does not operate as a physical absorber of any relevance. It may also be the case that the gibbsite, either before or after the conversion to porous particles, has a too low retention time in the bed to be able to physically absorb the (potentially) melting components. Since the particle size of the gibbsite is only around 100 µm, this might well be the case.

Surprisingly, willow showed agglomeration behaviour during a standard test at a temperature as low as 875°C. Willow generally is considered to show no tendency for agglomeration during thermal conversion. It's not clear what might be the reason for this.

Chemical analysis were carried out on bed material collected during gasification (after 4 hours at 750°C) of test 9 and test 20. From test 1 and 13 material was collected after the experiment where agglomeration was created. The analyses were done in order to see possible enrichment of certain elements of the coating of the bed material compared to the ash of the fuel. Table ... shows the main results focussed on the concentration of K.

Table 3.12 *Chemical analyses, expressed as ratios, of bed material during and after several controlled agglomeration experiments*

fuel	fuel #2 Dutch straw	fuel #2 Dutch straw	fuel #1 verge grass	fuel #4 Danish straw (weathered)
test#	9 *	20	1	13
sample	after 4 hours at 750°C	after 4 hours at 750°C	after controlled agglomeration	after controlled agglomeration
$(K/Na)_{bed} / (K/Na)_{fuel}$	0.68	0.63	0.81	0.14
$(K/Mg)_{bed} / (K/Mg)_{fuel}$	0.98	0.84	0.96	0.48
$(K/Al)_{bed} / (K/Al)_{fuel}$	0.73	0.24	0.15	0.19
$(K/P)_{bed} / (K/P)_{fuel}$	0.86	0.75	0.57	0.38
$(K/Ca)_{bed} / (K/Ca)_{fuel}$	1.01	0.83	0.89	0.85
$(K/S)_{bed} / (K/S)_{fuel}$	72	45	14	17

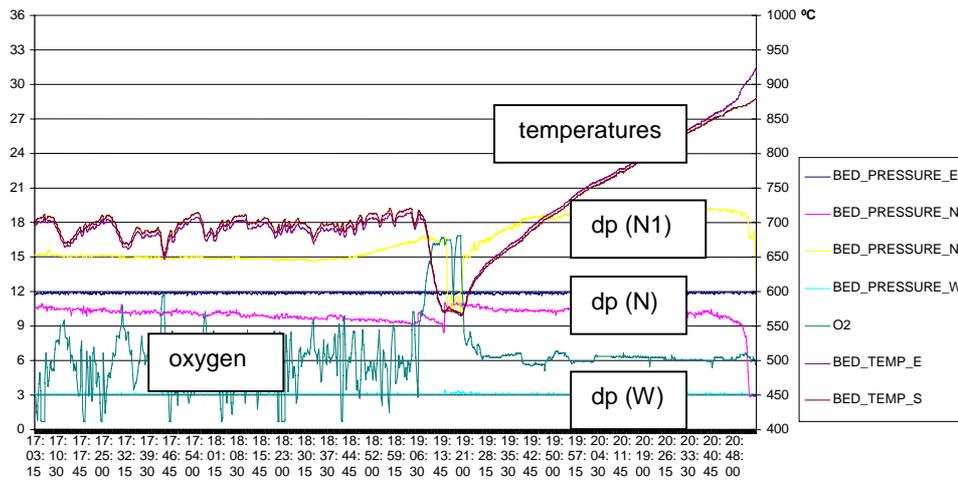
* kaolin (2 wt%) used as additive, composition of fuel plus additive has been used for calculating the ratios

It turns out that the ratios presented in the above table are close to unity. This might indicate that the bed materials coating has roughly the same composition as the fuel used in the experiment. The expected enrichment of K in the coating compared to the fuel is not found. The high ratios shown in the lower row are caused by the conversion of sulphur to H₂S during the test, taking away S to be used in the bed material coating.

3.6.3 BFBC: bubbling fluidized bed combustion facility (5 kWth) by Risø (ETC) (c)

Figure 3.14 shows a typical recording of a test performed with the bubbling fluidised bed combustion facility at ETC. Tables 3.13 and 3.14 summarise the main results of the agglomeration tests. It turned out that the ashing temperature (the temperature at which the fuel is combusted during the first phase of every experiment prior to increasing the temperature of the bed) is the main parameter influencing the agglomeration temperature. Other operational variables i.e. air flow, oxygen content, and size of sand particles have less influence on the agglomeration temperature. The influence of the ash concentration (determined by the amount of fuel feed into the system) has also a limited influence as long as there is sufficient amount of ash available to form an agglomeration mixture. Figure 3.15 shows the relation between the amount of fuel (ash) in the system and the agglomeration temperature.

Agglomeration Experiment 970623_risø_0006: Tashing= 694 °C, O2= 5.6 %, Taggl_init= 687 °C,
 Taggl_final= 855 °C



2151 g Dry Wheat Straw_rise-1 (6.3 % ash), 542 g Silversand (200-250 μm), 20 % fuel ash

Figure 3.14 Typical output from experiment with BFBC at ETC. In this case DK straw is used as a fuel. The experiment ends with a sudden decrease of pressure drop and a increase of temperature differences in the bed.

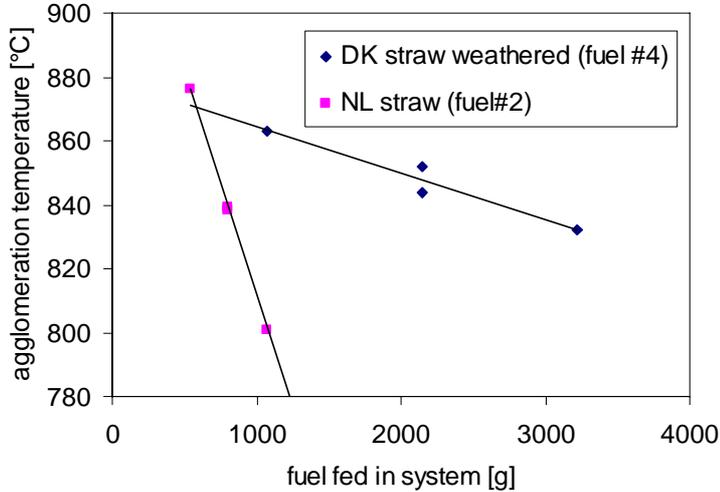


Figure 3.15 The effect of the amount of fuel whcih was fed into the BFBC and the observed agglomeration temperature

Table 3.13 *Agglomeration test results of three different straws as well as willow in ETC fluidised bed combustion facility*

test no.	fuel	fuel fed [g]	ashing temp. [°C]	agglomeration temp. [°C]
1	DK straw (fuel #3)	2151	659	891
9	DK straw (fuel #3)	2151	693	860
6	DK straw (fuel #3)	2151	694	855
10	DK straw (fuel #3)	2151	702	785
8	DK straw (fuel #3)	2150	727	732
33	DK straw weathered (fuel #4)	2151	745	852
34	DK straw weathered (fuel #4)	2151	748	844
35	DK straw weathered (fuel #4)	3225	750	832
36	DK straw weathered (fuel #4)	1075	747	863
55	DK straw weathered (fuel #4) with 3 wt% kaolin	1075	746	897
56	DK straw weathered (fuel #4) with 1 wt% kaolin	1075	748	849
43	NL straw (fuel #2)	538	749	876
47	NL straw (fuel #2)	807	747	839
46	NL straw (fuel #2)	807	753	838
45	NL straw (fuel #2)	1076	745	801
48	willow (fuel #7)	2000	691	898
49	willow (fuel #7)	2000	772	882
50	willow (fuel #7)	964	774	892
51	willow (fuel #7)	3500	774	892

Table 3.14 *Agglomeration test results of pure sewage sludge and straw/sewage sludge mixtures (two kinds, a: Egaa, b: Østdeponi) in ETC fluidised bed combustion facility*

test no.	fuels	straw in mix [wt%]	total fuel fed [g]	ashing temp. [°C]	agglomeration temp. [°C]
18	sewage sludge ^a (fuel #5)	0	525	885	970
37	sewage sludge ^b (fuel #5)	0	525	798	939
21	DK straw (fuel #3) and sewage sludge ^a (fuel #5)	9	578	802	974
22	DK straw (fuel #3) and sewage sludge ^a (fuel #5)	9	578	891	956
23	DK straw (fuel #3) and sewage sludge ^a (fuel #5)	34	790	804	968
24	DK straw (fuel #3) and sewage sludge ^a (fuel #5)	50	1050	804	915
25	DK straw (fuel #3) and sewage sludge ^a (fuel #5)	59	1292	800	899
26	DK straw (fuel #3) and sewage sludge ^a (fuel #5)	71	1838	799	942
27	DK straw (fuel #3) and sewage sludge ^a (fuel #5)	50	1050	798	937
28	DK straw (fuel #3) and sewage sludge ^a (fuel #5)	75	1050	800	974
29	DK straw (fuel #3) and sewage sludge ^a (fuel #5)	86	918	799	944
30	DK straw (fuel #3) and sewage sludge ^a (fuel #5)	86	918	750	956
38	DK straw (fuel #3) and sewage sludge ^b (fuel #5)	67	800	798	932
39	DK straw (fuel #3) and sewage sludge ^b (fuel #5)	80	1338	800	919
40	DK straw (fuel #3) and sewage sludge ^b (fuel #5)	89	2414	800	914
41	DK straw (fuel #3) and sewage sludge ^b (fuel #5)	86	1876	795	920

From the experiments with fuel #3, the relation between ashing temperature and agglomeration temperature becomes clear, see figure 3.16.

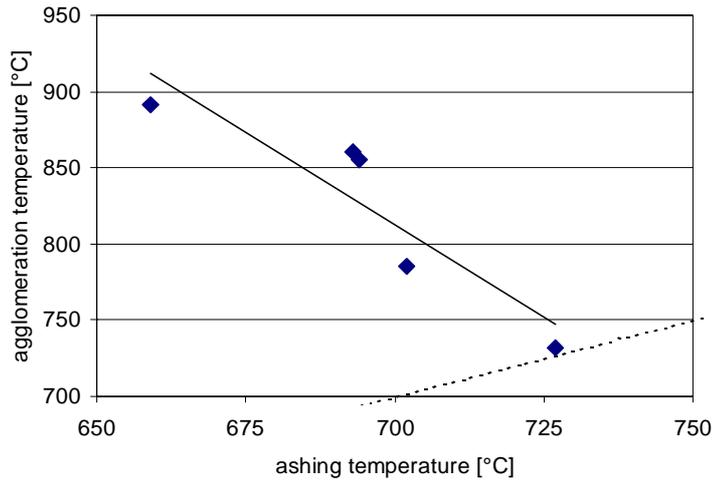


Figure 3.16 *The relation between agglomeration temperature and ashing temperature in BFBC experiments with DK straw (fuel #3). The dotted line represents the minimum agglomeration temperature (equal to ashing temperature)*

Furthermore, sewage sludge seems to have a positive effect on preventing agglomeration. In all cases the addition of sewage sludge increases the agglomeration temperature as can be seen in figure 3.17. Also kaolin as an additive improves the process, 3% kaolin increases the agglomeration temperature with about 30°C.

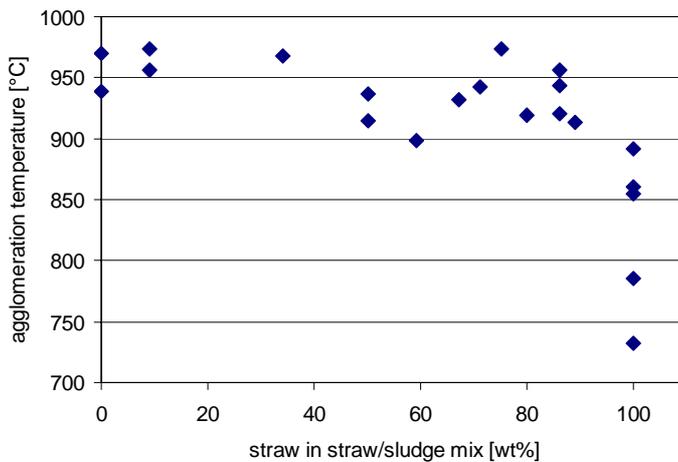


Figure 3.17 *The effect of sewage sludge in a mixture of straw and sewage sludge*

The FTIR pyrometric measurements turn out to clearly show the temperature distribution of the particles in a fluidized bed during combustion. Figure 3.18 shows the temperature distribution during test 6 (DK straw, fuel #3) during the combustion at 694°C. It is clear that the range of temperature broadens because of the combustion process. Particles have temperatures up to 100°C higher than the median value. On the other side, colder particles exist, probably freshly (cold) fuel particles.

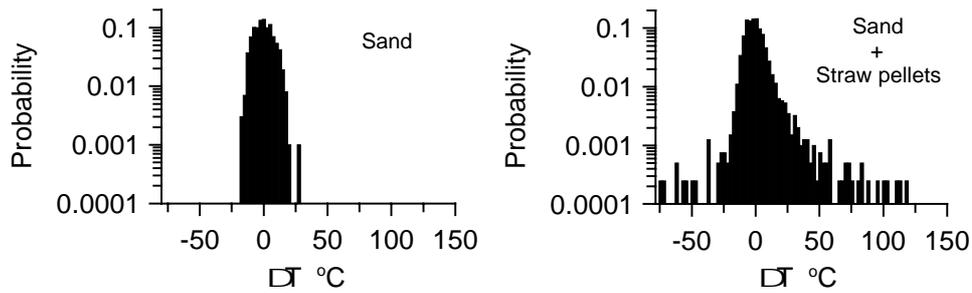


Figure 3.18 Measured temperature distribution in BFBC at ETC during test 6 (DK straw, fuel #3) at 694°C bed average temperature at 80 mm above distributor plate (approx. 70 mm above bed)

Table 3.15 shows the measured particle temperatures during several tests. It can be seen that particles can have 50-100°C higher temperatures than the bed temperature. Peaks up to 130°C have been measured. Needless to say that this can have significant effects on the agglomeration behaviour. This might be one of the main reasons for the relation shown in figure 3.16 where the agglomeration temperature drops when the ashing temperature increases. At high ashing temperatures there is a relative high probability that some particles have temperatures high enough to initiate agglomeration.

The over-temperature apparently existing during combustion, is probably dependent on the fuel material. Not only the type of material, but also physical characteristics as moisture content and particle size. In the above-described experiments, all fuel were palletised. Because this might decrease the overall reaction rate because of limitations of heat and mass transfer, excess temperatures are probably less than in cases where fuel is fed in a non densified form.

Table 3.15 Overview of measured particle temperatures during the combustion tests in the BFBC at ETC. ΔT_{par} is the average of the 10 hottest events, $\Delta T_{par, max}$ is the highest value measured during the test, both temperatures shown as difference with bed temperature

test no	bed temp. [°C]	O ₂ in gas [vol%]	fuel	probe position [mm above distributor]	ΔT_{par} [°C]	$\Delta T_{par, max}$ [°C]
2	784	7.2	DK straw, fuel #3	80	63	96
3	739	6.5	DK straw, fuel #3	103	42	64
4	737	10.2	DK straw, fuel #3	103	53	67
5	730	3.8	DK straw, fuel #3	58	42	58
6	694	5.6	DK straw, fuel #3	80	58	95
7	735	11.4	DK straw, fuel #3	80	85	119
8	727	4.2	DK straw, fuel #3	80	90	123
9	693	5.4	DK straw, fuel #3	80	75	120
10	702	5.6	DK straw, fuel #3	80	98	120
16	694	7.6	sewage sludge, fuel #5	80	62	67
17	686	5.7	sewage sludge, fuel #5	103	80	129
18	885	5.3	sewage sludge, fuel #5	103	35	69
19	703	5.7	sewage sludge, fuel #5	80	43	67

3.6.4 CFBG: circulating fluidized bed gasification facility (500 kW_{th}) at ECN (d)

The 500 kW_{th} circulating fluidized bed gasification facility at ECN has been used to convert wheat straw pellets from the Netherlands (fuel number 2) during a 10 hour experiment. The gasification temperature was chosen to be low: 750°C. Table 3.17 sums up the main results of the experiment. Also shown are some results obtained with other fuels in the same facility. What is clear from the figures is that the carbon conversion of the straw during the low-temperature test was low, as low as 75%. This is one of the penalties for the choice of a low process temperature. This however is not always the case. It is known that K, considered as the

major evil element for agglomeration, can also have a catalytic function for gasification reactions. In a confidential experiment in the same facility using chicken manure, very high carbon conversion rates were obtained unless the low process temperature (750°C). This was expected to be the result of the relatively high content of calcium and potassium as catalytic active elements for gasification.

The chlorine analysis of the second cyclone ash revealed that about 50% of the chlorine originally present in the straw is retained in the ash. This is a very high fraction compared to other experiments (at temperatures between 800 and 850°C) where this fraction is 10-20%. Probably, chlorine compounds like KCl are preferably attached to solid particles at temperatures around 750°C. Table 3.16 shows the transfer coefficient of some elements in the ash from the second cyclone.

During the test, every hour bed material samples were taken from the sealpot and analysed for K-content. Figure 3.19 shows the concentration profile.

Table 3.16 *The fraction of some elements from fuel appearing in cyclone ash (transfer coefficient)*

	verge grass	Dutch wheat straw	cacao shells	average value for CFBG at ECN
Al		0.90		0.9
As	0.93	< 0.48	< 0.60	0.6
B		0.87		0.8
Ba		0.95		0.9
Ca	1.00	0.92	1.73	0.8
Cd	< 0.04	< 0.12	< 0.04	0.1
Cl		0.48		0.4
Co	0.50	0.31	0.78	0.5
Cr	0.84	1.00	1.50	0.6
Cu	0.93	1.43	1.24	0.7
Fe		0.94		0.7
K	0.34	0.79	0.52	0.6
Mg	0.49	1.05	0.58	1.2
Mn	0.47	1.03	0.75	0.7
Mo		0.87		1.1
Na	0.47	1.29		0.6
Ni	2.62	1.05	0.83	0.8
P	0.41	0.95	1.32	0.7
Pb	< 0.12	1.60	0.08	0.3
S	0.34	0.21	0.29	0.3
Sb	0.51	< 0.16	< 0.24	1.3
Se	< 0.44		< 0.36	1.3
Si	0.42	1.12	0.46	0.6
Sn	0.10	< 0.18	< 0.04	0.8
Sr		0.97		0.8
Ti		0.96		1.0
V	0.67	0.95	0.78	0.7
Zn	0.71	1.03	1.53	0.6

Table 3.17 Numerical results of the gasification tests using different biomass fuels in the CFBG at ECN. Abbreviations: ar: as received (wet basis), HHV: higher heating value, CC: carbon conversion, CGE: cold gas efficiency, na: not analysed

fuel		fuel #1 verge grass	fuel #2 Dutch wheat straw	fuel #6 cacao shells	fuel #7 willow
reference		[1]	this project	[1]	[1]
<i>PROCESS CONDITIONS</i>					
fuel	kg/h ar	102.6	105	59.8	69
fuel water content	wt% ar	7.3	9.2	13.4	17.5
energy input (HHV)	kW	450	447	275	323
temperature	°C	815	750	822	827
<i>FUEL GAS</i>					
CO	vol% dry	10.64	12.85	8.00	9.40
H ₂	vol% dry	8.45	4.68	9.02	7.20
CO ₂	vol% dry	15.18	14.06	16.02	17.10
CH ₄	vol% dry	2.79	3.56	2.34	3.30
C ₂ H ₄	vol% dry	1.04	1.39	1.13	1.10
C ₂ H ₆	vol% dry	0.04	0.18	0.05	0.10
benzene	vol% dry	0.13	0.18	0.16	0.21
toluene	vol% dry	0.041	0.063	0.06	0.065
xylene	vol% dry	0.005	0.012	0.03	0.013
H ₂ S	vol% dry	na	na	0.002	0.005
HCl	vol% dry	0.0002	0.0007	0.0001	na
NH ₃	vol% dry	1.25	0.29	0.81	0.180
Ar (calculated)	vol% dry	0.60	0.57	0.58	0.58
N ₂ (calculated)	vol% dry	59.5	62.2	61.5	60.5
H ₂ O (calculated)	vol% wet	8.4	22.7	10.3	14.3
light tars	mg/m _n ³	na	5400	na	na
heavy tars	mg/m _n ³	273	na	78	510
dust	g/m _n ³	6.0	22.9	13.1	1.7
HHV fuel gas (calc.)	MJ/m _n ³ dry	4.90	5.12	4.61	4.92
dry fuel gas flow (calc.)	m _n ³ /h dry	206	155	131	151
wet fuel gas flow (calc.)	m _n ³ /h wet	224	190	145	172
<i>BALANCES and OTHER VALUES (calculated)</i>					
total mass balance	%	96.2	102.7	99.3	101.0
C-balance	%	99.5	97.7	103.3	104.3
O-balance	%	93.9	104.7	98.6	101.6
inert-balance	%	66	131	77	88
E-balance (HHV)	%	97.5	98.5	109.5	102.2
CC	%	92.7	75.2	85.9	97.0
GCE	%	64	50	62	66
ER		0.36	0.24	0.34	0.37
linear gas velocity	m/s	7.9	6.3	5.2	6.1
NH ₃ /fuel-N	%	83	45	42	73
H ₂ S/fuel-S	%			4	49

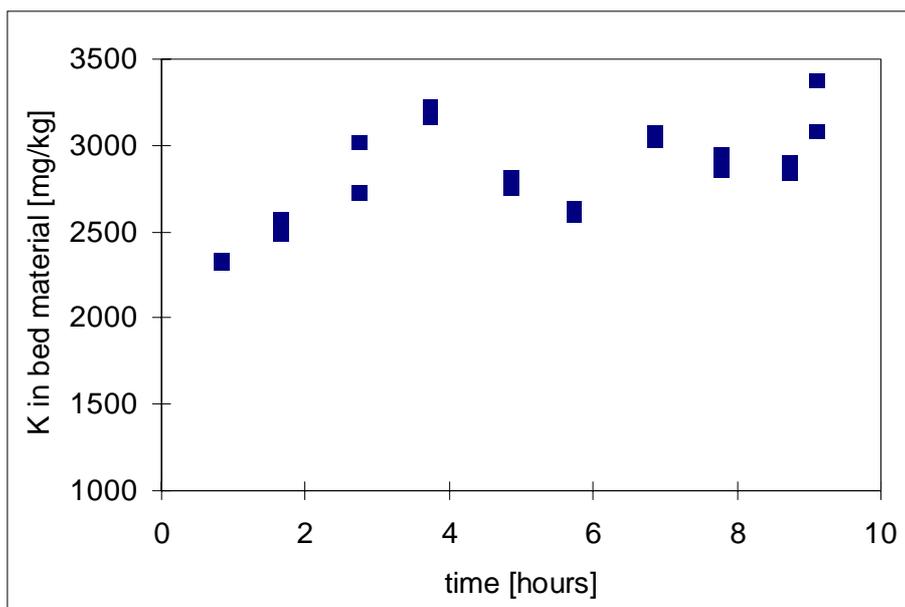


Figure 3.19 *The K-concentration in the bed material taken from the sealpot during the gasification test with Dutch wheat straw (fuel #2)*

From figure 3.19 it is clear that the K-concentration in the bed does not increase significantly during the test: the increase of concentration of 1000 mg/kg in 10 hours corresponds to a retention in the bed of less than 0.5% of the K from the fuel. So, most of the K leaves the gasifier without some kind of bonding to bed material.

The absence of an increase of K-content is not what has been observed during the chicken manure test already mentioned earlier. In this test (also at 750°C), the K-content of the bed material increased from about 2000 to 10000 mg/kg after 10 hours of testing. The difference may be related to the difference in carbon conversion. In the case of straw, much carbon having mineral components attached to it, are removed from the system. This way, elements like K are removed from the system partially, preventing a fast build-up in the system. The gasification of chicken manure showed high carbon conversion and therefore probably didn't remove the K from the system fast enough.

Another difference between straw and chicken manure is the molar ratio K/Cl. This is 3.5 for the manure and 1.7 for the straw indicating that the K in straw is more mobile. This might be one of the reasons for the build-up of K when firing chicken manure.

3.6.5 DTA/TGA: differential thermal analysis and thermo-gravimetric analysis at ECN and Risø (e)

The ECN and Risø results show good agreement, especially concerning the characteristic temperatures of mass losses. Some minor disagreement is seen concerning the extent of mass loss. This is probably reflecting the problem of obtaining fully representative fuel samples.

The difference between inert (N₂) and oxidising atmosphere turns out to be small. Furthermore, no heat effects were noticed during cooling and second heating cycles, which indicates that all processes were non-reversible. Melting is associated with volatile potassium which evaporates from the melt at the high temperatures of 1000°C and 1200°C, thereby preventing substantial solidification effects in the cooling cycle. The high mass loss (>12 %) for pure ashes ashed at 450 or 550°C and low mass loss (a few %) for ashes ashed at 650°C supports this.

Visual inspection revealed that nearly all of the pure straw ash samples were completely fused at 1000°C while willow ash was typically only partly sintered. The tests performed on various mixtures of ash and (100-125 micron) quarts sand revealed that the sand mainly behaves as inactive and inert.

Figure 3.20 shows a typical result. It can be seen clearly that large endothermic effects take place between 700 and 800°C probably due to melting of potassium chloride (melting point 770°C) or potassium silicates (melting point 740-780°C).

Tables 3.18 to 3.20 summarise the main results of the experiments in nitrogen atmosphere. Table 3.21 gives the results concerning experiments with straw ash (550°C) mixed with sand particles (100-125 micron) with varying ratio.

Table 3.18 *Summary of DTA/TGA-measurements with ash from unweathered wheat straw (fuel #3) in nitrogen atmosphere. The bold numbers indicate where melting may start (large heat effect)*

ashing temp.	mass loss (TG)	mass loss rate (DTG)	heat effects (DTA)
450°C	2-4% moisture 150 - 690°C: 5-5.5 % 690 - 1000°C: 6.5-8.5 %	increase from: 650 - 875°C max. 725°C max. 835°C	simultaneous large endotherms: 690 - 875°C 750 - 800°C max. 780°C
550°C	0.5-3% moisture 150 - 680°C: 2-2.7% 680 - 870°C: 7.2-9.2% 870 - 1200°C: 1.5-4.1%	increase from: 680-870°C max. 720-735°C max. 840-845°C	small and broad endotherm (Risø): max. 725°C large endotherm (ECN): 700 - 800°C max. 770°C
650°C	1-2% moisture 150 - 680 °C: 1.7-2% 680 - 1200 °C: 9-12%	increase from: 680 - 875°C max. 730-760°C max. 815-825°C	small and broad endotherm (Risø): max. ~ 750°C simultaneous large endotherms (ECN): 680 - 875°C 770 - 800°C max. 780°C

Table 3.19 *Summary of DTA/TGA-measurements with ash from weathered wheat straw (fuel #4) in nitrogen atmosphere. The bold numbers indicate where melting may start (large heat effect)*

ashing temp.	mass loss (TG)	mass loss rate (DTG)	heat effects (DTA)
450°C	4.5-5.5% moisture 150 - 550°C: 4-5% 550-680°C: 5-6.5% 680-1000°C: 6-8%	continuous from 150°C with a clear increase between 530 and 680°C max. 675°C	two large endotherms: 625-700°C 740 - 950°C max. 685°C max. 880°C
550°C	5 % moisture 150 - 570°C: 5.5% 570 - 670°C: 3% 670 - 1000°C: 11.5% total *: 20%	continuous from 150°C with a small increase between 570 and 670°C and a larger "twin peak" between 710 - 885°C max. 760°C	endotherms: 635°C 770°C max. 635°C max. 770°C
650°C	1.5 % moisture 150 - ~ 800°C: 3% 800 - 1000°C: 5.5%	continuous from 150 - 800°C increase between: 800 - 990°C max. 950°C	small endotherms: 580°C 930°C (?) max. ~ 580°C max. ~ 930°C (?)

Table 3.20 *Summary of DTA/TGA-measurements with ash from willow (fuel #7) in nitrogen atmosphere*

ashing temp.	mass loss (TG)	mass loss rate (DTG)	heat effects (DTA)
450°C	0.5-1% moisture 150 - 640°C: 1-2% 640 - 740°C: 9-13%	strong increase: 620 - 740°C max. 700°C	endotherm coinciding with mass loss: 620 - 730 °C max. 700 °C
550°C	1.5% moisture 150 - 520°C: 2% 520 - 710°C: 7%	strong increase: 520 - 710°C max. 650°C	endotherm coinciding with mass loss: 610 - 710°C max. 670°C
650°C	1.0% moisture 150 - 520°C: 1.5% 520 - 660°C: 1.5%	increase from 520 - 660°C max. 630°C	small endotherm coinciding with mass loss: 610 - 660°C max. 645°C

Table 3.21 *Summary of DTA/TGA-measurements with ash from unweathered straw (ashed at 550°C, fuel #3) mixed with silica sand (100-125 micron) in nitrogen atmosphere*

wt% sand	mass loss (TG)	mass loss rate (DTG)	heat effects (DTA)
0%	3% moisture 150 - 650°C: 4% 650 - 1000°C: 11.5%	two peaks between: 650 - 980°C max. 730°C max. 875°C	strong endotherm in very broad range around 720°C max. 720°C coinciding with mass loss peak
50%	1.5% moisture 150 - 650°C: 2% 650 - 900°C: 5%	two peaks between: 650 - 900°C max. 730°C max. 840°C	endotherm in broad range around 730°C max. 730°C coinciding with mass loss peak
75%	1.5% moisture 150 - 650°C: 2% 650 - 900°C: 5%	two peaks between: 650 - 900°C max. 730°C max. 840°C	endotherm in broad range around 730°C max. 730°C coinciding with mass loss peak
90%	0.5% moisture 150 - 650°C: 0.5% 650 - 830°C: 1%	small increase between: 650 - 830°C max. ~ 780°C	very small endotherm at 570°C max. 570°C
100%	0% moisture	essentially no increases	very small endotherm at 570°C max. 570°C

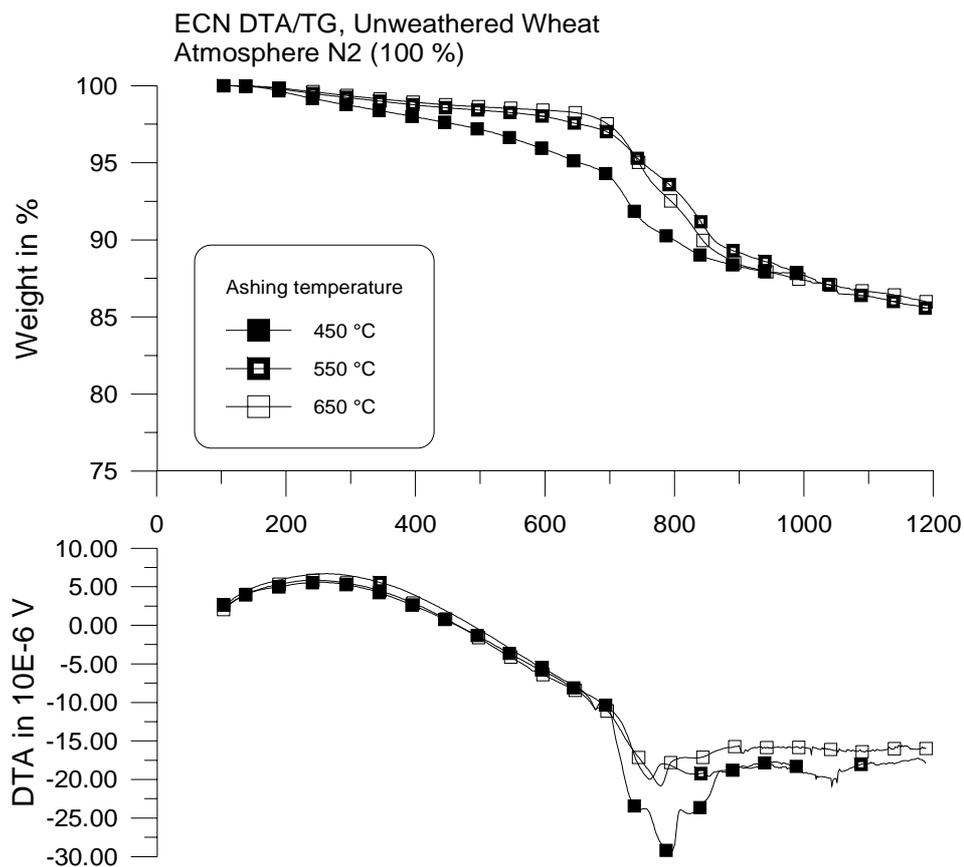


Figure 3.20 *DTA and TGA signal of unweathered wheat straw in a nitrogen atmosphere, top: weight as function of temperature, bottom: thermal effect (dip is endothermic)*

Table 3.22 summarises the “dangerous” temperatures for the different biomass materials. It is the result of a combination of both the DTA/TGA-results as shown above and the chemical analysis of the samples.

Table 3.22 *Temperatures at which agglomeration might occur according to DTA/TGA-experiments*

fuel # and name	“dangerous” temperature [°C]	remarks
fuel #3: unweathered Danish wheat straw	700°C	substantial melting around 770°C, probably due to melting of potassium chloride (melting point 770°C) or potassium silicates (melting point 740-780°C)
fuel #4: weathered Danish wheat straw	750°C	substantial melting around 850°C, probably due to melting of potassium silicates (melting point 740-780°C) considering the low chlorine content
fuel #7: willow	no signs of melting below 1000°C	only calcination occurs

Mixing wheat straw ash with sand resulted in roughly the same pattern as found in case where no sand was added. No new peaks appear which indicates that silica sand has not a very big influence on melting behaviour. This might be expected when considering that the pure ash already contains considerable amounts of silica.

3.6.6 Compression strength measurement facility by Risø (TNO) (f)

Five materials were selected for compression strength measurements according to the standard method described in chapter 3.3.6. The total carbon after ashing the samples was between 1 and 3% by weight, see table 3.23. It turned out that more than 80% of the carbon was inorganic except for the straw where only 40% or less was inorganic carbon.

Table 3.23 *Carbon content of different ash samples prepared for compression strength measurements*

ash sample	fuel #	carbon content in ash [wt%]
verge grass	1	1.7
Dutch straw	2	0.8
Danish straw	3	2.2
Danish straw (weathered)	4	2.3
cacao shells	6	2.7
chicken manure		1.1

Figure 3.21 shows the compression strength of ashed samples of the materials as indicated. Also shown is the curve for chicken manure. The results for Danish straw (both dry and weathered) turned out to be impossible to obtain. The ash pellets changed to a sort of spongy structure during heat treatment. The outer surface turned out to a smooth and molten structure with grey-brown colour. SEM-analysis revealed an enrichment of silicon, potassium and sulphur in the outer layer. Similar behaviour has been reported by [8].

The only explanation for the swelling behaviour during heating of the straw pellets is the following. Because the outer surface melts, an impermeable layer is formed. During heating, CO₂ by the dissociation of carbonates, and possibly other gaseous products, are formed. The impermeable outer layer prevents the gases to escape resulting in a swelling of the pellets. If this is the reason this indicates that the temperature where melting occurs is lower than the temperature where inorganic carbonates dissociate (650-750°C).

From the figure it can be seen that the curves for verge grass and chicken manure show the expected increase of compression strength with increasing temperature. It can be concluded that sintering occurs between 800 and 850°C for verge grass and between 900 and 950°C for chicken manure. For cacao shells, temperatures probably were not increased to high enough values to see any sintering. This means that cacao shells show sintering, according to compression strength measurements, above 900°C. Dutch straw shows strange behaviour. This probably is caused by the same effect as mentioned earlier for the other straw samples. In this case however, the effect is not so dramatic. This might well be related to the relative low carbon content of the Dutch straw ash, see table 3.23. Table 3.24 summarises the results of the compression strength measurements.

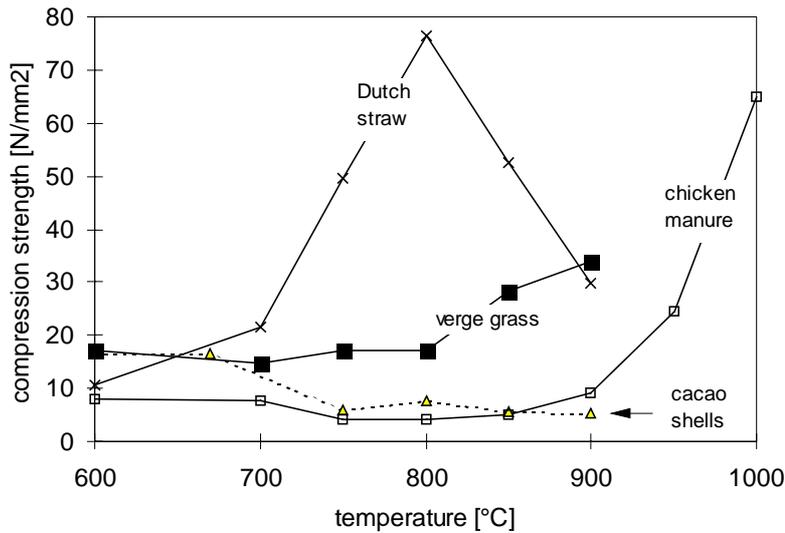


Figure 3.21 *Compression strength measurements on different materials after ashing and heating to indicated temperature*

Table 3.24 *Sintering temperatures according to compression strength measurements with ash*

ash sample	fuel #	“sintering” temperature [°C]
verge grass	1	800-850°
Dutch straw	2	< 750°
Danish straw	3	< 750°
Danish straw (weathered)	4	< 750°
cacao shells	6	> 900°
chicken manure		900-950°

3.6.7 Standard facilities for measuring standard ash melting temperatures by ECN (NMI) and Risø (DK-TEKNIK) (g)

Using standard techniques the melting temperatures were determined of ashes of three materials ashed at three temperatures each. Figure 3.22 shows the different temperatures as measured in a reducing atmosphere. Figure 3.23 shows the difference between reducing and oxidising atmosphere for two samples.

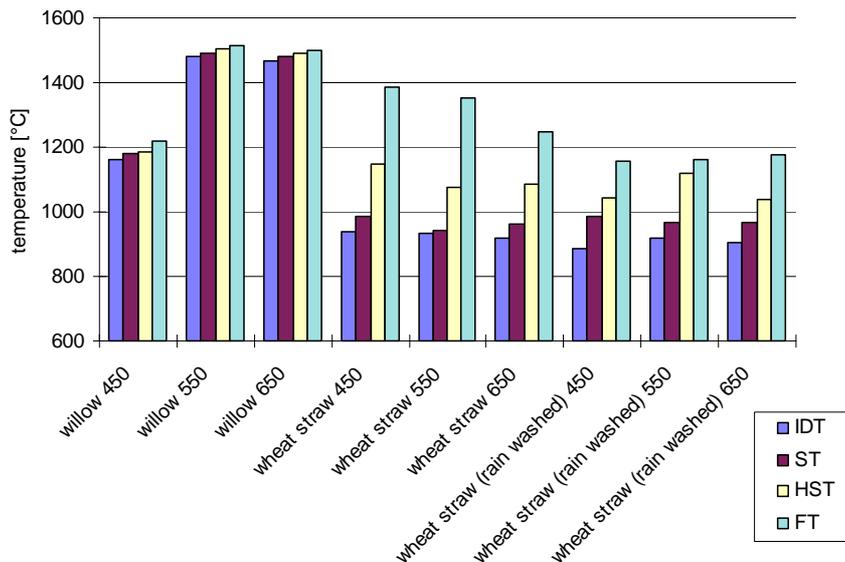


Figure 3.22 Melting temperatures for three fuels ashed at three temperatures (450, 550 and 650°C) in a reducing atmosphere (20% CO in nitrogen)

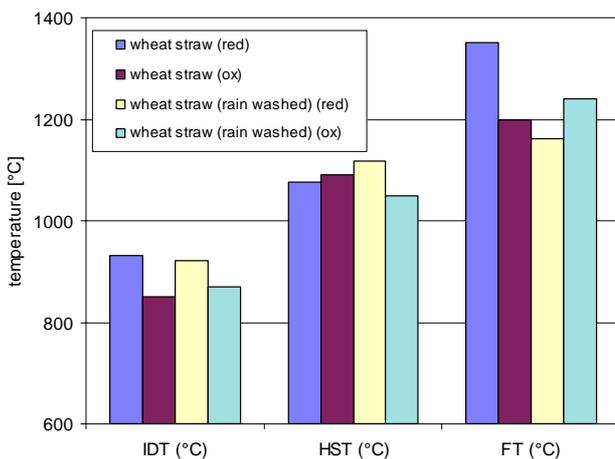


Figure 3.23 The influence of atmosphere on standard melting temperature of two wheat straw ash samples ashed at 550°C, red: reducing (20% CO in nitrogen), ox: oxidising (air)

3.6.8 SEM and HTM: high temperature microscope at Risø (h)

A comprehensive set of SEM measurements has been performed on the main part of the samples taken from the ETC fluidised bed agglomeration experiments and they confirm that the particles in general are covered with a more or less homogeneous surface layer. The measurements are taken both at different locations on the surface of the particles before and after agglomeration, and if possible also at the “bridge” between agglomerated particles. These measurements will be very useful in modelling of agglomeration when fundamental thermodynamic data for intermediate phases become available. It is interesting to notice that the spectroscopic data from all the sludge experiments are nearly independent of experimental conditions including the mass ratio between straw and sludge.

Ash taken from the ETC fluidized bed at the end of the ashing process and before agglomeration has been used in the HTM microscope. The samples were heated in the hot stage but it was not possible to detect any change in the picture as a function of stage temperature. When not agglomerated samples, which had proved in the fluid bed that they could agglomerate, were heated in the HTM to a temperature where they definitely should agglomerate they sometimes agglomerate and sometimes not and there was no difference in the pictures. Several samples taken from different fluidized bed experiments gave the same negative response. The method could therefore not be used to observe at which temperature agglomeration occurred.

A reason for the negative result may be that the atmosphere (vacuum) in the ESEM instrument during the heating of the samples is very different from the condition in a fluid bed. In particular volatile components may be removed from the sample by the pumping system of the microscope.

3.6.9 BFBC: bubbling fluidized bed combustion facility by Risø (VTT) (i)

Both the “dry” Danish straw and the weathered Danish straw turn out to result in defluidization at 775°C while at 750°C no sintering occurred. In both cases no visual agglomerates could be detected afterwards. However, by microscopy the agglomerates could be seen clearly. The sintering behaviour seems to be more pronounced using fuel #3 than the weathered straw (fuel #4).

3.7 TASK 7: Description of the total methodology for prediction of ash agglomeration and related problems, and identification of potential solutions

In the present project, the focus has been on methods for the prediction of agglomeration and related problems. This however is only useful if measures can be taken to avoid the problem. In this chapter several solution methods will be shortly described. In table 3.25 the different methods are given.

Table 3.25 *Solution methods, divided into different categories*

solution category	method
- growing and harvesting	using fertiliser with low content of chlorine postponing the year of harvest in short rotation forestry avoid contamination with soil particles leave some of the growth layer biomass components behind in the field/forest allow weathering
- fuel pre-treatment	removing non fuel components degrading oversize fuel material removing silica contamination washing out alkaline and chlorine homogenisation blending with coal and other fuels avoiding certain fuel combinations
- blending	combinations of high alkaline and high chlorine fuels high sulphur coal and high alkaline biomass high alkaline biomass and high silica coal/biomass
- fluid dynamic control	choose proper gas velocity with given particle size staged air or increased cross section at bottom secure good air distribution at all loads high fluidisation velocity frequently/occasionally increasing fluidization velocity limiting the turn down ratio
- bed particle management	<i>remove oversize material from the bed</i> addition of fresh bed material <i>limiting the retention of small particles</i> selectively draining problematic components additives
- temperature control	avoiding temperature excursions limiting the reaction temperature, special reactor concepts limiting single particle temperatures avoiding hot internal surfaces in critical areas choosing a sufficiently high temperature
- other measures	avoid condition of re-carbonation of CaO avoid condition of sulfidation of static Ca-compounds avoid condition of sulfidation of K/Na-compounds

3.7.1 Growing and harvesting

The elements considered to be (partly) responsible for agglomeration are: K, Na, Cl, P, S and Si. Chlorine is not essential for growth. The chlorine content of biomass therefore is mainly the result of *soil condition (location near the sea) and fertilisers* used. Most fertilisers contain chlorine because these (KCl) generally are cheaper than e.g. sulphates.

Alkali's (mainly K) is essential for growth and therefore is concentrated in fast growing parts. This explains the high concentration in annual crops but also the relative high amounts in young branches, leaves and needles from trees. One way to *reduce the share of young biomass* is to postpone the harvest or leave those materials in the wood as natural fertilisers.

The *presence of silica, generally soil components*, in the biomass fuel can be avoided by careful harvesting. It may be worthwhile accepting some waste by not sampling too close to the ground.

The concentration of alkali's and chlorine in biomass can be reduced considerably by *allowing rain to leach K and Cl*. Large reductions can be achieved. Some disadvantages are the delaying effect on potential subsequent crops, a decrease in biomass yield and the mentioned tendency for higher contamination with soil material. Also the material has to be dried.

3.7.2 Fuel pre-treatment

In practice stones, pieces of iron and other tramp materials will find their way into the feedstock. Such heavy components may accumulate in the bottom of the reactor/bed and obstruct the normal flow conditions, which can limit the local mass and heat transport and lead to severe agglomeration. Therefore whenever there is a risk of heavy non-fuel components in the fuel supply the fuel preparation and/or the feeding system should comprise means for *trapping the unacceptable components*.

A too large fraction of coarse fuel particles will negatively impact the quality of fluidisation. Especially under slow reaction conditions coarse char particles may accumulate to a concentration that negatively influences and eventually destabilise the fluidisation. Such destabilisation easily leads to hot spots that promotes local sintering due to the obstructed heat transport and within a short time a large part of the whole bed may be involved in this irreversible process. Paradoxically, this risk is especially present in fluidised bed systems operated at low temperature, where the reactivity is low. Mechanical breaking and crushing may be a solution. It should be mentioned that the resulting fuel should not contain too much fines because of the risk of excessive carbon losses in the process caused by the relatively low residence time of fine particles.

Soil (mainly silica) attached to the fuel may be separated from the fuel by washing, sieving or fluid dynamic separation. The attached sand can be removed from the soil more easily if the fuel is dry, which might be relevant when sieving is the pre-treatment. However the mentioned precaution is probably not worthwhile considering if not also limiting or completely avoiding the addition of silica along with a potential addition of supplementing bed material. This means that the benefit from removing (non-fuel inherent) silica contamination is also doubtful when the inherent fuel ash contains a high concentration of silica. In such cases the best strategy might as well be the opposite, i.e. to try to “flush” the alkaline/trouble components out of the bed by allowing a large addition of silica with the fuel.

Alkali's and chlorine can be washed out using hot water as a fuel pre-treatment. This solution is evaluated by both of the Danish power companies ELSAM and ELKRAFT and the Institute of Chemical Engineering at the Danish Technical University and a demonstration facility is expected to be build at the power plant Studstrupværket.

Agglomeration and deposition problems are sometimes seen even though fuel analyses indicate an unproblematic fuel. The reason may be that the fuel quality varies beyond what was indicated by even frequent fuel analyses. Besides this, changing fuel composition leads to changes in process temperature, which increases the risk of agglomeration. In order to limit the risk of frequent agglomeration and deposition problems due to such fluctuation in fuel quality, *homogenization of the feedstock* may be worthwhile.

3.7.3 Blending

Gasification tests conducted by the Danish power companies ELSAM and ELKRAFT at VTT and Enviropower test facilities showed that even straw with a high content of alkaline and chlorine may be efficiently gasified without agglomeration and deposition problems if *mixed with coal*. The mechanism primarily considered responsible for the positive influence of co-firing with coal is that a major part of alkaline from straw are bound into high melting aluminium silicates found in the coal. Furthermore a lower content of alkaline and chlorine in coal gives a diluting effect that may also be obtained by co-firing other less problematic types of biomass such as wood.

Furthermore there may exist some “*lucky*” combinations of biomass-biomass and biomass-waste fuels, i.e. combinations that give less trouble than either of the fuels used separately. From the present study, sewage sludge and straw seem to profit from each other: agglomeration risk seems low.

On the other hand, *combination of fuels having high alkali and high chlorine concentrations should be avoided*. Chlorine mobilises the alkali’s which otherwise might not have been active as far as agglomeration processes are concerned. In this study, this phenomenon has been demonstrated by the fact that cacao shells (high K, low Cl) do not show the expected agglomeration problems.

Also the *combination of fuels rich in KCl (e.g. straw) and sulphur (some coals) should be avoided*. As experienced at the Grenaa CFBC plant, large depositions form on heat absorption surfaces. The main mechanism is suspected to be KCl condensation and the subsequent reaction between KCl and SO_x forming KSO_x .

Furthermore, the *combination of high alkali and high silica fuels should be avoided*. This however is only worthwhile when alternative bed material (not silica) is used to solve the agglomeration problem.

3.7.4 Fluid dynamic control

In general the phenomena’s designated as deposition, bed sintering and agglomeration can be seen as the result of a competition between adhesion of particles to surfaces of the construction and/or neighbour particles at one hand and on the other hand wear on the adhered particles due to mechanical forces induced by e.g. other particles. Furthermore the movement of particles is also important because of the corresponding transport of energy. In many fluidised bed reactors this transport is so effective that temperature differences are kept down to only a few °C across the square section of the bed. However, an ineffective/obstructed particle movement can easily lead to local temperature derivations resulting in a further and potentially self-enforcing obstruction of the particle movement. So, two good reasons exist (mechanical forces on particles and temperature homogeneity) why fluid dynamics are playing a major role in the process of agglomeration. More specific points are described below.

Especially for small particles and large cross sections the *superficial gas velocity should always be kept several times the theoretical minimum fluidisation*. Important to realise that the particle size (and distribution) of the bed material does change during operation. This means that choosing proper gas velocities must be seen together with what is often called “particle management”, see later.

In CFB-reactors, usually a nominal gas velocity in the range of 5 – 10 m/s is chosen. In the resulting flow field it is only the sufficiently small particles (e.g. < 0.2-0.3 mm) that can be efficiently suspended by the upwards drag forces. Larger particles concentrate at the bottom of the reactor, possibly creating temperature inhomogeneity and obstructions, increasing the risk of agglomeration. On the other hand, in bubbling beds the additional effect of buoyancy forces allows also large particles to be suspended. It is possible (and also very usual) to benefit from this effect in CFB’s, either by *adding only a part of the reactant gas in the very bottom or by enlarging the square section of the bottom of a CFB reactor*. In the first case this means that a considerable part of the reactant gas is added as secondary or tertiary gas some distance above the openings for adding the primary gas.

The risk of uneven gas distribution through the different nozzles becomes real when the flow of gas (usually air) is reduced. This might induce inhomogeneous distribution of material and

temperature, finally increasing the risk of agglomeration. Therefore in cases where a high turn down ratio is wanted, *gas should be added via individually controllable lines*.

High fluidisation velocities always lower the tendency for agglomeration and deposition problems because of the already mentioned competition between particle adhesion and friction forces.

In some occasions it is seen that agglomerates already formed can be disintegrated by *temporarily increasing the gas velocity*. Increasing the gas velocity will mainly work on weakly bounded agglomerates that are typically formed rather fast at relatively high temperatures [9]. Agglomerates formed in the BFBG at ECN, used in the present project as a result of the standard test, turn out to be weak (like a sandcastle). Generally, emptying the bed by removing the bottom creates enough forces to render the major part of the reactor contents into individual particles.

Increasing the gas velocity may also work in a negative direction. This is when the agglomerates are stronger and the settlement on the base of the bed is already pronounced. Strong and slowly settling agglomerates are more typically formed in the lower temperature range. Increasing the gas velocity in the primary zone may then give a worse situation by reducing the bulk density in the still fluidised areas adjacent to the agglomerates and thereby reducing the buoyancy forces acting on the agglomerates. In this case a better strategy is to frequently or occasionally drain/remove the agglomerates from the bed even if the plant has to be stopped. It should be mentioned that a sudden increase of air flow can also result in an increase of temperature, which might worsen the situation.

Fluidised bed reactors used for energy production are often operated at part load conditions i.e. at reduced gas throughput. Due to reasons already mentioned, this situation typically constitutes the worst case concerning proper distribution of the fluidising gas and the quality of fluidisation. If problems occur and the already suggested measures shows insufficient, it may be necessary to *consider a less ambitious turn down ratio*.

3.7.5 Bed particle management

In lab-scale (short time) experiments, steady state is hardly obtained with respect to the composition of the bed material. In fact the bed composition during the test period may be close to the composition of the particles initially loaded. When running a “real world plant” on a more continuous basis, the bed material (composition and size) may after some days be very different from the particles initially loaded. The bed is more the result of the choice of fuel and other design and the operating parameters such as type and extent of bed additives, the efficiency characteristic of particle separators, the re-circulated share of separated particles, the location of bed particle drains and rate of draining and the classification and partially re-introduction of drained particles. The importance of such parameters was recognised during the 80’s and the covering phrase “particle management” was invented. Some related potential solutions to agglomerating problems are mentioned below.

In cases where there is a risk that agglomeration takes place and/or it is not possible to remove oversize particles by fuel preparation (as earlier mentioned) the reactor should be designed in such a way that even the worst possible types of tramp material passing through the preparation and feed system as well as agglomerates formed in the bed can be *effectively drained* out. Some of the major design means for effective draining is:

- designing for a heavy state of fluidisation in the bed bottom (choice of low fluidisation velocity and/or coarse particles) in order to make even relatively coarse particle float by buoyancy.

- on the other hand the gas flow in the reactor bottom should be high enough to keep the fluidisation vigorous and stable at all times.
- providing overall particle flow conditions that provides upwards (gulf-) streams in critical areas
- inclining the bed bottom against draining openings/means
- using “directional” air/gas nozzles
- using nozzles shaped in order not to hold up irregular bed components
- providing an open type of bed bottom (e.g. a so-called sparge pipe distributor) in stead of a base plate with nozzles.

The *addition of new bed material* can keep the bed content sufficiently well sized and chemically correct. In this way, the accumulation of certain elements is prevented. This method is used at the CFB combustion plant in the Danish town Grenaa, where the fuel is low sulphur coal in combination with straw (maximum 60 % straw by energy). By adding approximately 20 t of coal ash and 4 t of silica sand every 24 hours, the concentration of water soluble K compounds in loop seal particles are kept below 2000 ppm. In this case the limit is also set in order to avoid excessive deposition on the superheater tubes in the back pass.

The potential needs for adding “fresh” bed particles is sometimes fully or partly covered by adding particles that are chemically active in absorbing particularly sulphur or chlorine, catalytic cracking of tars in gasifiers or absorbing alkaline components in high melting components usually called “getter” materials.

Different identified or anticipated effects of various *additives* have been reported or can be suspected:

- physical absorption of melted phases within porosity of added particles
- chemical absorption of alkali metals into stable components with high melting points
- powdering that makes melted phases act less sticky to the surfaces of other particles
- interaction that change the melting/strength characteristics of problematic components in a positive direction

The table below includes additives that at least in some cases are suspected to offer the above mentioned positive effects.

Table 3.26 *List of possible additives preventing agglomeration*

type of effect	additive	principal components
physical absorption	limestone	CaCO ₃
	pre-calcined dolomite	CaO.MgO
	sintered magnesite	MgO
	gibbsite	Al(OH) ₃
chemical absorption	coal ash	
	aluminosilicates	Al _x Si _y O _z
	bauxite	SiO ₂ 7.0-10.0 %, Al ₂ O ₃ 81.5-88.0%
	diatomaceous earth	SiO ₂ 92 %, Al ₂ O ₃ 5%
	kaolin	Al ₂ O ₃ ·(SiO ₂) ₂ ·(H ₂ O) ₂
powdering	coal fly ash	Al _x Si _y O _z , Ca-/MgO, etc
		CaCO ₃
		CaO
		MgO
		CaMg(CO ₃) ₂
		CaO.MgO

Limiting the retention of small particles reduces the risk of agglomeration. The retention of especially small particles/fines may enhance sintering and agglomeration due to various reasons:

- the large specific surface area generally enhances surface phenomena's and e.g. adhesion forces dominate compared to inertia and gravity forces

- volatile ash components such as many alkaline components tend to concentrate on the large surface area of fine particles by condensation and absorption
- also less volatile ash components that includes problem components tends to be liberated mainly as small particles, i.e. these components tends (“conveniently”) to be elutriated and lost if not re-circulated

A high degree of particle re-circulation has also in BFB reactors been emphasised due to the positive influence on carbon conversion, tendencies for lower boiler emissions and decreased needs for adding fresh bed material. However, and as noticed by [10], the consequence has often been agglomeration problems. Limited retention of ash components is probably also part of the explanation for some mainly successful tests conducted at the HTW gasifier at RWTH, Aachen in Germany [11]. In this case miscanthus, triticale, barley and even highly chlorine containing ray grass are efficiently gasified.

3.7.6 Temperature control

Agglomeration is in most cases caused by melted ash or ash derived components condensed at particle surfaces and acting as to glue particles together. It is therefore obvious to try to avoid agglomeration by keeping a sufficiently low temperature. However, there are several other temperature-related mechanisms to consider.

Temperature overshooting during start up in combustors and gasifiers (start up and shut down usually in “combustion mode”) is a serious problem. The delayed reaching of the set point temperature often results in a major increase in fuel feed rate due to the very natural impatience of the operator. The result may be a situation with an unrecognised excessive amount of char in the bed. Typically this char start to react at a much faster rate shortly before reaching the pre-set operation temperature. The response to a decreased fuel feed rate at this stage may be an even faster temperature increase due to the lack off the temperature moderating effect of moisture evaporation and pyrolysis reactions. A similar risk exists when shifting to a less reactive fuel. In this case the natural reaction of bringing in more fuel when the temperature initially falls (during building up the new balance concentration) may lead to more or less the same situation. A good test during start up is to see the temperature response on a short feeding stop e.g. 50°C before the operation temperature is reached. If the temperatures do not start to level out within a few minutes, this can be an indication of a dangerously large char accumulation. It is also a good idea not to exceed a previously experienced or calculated feed rate when approaching the operation temperature. So, *avoid temperature excursions during start-up and shut down by simply being patient and careful.*

Simply lowering the process temperature generally results in unacceptable carbon losses due to the low reaction rates. *Special concepts* can solve this dilemma. One of the possibilities is the concept by DFBT where char is converted at low temperature and long residence times [12].

Local temperature peaks should be avoided. Several measures can be mentioned:

- improving the distribution of fuel and oxygen
- moderating the temperature near gas nozzles e.g. by adding steam to gasifiers or re-circulating flue gas to combustor
- better mixing by e.g. providing a more aggressive state of fluidisation in critical areas
- inducing in-bed “golf streaming” through critical in-bed areas
- allowing a higher particle flux through the freeboard or other critical parts of a CFB reactor
- addition of properly distributed heat absorption surfaces. E.g. providing “wing/panel” walls in the free board of a BFB or the upper part of a CFB reaction chamber

It is well known that especially in areas of a reaction chamber with a high oxygen concentration the temperature of burning char particles may be considerably higher than the mean temperature of the surroundings of the particles. In this report this is reported as well. Some counteractions against the above problems would be *to avoid high concentrations of oxygen in areas with high concentrations of char*. Measures such as improved distribution of combustion air or gasification agent (improved grid and nozzle design e.g. staged oxidation) may be a solution. Furthermore, it could be considered to oxidise the char in areas with low concentrations of silica particles that may contribute to the formation of eutectics. Eventually oxidation at low (mean) temperatures should limit the mentioned problem due to the generally slowed down reactions kinetics and higher margin from bed temperature to temperatures of melting and eutectics formation.

It is well known that sticky particles have much higher tendency to stick to high temperature surfaces than to surfaces at low temperatures. If sticky particles can not be avoided in certain areas in a reaction chamber or downstream passages it may therefore be a solution to use a sufficiently cooled wall construction instead of insulating refractory liners.

At high temperatures, salts might not condense and result in sticky substances. It is therefore possible that agglomeration can be avoided not only by decreasing but also by *increasing the process temperature*. Some evidence for this is seen from experimental results presented by [13]. In several cases during slowly increasing the temperature of beds of various compositions some self-dissolving “thickening” tendencies of the fluidisation are observed at temperatures above 800°C. However, the alkali’s evaporated may condense and cause problems at lower temperatures downstream and during the temperature increase some of the alkali’s may recombine into other sticky components with lower vapour pressure.

3.7.7 Other measures

One of the main types of agglomeration mechanisms is not based on the presence of melted phases and is some times called “sintering/agglomeration by chemical reaction”. Occurring on the interface between adjacent particles some reactions can form a solid bridge between the particles. Such a reaction is the re-carbonation of CaO to CaCO₃:



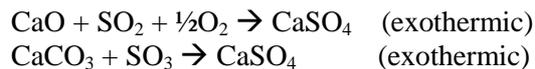
It can be seen that the potential for this reaction to take place can be increased by:

- the presence of a high concentration of CaO
- a high partial pressure of CO₂
- decreasing temperature

The risk of sintering/agglomeration due to re-carbonation is particularly present when using highly Ca-containing fuels, bed materials and/or additives and in locations of the process where the temperature is decreased enough to make the carbonate the thermodynamically stable Ca component (below approximately 700°C in atmospheric reactors). However practical experiences shows that a further important (necessary) circumstance is particle stagnation, i.e. the problem tend to appear in slowly / badly fluidised areas or as deposition on cooled surfaces. Severe problems are seen in especially the loop seals of petro coke fired boilers. The risk for problems due to re-carbonation are high in a pressurised plant which has clearly been experienced at the bio-IGCC plant in Varnamo [14], where depositions in the raw gas cooler have been experienced when gasifying woody fuels at up to 18 bar. However, these problems seem to be solved by using magnetite as bed material [15]. Depending on the application / choice of fuel some solutions that may be worth considering are:

- avoid combinations of temperatures total pressures that enhance the tendency for Ca-compounds to alternate between calcinating and re-carbonating conditions.
- avoid stagnant zones near gas distribution grids and in particle return ducts and particle coolers.
- limit the CO₂ concentration in critical areas (e.g. limiting the char concentration and/or adding steam or nitrogen in stead of air/oxygen).
- choose proper bed materials/additives.
- precautions against deposition in design of flue gas and product gas coolers.

A further example on “sintering/agglomeration by chemical reaction” is based on the sulphating of Ca compounds, e.g. by reactions:



Except for the “replacement” of CO₂ with SO₂/SO₃, it can be seen that the nature of the potential agglomeration mechanism is similar to the mechanism based on re-carbonation. Avoiding problems due to sulphating of Ca/CaCO₃ may involve:

- avoid stagnant zones near gas distribution grids and in particle return ducts and particle coolers.
- limit the SO_x concentration in critical areas (e.g. designing the reactor in such a way that the liberation of SO_x as well as its subsequent absorption are primarily taking place e.g. in the vigorously fluidised main reaction chamber.
- provide sufficient clearance and cleaning in heat absorption surfaces.

One of the risks in biomass fired FB/CFB boilers is the formation of agglomerates/deposits based on condensation of KCl on heat absorption surfaces and the subsequent formation of K₂SO₄ according to the reaction:



Very severe deposition problems experienced at the Grenaa CFB boiler when using high alkaline straw in combination with a high sulphur coal have been explained by this. It is reasonable to assume that the same reaction goes on in relation to KCl contained in/on fluidised/suspended particles and perhaps also from KCl in the gas phase, but it is not clear to what extend such reactions are causing agglomeration problems. Some possible solutions are:

- avoid the combination of large inputs to the process of K/Na, chlorine and sulphur (e.g. avoid co-firing straws/grasses and high sulphur coal).
- limit the release of K/Na to the gas phase and/or promote its rebinding into non-sticky solid phases inside the reaction chamber.
- provide some rows of so called screening tubes in front of superheater surfaces in the convection pass (deposits will form on the screening tubes but tend to peel off due to thermal stresses induced by a relatively low surface temperature.
- provide sufficient clearance and cleaning in/of heat absorption surfaces.

It should be mentioned that concerns about corrosion unfortunately points away from the first of the stated solutions (avoid combination of K and S). The sulfation of KCl on superheater surfaces helps to avoid the risk of severe Cl-corrosion by removing chlorine from the deposits [16]. According to this some input of sulphur may be an advantage.

3.8 TASK 8: Conclusive evaluation

In the following table, the resulting agglomeration temperatures are summarised as determined using the methods as described in chapter 3.3 and 3.6 of this report. Figure 3.24 shows the results in a graphical way.

Table 3.27 *Agglomeration temperatures (or range if more tests are done) measured within the project with different methods for different fuels*

fuel#:	1	2	3	4	5	6	7	remarks
	verge grass	Dutch straw	Danish straw	Danish weathered straw	sewage sludge	cacao shells	willow	
test method								
a chemical analysis								no temperature output
b BFBG, gasification (5 kWth)	825	810		800		900	875	0.5 mm sand, standard X-test
c BFBC, combustion and controlled agglomeration (5 kWth)		800-880	730-890	830-860	940-970			dependent on ashing temperature
d CFBG, gasification (500 kWth)	> 810	> 750				> 820	> 860	no agglomeration occurred
e DTA/TGA, melting temperature of ash and ash/bed			700	750			> 1000	
f compression strength of sintered ash pellets	800-850	< 750	< 750	< 750		> 900		
g standard ash melting temperature			930	905			1370	IDT, average value for the three ashes
h HTM, heating while observing ash/sand								not possible
i BFBC, combustion and controlled agglomeration (5 kWth)			775	775				

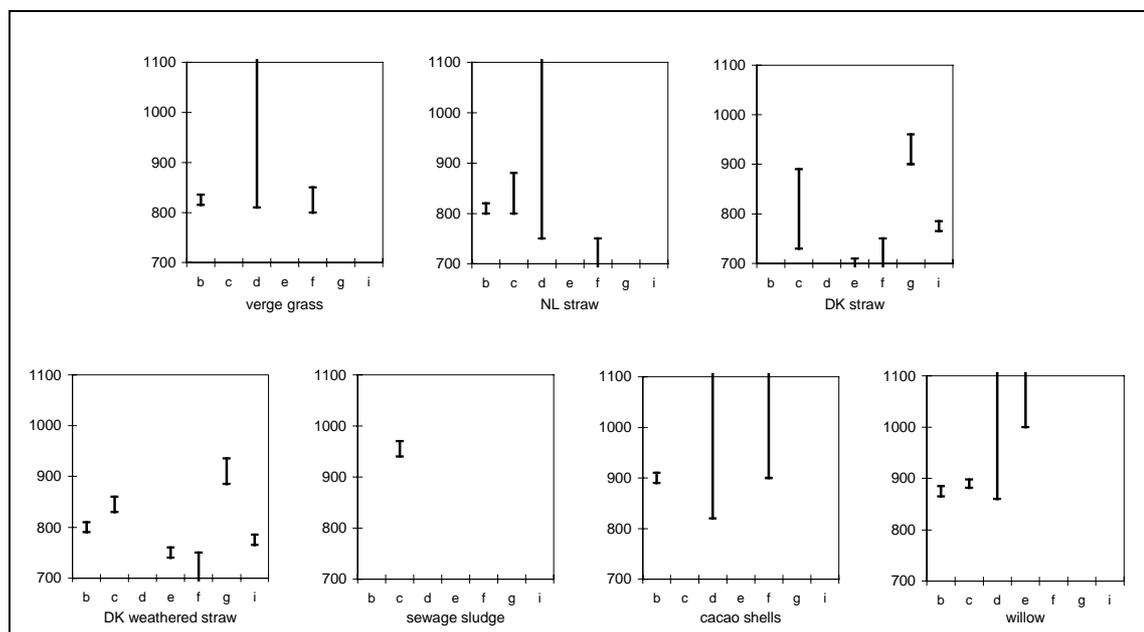


Figure 3.24 *Graphic representation of results from table 3.27, agglomeration temperatures measured within the project with different techniques. (b): BFBG, lab-scale gasification at ECN, (c): BFBC, lab-scale combustion at ETC, (d): CFBG, bench-scale gasification at ECN (e): DTA/TGA, (f): compression strength of sintered ash pellets, (g): standard ash melting temperature, (i): BFBC, lab-scale combustion at VTT. Large error bars are caused by the measurement of only a minimum or maximum value.*

Chemical analysis of the fuel can give a first indication of whether there might be an agglomeration problem during thermal conversion. In general a high K-content means a risk for agglomeration. However, cacao shells (very high K-content, roughly twice that of straw) do have significant less tendency for agglomeration than straw as found using the BFBG at ECN (b). Probably the very low Cl-content of cacao shells renders the K less mobile and therefore less reactive. The result of this relative low K-mobility is that agglomerates are not formed by the melting of K-salts (like KCl) but by the formation and melting of K-silicates (with e.g. bed material), which means that the agglomeration temperature shifts to (50-100°C) higher temperatures.

If high-K / high-Cl fuels show agglomeration by simply forming and melting salts, this implicate that bed material is not playing a major role. This is shown in experiments with the BFBG at ECN (b) with different bed materials (silica, alumina and mullite) with straw as fuel. The agglomeration temperature in all cases was 840°C.

From the methods used in the project, laboratory fluid bed agglomeration experiments seem to give the most reliable information about conditions and temperatures where agglomeration takes place. However care must be used when comparing results from different facilities as both experimental conditions (including fuel preparation) and the design of the fluid bed will influence the result. Fluid bed systems offer the possibility to easily compare different measures like additives and bed materials. Contrary to methods like DTA, compression strength and ash melting temperatures, fluidized bed experiments combine all processes that might be relevant for agglomeration.

From particle temperature measurements in a BFB combustion facility at ETC (c) it turns out that burning particles can easily have temperatures of up to 100°C in excess of the mean bed temperature. This has a large influence on agglomeration behaviour. This relation also is illustrated by the relation that is found between ashing temperature (at which the fuel is combusted prior to an increase of temperature up to the agglomeration) and agglomeration temperature, see chapter 3.6.3. Because gasification, contrary to combustion, is a process where peak temperatures are lower or even absent, one might expect that agglomeration during gasification will occur at higher temperatures than during combustion. This however can not be concluded from the experiments, once again illustrating the importance of other factors like the design of fluid beds (the gas distribution, the type of nozzles, etc.).

The use of additives is one solution which might be used to mitigate agglomeration problems. It has been shown that kaolin, magnesite and dolomite (2 wt% of fuel flow) increase the agglomeration temperature with at least 60°C during gasification. During combustion tests a 30°C improvement has been demonstrated for kaolin (3 wt%) added to straw. Also the addition of sewage sludge shifts the agglomeration temperature to considerable higher ranges. This already is significant at the lowest sludge/straw-ratio tested (14wt% sludge in mix). It might well be that sludge slows down the combustion reactions and therefore decreases peak temperatures. As sewage sludge is available in enormous quantities, and represents a waste problem in itself, this may be one way to reduce/eliminate the agglomeration problems when using alkaline rich biofuels. Gibbsite, thought to be a physical getter for alkali's, does not change the agglomeration temperature.

In the lab-scale fluidised bed facilities at ECN (b) and ETC (c), the effect of accumulation of elements is shown. More fuel/ash in the bed decreases the agglomeration temperature. An increase of fuel (ash) fed to the system by a factor of 3 decreases the agglomeration temperature with about 25°C. For Dutch straw in the ETC combustion facility this was even circa 75°C.

DTA/TG investigations (e) can at present only give an indication of a temperature range where agglomeration might occur because the energy exchange from the agglomerating components is to some extent hidden by other chemical reactions. However, the method might be improved by

including other possible chemical reaction mechanisms and their influence on the energy balance and from this introduce a correction term to the measured temperatures.

Compression strength measurements (f) may give an indication of the temperature where agglomeration may start to occur. In practice, some problems exist. For example unweathered wheat straw was swelling during the heat treatment and compression strength measurement could not be performed.

ESEM/HTM measurements (h) do not give any reliable indication of agglomeration during the heating process in the microscope and a following examination of the samples was also unsuccessful.

SEM measurements give very useful information of the composition of the surface layer of the different bed particles and of how agglomeration is distributed. These measurements give vital information for modelling a possible surface interaction between bed particles.

Thermo-chemical modelling of the processes taken place between interacting particles is at the present still in an early stage, but fundamental work may be a realistic way to improve the accuracy. Further investigations in e.g. fluid beds may not be the best way to improve the understanding of the fundamental mechanisms, which are involved in the agglomeration process.

Experiments in the CFBG facility at ECN (d) did not result in agglomeration. A CFB is less suitable than a BFB as a tool for agglomeration research because temperatures in a CFB are less homogeneous (differences of 10-20°C are normal) and agglomeration therefore is not as sharply recognisable as it is when using a BFB (temperature differences of only a few degrees). During the experiment with straw, The K-content of the circulating sand reached a constant level of about 3500 mg/kg, already after a few hours. The bulk of the K (80%) and many Cl (50%) was found in the ash separated by the second cyclone. The rest is probably leaving the system with the gas. Apparently the first cyclone of the CFB has a relatively low efficiency for small (ash) particles, preventing these from circulating and accumulating in the reactor. This has been demonstrated before by the fact that bed material with 270 µm (instead of the normal 500 µm) was completely blown out of the system within a few hours. During the test with straw at low temperature (750°C), much carbon left the system unconverted. Because this means that captured minerals are leaving the system as well, the (generally unwanted) low carbon conversion has a positive effect. So, conversion at low temperature prevents agglomeration for two reasons: the low temperature and the removal of significant amounts of minerals with badly converted fuel.

Standard ash melting temperatures (g) proved to be not related to agglomeration in a way that can be used when trying to predict agglomeration. The difference between reducing and oxidising atmosphere couldn't be shown unambiguously.

As main conclusion it can be said that elemental analysis always should be performed since it gives a good first indication of the risk of agglomeration. Fluidized bed experiments combine all relevant processes taking place in real conversion plants and therefore suitable to be used as prediction tool. Especially BFB's, because of the high temperature homogeneity, have shown to be accurate and reproducible tools to compare different fuels and solutions for agglomeration. However, the temperatures where agglomeration starts might be different from the temperature in real plants since different hydrodynamics, nozzle design, etc. have large influence on the agglomeration process. Furthermore, during combustion actual local temperatures can be considerably (over 100°C) higher than measured using normal thermocouples.

4. COMPARISON OF PLANNED ACTIVITIES AND WORK ACCOMPLISHED

The results achieved in the project are according to the planned activities with a few exceptions. Within task 1, material should have been collected from full-scale facilities. When the project started, the Grenaa plant had changed to a less problematic fuel combination and also had made some design changes to reduce the agglomeration problems. It was therefore decided to use problematic fuels in the lab scale experiments.

Within task 5, the modelling activities were less comprehensive than planned. This is mainly due to a lack of thermodynamic data, see chapter 3.5. On the other hand, a total of 7 fuels have been selected in the project, whereas only 3-4 have been planned in the original project. Because of this, the amount of tests within (task 6: performance of lab-scale tests) was larger than planned.

5. CONCLUSIONS

Chemical analysis of the fuel can give a first indication of whether there might be an agglomeration problem during thermal conversion. In general a high K-content means an increased risk for agglomeration. However, the K-content alone is not a good indicator. Also the amount of chlorine was found to be crucial. It has been shown in standard test that cacao shells, having a K-content of roughly twice the K-content of straw, show agglomeration at circa 100°C higher temperatures than in case straw is used. The very low chlorine content of cacao shells probably causes this.

From the methods used in the project, laboratory fluid bed agglomeration experiments seem to give the most reliable information about conditions and temperatures where agglomeration takes place. Contrary to methods like DTA, compression strength and ash melting temperatures, all processes that might be relevant for agglomeration actually can occur during fluid bed experiments: fuel-bed material interactions, volatilization and condensation, shear forces, temperature homogeneity and accumulation. Standard tests have been developed where process temperature is gradually increasing until agglomeration. These tests have been applied in the project at three different laboratories: ECN (NL), ETC (S) and VTT (FIN). They have proved to be accurate and reproducible. Standard agglomeration tests therefore seem good tools for agglomeration research.

It has been shown with standard tests in lab-scale fluidized bed facilities that the addition of kaolin, magnesite, dolomite and sewage sludge significantly decrease the actual temperature of agglomeration. The agglomeration temperatures increased with at least 60°C in these cases. During combustion experiments, measured particle temperatures appeared to have up to 100°C in excess of the bed temperature. This might have a large influence on agglomeration. Because gasification, contrary to combustion, is a process where peak temperatures are lower or even absent, one might expect that agglomeration during gasification will occur at higher temperatures than during combustion. This however can not be concluded from the experiments, illustrating the importance of other factors like the design of fluid beds (the gas distribution, the type of nozzles, etc.).

Simply choosing a low temperature for the conversion in order to prevent agglomeration to occur, has proven successful during a 10-hour test with straw in a CFB gasifier. Apart from preventing melting and formation of eutectics to happen, also some important elements like K are removed from the system with the relative high fraction (25%) of unconverted char.

Compression strength measurements, DTA/TG, standard ash melting temperature measurements and high temperature microscopy as means to predict agglomeration do not seem worthwhile. However, DTA/TG and electron microscopy can be useful as a research tool.

It can be concluded that not only the type of fuel and other chemical “input” is determining the agglomeration temperature, also other factors like gas distribution, size of bed material, type of nozzles, cyclone efficiency in CFB’s, etc. can have an important role. This means that results from lab-scale facilities can be interpreted in a relative way (comparing fuels and evaluate possible solution) but should always be used with great care when trying to draw conclusions for full-scale plants. Nevertheless, standardised lab-scale bubbling fluidized bed experiments, as developed and used in this project, seem to be the most reliable tools for the prediction of agglomeration.

6. REFERENCES

1. A.van der Drift, J.J. Vermeulen: *Ten residual biomass fuels for circulating fluidized bed gasification*, submitted for publication in Biomass and Bioenergy (1999).
2. G.C.A.M.Heemskerk: *Best practice list for biomass fuel and ash analysis*, Utrecht, Novem-EWAB no.9820, 58 p. (1998).
3. Description of the CFB gasification plant at ECN on the internet: http://www.ecn.nl/unit_fb/bivkin/index.html (1998).
4. M.Öhman, A.Nordin, B.Skrifvars, R.Backman and M.Hupa: Accepted for publication in Energy & Fuels (1999).
5. M.Öhman and A.Nordin: Accepted for publication in Energy & Fuels (1999).
6. B.Skrifvars, M.Hupa, R.Backman and M.Hiltunen: Fuel **73** (2) 171-176 (1994).
7. Biomassa and waste composition database on the internet: <http://www.ecn/phyllis> (1999).
8. B.Olanders and B.M.Stenaari: *Characterisation of ashes from wood and straw*. Biomass and Bioenergy **8** (2) 105-115 (1995).
9. W.Lin, G.Krusholm, K.Dam-Johansen, E.Musahl and L.Bank: *Agglomeration phenomena in fluidized bed combustion of straw*. In: Proceedings of the 14th International Conference on Fluidized Bed Combustion, 11-14 May 1997, Vancouver, Canada (Ed. D.S.Preto), pp. 831-838 (1997).
10. A.Brown: *Phase composition of sintered masses formed in fluidized bed combustors*, Studsvik Nuclear, report Studsvik/NS-90/73 (1990).
11. W.Hahn: *Gasification of renewable feedstocks in a circulating fluidised bed. Implementing CO₂ reduction targets through power-and-heat cogeneration with integrated biomass gasification*, Technische Hochschule Aachen (Germany). Fakultät für Bergbau, Huettenwesen und Geowissenschaften (1994).
12. P.Stoholm, R.G.Nielsen, H.Nygaard, L.Tobiasen, M.W.Fock, K.Richardt and U.Henriksen: *Low temperature CFB gasifier, conceptual ideas, applications and first test results*. In: submitted for presentation during the 1st World Conference and Technology Exhibition, 5-9 June 2000 in Sevilla, Spain (2000).
13. F.Zintl and T.Öhman: *Alkali-induced particle agglomeration and bed-fluidization on CFB-combustion of biomass - Test of common and alternative bed materials*. In: Biomass for energy and industry. Proc. 10th European conference and technology exhibition (Eds. H.Kopetz et al.), pp. 1348-1350, C.A.R.M.E.N., Rimpf (Germany) (1998).
14. K.Ståhl and M.Neergaard: *Experiences from the biomass fuelled IGCC plant at Värnamo*. In: Biomass for energy and industry. Proc. 10th European conference and technology exhibition (Eds. H.Kopetz et al.), pp. 291-294, C.A.R.M.E.N., Rimpf (Germany) (1998).
15. K.Ståhl and M.Neergaard: *Experiences from the Värnamo IGCC demonstration plant*. In: VTT Symposium 192: Power production from biomass III. Gasification and pyrolysis R&D&D for industry (Eds. K.Sipilä and M.Korhonen), pp. 73-86, VTT Energy, Espoo (Finland) (1998).
16. H.Junker, F.Fogh, L.Baxter and A.Robinson: *Co-firing biomass and coal. Experimental investigations of deposit formation*. In: Biomass for energy and industry. Proc. 10th European conference and technology exhibition (Eds. H.Kopetz et al.), pp. 1482-1485, C.A.R.M.E.N., Rimpf (Germany) (1998).
17. B.-J.Skrifvars, M.Hupa, M.Öhman and A.Nordin: *Predicting bed agglomeration tendencies for biomass fuels. A comparison of three different techniques*. submitted for publication in Energy and Fuels (1999).

18. M.Öhman: *A new method to quantify fluidized bed agglomeration in the combustion of biomass fuels*. Licentiate thesis, Umea University, 23 p. (1997).
19. NREL: *Alkali deposits found in biomass boilers, The behaviour of inorganic material in biomass-fired power boilers - Field and laboratory experiences, Vol II*, NREL/TP-433-8142, SAND96-8225 (1996).
20. B.Skrifvars, J.P.lomquist, M.Hupa and R.Backman: *Predicting the ash behaviour during biomass combustion in FBC condition by combining advanced fuel analyses with thermodynamic multi-component equilibrium calculations*. In: Pittsburgh coal conference, USA, 14-18 Sept. 1998.
21. E.A.Osman: *A study of the effects of ash chemical composition and additives on fusion temperature in relation to slag formation during gasification of biomass*, PhD-thesis, University of California (1982).
22. T.F.Wall, R.A.Creelman, S.Gupta, C.Coin and A.Lowe: *Coal ash fusion temperatures- New characterisation techniques and associations with phase equilibria*. In: Applications of Advanced Technology to Ash-Related Problems in Boilers (Eds. L.Baxter and R.DeSollar), pp. 541-556 (1996).
23. B.M.Steenari: *A practical and theoretical study of sintering of coal ash and limestone in a fluidized bed combustor*, Staten energiverk, FBT-87/34 (1987).
24. B.-J.Skrifvars, R.Backman and M.Hupa: *Characterization of the sintering tendency of ten biomass ashes in FBC conditions by a laboratory test and by phase equilibrium calculations*. Fuel Process. Technol. **56** (1) 55-67 (1998).
25. A.Nordin, M.Öhman, B.J.Skrifvars and M.Hupa: *Agglomeration and defluidization in FBC of biomass fuels- mechanisms and measures for prevention*. In: Proc. 1995 Eng. Found. Ash Conf., Waterville Valley, 16-22 July 1995 (1995).
26. A.Nordin and R.Backman: *Heavy metal behaviour during combustion and gasification of biomass fuels - comparison between chemical equilibrium and experimental results*. In: Ashes and particulate emissions from biomass combustion, Vol. 3, edited by I. Obenberger, dbv-Verlag, Graz, Austria (1998).
27. A.Ljung and A.Nordin: *Theoretical Feasibility for Ecological Biomass Ash Recirculation: Chemical Equilibrium Behaviour of Nutrient Elements and Heavy Metals during Combustion*. Environmental Science & Technology **31** (9) 2499(1997).
28. R.Backman and A.Nordin: *High temperature equilibrium calculations of ash forming elements in biomass combustion / gasification systems - state-of-the-art, possibilities and applications*, Ashes and particulate emissions from biomass combustion, Vol. 3, edited by I. Obenberger, dbv-Verlag, Graz, Austria (1998).
29. M.Blander, T.Milne, D.Dayton, R.Backman, D.Blake, V.Kühnel, W.Linak, A.Nordin and A.Ljung: *Equilibrium chemistry of biomass combustion: A round-robin set of calculations using available computer programs and data bases*. In: Impact of mineral impurities in solid fuel combustion (Eds. T.F.Wall and L.L.Baxter) (1997).
30. M.Blander and A.D.Pelton: *The inorganic chemistry of the combustion of wheat straw*. Biomass and Bioenergy **12** (4) 295-298 (1997).
31. L.A.Hansen, H.P.Michelsen and K.D.Dam-Johansen: *Alkali metals in a coal- and biomass-fired CFBC - Measurements and thermodynamic modelling*. In: Fluidized Bed Combustion, Volume 4, ASME 1995, pp. 39-48 (1995).
32. P.Kallner, A.Nordin and R.Backman: *Fate of ash forming elements in gas turbine combustion of pulverized wood - chemical equilibrium model calculations*. In: ASME9620 (1996).
33. R.W.Bryers: *Fireside slagging, fouling and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels*. Progress in Energy and Combustion Science **22** (1) 29-120 (1996).

34. B.Olanders and B.-M.Steenari: *Characterization of ashes from wood and straw*. Biomass and Bioenergy **8** (2) 105-115 (1995).
35. M.K.Misra, K.W.Ragland, L.L.Baxter, B.M.Jenkins and L.L.Oden: *Alkalis in alternative biofuels*. FACT **18** 211-220 (1998).
36. W.R.Livingston: *Straw ash characteristics*, Babcock Energy Limited , DE92 519748, 23 p. (1991).
37. N.Padban, Z.Ye and I.Bjerle: *Alkali removal and bed material agglomeration studies applied to biomass gasification*. In: Developments in thermochemical biomass conversion, Vol 2 (Eds. A.V.Bridgwater and D.G.B.Boocock), pp. 1031-1044, Blackie Academic & Professional, London (1997).
38. B.J.Skrifvars, M.Hupa, A.Moilanen and R.Lundqvist: *Characterization of biomass ashes*. In: Proc. Applications of advanced technology to ash-related problems in boilers (Eds. L.Baxter and R.DeSollar), pp. 383-398, Plenum Press, New York (1996).
39. E.J.Raask: Thermal Anal. **16** 91(1979).
40. E.J.D.Smith: Journal of the Institute of Fuel **29** 253(1956).
41. M.J.Gluckman, J.Yersuhalmi and A.M.Squires: *Defluidization characteristics of sticky or agglomerating beds*. In: Proc. of the Int. Fluidization Conf., California, U.S.A, pp. 395-422 (1976).
42. A.R.Manzoori: *Role of the inorganic matter in agglomeration and defluidization during the circulating fluid bed combustion of low-rank coals*, PhD-thesis, University of Adelaide (1990).
43. I.W.Cumming, W.I.Joyce and J.H.Kyle: J. Inst. E. **58** (1985).
44. I.W.Cumming and A.Sanyal. In: Proceedings of the Engineering Foundation Conference, 12-17 July 1981 (1981).
45. R.E.Conn: *Laboratory techniques for evaluating ash agglomeration potential in petroleum coke fired circulating fluidized bed combustors*. Fuel Process. Technol. **44** (1/3) 95-103 (1995).
46. J.R.Gibson and W.R.Livingston. In: Engineering Foundation Conference on Inorganic Transformations and ash deposition during combustion, Palm Coast, Florida, pp. 425-447 (1991).
47. N.Padban, S.Kiuru and A.L.Hallgren: *Bed material agglomeration in PFB biomass gasification*. Preprints of Papers, American Chemical Society, Division of Fuel Chemistry **40** (3) 743-747 (1995).
48. E.Natarajan, M.Ohman, M.Gabra, A.Nordin, T.Liliedah and A.N.Rao: *Experimental determination of bed agglomeration tendencies of some common agricultural residues in fluidized bed combustion and gasification*. Biomass and Bioenergy **15** (2) 163-169 (1998).
49. M.Öhman: *A new method for Quantification of fluidized bed agglomeration tendencies: A sensitivity analysis*. Energy & Fuels **12** 90-94 (1998).

ANNEX A. A LITERATURE SURVEY ON AGGLOMERATION, MECHANISM, PREDICTION AND PREVENTION

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SUMMARY

Agglomeration mechanisms

Agglomeration problems in fluidised-beds are associated with a high content of organically-bound (volatile) alkali metals in the fuel. In biomass, alkali metals (esp. potassium) concentrate in regions of most vigorous growth. Likely problematic fuels are therefore residues of agricultural crops, young energy crops and all other fuels containing high amounts of young organic material. Problems are more severe when a high alkali content is combined with high contents of sulphur (in combustion), chlorine, silica and phosphorus. These elements form low-melting compounds or eutectics, which become deposited on the bed particles, coating them with a sticky ash layer.

Influence factors promoting agglomeration

Apart from ash chemistry, system design and operational conditions are very important factors determining the time-scale of the process. Problems are sometimes associated with temperature excursions, and it seems that the higher the temperature the more severe the problems. However, for high-sulphur fuels there appears to be a temperature window where in-bed sulphur retention is less and agglomeration problems are reduced. The use of silica-sand bed material promotes agglomeration due to reaction of alkali compounds with the silica to form low-melting surfaces on the particles. The time-scale of the agglomeration process and maximum allowable temperatures in the bed are furthermore strongly influenced by fluidisation conditions, gas atmosphere, bed and fuel particle size, and ash re-circulation from cyclones (in CFB's).

How to prevent agglomeration?

Adding inert high-melting minerals (CaO, MgO), sulphur-sorbents (limestone, dolomite) and alkali-sorbents (clay minerals) to the bed are reported to reduce agglomeration problems in fluidised-beds, but mechanisms are not fully understood. In some reported cases, sulphur-sorbents even decreased ash deformation temperatures and increased fouling. Blending of straw with wood and coal is reported to be successful to some extent. In full-scale practice, the bed-material is refreshed regularly before a critical ash-accumulation (alkalis) or agglomeration level is reached.

How to predict agglomeration?

A lot of indices based on the ash chemical composition are reported to assess the fouling and slagging propensity of coals in pulverised fuel boilers. These are fuel specific and often do not include system design parameters and operational conditions. No such indices were found for fluidised-bed gasification of biomass. Some attempts have been undertaken to determine a critical alkali accumulation in the bed on laboratory-scale for different bed materials, but values were substantially different from full-scale values. A lot of laboratory sintering methods were developed to predict the agglomeration and sintering behaviour of coal and biomass ashes. All suffer from the limitation that gas-phase reactions, reactions between gas components and the ash, condensation of alkali vapours, the influence of particle-to-particle collisions in fluidised-beds, and partitioning of elements can not be adequately simulated in the laboratory. Furthermore, thermal ashing to prepare a laboratory ash can create artefacts in the ash and, more important, gives a substantial alkali-loss, artificially increasing the ash-fusion temperatures. These methods can therefore not give absolute agglomeration temperatures, but some seem useful for gaining a more fundamental understanding of ash behaviour in thermal conversion.

1. INORGANIC MATTER IN BIOMASS AND ITS TRANSFORMATIONS

1.1 Chemical composition of biomass-ash

Reported ash contents and compositions for biomass differ considerably with fuel-type and for the same fuel-type with soil, fertilisers, climate, maturity, harvesting, handling, etc., and also with ashing temperature and analysis method employed. Important inorganics in biomass, from a point of view of agglomeration problems, are the refractory element silicon, the alkali elements potassium and sodium, the alkaline earth element calcium and the non-metallic (anionic) elements chlorine, sulphur and phosphorus. For indicative purposes, some general trends are described below for woody fuels and agricultural residues.

A database of biomass composition, ash composition and ash fusion temperatures is available on the internet: <http://www.ecn.nl/phyllis>. The database is made by ECN and is called Phyllis, the Greek goddess of trees and wisdom. Some important information: wood generally has a very low ash content (1-3 %), of which 50 - 60 % is calcium (predominantly as CaO), 5 - 10 % is potassium and 10 % or less is silica. Some extraneous clay and quartz may be present from contamination with soil. Ash melting temperatures are generally very high. Sulphur and chlorine are very low, giving rise to little problems in combustion. Agricultural residues have a higher ash content, consisting largely of silicon, potassium and phosphorus. Their ash melting temperatures are therefore lower than for wood, usually between 800 and 1000°C. Straws and grasses may also contain relatively high concentrations of chlorine and sulphur. The ash content of these fuels shows a large variance, ranging from 2 % to sometimes more than 20 %.

Bryers (1996) distinguishes three different biomass-ash systems:

- *high-silica/high-potassium/low-calcium ash* with low fusion temperatures (agricultural residues)
- *low-silica/low-potassium/high-calcium ash* with high fusion temperatures (wood)
- *high-calcium/high-phosphorus ash* with low fusion temperatures (manure)

1.2 Forms of inorganics in biomass

The form in which an inorganic element occurs in a solid fuel has a decisive influence on its reactivity and volatility in combustion and gasification. According to Baxter (1993) inorganic material in solid low-rank fuels (lignites and biomass) can be roughly divided in two fractions: 1) atomically dispersed inherent inorganics and 2) extraneous discrete minerals added through geologic or processing steps. Inherent inorganics in biomass and low-rank coals are largely associated with oxygen-containing functional groups (hydroxyl, carboxyl, ether and ketone groups) as chelates or cations, or are in solution in inherent moisture as salt or precipitated as a crystalline salt (like sodium chloride).

Bryers (1996) gives a short overview on the modes of occurrence and origins of the main inorganic elements in biomass. Sulphur is in the form of sulphates and organic sulphur. Chlorine occurs as a chloride ion. Silicon is from absorption of silicic acid from the soil and deposits as hydrated oxide in amorphous form. Potassium occurs as univalent ion and has an important function in osmotic processes. It concentrates in the regions of most vigorous plant growth and is highly mobile. Sodium is not an essential element in plants, but may be

introduced through intrusion of salt water during transport or trough fuel processing. Calcium is essential for cell wall stiffening and forms exchangeable bonds with cell walls. Aluminium is toxic and its presence is usually a marker of contamination via dust, dirt or other soil constituents.

Miles et al. (1996) determined the modes of occurrence of inorganics in very different biofuels in terms of their solubility in increasingly aggressive solvents. The fuels analysed included rice and wheat straws, grasses, urban wood fuel, Almond hulls and shells, olive pits and non-recyclable paper. The analysis procedure distinguishes between the following four modes of occurrence:

solubility	likely form in the fuel
- water soluble	water soluble salts
- soluble in ammonium acetate acid (ion-exchangeable)	organically bound as cations
- soluble in hydrochloric acid	acid soluble salts as carbonates and sulphates
- insoluble	mineral form as oxides, silicates or sulphides

All of the refractory elements (Si, Ti and Al) are in the form of oxides and were insoluble. Titanium and aluminium were present only in trace concentrations. The alkali and alkaline earth elements (K, Na, Ca and Mg) were predominantly in a soluble form. In non-contaminated (no soil) fuels, over 90 % of potassium was in a water-soluble or ion-exchangeable form and thus highly volatile. Calcium was largely in an ion-exchangeable or acid soluble form and thus less volatile than potassium. Sodium and magnesium were present only in trace concentrations. In the non-recyclable paper and urban wood fuel, clay contamination gave rise to a large fraction of insoluble and thus non-volatile potassium. Almost all the chlorine was in a water soluble and thus highly volatile form. Sulphur can be a significant component in straws and grasses and occurs in variable forms, ranging from completely water soluble in wheat straw to completely insoluble in switch grass. However, the volatility of sulphur is not so much depended on its form in the fuel, as it is oxidised in combustion to gaseous SO₂ and released as H₂S in gasification. Phosphorus only occurs in significant concentrations in manure and litters and its form is variable. Iron in biomass is present in very low concentration and does not play an important role in slagging, fouling or bed-agglomeration.

1.3 Mineral matter transformations

The physical and chemical transformations of mineral matter in combustion of biomass in conventional boilers as elucidated by the Alkali Deposit Investigation of NREL, U.S. (Miles et al., 1996) are illustrated in figure A1.1

Table A1.1 *Change in crystalline (no amorphous phases) phases on slow heating in air (equilibrium composition) of low temperature ash (LTA) of straw and wood mixtures (Olanders and Steenari, 1995)*

temperature [°C]	crystalline phases in wood ashes	temperature [°C]	crystalline phases in straw ashes
400	CaCO ₃ , SiO ₂ (quartz), traces of K ₂ SO ₄ and carbonates	400	CaCO ₃ , SiO ₂ (quartz), K ₂ SO ₄ , KCl, KAlSi ₃ O ₈
650	CaCO ₃ , SiO ₂ (quartz), traces of K ₂ SO ₄ and carbonates	650	K ₂ SO ₄ , KCl, KAlSi ₃ O ₈ , traces of SiO ₂
700	CaO, SiO ₂ (quartz)	700-750	K ₂ SO ₄ , KCl, K ₂ CaSiO ₄ , KAlSi ₃ O ₈ , traces of SiO ₂
750	CaO, SiO ₂ (quartz), MgO	800-1000	K ₂ SO ₄ , KCl, K ₂ CaSiO ₄ , KAlSi ₃ O ₈ , traces of SiO ₂
800	CaO, MgO, traces of SiO ₂ (quartz) and silicates		
850	CaO, MgO, traces of SiO ₂ (quartz) and silicates (K ₂ CaSiO ₄)		
900	CaO, MgO, K ₂ CaSiO ₄ , Ca-silicates		
1000-1150	CaO, MgO, Ca-(Mg)-silicates		

Fundamental investigations on alkali release have been undertaken by Campisi (1988), Manzoori (1990), Livingstone (1991), Misra et al. (1993) and French et al. (1994). In short, a large part of the soluble potassium will be released in the gas phase above 800°C. How much depends on many factors, as mentioned earlier.

Low-rank coals

Campisi (1988) compared the release of sodium from lignite (organically bound sodium) and brown coal (sodium chloride) with direct evaporation of sodium chloride, by heating small samples at different heating rates (25 to 1667°C/s) in a reducing atmosphere and analysing the evolving gas with AAS. Heating rate did not seem to have an effect on the release profiles. Vaporisation of sodium from the coals started at 800°C and was complete at 1700°C, while the release rate was highest at 1000°C. Release profiles were markedly different from that of evaporation of pure sodium chloride.

Manzoori (1990) studied the ash forming process in fluidised-bed combustion of high-sodium, high-sulphur low-rank coal, by conducting both pyrolysis and combustion experiments with single coal particles. Sodium in this coal was partly organically bound and partly as sodium chloride. In pyrolysis (700 - 830°C), a large fraction of the chlorine (40 - 70 %) was lost from the char after 120 seconds, while only less than 10 % of the sodium was lost. Combustion at 700°C showed more or less the same picture, although results were interfered by char fragmentation. He suggested sodium chloride dissociates or reacts with other compounds to form less volatile sodium and hydrogen chloride.

Wood and straw

Livingstone (1991) investigated the volatilisation of alkalis from several straw types by rapidly heating (500 - 1000°C/s) small samples in air to temperatures between 800 and 1200°C. The release depended on the straw type. Wheat and barley straws showed larger alkali loss than rape straw. For example, combustion at 800 and 1000°C of wheat straw gave a 20 and 50 % total potassium loss respectively, which corresponded with 30 and 80 % respectively of the water soluble and ion-exchangeable potassium. Sodium loss was relatively low below 1000°C, but increased up to 95 % of the soluble sodium (55 % of total) at 1200°C.

Misra et al. (1993) studied the composition of wood and bark ashes as function of temperature. On heating low temperature ash from 600 up to 1300°C they noticed a significant loss in potassium from the ash, starting between 800 to 900°C and resulting in 63 to 90 % of the total potassium released into the gas phase at 1300°C.

French et al. (1994) studied the gas phase release and speciation of alkalis during combustion of woody and herbaceous fuels, at 800 and 1100°C. Almost all the chlorine was released as HCl during devolatilisation, while a much smaller part of the alkalis were released during char combustion as chlorides or hydroxides. Alkali release was higher for the herbaceous fuels than for wood, due to both higher chlorine and alkali concentrations, and increased markedly with temperature. They estimated the release of potassium in switch grass combustion at 1100°C to be 20 %.

2. BED-MATERIAL AGGLOMERATION DURING GASIFICATION AND COMBUSTION

Despite the relatively low temperature in fluidised-bed thermal conversion and combustion, usually below the ASTM ash deformation temperature, problems with bed-agglomeration are reported, especially with agricultural residues and lignite. Most of these problems are associated with a high alkali content of the fuel, operational set-ups (temperature excursions), or systems originally designed for high-rank (low-alkali, low-sulphur) fuels.

2.1 Agglomeration mechanisms

2.1.1 Particle-to-particle bonding mechanisms relevant to bed-agglomeration in fluidised-bed processes

Particle-to-particle bonding or sintering starts when a neck is formed between particles, resulting in a initially porous network. Given time, the neck regions grow until individual particles can no longer be identified. Finally, a dense mass forms. The driving force for this process is reduction of the surface energy of the particles (Skrifvars et al., 1992a). Skrifvars et al. (1989, 1992a, 1992b and 1996) have studied the sintering behaviour of ashes from coal, peat and biomass under FBC conditions and consider three sintering mechanisms to be important: partial melting, viscous flow and chemical reaction. Which one occurs depends on the ash chemical and mineralogical composition, the temperature history of the ash particles and gas components.

Partial melting: sintering in the presence of a reactive non-viscous liquid phase consisting of molten alkali salts, where the solid phase is partly soluble in the liquid at the sintering temperature. The amount of liquid controls the neck formation. Cooling below the solidus temperature gives crystallisation of the bonding agent and densification of the agglomerate. This mechanism is predominant for fuels with ashes high in alkali, sulphur and chlorine. These elements form low-melting eutectics, causing sintering and agglomeration at temperatures even below 700°C. Skrifvars et al. (1992a) mention that sintering by partial melting can be predicted by thermodynamic equilibrium calculation of the amount of molten phase in the ash as function of temperature. Theoretically predicted initial melting temperatures of ashes correlated fairly well with experimentally determined initial sintering temperatures.

Viscous flow sintering or vitrification: sintering due to viscous flow of a vitreous silicate phase. When a silicate ash is heated above the solidus temperature, a highly viscous liquid phase forms. Due to its high viscosity, the liquid remains viscous on rapid cooling below the solidus temperature, forming a glassy phase. Bryers (1996) states that absorption of alkalis on silicate fly ash particles gives rise to formation of a low-melting silicate on the surface of the particles. When the temperature in a ash-deposit rises, due to reduced heat transfer, flowing of this viscous layer forms a neck between adjacent particles. On cooling this neck freezes to a glassy phase.

Vitrification of peat ash in an oxygen-blown HTW gasifier (750-950°C) gave rise to unexpected formation of deposits, hampering operation by clogging the gasifier outlet and cyclones (Moilanen, 1993). Ash fusion temperatures were above 1000°C. Sintering was ascribed to rapid heat up of the ash particles in flames of the oxygen-blown bed, to temperatures exceeding the

solidus temperature. On cooling the slag formed in the flames remained glassy with low enough viscosity to give rapid sintering in the freeboard zone by viscous flow at temperatures as low as 700 to 800°C.

The dependence of this mechanism on properties of fly ash particles is given by the ‘Frenkel’ formula:

$$x^2 = \frac{3 \cdot r \cdot \gamma \cdot t}{2 \cdot \eta}$$

where r = radius of particles
 x^2 = equivalent of contact area (neck) between particles
 γ = surface tension of the vitreous phase
 η = viscosity
t = time

Neck growth ($x(t)$) is thus controlled by time and viscosity, the latter varying with temperature and chemical composition of the slag. Moilanen (1991) mentions viscosities in the range of 10^7 to 10^9 Poise to be critical for agglomeration in fluidised-beds. Moilanen (1989) also studied the effects of temperature, ash chemical composition and atmosphere on sintering of peat ash. Sintering of 100 μm premelted (to obtain slag) ash particles was measurable between 700 and 800°C and increased with temperature and the basic-to-acid ratio of the ash. Surface crystallisation in the slag inhibited sintering, which was achieved by adding sodium and phosphorus. Normally, these elements have a strong fluxing effect. Sintering was much stronger in a reducing than in a oxidising atmosphere. This was ascribed to oxidation and crystallisation of iron to hematite.

Chemical reaction: sintering due to reaction between the particles or the particles and the gas, to form a third compound binding the particles together. Skrifvars et al. (1992a and 1996) concluded that this mechanism is responsible for sintering of coal and biomass ashes rich in calcium. These ashes show increased sintering in CO_2 atmosphere at temperature between 600 and 800°C and with SO_2 in the gas at all temperatures (above 500°C), when compared to sintering in dry air. The effect of CO_2 was only noticeable for ashes in which calcium was as oxide and not when it was as carbonate. It was concluded that carbonation of CaO in a gas with high CO_2 partial pressure gives particle-to-particle bonding via CaCO_3 crystals. Above 800°C these again decompose to CaO and CO_2 . They mention that this sintering mechanism could be relevant to deposit hardening in combustion, where ash is first formed at high temperatures above 800°C, decomposing the carbonates to oxides, and then cooled in the post combustion zone in a CO_2 -rich environment. Sulfation of CaO to CaSO_4 , due to SO_2 in the gas, gives the same kind of bonding by crystals, stable over a wider temperature range.

Bryers (1996) also mentions calcium sulphate bonding to be an important deposit hardening mechanism when firing coals rich in organically bound calcium and sulphur or when adding finely ground limestone for sulphur capture. Submicron CaO particles deposit on tube surface through thermophoresis and then become sulphated by reaction with SO_2 or SO_3 . Local low oxygen partial pressures at the tube surface could additionally give rise to formation of the low melting eutectic CaSO_4/CaS (eutectic point 830°C).

2.1.2 Bed-agglomeration mechanisms in fluidised bed combustion and gasification

Fluidised-bed combustion of low-rank coals

Brekke and Karner (1982), Bobman, Hajicek and Zobeck (1985), Mann, Galbreath and Kalmanovitch (1992), and Manzoori (1990) all experimentally studied the mechanisms of

agglomeration in FBC of high-sodium, high-sulphur low-rank coals. They all identified an initial stage in which highly sulphated ash, rich in sodium and calcium, becomes deposited on the bed particles forming a sticky ash coating. The sodium in the coating is derived from the organically bound sodium and sodium chloride. This ash coating gives rise to particle agglomeration due to sulphate-to-sulphate sintering (chemical reaction) or liquid phase sintering (partial melting) due to the presence of low-melting point eutectics of sulphates of sodium, calcium and possibly magnesium. In later stages the ash reacts with the quartz sand bed material to form low-melting silicates on the surfaces of the particles. Viscous flow sintering then accelerates the process.

Brekke and Karner (1982) mention that problems are promoted by the use of high-sodium lignite, increased operation time, ash re-injection, temperature excursions, quartz sand bed material and ash accumulation in the bed. They report that the use of limestone as additive inhibits to some extent agglomeration. The agglomeration process occurred over a period of about 100 hours, when further operation was hampered by substantial defluidisation. Severe agglomeration was evident after 60 hours of .

Bobman, Hajicek and Zobeck (1985) noticed that there is an intermediate temperature range where agglomeration is reduced. Agglomeration was severe at high temperatures above 980°C and lower temperatures around 800-830°C, causing shut down after 50 to 80 hours operation. At 900°C agglomeration was however minimal even after 100 hours of operation. They noticed a correlation between agglomeration and the sulphur retention in the bed, but did not speculate on a cause/effect relation.

Mann, Galbreath and Kalmanovitch (1992) reviewed the results of the experimental work conducted on agglomeration at EERC of the University of North Dakota, U.S. and full-scale data and came to the following general mechanism for the formation of agglomerates in AFBC of high-sodium, high-sulphur low-rank coals:

1. Initial deposition/condensation of volatile sodium ash species on the surfaces of bed particles, followed by deposition of submicron calcium species (from organically bound calcium) on the initial sticky layer. Condensation is a gas-to-solid condensation, which may occur in combustion as the temperature of the burning char is higher than the temperature of the bed particles.
2. Reaction of the sodium and calcium with SO₂ in the gas to form sulphates, before, during or after deposition on the bed particles.
3. Entrapment of other larger ash particles in this initial sulphated ash layer.
4. Cohesion of bed particles due to sulphate-to-sulphate sintering (chemical reaction) or formation of low-melting eutectics of sulphates (partial melting).
5. Formation of larger agglomerates.
6. Partial defluidisation due to increasing fraction oversized particles in the bed, causing hot spots.
7. In the high temperature zones in the bed, low-melting-point silicates form due to the reaction of sodium and calcium with the quartz bed material. Temperatures exceeding the solidus temperature of the newly formed silicates give rise to viscous flow sintering, forming hard agglomerates and accelerating the agglomeration process.

A same kind of mechanism is proposed for the deposition of ash on in-bed heat exchange surfaces in FBC by Oakey, Minchener and Stringer (1990). They also mention the inherent propensity of very fine particles (< 5 µm) to sinter, independent of their composition. They claim therefore that some ash deposition on surfaces above 540°C is unavoidable.

Manzoori (1990, 1992, 1993 and 1994) reports that deposition of sticky ash on bed particles and subsequent agglomeration is reduced by a higher content in the fuel of fine-sized inert minerals, like silica, alumina and aluminosilicates, a lower volatile sodium content of the fuel and a lower

bed temperature. Agglomeration was accelerated by impregnation of the fuel with sodium chloride solution, which resulted in chlorine in the ash coating lowering its melting temperature. Below the initial sintering temperature of the spent bed material (700°C), as determined by thermal analysis, no bed-agglomeration occurred. Manzoori (1990) derived an expression for the rate of agglomeration in FBC in terms of the thickness and physical properties of the ash coating and the operational conditions.

Fluidised-bed gasification of low-rank coals

Mason et al. (1980), Marinov et al. (1992) and Williamson, et al. (1994) all discuss the important role of pyrite in the formation of agglomerates in FBG of iron-rich coal. Marinov et al. (1992) report that the pressurised fluidised bed gasification of a high-sulphur lignite at 930°C was hampered due to intensive ash agglomeration. The low-melting (924°C) eutectic of FeS and FeO was considered to be the agglutinating agent for coarse ash particles. Mason et al. (1980) state that this is due to rapid decomposition of pyrite (FeS₂) to pyrrhotite (FeS), followed by oxidation of FeS to FeO even at very low oxygen partial pressure. Williamson (1994) noticed that pyrite forms very fine sized ash particles which become attached to the larger clay-derived ash particles, coating them with low-melting material.

Fluidised-bed combustion and gasification of high-alkali biomass

A number of investigators report that agglomeration in FBC and FBG of high-alkali biomass is due to reaction of the alkalis with the silica sand forming low-melting eutectics on the bed particle surfaces (Grubor et al. 1995, Paisley and Litt 1993, Ghaly and Ergudenler 1993a, 1993b, 1994a and 1994b, Padban et al. 1996). Agglomeration occurred at temperatures as low as 750°C.

Representative of agglomeration in FBC of high-alkali biomass are the results obtained by Nordin et al. (1996). Combustion of Lucerne and olive flesh in a laboratory-scale fluidised-bed reactor at 850°C resulted for both fuels in severe agglomeration within less than 30 minutes. The process from initial agglomeration to total defluidisation was found to be very rapid. They noticed that the fuel particle temperature was much higher than the average bed temperature and suggest that ash melts at the surface of the burning fuel particle and then deposits on the bed particles. Controlled increase of the temperature of a air-fluidised mixture of ash and quartz sand followed by analysis of the spent bed particles revealed initial agglomeration was indeed due to a melt. In the case of Lucerne (low-silica, high-potassium) the initial agglomeration temperature was as low as 680°C and the bonding agent was a alkali salt melt (Ca, K, S, P, CO₃ and some Cl). For olive flesh (high-silica, high-potassium) agglomeration started at 940°C and a potassium-silicate melt (K, Ca and Si) was the glue. Analysis of agglomerates from real combustion showed agglomeration in the end stage of the process to be due to a molten potassium-silicate layer on the bed particles, likely formed by reaction of quartz sand with alkali compounds.

From these results it follows that deposition of low-melting high-alkali ash on bed particles is the initial step in agglomeration. This ash consists of alkali-silicates or alkali-salts (chlorides, carbonates and sulphates), depending on the ash chemical composition and temperature. Hot spots in the bed accelerate the process due to reaction of quartz particles with alkalis forming low-melting silicates on their surfaces.

2.1.3 Defluidisation of fluidised-beds due to ash chemistry

Basu and Sarka (1983) noticed that the minimum fluidisation velocity of a bed of coal ash minerals linearly increases with the bed temperature when the temperature rises above the initial sintering temperature of the bed (thermal analysis). They state that clinker formation is preceded by defluidisation. Reduced heat transfer gives rise to hot spots in the bed exceeding the deformation temperature of the coal ash. Defluidisation of the bed is a consequence of an extra

adhesive force between the bed particles, which become sticky above the sintering temperature. When the fluidisation velocity falls below the true minimum fluidisation velocity, the bed defluidises instantaneously. Smaller particles showed sintering and defluidisation at lower temperatures, which was ascribed to the larger contact area. Also according to Manzoori (1990 and 1994) defluidisation is an instantaneous process which may occur without preceding agglomeration of the bed material. He states that the ash chemistry causing defluidisation is the same as for agglomeration, but that both phenomena are not the same. He derived an expression for the onset of fluidisation in terms of the thickness and physical properties of the ash coating and the operational conditions.

2.1.4 Combustion versus gasification: some important differences

Major differences between combustion and gasification of high-sulphur fuels is that sulphates do not form in gasification and the much higher fuel particle temperature in combustion, sometimes several hundred degrees higher than the furnace temperature. Manzoori (1990) and Nordin et al. (1996) mention that volatilisation or melting of ash at the high fuel particle temperature may be the initiating step in agglomeration.

2.2 Influence factors promoting agglomeration

2.2.1 Ash chemistry

The important role ash chemistry is largely described in section 2.1. Most undesirable elements in the ash are potassium and sodium, especially in combination with high amounts of sulphur (in combustion), chlorine, phosphorus and silica. Calcium gives problems in the special case of co-combustion of a high-sulphur fuel with a fuel rich in organically bound calcium. Calcium is also an important bulk component in ash deposits, especially when adding limestone to the bed, but is mostly not responsible for the initiation of deposits.

2.2.1.1 Potassium

Potassium is by far the most important element in biomass responsible for ash-related problems. In oxidising conditions the thermodynamic stability of potassium compounds with increasing temperature is as follows: sulphates (< 1000°C) < silicates < chlorides. In reducing conditions sulphates do not form and silicates and chlorides are the stable compounds. These compounds all have relatively low melting points and can form even lower-melting eutectics. A high amount of volatile (organically bound) potassium in biomass combustion is therefore associated with slagging in the furnace due to fluxing of silicates, fouling and corrosion in convective passes due to condensation on the heat transfer surfaces as chlorides, sulphates, hydroxides or oxides and subsequent sulfation to sticky and corrosive sulphates, and agglomeration in fluidised beds due to formation of low-melting compounds or eutectics by reacting with silica (from the fuel or bed media), sulphur and chlorine. Volatilisation of potassium starts to be significant at temperature above 800°C, depending on the fuel-type.

2.2.1.2 Chlorine

Chlorine is almost completely released as HCl in the gas during devolatilisation. Chlorine greatly facilitates the release of alkali into the gas phase, due to the reaction of HCl with alkalis forming stable alkali chloride vapours. This can even release alkalis from aluminosilicate

minerals. The amount of alkali released into the gas phase is more related to the total chlorine than total alkali content. Chlorine also increases the danger of bed-agglomeration due to the low melting points of chlorides and the formation of low-melting eutectics. Manzoori (1990) noticed agglomeration was greatly accelerated by impregnation of coal with sodium-chloride solution. Furthermore, chlorine can accelerate high temperature corrosion.

2.2.1.3 Sulphur

In combustion sulphur is released as SO₂, which reacts with alkalis to form sulphates. Sulphates have very low vapour pressures and condense readily on cooler surfaces, such as heat transfer tubes and bed particles. In gasification, sulphur is largely converted in hydrogen sulphide and sulfation does not occur. Formation of low-melting silicates and stable alkali chloride vapours is then more likely.

2.2.1.4 Silica

Silica particles absorb alkalis creating low-melting surfaces due to the fluxing action of alkalis. Paisley and Litt (1993) report that agglomeration in gasification of switch grass and poplar in the Battelle pilot plant was due to formation of the low-melting eutectic K₂Si₄O₉-SiO₂ (eutectic point 760°C) by absorption of fuel potassium by the sand.

2.2.2 Bed material

From the literature it becomes clear that silica sand is not a suitable bed material in FBC and FBG of high-alkali fuels, due to formation of low-melting eutectics on the surfaces of bed particles by the reaction of silica with alkalis. Alumina does not react with the ash and may make higher temperatures possible. Pure hematite is reported as the most suitable bed material in combustion of high-alkalis biomass. Dolomite, sometimes used for its catalytic effect on thermal cracking of tars, can give rise to strong calcium-based ash deposition in the freeboard. The same goes for limestone, which is used for in-bed sulphur removal. Addition to the bed of limestone may in some cases even lower the ash melting temperature. Some illustrative experiences are reported below.

Grubor et al. (1995) conducted long term combustion tests with high-alkali corn cobs in a 150 kW fluidised bed with silica sand as bed material. Operation at 820°C had to be stopped after 60 hours due to extensive agglomeration, while this was necessary after 180 hours at 750°C. Severe fouling of the freeboard walls was also noticed, possibly due to the increase in freeboard temperature as a result of combustion of corn cobs on the top of the defluidised bed. There was a build up of sodium, potassium and iron in the bed with time, corresponding with deposition of 40 % of the alkalis fed with the fuel on the bed particles. Silica bed particles showed a glassy amorphous phase on their surface, resulting from the fluxing action of the alkalis. Heat treatment of mixtures of alkali salts and bed materials, including corundum (Al₂O₃), silica, hematite and hematite ore, revealed that hematite is the only suitable bed material for the FBC of high-alkali biomass fuels. Silica already showed sintering at 700°C, corundum at 800°C, while hematite did not show any sintering even at 900°C and a alkali content of 20 %. Feeding alkali salt solutions into a laboratory-scale fluidised-bed of hematite did not give any agglomeration at temperatures around 950°C. There was however a strong increase in fine particles elutriated from the bed, caused by attrition of the porous scale formed on the hematite particles by reaction with alkalis.

Ghaly and Ergudenler (1993a, 1993b, 1994a and 1994b) studied agglomeration of silica and alumina bed materials in the fluidised-bed gasification of straw. The silica bed agglomerated

once the temperature reached 800°C, resulting in defluidisation. No agglomeration was noticed at 750°C. The alumina bed agglomerated at 920°C, corresponding with the softening point of the straw ash of 921°C. Below 900°C, gasification of straw in alumina did not give any agglomeration problems. They mention that temperature is the key variable and not the ash content of the bed or the gas velocity. However, test runs were relatively short so that no real consideration was given to ash accumulation in the bed with increasing operating time. Heat treatment in air of mixtures of straw ash and bed material at different temperatures gave similar agglomeration temperatures, indicating this kind of simple tests can be valuable in assessing the agglomeration propensity of a bed material/fuel ash combination.

At VTT (Madsen and Christensen, 1995) 100% straw was gasified in a PDU-scale bubbling-fluidised-bed reactor in beds of alumina and dolomite. Sintering was especially noticed in the freeboard at temperatures around 800°C, which was severe with dolomite in the bed. Sintering in the bed at temperature around 750 was ascribed to the re-circulation of cyclone ash giving accumulation of low-melting straw ash in the bed.

2.2.3 Fluidisation conditions

Atakul and Ekinci (1989) studied the effects of fluidisation conditions, particle size, bed material and lignite type on agglomeration and defluidisation in FBC. They found that the agglomeration temperature could be lowered by:

1. Larger fuel particles: agglomeration temperature increased 60-70°C when the fuel particle size was increased from 1.4 to 4.5 mm.
2. Smaller bed particles: agglomeration temperature increased 50-70°C when the bed particle size was increased from 0.85 to 0.4 mm.
3. Higher fluidisation velocity.
4. The use of limestone and dolomite instead of quartz as bed material. This was ascribed to the lower density and thus lower minimum fluidisation velocity of these materials.

The static bed height did not have an effect, due to the concurring effects of poorer fluidisation and higher bed material to ash ratio.

2.3 How to prevent agglomeration?

Some measures to prevent or delay ash related problems for an existing installation include:

- chemical additives to the bed to increase the ash melting temperature,
- blending with wood or coal,
- lowering the bed-temperature below the ash sintering temperature,
- periodical refreshment of the bed inventory before critical ash build-up in the bed.

2.3.1 Chemical additives

Additives mentioned to reduce or delay bed-agglomeration and defluidisation in combustion and gasification are:

- Periclase (MgO)
- Calcite (CaO)
- Dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$)
- Limestone (CaCO_3)
- Clay minerals (aluminosilicates), like kaolin

The mechanisms are not fully understood. Some fine-grained additives, like limestone, can also have adverse effects by forming deposits on heat transfer surfaces and reactor walls (Miles et al., 1996) and are even reported to decrease ash deformation temperatures (Osman, 1982). Above mentioned additives are also reported to reduce problems with corrosion and erosion in biomass-fired fluidised-beds (Coe, 1996).

Mechanisms to prevent agglomeration by additives appear to be:

Increasing the melting temperature of the ash or reducing stickiness of ash coatings on bed particles

- periclase
- calcite
- alumina and clay minerals

Fixation of volatile alkali metals in high melting minerals

- kaolin

Removing sulphur before it reacts with the ash to form low melting compounds

- limestone
- dolomite

Reported experience

Skrifvars et al. (1992a) studied the effect of limestone and clay mineral on the sintering behaviour of coal ashes. Limestone and clay mineral decreased the sintering tendency of brown coal ash at 500 to 600°C, but increased the sintering tendency at 700°C. Further addition at 700°C above a Ca/S ratio of 1.3 again decreased the sintering tendency below that of the ash alone. This effect was slightly greater for the clay mineral. The results were not explained by chemical reactions taking place, but simply by dilution of the ash with high melting material.

Osman (1982) investigated the effect of CaCO₃, CaO and MgO on the standard deformation and fusion temperatures of biomass ashes. Addition of CaCO₃ increased the fusion temperature by 100°C, but the deformation temperature was reduced by 100°C. Addition of MgO increased both the deformation and fusion temperatures effectively above normal FBC and FBG temperatures. CaO gave only a moderate increase of these temperatures. Use of CaCO₃, MgCO₃ and CaO in a downdraft gasifier did not reduce slagging problems, as the ash melting temperature could not be increased above the temperature in the hot spots of the reactor. CaO was added to the raw straw as dry particulate matter, followed by pelletization. CaCO₃ and MgCO₃ were added by spraying a solution of these compounds on the fuel.

Manzoori (1990) noticed that a high content of fine-sized extraneous inert minerals in a high-sodium, high-sulphur low-rank coal, inhibited agglomeration in fluidised-bed combustion at 850°C. The same coal with similar contents of sulphur, organically bound sodium and sodium chloride, but almost no inert mineral inclusions, gave total defluidisation of the bed after only 3.5 hours. The difference was ascribed to the fact that the fine inert minerals become embedded in the ash coating deposited on the bed particles, making it less sticky.

Paisley and Litt (1993) report that gasification of switch grass and poplar lead to formation of sand agglomerates in the combustor of the Battelle pilot plant, hampering circulation of the sand. The bonding agent was the low melting eutectic K₂Si₄O₉-SiO₂ (eutectic point 760°C) formed by reaction of fuel potassium with the sand. Addition of 2 % by weight of MgO with the feed prevented agglomeration problems with poplar, even at normal high combustor temperatures around 1050°C. Thermomechanical analysis of mixtures of sand, ash and chemical additives showed kaolinite is not effective in decreasing the sintering tendency, calcite (CaO) can only give a slight reduction in sintering, and periclase (MgO) can eliminate sintering.

Mann et al. (1992) report that addition of limestone in fluidised-bed combustion of low-rank coals reduces problems with ash deposition and bed-agglomeration. They ascribe this to removal of sulphur, so that it no longer reacts with the alkalis and calcium from the fuel.

Particle size seems to be important as they noticed that deposition of fine-grained CaO from the fuel on heat transfer surface followed by sulfation is an important deposit initiating mechanism. Addition of limestone can have adverse effects, which follows from the following reported experience. Miles et al. (1996) report that limestone addition in fluidised-bed combustion of biomass blends gives rise to deposits consisting largely of calcium sulphates. The deposit initiating step is unclear and may be related to fuel inorganics. Delvinquier et al. (1995) noticed that addition of fine-grained limestone to a fluidised bed of silica sand at 850°C caused defluidisation after only 10 minutes. This was ascribed to reaction of very fine calcined lime particles (3 µm) with potassium-aluminosilicate impurities in the surface of the silica sand bed particles, binding the particles together. When SO₂ was added to the air this no longer occurred. Sulfation of CaO makes it less reactive towards the aluminosilicate impurities. Anthoney et al. (1995) report that sulfation of added lime particles caused agglomeration and fouling in CFBC of petroleum coke. Petroleum coke is a fuel with very low ash and very high sulphur content. Agglomerates consisted entirely of sintered limestone-derived particles which were highly sulphated (CaSO₄). Addition of MgO reduced the problems. MgO does not become sulphated and forms inert barriers between the limestone particles which prevents good contact and so extensive chemical hardening.

Mann et al. (1995) report that kaolin is suitable for in-bed removal of sodium in FBC of Beulah lignite. They noticed a 93 % reduction, from 3.6 ppm to 0.27 ppm, in the vapour phase alkali concentration in the flue gas with addition of fine-sized kaolin to the bed. The particle size of the kaolin had a significant effect on the alkali capture efficiency. Alkali absorption lowers the melting point of the clay mineral, which may be of some concern. A frequently mentioned reaction product of kaolin is nepheline, which has a melting point of 1500°C. However, it is likely that also non-stoichiometric phases form with lower melting points. Padban et al. (1996) tested Quartz, Baskarp and Fyle sands, all based on silica but with different impurities, for their alkali absorbing potential by heat treatment of mixtures of sand and different alkali salts in a TGA. Alkali capture depended on both sand type and alkali salt (KCl, NaCl and KNO₃). They noticed an optimum temperature for alkali capture around 890°C, ascribed to the opposite effects of temperature on physisorption and chemical reaction. At temperatures between 680 and 1100°C the alkalis always caused considerable agglomeration, making these materials unsuitable for alkali capture in FBG of high-alkali biomass. Alkali gettering by aluminosilicates in down stream fixed-beds has been studied quite extensively for the purpose to remove alkalis from hot fuel gas (Scandrett and Clift 1984, Uberoi 1990, McLaughlin 1990). Alkali gettering by minerals has also been studied with respect to alkali loss in catalytic coal steam gasification (Kuhn and Plogmann 1983, Formella et al. 1986, Bruno 1986). Conditions were however quite remote from those in fluid-bed gasification. Potential getters according to McLaughlin (1990) are characterised by a open layered crystal structure. Kaolin, emathlite and calcium montmorillonite were found to be very good getters. Water vapour in the gas increases gettering, while HCl substantially decreases gettering. The latter effect may limit the use of aluminosilicates to low-chlorine fuels. Furthermore, the getter efficiency decreases with temperature. Waste paper contains a high concentration of kaolin, making blending with this fuel possibly attractive.

2.3.2 Fuel blending

One way to achieve a higher ash melting temperature or lower alkali input into the system is to blend a problematic fuel with coal or wood. When blending fuels one must always keep in mind that it is the interaction between alkalis, alkaline earth elements and silica, chlorine, phosphorus and sulphur that causes the problems. Bryers (1996) for example mentions that co-firing of non-problematic wood with a high-sulphur fuel, like heavy oil, is almost sure to give serious fouling due to the combination of organically bound calcium and sulphur, giving rise to calcium sulphate bonded deposits.

Fist rules biomass fired boilers

From full-scale experience and fuel compositions, Miles et al. (1996) give some fist rules to avoid excessive fouling problems in biomass-fired boiler. One concerns the maximum alkali input, (Na₂O+K₂O) in kg/GJ, into the boiler: 0-0.17 does not give problems, 0.17-0.34 becomes problematic and would make it necessary to have frequent outages and lower furnace exit temperatures, while > 0.34 gives rise to unmanageable problems.

Experience with co-gasification

Madsen and Christensen (1995) report experience at VTT (PDU-scale) and Enviropower (pilot-scale) with co-gasification of straw and coal. At VTT blends with 54 % straw could be gasified at temperatures between 960 and 970°C in the bed and 970 and 990 in the freeboard without any problems. The bed material consisted of limestone and char and ash from the coal. At Enviropower blends of 50 % straw could be gasified at temperatures of 940°C in the bed and 950°C in the freeboard. Gasification at 980°C of a blend with 25 % straw gave strong bed-agglomeration, resulting in plant shutdown after only 12 hours. This indicates that temperature is a very critical variable.

Experience with co-combustion

Salour et al. (1993) investigated co-combustion of wood and rice straw and report that bed-agglomeration could be delayed by addition of at least 50 % wood. The reason for this high percentage is the low ash content of wood. Nordin et al. (1996) noticed severe bed-agglomeration within less than 30 minutes when combusting Lucerne and olive flesh in a fluidised-bed at 850°C. Blending with coal (50 wt. %) eliminated the problems, making stable operation possible for the entire duration of the test runs (10 hours). Additionally, a high sulphur retention in the ash of 80% was obtained with blending. Initial agglomeration temperatures for the fuels were raised by blending from 670°C in the case of Lucerne and 940°C for olive flesh to 950°C and more than 1050°C respectively. The agglomeration temperatures correlated very well with initial sintering temperatures from a compression strength sintering method.

2.3.3 Periodical refreshment bed material

Regular sampling and analysis of the bed material during operation and refreshing the bed inventory before the a critical alkali concentration or critical agglomeration level is reached may be a necessary measure when firing of gasifying a high-alkali fuel alone. Grubor et al. (1995) tried to determine a critical alkali content by spraying alkali salt solutions into a fluidised-bed until defluidisation. However, they found a considerable difference between critical concentrations determined on lab-scale and those found from larger scale combustion experiments with corn cobs.

2.3.4 Lowering the bed temperature

Lowering the bed-temperature below the initial sintering temperature of the bed material/ash mixture would be the most logical measure to prevent problems. Reducing the air to fuel ratio in gasification is however undesirable, as this generally gives a lower carbon conversion and higher concentrations of tar in the gas. Increasing the air excess ratio in combustion is also difficult as it can cause extinction of the flame in the bottom of the bed. Furthermore, a low bed-temperature may give high CO emissions (Grubor et al 1995). Better ways to achieve a lower bed temperature for a given air to fuel ratio may be addition of steam to the fluidising gas or additional heat transfer surface in the bed or freeboard. Freeboard temperatures in biomass combustion are generally 100°C higher than in the bed, due to combustion of volatiles. Osman (1982) studied the effect of lowering the bed temperature by steam on slagging in downdraft gasification of agricultural wastes. By mixing steam with the combustion air he was successful

in keeping the bed temperature below the determined standard ash deformation temperature, which resulted in slagging free operation.

2.4 How to predict agglomeration?

Many laboratory methods are mentioned in the literature for assessing the slagging, fouling or agglomerating propensity of a fuel. All suffer from the fact that ash produced in the laboratory is significantly different from the ash formed in real combustion and gasification, due to the many influence factors in ash formation that can not be adequately simulated in the laboratory. Important in this respect are partitioning, gas-solid reactions and re-condensation of alkali vapours on fly ash. The predictive value of below mentioned laboratory methods is therefore hard to assess, also because results were not always compared to full-scale experience. Below mentioned methods should be combined with larger-scale tests in fluidised beds and modelling to gain a more fundamental understanding of ash formation and agglomeration.

2.4.1 Fuel analyses

Slagging/fouling indices derived from standard ash chemical composition

Osman (1982) discusses some empirical indices correlating the ash chemical composition to the standard deformation and fusion temperatures of coal ashes. Bryers (1996) gives several empirical correlations for slagging and fouling. He mentions that this kind of indices are fuel specific and do not take into account important operational and design parameters.

Reactive alkali and chlorine content: chemical fractionation

Miles et al. (1996) give a procedure to determine the modes of occurrence of inorganics in biomass in terms of their solubility in increasingly aggressive solvents. Leaching a biomass sample with water extracts the loosely bound inorganics and simple inorganic salts. Leaching with 1 M ammonium acetate extracts all ion-exchangeable inorganics (organically bound). Finally, leaching with 1 M hydrogen chloride extracts the acid soluble salts, like carbonates and sulphates. Inorganics in the residue are typically in silicates, oxides or sulphides. This procedure can yield 5 to 15 % higher total alkali concentrations than analysis of ash prepared at 600°C. Because water soluble and ion-exchangeable alkalis are in a volatile form, their concentration together with the chlorine concentration gives more information about the fouling propensity of a fuel than the total alkali content or standard fusion temperatures. This method of chemical fractionation is also used for analysing spent bed material and agglomerates to determine whether a reaction has taken place between volatile alkalis and bed material that would have changed the form of the alkalis (Manzoori 1990, Padban et al. 1996).

Recommended ashing procedures to produce laboratory ash for analysis

Results of ash characterisation tests to determine the sintering and melting behaviour of ash are strongly influenced by the ashing temperature. Ashing temperatures above 600°C give significant alkali loss, artificially increasing the fusion temperatures. Miles et al. (1995) therefore recommend an ashing temperature of 600°C. A lot of investigators on ash behaviour have used ashing procedures with temperatures around 500°C. Also oxygen plasma ashing is mentioned as a method to burn away the organic matter, while leaving the mineral matter intact. This may work for a high rank coal with all the inorganics in minerals, but in biomass the inorganics are largely associated with the organic matrix. Bryers (1996) warns that low temperature ashing with long oxidation times gives rise to the formation of artefacts from the organically bound inorganics, e.g. potassium nitrates and perchlorates, not normally found in biomass ash.

2.4.2 Ash melting, sintering and agglomeration temperatures

Standard ASTM ash fusion test

Standard ash fusion temperatures are determined according to ASTM-D1857. This method is developed to assess the slagging propensity of coal and coke in stoker fired boilers. It is based on visual observation of the deformation of a ash cone during heat treatment. This method is well known and many investigators report ash fusion temperatures of biomass ashes (Bining 1988, Miles et al. 1996, Bryers 1994, Skrifvars et al. 1996, Osman 1982). Apart from the difficulty of visual observation, there are some strong arguments against the predictive value of this method. Huffman (1981) reports that coal ash already substantially melts at temperatures 200 to 400°C below the visually determined initial deformation temperature. Furthermore, that further deformation of the cone is largely due a decreasing viscosity with temperature, rather than increased melting. Osman (1982) determined the ash deformation and fusion temperatures in air of 26 different biomass fuels. He mentions that the melting process is not a sharp phenomenon, but a gradual process. The change in cone shape differed markedly from sample to sample. Especially the detection of the fusion temperature was difficult, as the ash did not always deform to a lump. Osman further mentions that the temperatures determined by this method are affected by 1) the size, shape and inclination of the cone, fineness of the ash, the rate of heating and the nature of the atmosphere.

Empirical correlations between standard ash fusion temperatures and ash chemical composition

Osman (1982) concludes that phase diagrams can be used to predict measured deformation and fusion temperatures of biomass ash only when the ash consists of a two or three component system. Fusion temperatures of biomass ashes with four or more components can not be determined from phase diagrams. Wall et al. (1996) discuss correlations between fusion temperatures of coal ashes and eutectic points from phase diagrams and find a relatively good correlation. Steenari (1987) tried to explain sintering behaviour of coal ash and limestone in fluidised-bed combustion from the eutectic melting points of the oxide systems. However, ash is not only made of two to four oxides and furthermore these systems are often not fully investigated.

Differential thermal analysis/thermogravimetric analysis

A number of investigators (Skrifvars et al. 1996, Bryers 1994, Olanders and Steenari 1994, Misra et al. 1993, Livingstone 1991) have used DTA/TGA to characterise the melting and volatilisation behaviour of biomass ashes, or to study sorbents for alkali capture and reactions between bed material and alkali salts (Padban et al. 1996). The method is based on measuring heat effects in the ash sample (endothermic or exothermic processes) and simultaneous measurement of the weight loss. It can be a useful tool for determining initial melting temperatures and to estimate the volatilisation of elements. However, interpretation of the results without knowledge of the mineralogical composition of the ash is very difficult due to the many processes that can occur simultaneously in ash (decomposition, volatilisation, evaporation, reactions with the gas, melting) and the disturbing effects from absorption of gases and oxidation during storage, combustion of residual carbon, artefacts from low temperature ashing, etc.

Electrical resistance and shrinkage (thermo-mechanical analysis) method

Wall et al. (1996) discuss different methods based on electrical resistance and shrinkage for measuring the sintering tendency and initial melting temperatures of coal ashes and interpreted their results from phase diagrams. The different methods gave different results, already indicating the sensitivity of these methods for factors like ashing. Manzoori (1990) used thermo-mechanical analysis to identify the initial sintering temperature of spent bed material from CFBC and found a good correlation between this temperature and the temperature where agglomeration started in CFBC of high-sodium, high-sulphur low-rank coals. The initial sintering temperature from TMA was the same as the temperature where melting started in

DTA/TGA, so that partial melting was probably the sintering mechanism. Khan (1989) describes a apparatus for direct measurement of ash fusion and sintering by simultaneous measurement of electrical resistance and shrinkage at high temperatures and pressures. Sintering temperatures measured were considerably less than the standard initial deformation temperatures for the ashes.

Laboratory sintering method: pressure strength measurement of heat-treated ash pellets

Skrifvars et al. (1989) describe a laboratory method to measure the sintering tendency of ashes based on the compression strength of heat treated ash pellets. This method has been used by a number of investigators (Ots et al. 1995, Nordin et al. 1996, Skrifvars et al. 1996, 1992a and 1992b). Pellets of laboratory ash or mixtures of ash and bed material are heat treated in a relevant gas atmosphere. After cooling the crushing strength of the pellets is measured. The temperature where this crushing strength deviates from the base strength is then referred to as the initial sintering temperature. Comparison of lab-results with full-scale experience by Skrifvars et al. (1989, 1992a, 1992b and 1996) shows that this method is very useful in revealing the mechanism behind agglomeration (f.e. effect gas components) and comparing different fuels for their sintering and agglomerating propensity, but that it does not give absolute initial agglomeration temperatures due to the many other important factors besides ash chemistry.

Heat treatment mixtures of laboratory-ash and bed material and other similar agglomeration tests

Ghaly and Ergudenler (1994a and 1994b) used heat-treatment of mixtures of straw-ash and bed material to determine their agglomeration characteristics. The agglomeration temperatures determined corresponded very well with experience from lab-scale fluidised-bed gasification of straw. Padban et al. (1996) used heat treatment of low temperature ash (550°C) and silica sand to study agglomeration of biomass ashes with SEM. Moilanen et al. (1996) used heat treatment of low temperature ash to investigate the agglomerating propensity of a large number of Finnish and Italian biomass fuels. These kind of tests can be used to obtain a first indication and comparison of the agglomerating propensity of mixtures of bed material and ash, but do not give absolute initial agglomeration temperatures again due to the many other important factors besides ash chemistry.

Flow properties heat treated ash (relevant to loop seal)

Conn (1995) describes a method to evaluate the agglomerating propensity of ash from petroleum coke in CFBC, based on the “hot” angles of repose and internal friction. Ash from the j-valve of a CFBC was heat treated in a vertical stainless steel cylinder. When the desired temperature was reached the ash was allowed to flow from the cylinder through a small hole in the bottom. The repose and internal friction angles were then taken as an indication of the ease of flow of the ash in a real j-valve at the given temperature. These results were compared to results from the compression strength sintering method, electrical resistance method and SEM analysis of deposits from a full-scale CFBC to determine the mechanism of sintering. This allowed determination of the agglomeration mechanism for petroleum coke in CFBC.

3. REFERENCES OF ANNEX A

- Anthony, E.J., Iribarne, A.P., and Iribarne, J.V. A new mechanism for FBC agglomeration and fouling when firing 100% petroleum coke. *Fluidized bed combustion*, ASME, 1:523-533, 1995.
- Atakul, H. and Ekinçi, E. Agglomeration of Turkish lignites in fluidised-bed combustion. *Journal of the Institute of Energy (March)*:56-61, 1989.
- Basu, P. and Sarka, A. Agglomeration of coal ash in fluidized beds. *Fuel* 62(August): 924-926, 1983.
- Baxter, L.L. Ash deposition during biomass and coal combustion: a mechanistic approach. *Biomass and Bioenergy* 4(2):85-102, 1993.
- Baxter, L.L. Ash deposition and corrosion during biomass combustion. TNO-report. TNO-MEP-R96/307, 1996.
- Bining, A.S. Cereal straw ashes compositional analyses and their fusibility characteristics. The Combustion Institute Canadian Section Spring Technical Meeting. :40-43, 1988.
- Bitowft, B.K. and I.Bjerle, A generic study of the sintering aspects of biomass in a fluid bed gasifier. Proc. of 11th Annual Symposium on Energy from Biomass and Wastes, Orlando, 16 March 1987.
- Bobman, M.H., Hajicek, D.R., and Zobeck, B.J. A study of bed agglomeration resulting from the AFBC of low-rank coals. 8th International Conference on Fluidized Bed Combustion. Houston, Texas, DOE/METC-85/6021, 1985.
- Brekke, D.W. and Karner, F.R. Analysis and characterisation of atmospheric fluidized-bed-combustion agglomerates. DOE/FC/10120-T7, 1982.
- Brooker, D.D. and Oh, M.S. Iron sulfide deposition during coal gasification. *Fuel processing technology* 44:181-190, 1995.
- Brown, A. Phase composition of sintered masses formed in fluidized bed combustors. Studsvik Nuclear. Studsvik/NS-90/73, 1990.
- Bruno, G. et al. Correlation between potassium losses and mineral matter composition in catalytic coal steam gasification. *Fuel*(65): October 1986.
- Bryers, R.W. Fireside slagging, Fouling, and High-Temperature Corrosion of heat transfer surface due to impurities in steam-raising fuels. *Prog. Energy Combust. Sci.* 22:29-120, 1996.
- Campisi, A. A microcomputer-controlled AAS and electrothermal atomizer. State Electricity Commission of Victoria, Research and Development department, Report LO/88/003, 1988
- Coe, D.R. Successful experience with limestone and other sorbents for combustion of biomass in fluid bed power boilers. In: Proc. 1st biomass conference of the Americas, Vol 1 (Ed. D.L. Klass), pp. 382-392, National Renewable Energy Lab. Golden, CO (USA) (1993).
- Conn, R.E. Laboratory techniques for evaluating ash agglomeration potential in petroleum coke fired circulating fluidized bed combustors. *Fuel processing technology* 44:95-103, 1995.
- Delvinquer, V. Defluidization at high temperature in fluidized bed of sand by addition of calcium carbonate. *Fluidized Bed Combustion*. ASME. 2:801-806, 1995.
- Formella, K. et al. Interaction of mineral matter in coal and potassium during gasification. *Fuel*(65): October 1986.
- French, R.J., et al. The direct observation of alkali vapour species in biomass combustion and gasification. NREL: NREL/TP-430-5597, 1994.
- Ghaly, A.E. and Ergudenler, A. Agglomeration of silica sand in a fluidized bed gasifier operating on wheat straw. *Biomass and Bioenergy* 4(2):135-147, 1993a.
- Ghaly, A.E. and Ergudenler, A. Agglomeration of alumina sand in a fluidized bed straw gasifier at elevated temperatures. *Bioresource Technology* 43:259-268, 1993b.

- Ghaly, A.E., Ergudenler, A., and Laufer, E. Study of agglomeration characteristics of silica sand-straw ash mixtures using scanning electron microscopy and energy dispersive x-ray techniques. *Bioresource Technology* 48:127-134, 1994a.
- Ghaly, A.E., Ergudenler, A., and Laufer, E. Agglomeration characteristics of alumina sand-straw ash mixtures at elevated temperatures. *Biomass and Bioenergy* 5(6):467-480, 1994b.
- Grubor, B.D. et al. Biomass FBC combustion- bed agglomeration problems. *Fluidized Bed Combustion*. ASME. 1:515-522, 1995.
- Hald, P. Alkali metals at combustion and gasification -equilibrium calculations and gas phase measurings-. The Technical University of Denmark, Department of Chemical Engineering. PhD thesis, 1994.
- Huffman, G.P. et al. Investigation of the high-temperature behaviour of coal-ash in reducing and oxidising atmosphere. *Fuel*(60): July 1981.
- Khan, M.R. Apparatus for direct measurement of ash fusion and sintering behaviour at elevated temperatures and pressures. *Rev. Sci. Instrum.* 60(10):3304-3309, 1989.
- Kuhn, L. and H. Plogmann. Reaction of catalyst with mineral matter during coal gasification. *Fuel*(62): Februari 1983.
- Ligthart, F.S. Fate of sodium and potassium in fluidised-bed gasification and hot gas clean up. Delft University of Technology, Laboratory of Thermal Power Engineering: EV-report 1865, 1995
- Livingstone, W.R. Straw ash characteristics. Department of Energy: DE92-519748, 1991.
- Madsen, M. and E. Christensen. Combines gasification of coal and straw. In: Co-gasification of coal/biomass and coal/waste mixtures, APAS. Clean coal technology programme 1992-1994. European Comission.
- Mann, M.D., Swanson, M.L., and Yagla, S.L. Characterization of alkali and sulfur sorbents for pressurized fluidized-bed combustion. *Fluidized Bed Combustion*. ASME. 1:333-340, 1995.
- Mann, M.D., Galbreath, K.C., and Kalmanovitch, D.P. The role of ash chemistry and operating parameters on ash agglomeration and deposition in FBC systems. In proceedings of conference 'Inorganic transformations and ash deposition during combustion' :773-789, 1992
- Manzoori, A.R. Role of the inorganic matter in agglomeration and defluidization during the circulating fluid bed combustion of low-rank coals. PhD thesis, Department of Chemical Engineering, University of Adelaide, 1990.
- Manzoori, A.R. and Agarwal, P.K. The fate of organically bound inorganic elements and sodium chloride during fluidized bed combustion of high sodium, high sulphur low rank coals. *Fuel* 71(May):513-522, 1992.
- Manzoori, A.R. and Agarwal, P.K. The role of inorganic matter in coal in the formation of agglomerates in circulating fluid bed combustors. *Fuel* 72(7):1069-1075, 1993.
- Manzoori, A.R. and Agarwal, P.K. Agglomeration and defluidization under simulated circulating fluidized-bed combustion conditions. *Fuel* 73(4):563-568, 1994.
- Marinov, V., Marinov, S.P., Lazarov, L., and Stefanova, M. Ash agglomeration during fluidized bed gasification of high sulphur content lignites. *Fuel processing technology* 31:181-191, 1992.
- Mason, D.M. and Patel, J.G. Chemistry of ash agglomeration in the U-GAS process. *Fuel processing technology* 3:181-206, 1980.
- McLaughlin, J. The removal of alkali salt vapours from hot coal-derived gases. Guildford (UK): University of Surrey, Dep. of Chemical and Process Engineering. PhD thesis, 1990.
- Miles, T.R., et al. Alkali deposits found in biomass power plants: A preliminary investigation of their extent and nature. NREL: NREL/TP-433-8142, 1996.
- Miles, T.R., Bryers, R.W., Baxter, L.L., Jenkins, B.M., and Oden, L.L. Alkalies in alternative biofuels. *FACT* 18:211-220, 1994.
- Misra, M.K., Ragland, K.W., and Baker, A.J. Wood ash composition as function of furnace temperature. *Biomass and Bioenergy* 4(2):103-116, 1993.
- Moilanen A., The effect of temperature, chemical composition and gas atmosphere on sintering of peat fly ash. *Proc. Int. Coal Science*. Tokyo, Japan, 1: 397-400, 1989.

- Moilanen, A. The effect of ash viscosity on the sintering of peat fly ash, *J. Inst. of Energy*, 64: 21-25, 1991.
- Moilanen, A. Studies of peat properties for fluidized-bed gasification. Espoo:Technical Research Centre of Finland. VTT publications 149, 1993.
- Moilanen, A., Nieminen, M., Sipila, K., and Kurkela, E. Ash behaviour in thermal fluidised-bed conversion processes of woody and herbaceous biomass. 9th European Bioenergy Conference & 1st European Energy from BiomassTechnology exhibition. Copenhagen, 1996.
- Moseley, J.L. and O'Brien, T.J. A model for agglomeration in a fluidized bed. *Chemical engineering Science* 48(17):3043-3050, 1993.
- Muthukrishnan, M. Salient features and operating experience with world's first rice straw fired fluidised bed boiler in a 10 MW power plant. *Fluidized Bed Combustion*. ASME. 1:609-614, 1995.
- Nordin, A. et al. Agglomeration and defluidization in FBC of biomass fuels- mechanisms and measures for prevention. *Proc. of Conf. on 'Applications of Advanced Technology to Ash-related Problems in Boilers*. Baxter, L. and DeSollar, R., 1996.
- Oakey, J.E., Minchener, A.J., and Stringer, J. Ash deposition in atmospheric-pressure fluidised-bed combustion systems. *Journal of the Institute of Energy (March)*:208-219, 1990.
- Olanders, B. and Steenari, B.M. Characterisation of ashes from wood and straw. *Biomass and Bioenergy* 8(2), 1995.
- Osman, E.A. A study of the effects of ash chemical composition and additives on fusion temperature in relation to slag formation during gasification of biomass. PhD thesis, University of California, 1982.
- Ots, A., Skrifvars, B.J., Hupa, M., and Parve, T. Sintering and fouling characterization of ashes with high calcium oxide content. *Fluidized Bed Combustion*. ASME. 2:1393-1405, 1995.
- Overend R. P. Thermochemistry: the key to minerals separation from biomass for fuel use in high performance systems. In: *VTT Symposium 164: Power production from biomass II with special emphasis on gasification and pyrolysis R and DD* (Eds. K. Sipilae and M. Korhonen), pp. 197-214, VTT Energy, Espoo (Finland) (1996).
- Padban, N., Ye, Z., and Bjerle, I. Alkali removal and bed material agglomeration studies applied to biomass gasification. *Development in Thermochemical Biomass Conversion*. Banoff, Canada, 1996.
- Padban, N., Kiuru, S., and Hallgren, A.L. Bed material agglomeration in PFB biomass gasification. *American Chemical Society, Division of Fuel Chemistry*, 40 (3), pp 743-747, 1995.
- Paisley, M.A. and R.D. Litt. Evaluation of energy plantation crops in a high-throughput indirectly heated biomass gasifier. *Battelle*, 1993
- Salour, D., Jenkins, B.M., Vafaei, M., and Kayhanian, M. Control of in-bed agglomeration by fuel blending in a pilot scale straw and wood fueled AFBC. *Biomass and Bioenergy* 4(2):117-133, 1993.
- Scandrett, L.A. and R. Clift. The thermodynamics of alkali removal from coal-derived gases. *J. Inst. Energy*. Vol. 1, No. 433, pp. 391-397, 1984.
- Skrifvars, B.J., Hupa, M., and Moilanen, A. Measuring the sintering tendency of ash by a laboratory method. *Journal of the Institute of Energy (September)*:131-137, 1989.
- Skrifvars, B.J., Hupa, M., and Hiltunen, M. Sintering of ash during fluidized bed combustion. In proceedings of conference 'Inorganic transformations and ash deposition during combustion' 1992
- Skrifvars, B.J. and Hupa, M. Sintering of ash during combustion and gasification. *Liekki progress report*. 2:531-565, 1992a.
- Skrifvars, B.J., Hupa, M., and Hiltunen, M. Sintering of ash during fluidized bed combustion. *Ind. Eng. Chem. Res.* 31:1026-1030, 1992b.
- Skrifvars, B.J, M. Hupa, R. Backman and M. Hiltunen: Sintering mechanisms of FBC ashes. *Fuel* 73 (2) 171-176 (1994).

- Skrifvars, B.J., Sintering tendency of different fuel ashes in combustion and gasification conditions, PhD Thesis, Abo Akademi, Department of Chemical Engineering, 1994
- Skrifvars, B.J., Hupa, M., Moilanen, A., and Lundqvist, R. Characterization of biomass ashes. Applications of Advanced Technology to Ash-related Problems in Boilers. Baxter, L. and DeSollar, R. pp. 383-398, 1996.
- Steenari, B.M. A practical and theoretical study of sintering of coal ash and limestone in a fluidized bed combustor. Staten Energiverk. FBT-87/34, 1987.
- Uberoi, M. et al. The kinetics and mechanism of alkali removal from flue gases by solid sorbents. Progress in Energy Combustion Science. Vol. 1, pp. 205-211, 1990.
- Vassilev, S.V., Kitano, K., Takeda, S., and Tsurue, T. Influence of mineral and chemical composition of coal ashes on their fusibility. Fuel processing technology 45:27-51, 1995.
- Wall, T.F., Creelman, R.A., Gupta, S., Coin, C., and Lowe, A. Coal ash fusion temperatures- New characterisation techniques and associations with phase equilibria. Applications of Advanced Technology to Ash-Related Problems in Boilers. Baxter, L. and DeSollar, R. :541-556, 1996.
- Williamson, J., West, S.S., and Laughlin, M.K. The behaviour of bed material during fluidized bed gasification: The effects of mineral matter interactions. Fuel 73(7):1039-1045, 1994.

ANNEX B. OVERVIEW OF PREDICTION METHODS REPORTED IN LITERATURE

Method	Method description	Predictability	Remarks	References (chapter 6)
<i>fuel analysis</i>				
ASTM D1857, standard ash fusion test	Four characteristic temperatures are identified from an ash cone according to a standardised description (visual observation of the ash cone during heating in an oven). The characteristic temperatures are: initial deformation temperature IDT, softening temperature ST, hemispherical temperature HT, fluid temperature FT.	Predictability is very low. It predicts too high agglomeration temperatures and the predicted trends are false as well. Skrifvars: ASTM failed in all cases to predict the bed agglomeration temperature.		[17,18] and this report
Chemical fractionation	Increasingly aggressive solvents leach the same sample in a series of three sequential leachings, producing four samples (incl. raw material) for characterisation.	NREL: laboratory to laboratory variations can be large. Skrifvars: predictability is moderate.		[19,20]
<i>static procedures</i>				
Empirical correlation between standard fusion temperatures and chemical ash composition	Phase diagrams and thermodynamical calculations (eutectic melting points) are used to predict the deformation and fusion temperatures of biomass ash. Skrifvars: thermodynamically calculated temperature at which 15% of the ashes is melted ($T_{\text{melt } 15\%}$) is a measure for the sintering temperature.	It is still hard to predict the agglomeration temperature with a thermodynamical model. However, models and programs are improving fast. Even with a simple model the predicted temperatures are not worse than a laboratory experiment. Skrifvars: good correlation of T_{sint} with $T_{\text{melt } 15\%}$ for 6 of 10 ashes. Nordin: a complete non-ideal data-set was not available but the general results, as well as the trends obtained agree well with the experimental results obtained (compression strength sintering test and lab-scale FBC).	ash-mixtures are very complex and hard to model (esp. silica), unknown which part of the ash has to be melted before agglomeration is a fact, kinetic parameters are not considered but probably relevant	[21,22,23,24,20,25, 26,27,28,29,30,31,32] and this report
DTA/TGA: differential thermal analysis/ thermogravimetric analysis	The heat effects (endothermic or exothermic processes) in the ash sample and the weight loss of the sample are measured simultaneously. Detectable processes are melting processes, decomposition processes and chemical reactions.	The DTA measurements do not clearly support the melt formation which is measured with the compression strength based sintering test and/or thermodynamically calculated.	Can be used to reveal the mechanism behind sintering	[33,34,35,36,37,38] and this report
Dilatometric shrinkage test	The change in length of a pulverised ash sample is measured during heating. Shrinkage indicates sintering.	Öhman: The shrinkage method is superior to the ash fusion tests, but should be supplemented with continuous measurements of the conductance.	Gluckman relates sintering to ration of velocity and minimum fluidisation velocity	[18,39,40,41,42]
Thermal- and electrical conductance test	The thermal or electrical conductance of an ash sample is measured. As the cross sectional area of sinter bonds between the particles grows, the conductance path is increased.	unknown	Satisfactory contact between ash and electrodes is essential but hard to achieve.	[18]
Electrical conductance test and shrinkage test	Simultaneous measurements	unknown	Good contact between ash and electrodes is essential but hard to achieve. This method is in the literature used for coal ashes only.	[18,43,44,45,46]
Compression strength based sintering test	The ash sample is crushed and pelletised to a cylindrical pellet and heated in a controlled gas atmosphere. After cooling, the pellets are crushed in standard compression-testing equipment, and the compression strength is taken as measure of the degree of sintering.	This test is good for predicting bed agglomeration trends except for cases at which interaction between the bed material and the ash takes place. Skrifvars investigated 10 biomass-ashes: for 5 the result correlated with fluidized bed tests.	Very useful in revealing the mechanism behind agglomeration	[33,17,18,25] and this report

Method	Method description	Predictability	Remarks	References (chapter 6)
<i>static procedures (cont.)</i>				
Heat treatment and subsequent SEM analysis.	Mixtures of ash and bed material are heated in an oven for a certain period. The heat-treated samples are chemical analysed (X-ray fluorescence spectroscopy, atomic adsorption spectro-photometry, ion chromatography) and the particle surfaces are analysed by the SEM.	Not used to predict agglomeration temperatures.	Used to reveal the mechanism behind sintering/agglomeration.	[47] and this report
Flow properties heat treated ash	Ash is heat treated in a vertical stainless steel cylinder. When the desired temperature is reached the ash is allowed to flow from the cylinder through a small hole in the bottom. The repose and internal friction angles are then taken as an indication of the ease of flow of ash in a L-valve of a CFBC.	No temperature is predicted and the predictability of this method is not very promising.	In combination with other methods this method contributes to the determination of the agglomeration mechanism of petroleum coke.	[45]
Viscosity measurements	A critical viscosity is required for adhesion of ash particles, this fact can be used to predict an agglomeration temperature. At high temperatures viscosity measurements are mostly carried out using a rotating crucible viscometer. Viscosity of less fluid slags can be measured by a rod penetration viscometer.	No prediction of the agglomeration temperature is mentioned.	This method is in the literature used for coal ashes only.	[18]
<i>dynamic procedures</i>				
Bubbling Fluidized Bed Combustion Facility: BFBC (at ETC)	Combust a certain amount of fuel at fixed temperature ("ashing temperature") and subsequently stop the biomass fuel feeding and raise the bed temperature externally (by supplying propane flue gas with the same oxygen concentration as the biomass flue gas) with 2-3°C/min until agglomeration occurs (sudden drop in pressure and a sudden change in temperature). The particle temperature (both sand and biomass/char) is measured using a FTIR pyrometer of which the probe is mounted in the bubbling bed.	Method includes interaction between bed material and ash. Skrifvars: It is expected to give accurate predictions of possible bed agglomeration but no full-scale tests are carried out.	Particle temperatures can be 100° higher in temperature than the bed during combustion.	[17,9,48,25,18,49]
Bubbling Fluidized Bed Gasification Facility: WOB (at ECN)	The biomass material is converted by air-blown gasification at 750° during 4 hours while feeding the material with about 1 kg/h. Subsequently the temperature of the bed is raised stepwise (by adjusting the electrical heating of the gasification vessel) with 25° every 30 minutes until agglomeration occurs. Both the fuel feeding rate and airflow remain unchanged. The 4 hours of stationary operation makes up the biggest part of the total duration of the experiment. This ensures a certain ash accumulation in the system, which is independent of the agglomeration behaviour of the fuel tested.	Method includes interaction between bed material and ash. Fuel supply until agglomeration ensures constant presence of volatile components (like alkali's). Gasification generally leads to better temperature homogeneity (lower peak temperatures).		this report
Bubbling Fluidized Bed Combustion Facility: BFBC (at VTT)	At a fixed temperature, a fixed amount of fuel (50 gram) is combusted in the bed containing 65 gram of bed material. After the fuel batch is fed, the reactor is emptied and a new experiment starts at a higher temperature (steps of 25°C) until signs of ash sintering are observed.			this report

ANNEX C. PUBLICATIONS, CONFERENCE PRESENTATIONS AND PATENTS

Publication:

F. S. Ligthart, A. van der Drift and A. Olsen, Bed-agglomeration in fluidised bed conversion of biomass, Proc. 10th European conference and technology exhibition: Biomass for energy and industry, Würzburg (Germany), 8-11 June 1998 (Eds. H. Kopetz et al.), pp. 1765-1768.

Conference presentation:

A. van der Drift and A. Olsen, Prediction and solution methods for ash agglomeration and related problems during biomass conversion, submitted for presentation at 1st World Conference and Technology Exhibition, 5-9 June 2000 in Sevilla, Spain (submitted).

Patent:

none.