

**OPERATIONAL PROBLEMS,
TRACE EMISSIONS AND BY-PRODUCT MANAGEMENT
FOR INDUSTRIAL BIOMASS CO-COMBUSTION**

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on behalf of



Executive Summary

Based on the work of the different partners, the project provides a comparison of different biomass co-utilization concepts with regard to fouling, slagging, corrosion, ash utilization and trace emissions. In detail the project incorporated biofuels like wood, wood pulp, bark, straw, wood matter from pressed olive stones and sewage sludge.

The major operational problems like slagging, fouling and corrosion were investigated in both PF and FB units of various scales. Further on, emphasis was put on the subsequent emissions and their minimization of the problematic species of HCl and of the trace organic compounds like dioxins and furans, PCBs and VOCs. The detailed laboratory scale studies of biomass/coal co-combustion were used to validate mathematical modelling techniques. Finally the effect of co-combustion on the by-product management - handling, utilization and disposal have been evaluated and compared with a pure coal or pure biomass combustion system, respectively.

As a further approach to avoid the above problems of co-utilization the pretreatment of biomass to remove the undesired components before combustion has been investigated by washing, pyrolysis or gasification prior to combustion. The potential of utilization the gaseous product from pyrolysis or gasification as reburn fuel for NO reduction was evaluated.

As the final result of the project the phenomenical and fuel dependent restrictions of co-combustion have been determined and solutions for the prevention of operational problems and the reduction of hazardous effects on the environment are provided in order to propose the best suitable and most economical technique.



Objectives of the Project

In comparison to other renewable energy sources, thermal utilization of biomass or waste is a cheap and technically feasible option to contribute to reducing the net CO₂-emissions. Co-combustion of biomass or wastes together with coal in existing large-scale firing systems offers several advantages, e.g. the possibility to utilize a large quantity of biomass or lower investment costs compared with systems exclusively fired with biomass. Utilization of biomass or wastes, however, may have consequences on combustion behaviour, emissions, corrosion, and residual matter.

Based on the experience of the APAS programme, the objective of this project was to concentrate the research effort on the problem areas like slagging, fouling, corrosion, ash utilization and trace emissions for different co-combustion systems and carefully investigate technical options to avoid these negative effects. The solution of these technical problems is essential for a technically and economically feasible and environmentally advantageous co-combustion and will promote a widespread utilization of existing biomass resources.

Based on the work of the different partners, the final goal was to compare the different methods of co-combustion (PF, FB, pretreatment) with regard to technical, economical and environmental issues.

The objectives of the project have been in detail:

- to find out the optimum co-combustion technique with regard to operation, by-product management and trace emissions
- to point out measures for eliminating operational problems and reducing environmental impacts or to show the restrictions of co-combustion in dependence on the biomass fuel



- to promote utilization of by-products from co-combustion
- to evaluate the effect of co-combustion on trace emissions
- to demonstrate the technical and economical feasibility of biomass co-combustion
- to techno-economically compare direct co-combustion and pretreatment by pyrolysis and gasification

Scientific and Technical Description of the Project

4.1 Work Programme

Coordination: "Operational problems, trace emissions and by-product management for industrial biomass co-combustion"		
Direct Co-combustion		Pyrolysis/gasification as pretreatment
slagging and fouling in dry and molten ash PF (IVD)	toxic organic compounds (CRE, Leeds, ICSTM Ch.E.) operation behaviour in a 43 MW CFBC (CRE)	entrained flow pyrolysis and reburning (IVD)
mineral ash transformation (ICSTM, M.E.)	operation slagging, fouling, corrosion, 30 MW CFBC + 100 MW BFBC (VAB)	pyrolysis, char wash + combustion, techn / economic study (Elsam / DTU)
fuel preparation, operation, slagging, fouling (SEAB)	corrosion in ash cooler (Elsam / LLB)	FB gasification, gas cleaning, reburning, bench + pilot scale (TPS)
modelling ash behaviour (AA)	sintering (DTU)	
ash utilization (Cerchar/mpa)	slagging and fouling (NTUA)	
corrosion (SMAB)	volatile release (TPS)	
technical / economical assessment studies (UU, IVD, all)		

Figure 1 *Technical overview and task structure*

Within this project different biomass co-utilization concepts are compared with regard to fouling, slagging, corrosion, ash utilization, and trace emissions. Figure 1 gives a technical overview on the tasks of the involved partners.

4.1.1 Direct Co-Combustion

The cheapest possibility is direct co-combustion, using coal and biomass as a feedstock and burning it together in a coal-fired boiler. The effects of co-combustion of different kinds of biomass, especially complicated fuels like straw, on slagging, fouling, and corrosion have been considered carefully. Also the effects of co-utilization on the ash have been evaluated and compared to a pure coal or biomass combustion system.

Besides coal and oil, wood, wood pulp, bark, straw, wood matter from pressed olive stones and sewage sludge were used as feedstock materials.

The combustion concepts under consideration were:

- pulverized fuel combustion



- fluidized bed combustion (bubbling, circulating)
- slagging combustor

Pulverized Fuel Combustion

The work of IVD, Imperial College and Stockholm Energi focussed on the co-utilization of biomass in pulverized fuel systems. IVD extended its experience of co-combustion at a 0.5 MW pulverized fuel facility to a high temperature slagging combustor. The dry and molten ash combustion systems have been compared with regard to fouling, slagging, corrosion and ash utilization. The Imperial College of Science, Technology and Medicine (ICSTM), Department of Mechanical Engineering investigated the transformation of inorganic constituents to evaluate operational problems if part of the total fossil fuel is substituted by biomass or sewage sludge. The work of Stockholm Energi concentrated on the optimization of a co-combustion process using biomass and oil in a converted coal fired pf boiler with special emphasis on fuel handling, fuel preparation, operational behaviour, slagging, fouling and emissions. Stockholm Energi AB was officially not a partner of the project. They joined the project in 1996 to contribute with their experience and results to the research work of the project.

CFB-Combustion

The aim of CRE, Imperial College and Leeds University was to optimize operational and environmental impacts of co-firing coal and biomass in FBC systems. The programme includes elements of laboratory-scale studies in conjunction with mathematical modelling techniques, and studies of the impact of biomass addition on the operability and pollutant emission profile of a 43 MWth CFBC. Of particular concern was the effect on the atmosphere of emissions of HCl and trace organic species such as dioxins and furans, PCB's and VOC's. A detailed assessment of the operational and environmental constraints on the performance of the boiler has also been undertaken.

Based on the experience of corrosion measurements in a 80 MWth coal/straw fired CFB boiler, Elsamprojekt and LLB Lurgi Lentjes Energietechnik GmbH were looking for possibilities to reduce the corrosion in an ash cooler. A test box has been constructed and tested in a bypass flue gas stream at the Grenaa CFB boiler. The project part of TU Denmark concentrated on the sintering in the bed of a biofuel co-fired FB boiler. The National Technical University of Athens (NTUA) has determined necessary measures in order to reduce operational problems for the co-combustion of straw and pressed olive stones together with brown coal.

Because of the higher volatile content of biomass compared to coal, a uniform distribution of the fuel is important for FB combustion. In order to avoid operational problems, TPS investigated methods to optimize the volatile release distribution by changing the bed circulation pattern or by location of fuel inlets.

Within this project Vattenfall investigated operational problems at two combined heat and power (CHP) plants, a 35 MWth Circulating Fluidized Bed (CFB) at Nässjö and a 100 MWth Bubbling Fluidized Bed (BFB) at Nyköping. The BFB plant in Nyköping had severe deposit problems on the superheaters and enrichment of unwanted species in the deposits, which led to corrosion in the [mm] scale. The scale of the fouling problems in Nyköping resulted in the focus of the project being directed towards this plant. The investigations of slagging and fouling, material corrosion and ash quality at this plant have been done in cooperation with Åbo Akademi University and Studsvik Material AB. Fuel and ash from the plants have been used by other partners for further chemical analyses.



Studsвик Material and Åbo Akademi University have also provided support to other partners with regard to corrosion and slagging. The by-products from co-combustion in the combustion systems of the partners have been analysed by mpa and Cerchar in order to determine the possibility of utilization.

4.1.2 Washing/Pyrolysis/Gasification of Biomass as Pretreatment

A further approach to avoid the above mentioned problems of co-utilization is to pretreat the biomass in order to remove the undesired components before the combustion process. One way to do this could be a pyrolysis/gasification process and the utilization of produced gas in a different boiler. By removing alkali and chlorine from the gas from pyrolysis and gasification no impact on corrosion and slagging/fouling is to be expected in the boiler. Additionally, the gas can be used as reburn fuel for NO_x reduction. If the yield of the remaining char is too high, a treatment and combustion of the ash has to be taken into account.

By keeping the ashes separated in the gasification/reburning process, there is no change in the coal ash property. The biomass ash from the gasifier can be utilized as fertilizer on farmland or in forest.

The partners who were involved in this task are TPS, Elsamprojekt, TU Denmark, NTUA and IVD. TPS concentrated on the gasification in an FB reactor, on gas cleaning and the use of the LCV gas as reburn fuel. The tests were done in bench and semi-industrial scale. IVD University of Stuttgart carried out pyrolysis tests of straw and determined the reburn efficiency of the pyrolysis gas. Elsamprojekt together with TU Denmark investigated the pyrolysis of straw and the char combustion. As a further possibility to pretreat biomass washing was studied by Elsamprojekt, TU Denmark and NTUA.

4.1.3 Techno Economic Assessment Studies

The University of Ulster carried out technical, environmental and economical assessment studies of the different biomass co-combustion concepts which have been investigated by the partners of the project.

4.2 Results on Slagging

4.2.1 General

Ash related problems such as slagging and fouling in different kinds of combustion boilers, continue to be the most usual single reasons for unscheduled shut downs of the boiler. They decrease the boiler efficiency, plug the flue gas channel, damage the boiler and may lead to corrosion and erosion problems. The formation of fly ash particles and its deposition is a very complex mechanism in a boiler, which is shown in Figure 1.

Deposition of ash can occur on all heat exchangers - both water walls and convective path - within a boiler. Whereas slagging is normally restricted to the furnace, fouling (loosely bonded deposits) is observed in the convective heat exchangers. For fluidized bed combustion, additionally sintering can occur in the bed, resulting in a loss of fluidization.



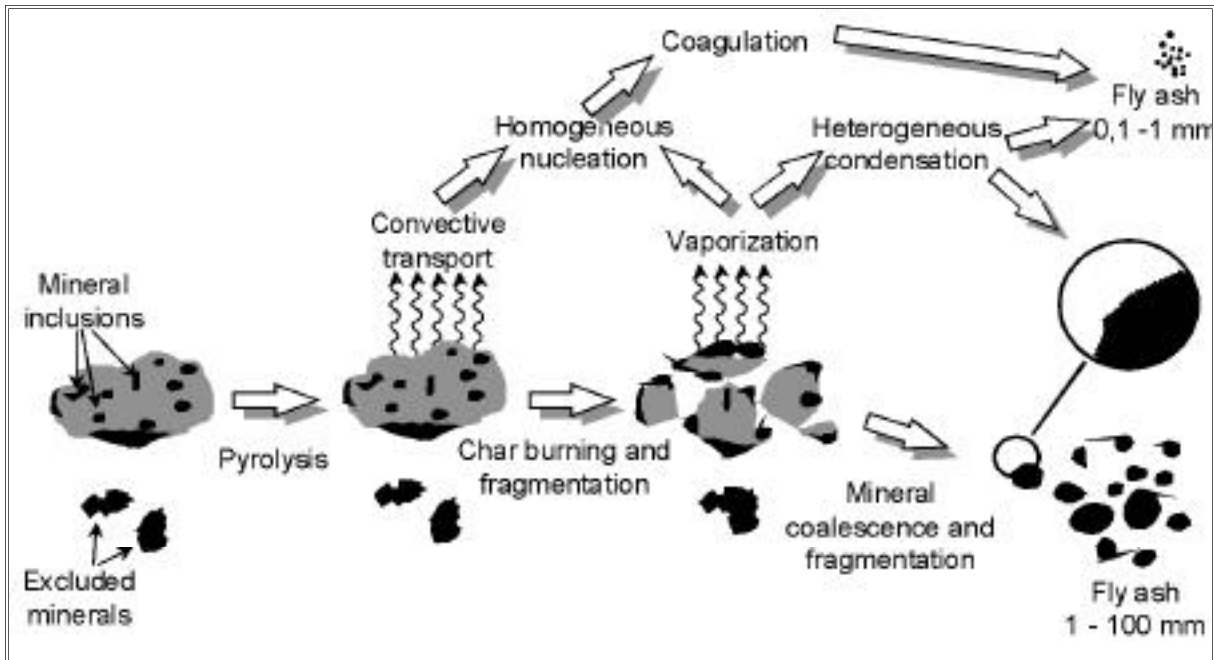


Figure 1 *Formation of fly ash from coal*

Ash related problems are dependent on the firing system and the fuel. Biofuels are known as difficult fuels, because they contain ash forming elements like alkalis, which produce low melting deposits and may cause corrosion.

4.2.2 Fluidized Bed

Fluidized bed combustion is considered as an option for power generation from bio-mass due to a comparably low effort of biofuel treatment. However, biomass ash normally has a high alkali content, which can form compounds with low melting temperature during combustion or gasification. The low melting ash constituents can induce in-bed-agglomeration, in addition to fouling and corrosion problems. The agglomerates are composed of sand and ash particles bound by fused, glassy materials. Accumulation and sintering of these agglomerates can lead to loss of fluidization (defluidization) and shutdown of the plant. In order to overcome the problems, a better understanding of the mechanisms is of importance.

The aim of DTU in this project was to investigate the agglomeration phenomena in a laboratory fluidized bed combustor to burn one of the most troublesome biofuel -straw- and to co-fire straw with coal. Development of agglomerates was monitored by the pressure drop over the bed and the axial temperature profile inside the bed. The change of pressure drop and temperature profile are shown in Figure 4. At initial stage of combustion little agglomerates are formed, thus the average value of the pressure drop remains constant and the bed temperature is uniform. When a significant amount of agglomerates are formed, the pressure drop starts to decline and a temperature gradient appears at the bottom part of the bed. The pressure drop decreases continuously and the bed is defluidized eventually. The defluidization is indicated by a sudden decrease of the pressure drop over the bed to a low level, as illustrated in Figure 4. The decline of the pressure drop before defluidization indicates a segregation of large agglomerates in the bottom of the bed.



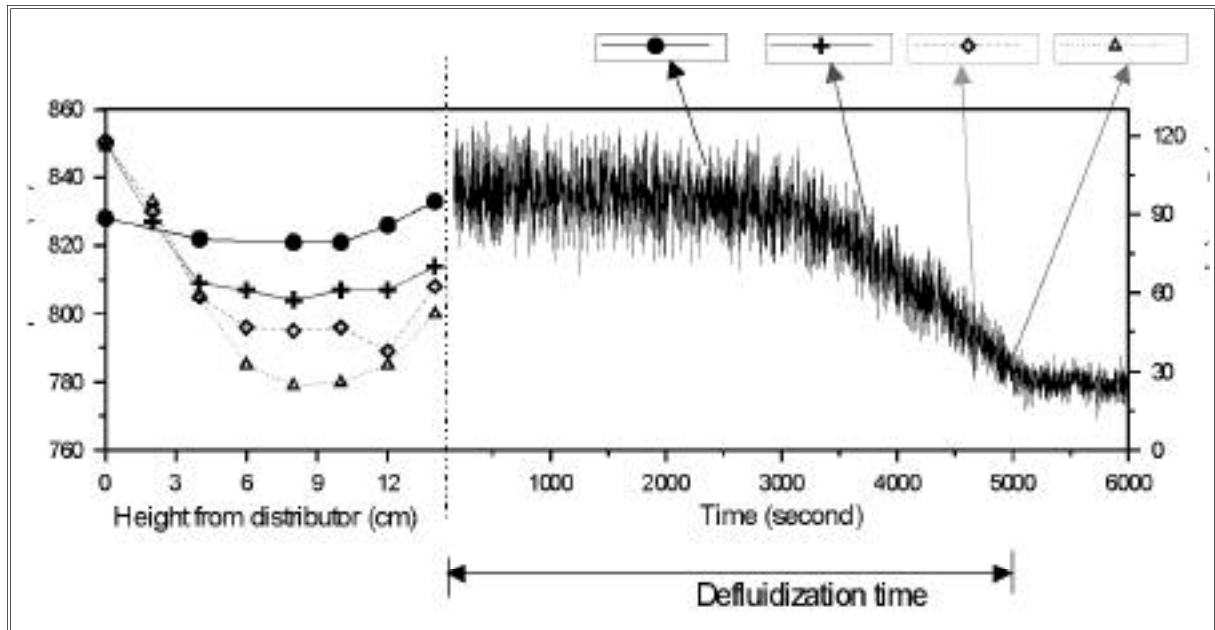


Figure 2 *Temperature and pressure drop profile*

The results show that temperature has the most pronounced effect on the agglomeration tendency. As bed temperature increases, the defluidization time decreases sharply, which indicates an increasing tendency of agglomeration. It is most probable that agglomerates are initiated from burning char particles. This may be the dominant way for the potassium constituents in the ash to be transferred to the sand surfaces, forming a coating layer.

By using various experimental techniques, it is revealed that the potassium in straw experiences transformation from organic and inorganic forms to low melting point K_2O-SiO_2 -compounds during combustion. Within the typical FBC temperature range of 720 - 920°C, most of the potassium compounds tend to remain in the bed. The melting of K_2O-SiO_2 compounds is clearly identified as a coating layer on the sand surfaces by SEM/EDX analysis. The sticky layer causes the formation of agglomerates and eventually defluidization.

A simple model has been developed by DTU to describe the defluidization time as a function of parameters such as temperature, fluidization velocity and particle size. The agreement between model and experimental data is fairly good.



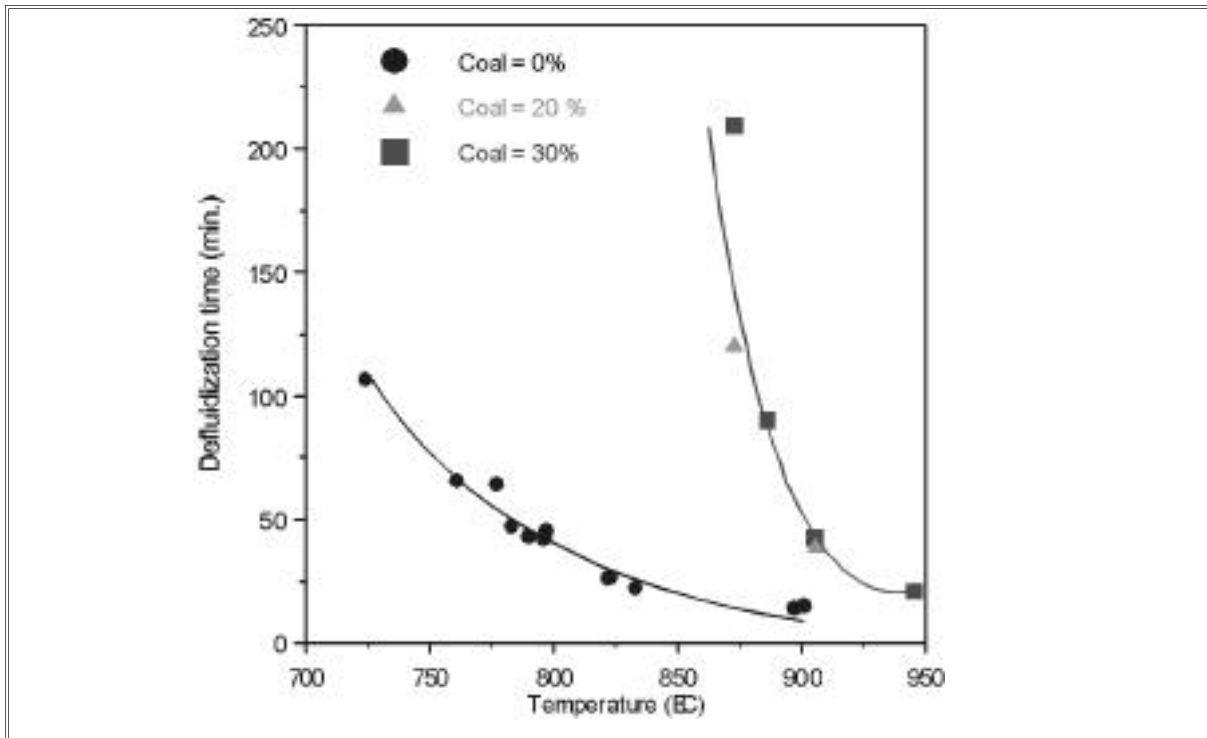


Figure 3 *Measured defluidization time*

Co-firing straw with coal can significantly extend the defluidization time, corresponding to a reduction of the agglomeration tendency. Both the coal ash and its sulphur content contribute to this. Combination of co-firing straw with coal and controlling the bed temperature properly may minimize the agglomeration problem in FBC effectively, see Figure 3. Similar conclusions were also drawn by research at NTUA. Furthermore, it was demonstrated that the performance of the leaching process on the raw biomass material – i.e. both for straw and pressed olive stones – improves considerably the ash behaviour at high temperatures.



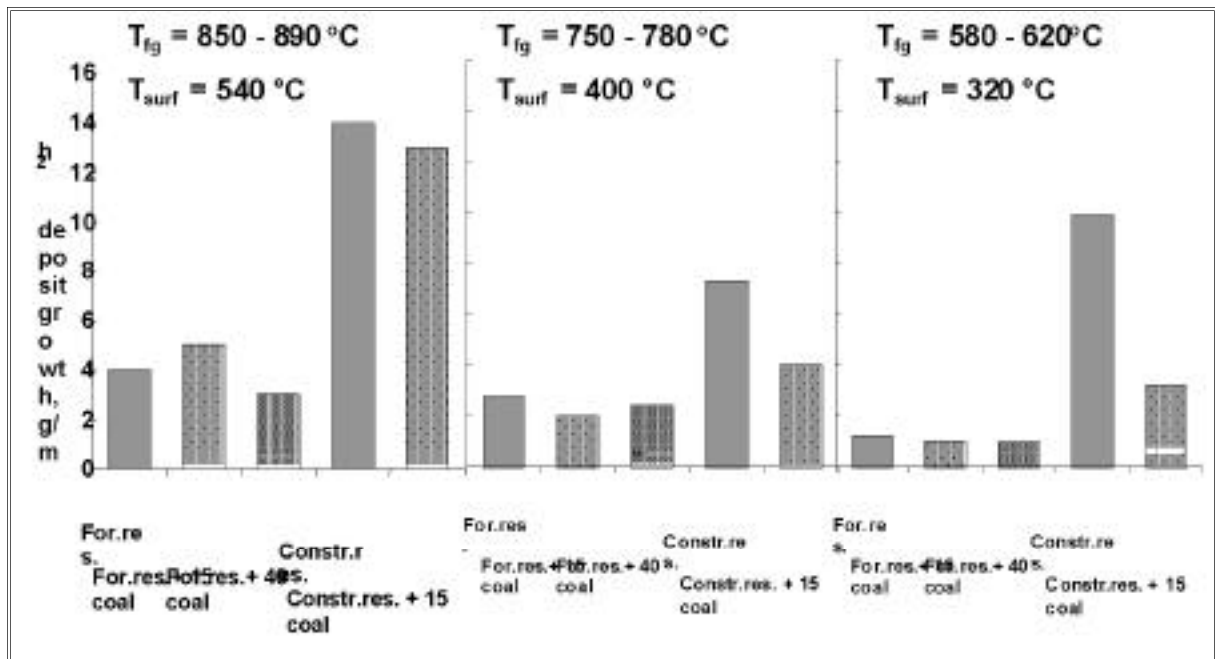


Figure 4 Deposition measurement at 100 MWth BFB

Figure 4 shows the deposition growth measured by Vattenfall and Åbo Akademi University (ÅA) at a 100 MWth Bubbling Fluidized Bed (BFB) at different locations and temperatures and with different fuels. Firing with a mixture of construction and packaging waste led to severe corrosion and fouling problems. The addition of coal reduces the deposition growth compared to firing with 100% biomass. Flue gas and deposit analyses showed that when co-firing with coal in the BFB boiler more HCl and SO₂ remained in the flue gas and less potassium and chlorides were found in the deposits. It is known from other applications that excess SO₂ in the flue gas may drive out or inhibit chlorine in the deposit. Compression strength tests carried out by ÅA indicated that the results allow to detect different sintering behaviour for various ashes. The measured ash sintering tendencies correlated also in many cases with known problematic behaviour of ashes in full scale combustion systems. Therefore the compression strength based sintering test is well suited for rating fuel ashes with respect to their potential problems they may cause in a boiler when the fuel is fired. The test is more accurate than the standard ash fusion tests since the compression strength test detects any process that affects particle-to-particle bondings in the ash.



In this project ÅA studied the ash chemistry and melting behaviour with the thermodynamic equilibrium analysis in two different ways. Firstly the sintering tendencies determined by compression strength test were compared with their calculated melting behaviour. The measured sintering temperatures show a reasonable agreement with the T10 temperature (10% melt in the slag).

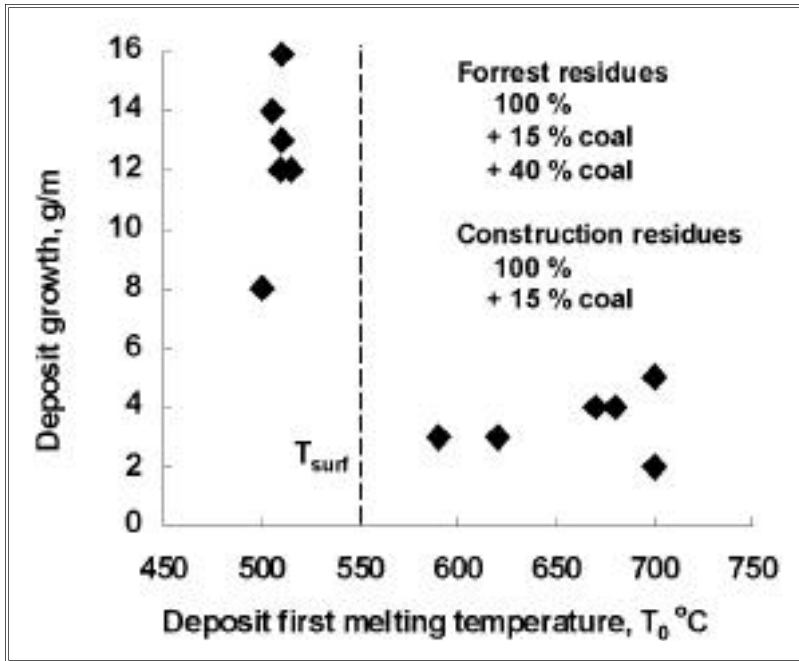


Figure 5 Correlation of deposit growth and melting temperature

Secondly the measured deposit growth rates in an BFB boiler were correlated with the calculated melting behaviour of a deposit. Figure 5 shows the correlation between measured deposition growth at the large scale boiler and the calculated first melting temperature. It can be seen that the deposition growth is clearly higher, when the first melting temperature is below the deposit probe surface temperature. The melting of the ash was most likely the dominating deposit forming mechanisms in the hottest measurement location of the FBC boiler. That implies that melting behaviour calculations may well be used for defining stickiness criteria for ash particles to form deposits but also other deposit formation mechanisms should be used.

4.2.3 Pulverized Fuel

The slagging and fouling in pulverized fuel firing systems was studied by IVD, University of Stuttgart at two different pilot scale test facilities. Besides testing co-combustion of straw in a dry ash removal PF combustor, which represents the commonly used coal combustion system nowadays, additionally, pure biomass combustion and co-combustion was investigated in a 0,3 MW slag tap furnace. In some European countries i.e. Germany slag tap furnaces had been the most common firing system in the sixties and are still operated today.

Although biomass ash is known to form low melting slags, the slag, which formed in the slag tap furnace at 100% straw combustion had such a high viscosity at 1500°C furnace temperature that it did not flow down the walls.



Due to the high temperature potassium is vaporized, and its loss results in a shift of slag viscosity, which is mainly composed of SiO_2 with minor Al_2O_3 and CaO . The potassium condenses in the flue gas path on cooled tubes, forming KCl and K_2SO_4 .

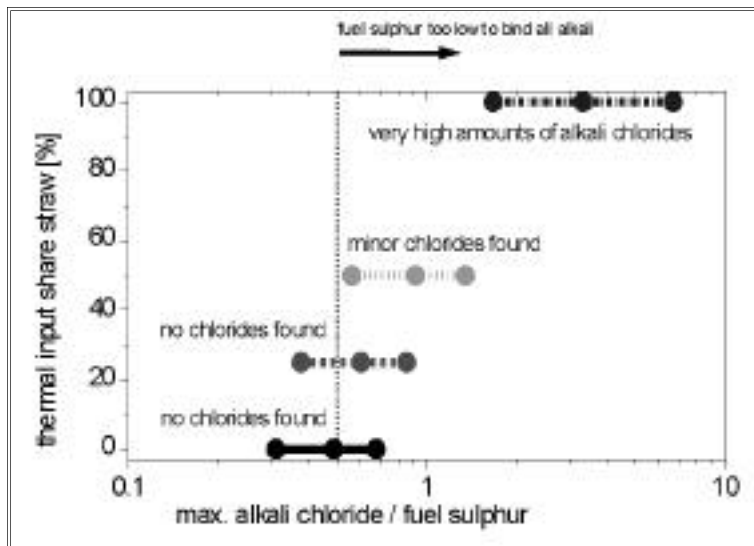


Figure 6 Impact of alkali/sulphur ratio

For co-combustion of straw together with coal, the furnace was operated with continuous slag flow and slag discharge. In co-combustion with coal potassium was mainly found in sulphates and aluminium silicates. Depositions contain less or no alkali chlorides. The alkali chloride formation is most probably related to the ratio of the chlorine, which can form alkali chlorides, to sulphur. If the available sulphur is too low, potassium chloride is formed, see Figure 6.

As a conclusion, the vaporization of potassium will increase the melting temperature of the remaining ash. This is of disadvantage for wet bottom firing systems, as demonstrated in the investigations of IVD especially for pure biomass combustion, however, it is of advantage for PF firing system with dry ash removal and will reduce the risk of slagging.

On the other side vaporized components may condense in the connective heat exchanger, causing fouling and corrosion. The high temperatures in PF combustion systems (in contrast to FB systems) and the sulphur dioxide in the flue gas (from coal) promote interactions of vaporized components with sulphur and the fly ash. Therefore potassium silicates and potassium sulfates are expected to dominate rather than potassium chloride. Although sulphates also cause fouling, they are considered to be better than chlorides.

Imperial College, Department of Mechanical Engineering developed a mathematical model, based on computer controlled scanning electron microscopy (CCSEM) and Computational Fluid Dynamics modelling techniques, which is capable of predicting the slagging performance of pulverized sewage sludge flames compared with those of sewage-coal co-utilization. The validation of the model has been provided for in a parallel experimental regime undertaken in the 150 kW laboratory scale furnace.



4.2.4 Conclusions Regarding to Slagging

- The alkali content of biofuels may cause severe sintering, slagging and fouling problems. The occurrence and behaviour of alkalis is dependent on the firing system and the fuel. In case of high alkali to sulphur ratios, alkali chlorides are formed, which may cause severe fouling and corrosion. If sufficient sulphur is available, alkali chlorides are avoided.
- In comparison to pure biomass combustion, the addition of coal considerably reduces operational problems
- In deposits from PC fired units alkali chlorides are missing compared to results from the FB plants where alkali sulfates and chlorides were found. This effect comes from that the chlorine most likely leaves the boiler in a PC fired system with the flue gases as HCl most likely due to the fact that most alkali is tied up with the silicates and therefore is not available for the chlorine. This is again most likely due to the higher temperature in the PC furnace compared to the FBC.
- Under FB conditions, due to the insitu desulphurization sulphur dioxide is not available in the flue gas, thus resulting in the formation of potassium chloride, which may cause fouling and corrosion even for fuels with low chlorine content.
- The higher temperatures under PF conditions and the available sulphur dioxide in the flue gas promote the formation of potassium silicates and sulphates, which are considered to cause less fouling problems.
- The vaporization of potassium under PF conditions increases the melting temperature in the remaining ash, which reduces slagging problems in pulverized fuel combustion with dry ash removal. In slagging combustion, the slag flow may be negatively affected.
- The testing procedures, which are available and commonly used today, are not able to consider fuel dependent problems. There is consequently a great need to develop prediction methods that could foresee potential ash related problems easily and cost effectively. Methods like lab scale fluidized bed sintering test, compression strength measurement, and thermodynamic multi component calculation have given encouraging results and have to be further developed.

4.3 Results on corrosion

4.3.1 General

High temperature corrosion is a problem often associated with combustion and co-combustion of biofuels. The problem is primarily related to one-year crops which have a relatively high content of chlorine, typically in the range of 0.1-1% of the fuel. Elder biomass types, such as wood, may cause problems as well - usually due to contamination from other sources (e.g. sea water, soil, paint rests, adhesives).

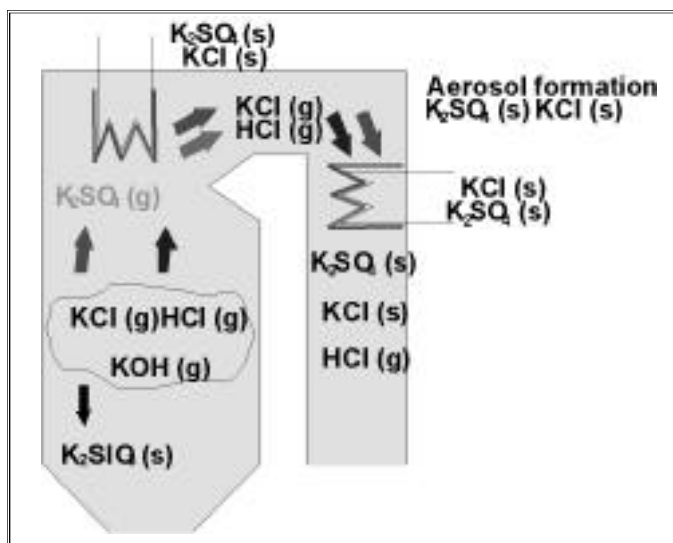


Figure 7 Behaviour of potassium and chlorine in a boiler



To reduce high temperature corrosion it is important to understand the mechanisms. In conventional power plants the usual corrosion mechanism is oxidation, which is a rather slow process giving corrosion rates in the order of 1-2 mm/100,000 hours. At higher metal temperatures (650-700°C), sulphate melts could be formed and the corrosion rate will increase substantially. Sulphate melt corrosion does not occur in well-designed conventional boiler, not even in ultra super critical boilers.

In a co-fired biomass boiler, KCl could be released and condensed on tube surfaces. Above a certain metal temperature, alkali chlorides deposited on the tube surfaces will lead to high corrosion rates through one or two corrosion mechanisms or a combination of the two.

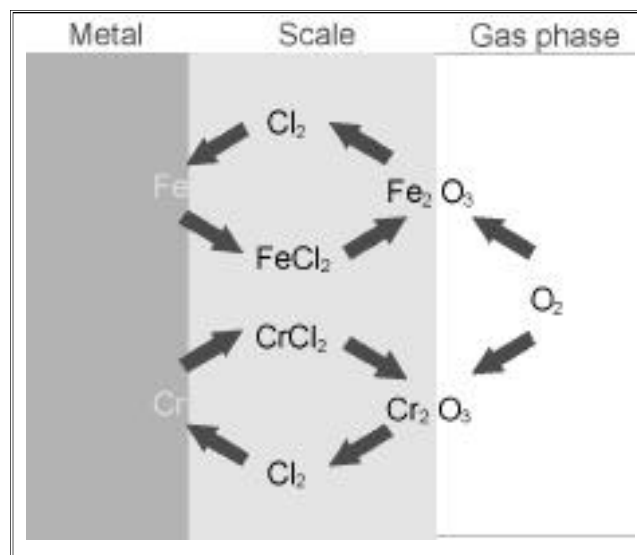


Figure 8 The active oxidation mechanism

The critical corrosion mechanism for biomass co-combustion are illustrated in Figure 7 and Figure 8. KCl in the fuel could be released as KCl or converted into HCl, potassium silicate and K₂SO₄. KCl is in the gas phase at combustion temperature and condenses at the heat surface, as well as in gas phase to K₂SO₄. Condensed KCl on the tube surfaces could form low melting eutectics, leading to an increased corrosion rate. Release of chlorine in the deposits could initiate the so-called active oxidation. A reaction between deposited KCl and SO₂ releases chlorine gas close to the metal surface. The chlorine reacts with the metal forming metal chlorides with high partial pressures. At increasing oxygen partial pressures away from the metal surface the metal chlorides will be transformed to oxides again with a release of chlorine. There is a closed loop which can be feeded by sulfation of more KCl.

Corrosion in biomass co-fired plants is influenced by the following service parameters.

- Fuel combination (The K/Si and the S/Cl ratios in fuel, which determine how much K that could be transformed to K-silicates or K₂SO₄).
- Combustion temperature (High combustion temperature in PF boilers favours formation of potassium silicates).
- Flue gas temperature around the heat transfer surface (high partial pressure of KCl and high driving force).
- Metal temperature/Steam temperature (Corrosion rates increases).
- Plant design (mixing and cleaning devices).
- Materials (high alloyed materials form a better protective oxide layer).

4.3.2 Corrosion in CFB Boilers

Within this project, Vattenfall has made corrosion measurements at the Näsjo Power plant firing coal and wood chips. The results indicate that acceptable corrosion rates can be achieved. In the APAS programme, the precursor of the OPTEB programme, ELSAM found that co-combustion of coal and straw increased the corrosion up to 25 times compared to coal. In the temperature range of 450-520°C.



The corrosion rate is increased, however, it is acceptable in most cases, but the actual corrosion rate depends highly on the straw quality and combustion temperatures.

Vattenfall found that co-firing a mixture of packaging waste and wood, the corrosion attack had many similarities to straw combustion. Potassium chloride was found in the deposits, although the Cl-content in the fuel was difficult to detect. The corrosion rate increased to a level more or similar to what ELSAM has found by co-firing straw. The results indicate that even rather small contents of chlorides in biomass can cause problems in fluidized bed boilers.

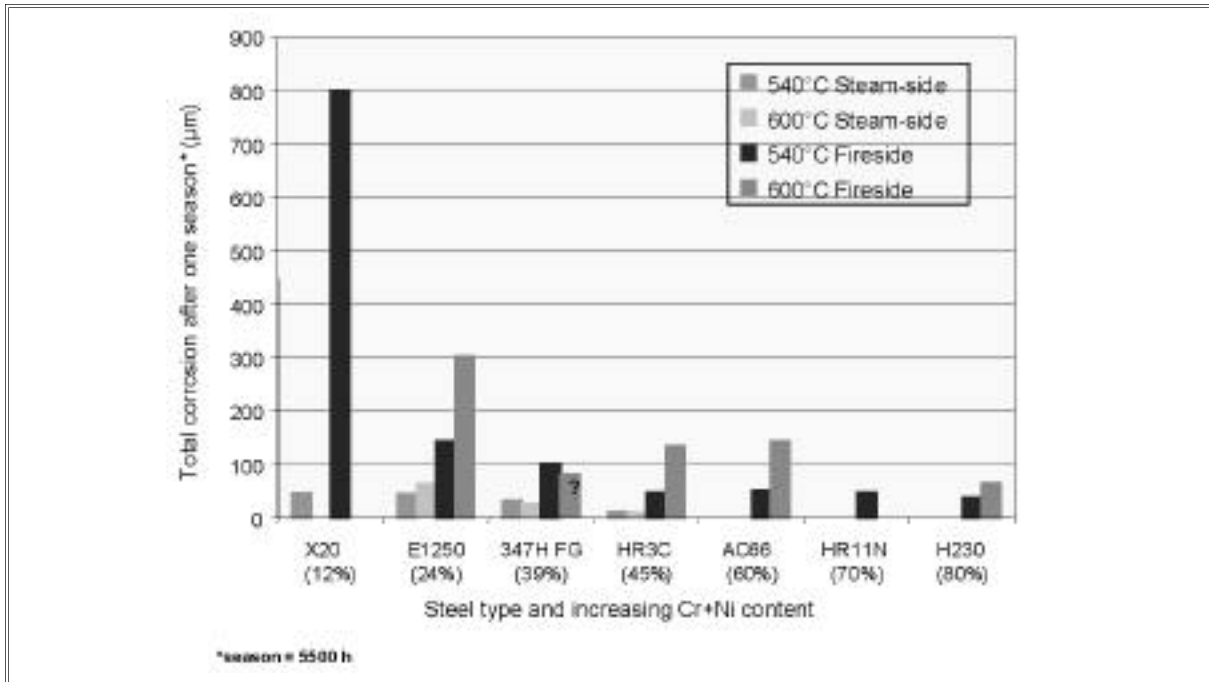


Figure 9 Corrosion measurements at 30 MW CFBC

Figure 9 clearly indicates high corrosion rates especially for the 12% Cr steel X20CrMoV121. Higher content of Cr and Ni had a positive effect on the corrosion rate. Table 2 summarizes high temperature corrosion at co-combustion for various fuel combinations.

Table 2 Corrosion data for various fuel combinations used in CFB boiler at steam temperatures ranging from 450 - 600°C

Steam Temperature	450 - 520°C	520 - 560°C	560 - 600°C	> 600°C
Coal + Wood	1	1	1	+ ?
Coal / Packaging waste + Wood	o ?	-1	-1	-1
Coal + 10 - 20% Straw	o ²	-2	-2	-2

+ acceptable corrosion rates, o may be acceptable or not, - unacceptable corrosion, ? to be verified
 1) Vattenfall (OPTEB), 2) ELSAM (APAS)



4.3.3 Corrosion in PF boilers

In PF boilers, corrosion is less than in FB boiler due to a higher conversion of the KCl in the fuel - to primarily silicates and to some extent sulphates. Co-firing wood and coal is not a problem according to Vattenfall studies. Co-firing straw up to 20% is not a problem according to ELSAM studies. Corrosion may occur at high metal temperatures due to higher concentrations of sulphates in the flue gas compared to coal firing.

Table 3 *Corrosion for various fuel combinations used in PF boiler at steam temperatures from 450 - 600°C*

Steam temperature	450 - 520°C	520 - 560°C	560 - 600°C	> 600°C
Coal + Wood	1	1	1	1
Coal + 10 - 20% Straw	2	2	2	?
Coal + > 20% Straw	-3	-3	-3	-3
Oil + Wood	4	4	?	?

+ acceptable corrosion rates, o may be acceptable or not, - unacceptable corrosion, ? to be verified

1) Vattenfall (OPTEB), 2) ELSAM, 3) IVD 4) Stockholm Energi

All potassium is converted to KCl according to studies done by IVD, University of Stuttgart. This will lead to a higher corrosion rate. These high straw shares have not been tested in full scale.

Stockholm Energi has investigated co-combustion of oil with 80% wood without seeing corrosion even at temperatures up to 600°C (see table 2), but another oil quality may cause problems with vanadate melt corrosion.

Test results from Stockholm Energi made in collaboration with Studsvik Material show that the corrosion rate is lower when firing oil and wood than in fluidized boiler. For standard austenitic steel like 347 H with Cr+ Ni contents of 40%, the corrosion rate is acceptable even at 650°C metal temperature.

4.3.4 Design Improvements to Reduce Corrosion

It has been shown that in some cases corrosion can be a serious problem when co-firing biomass with fossil fuels. In the following some design improvements investigated in the OPTEB programme in order to reduce high temperature corrosion are presented. The investigated methods are listed in Table 4.



Table 4 Investigated methods for reduction of corrosion potential in biomass co-fired plants

Method	Partners involved
Pretreatment: Straw leaching	NTUA, Elsam
Pre-treatment: "Cold" - Pyrolysis +Char wash	Elsam, DTU, IVD
Design modification of CFB/external ash cooler	Elsam, LLB
Improved mixing in CFB	TPS
Melt prediction - adjustment of service parameters	AA
Materials	Studsvik Material

Pre-Treatment

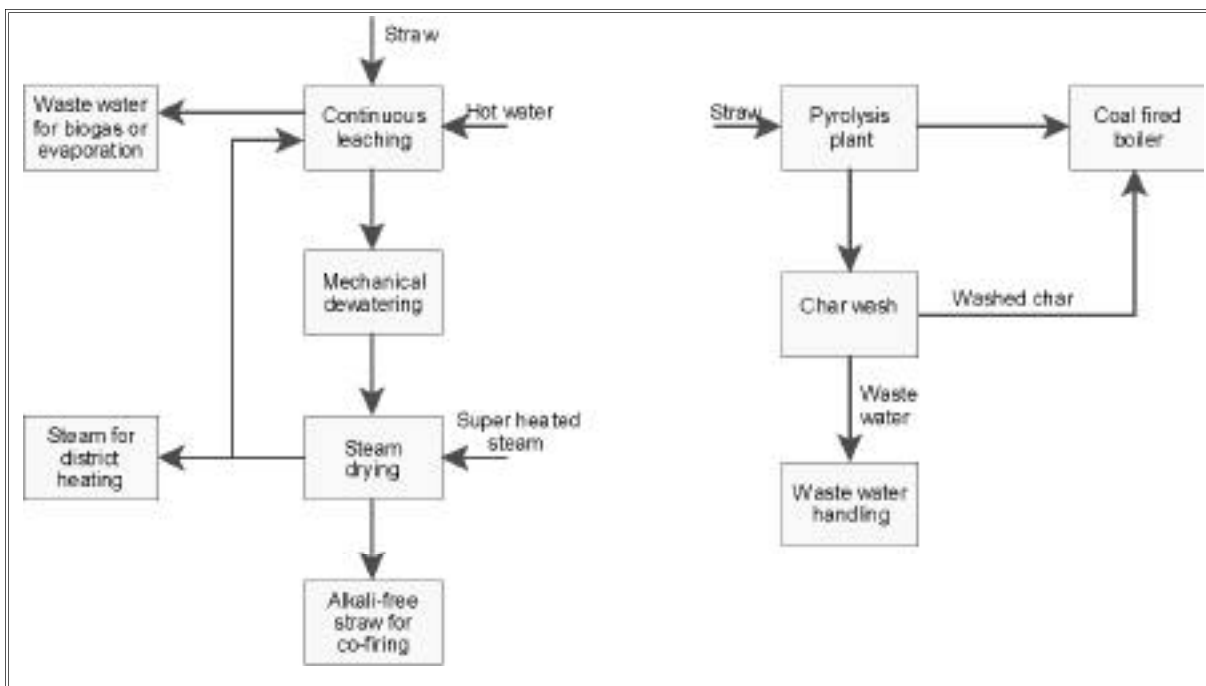


Figure 10 System configuration by pre-treatment: leaching - pyrolysis / char wash

The first example shows the system configuration for the pretreatment processes investigated by ELSAM and the Technical University of Athens, see Figure 10. The left side diagram illustrates a biomass leaching process integrated into a coal fired boiler with district heating. The biomass - in this case straw - is leached, dewatered and dried and could then be used in a PF boiler without problem.

The diagram to the right illustrates a pyrolysis process in combination with a char wash integrated with a coal fired boiler. Straw is pyrolysed at low temperature in order to keep KCl in the char. The pyrolysis gas is led to the boiler and could be burned without causing corrosion, without contaminating the waste



products with potassium and without fouling catalysts. The char is washed, and when KCl is washed out the char is led to the boiler.

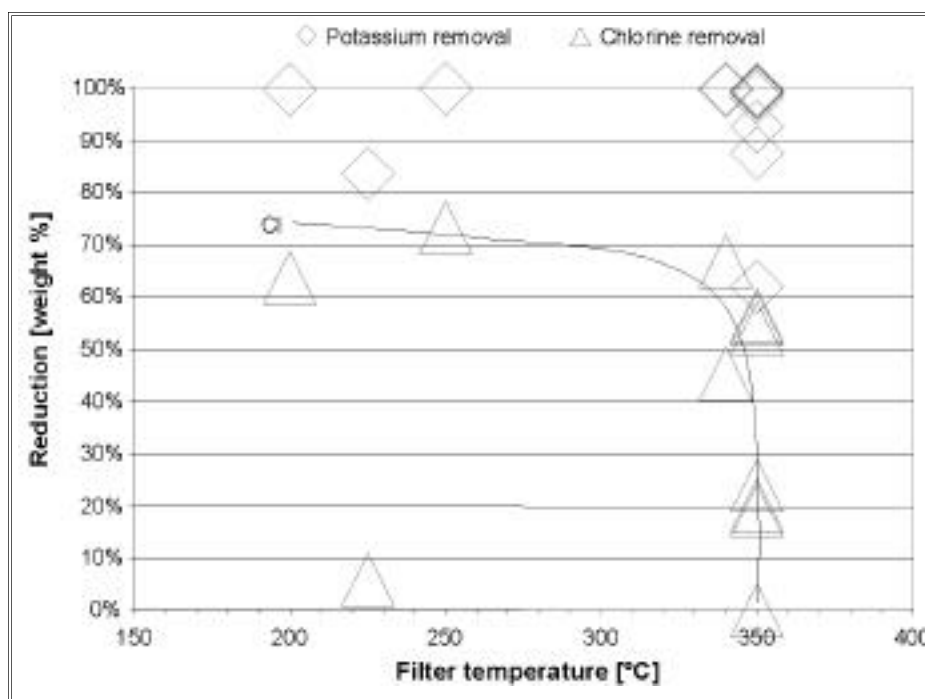


Figure 11 Potassium / chlorine removal as a function of filter temperature

Results show that more than 90% of potassium is leached out within 2-3 minutes potassium in 60°C water.

The results of the pyrolysis tests have shown that chlorine is released already from approx. 200°C, probably released as HCl. Potassium release starts at temperatures above 600°C together with a second release of chlorine indicating the release of KCl.

The potential for removing virtually all of the potassium, and most of the chlorine, from a gasification gas has been demonstrated by TPS in Figure 11. The desired degree of gas cleaning has been achieved by passing the LCV gas through a filter at temperatures in the region of 300 °C. In this convincingly demonstrated concept the biomass derived gas is used for NO reburning of a PF coal flame.

Modified CFB Design

ELSAM has been studying advanced CFB plants for co-combustion of straw and coal with steam temperatures up to 580°C, this implies the risk of high and unacceptable corrosion rates. Therefore, ELSAM has considered a plant, where the heat exchangers located in the convective pass of the boiler are limited to a steam temperature of 450°C. The final superheater with steam temperatures up to 580°C is located in external ash coolers, which only receives the hot ash particles which in theory should have released all KCl. In practice not all particles entering the external ash cooler have released all KCl, and previous ELSAM studies show that high corrosion rates in the external ash cooler environment are likely. In this project, ELSAM and LLB have made a test facility coupled to the Grenå Boiler, where it is possible to vary the environment. KCl in the gas phase is reduced substantially and deposition of KCl on cooled probes stops.



Improved Mixing in CFB

Improved mixing in a CFB has been studied by TPS, although it has not been the main purpose of this study to improve corrosion conditions. TPS has studied methods to improve the mixing in the combustor of a fluidized bed. A better dispersion of the fuel particles increases the residence time and will, in that way, decrease the transport of chlorides to the external ash coolers in a CFB. Three parameters have been studied: Increase of the bed height, un-even air fluidization and more fuel injection points. The results have shown, that increasing bed height and fluidization velocity increase the dispersion coefficient. Using an un-even air distribution a higher transverse transport of particles is achieved. The most efficient way to improve the mixing is probably by using multi fuel injection. TPS has developed a model to predict pyrolysis and particle dispersion in fluidized bed boiler. Using this model the effect of increasing the number of fuel injection points from one to four points has been calculated.

Melt Prediction

Prediction of the melt behaviour in combination with adjustment of the service parameters could be used to affect the deposition and the corrosiveness of the deposits. This is further described in the previous section about slagging and fouling.

Materials

The more traditional way of solving corrosion problems is to use more corrosion resistant materials. Studsvik Material has investigated this possibility of co-combusting coal and wood and coal and olive waste. The materials solution have the disadvantage that it only affects corrosion and not related problems such as fouling, which often occurs at the same time. In cases where corrosion is the main problem better materials might be an easy solution to implement.

4.3.5 Conclusions Regarding Corrosion

- Severe corrosion in co-fired coal-biomass boilers is related to alkali chlorides in the deposits. The alkali chlorides are released during combustion and condense on the heat surfaces.
- The presence of alkali chlorides in the deposit is dependent on the boiler design, biomass type and coal/biomass ratio. In PF boilers, KCl is converted to potassium-silicates, K_2SO_4 and HCl, and no KCl is found in deposits, and corrosion rates are similar to coal combustion. In fluidized bed boilers, KCl is only partly converted and KCl is found in deposits leading to high corrosion rates. Design modifications are needed in fluidized bed boilers if the corrosion rate should be reduced to acceptable levels in plants.
- The OPTEB programme has identified process modifications, which can decrease high temperature corrosion co-fired coal and biomass plants. These measures include biomass pretreatment, modification of the CFB design, material optimisation and operational changes.

4.4 By-Product Utilization

Co-combustion solid residue utilization must be viewed against a background of current coal ash utilization (varying between 10 % in Austria to 100 % in Netherlands) mainly in cement and concrete manufacture. Current European legislation (EN 450) permits the use of fly ash from pulverized firing of anthracite and bituminous coal only. Co-combustion wastes are excluded, similarly fluidized bed ashes, from coal or co-combustion, are excluded, although some usage is permitted under national rules.



The OPTEB project has focussed attention on the characterization of both PF and FB (and CFB) co-combustion ashes. A wide range of chemical and physical properties have been measured. Some of the properties of CFBC ashes have been compared with ASTM C618 mineral admixture classes by Cerchar. Here it is apparent that the SO_3 and $[\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3]$ levels are roughly satisfactory although the LOI (loss of ignition) is high. However, excellent physical properties in terms of strength and contraction are demonstrated, where co-combustion ashes are seen to be superior in strength to the reference standard. In concluding for the FBC system, the addition of up to 50% biomass is observed to make only minor modification to the chemical characteristics of coal ash. The trace element content of co-combustion ashes is well below reference standards. Leachability is very satisfactory except for $[\text{SO}_4^{2-}]$ and $[\text{Cr}^{6+}]$. Chemical and physical properties (except LOI) are very encouraging for use in the construction industry.

mpa analysed and characterised residues which several parties produced in different combustion systems varying in both plant and equipment and in the method of combustion. In addition to residues from industrial plants (Vattenfall, Nässjö – Sweden, FBC) and small-size technical trials (Cerchar – FBC, CFBC), mostly ashes from laboratory scale systems obtained by different combustion technologies (IVD – PF; NTUA – FBC) were studied.

Chemical, physical and mineralogical analyses were made of residues, and their suitability as building material was also studied by mpa. The important findings from the project work undertaken by mpa are in the area of material studies of the supplied samples, on the one hand, and the development of analytical methods, on the other. The latter include a method to analyse the chemical composition of minute sample quantities by means of EDX and the quantitative analysis of selected mineral phases by XRD.

In this, the major differences among the ashes from various methods of combustion (PF, FB) were identified both materially and morphologically, as was the type and quantity ratio of different biomass in the original coals.

For the interpretation of the results, it is important to determine the changes of the material parameters observed during the stepwise increase in the biomass proportion.

Generally, it can be said that the data of the chemical analysis change as follows:

- increase in the proportion of non-burned residue
- increase in the contents of K_2O and SO_3
- increase in the content of SiO_2
- reduction of the content of Fe_2O_3

Similar results were obtained from the leaching test studies of the aforementioned samples.

The mineralogical studies also showed that when the biomass ratio increased, an increase resulted also for the alkaline and chloride-containing mineral phases.

Clear differences between different PF and FB residues exist in the grain size distribution and grain shapes. Depending on the method of combustion, PF ashes, which are produced at higher combustion temperatures, contain more amorphous particles. These particles are produced when the mineral components of the fuel coal and biomass, respectively, fuse. The melt phases that exist temporarily during the combustion process take on droplets, which can retain their spherical shape after solidification in the cooler reaches of the flue gas ducts. Extensive scanning electron microscopy made clear and documented the differences in the morphology of the ash particles of PF and FB ashes in the various ash fractions. The lower combustion temperatures of FB boilers have only little morphological



influence on the original mineral inventory, causing irregularly shaped particles to form under these conditions of combustion. When biomass is added, the proportion of irregularly shaped particles in the PF ashes also increases slightly.

The following statement can be made with regard to the grain distribution in PF ashes: The proportion of $< 20 \mu\text{m}$ becomes the higher the more biomass is added. This is true, most of all, of PF residues. A similar trend was found for fine-grain FB fly ash.

The most surprising results were obtained from the compression strength studies of the finer ash batches. It was found that PF residues (IVD) and FB fly ashes (Cerchar) in comparison with cement standard tests yielded similar or even better absolute results. Scanning electron microscopy and microanalytical studies suggested an interpretation of the hydration mechanism in that the thermal treatment activates the SiO_2 in the biomass and, in addition, causes the formation of strength-producing CSH phases in the cement paste.

These positive results were confirmed by the work carried out by Cerchar.

Regrettably, for some tests with high biomass shares the measuring data exceed several material parameters in the list of requirements for the fly ash European norm (EN 450). This applies to the content of non-burned residue, free lime and sulphate. This means that for the time being there exists no legal framework for the production of ready-mixed concrete or concrete products for use in building constructions.

In conclusion, the need for new European legislation to permit utilization of co-combustion ashes from both PF and CFBC is highlighted, given by the many excellent ash properties observed during the OPTEB studies.

4.4.1 Conclusions Regarding By-Product Utilization

- Residues from biomass co-combustion showed excellent properties of co-combustion ashes as potential construction materials.
- Utilization of by-products plays a key role for further development of co-combustion. The European Norms consider only pulverized coal fly ash from pure combustion for utilization. A review of the European legislation on ash disposal and usage or national amendments are required.



4.5 Emissions, Trace Emissions

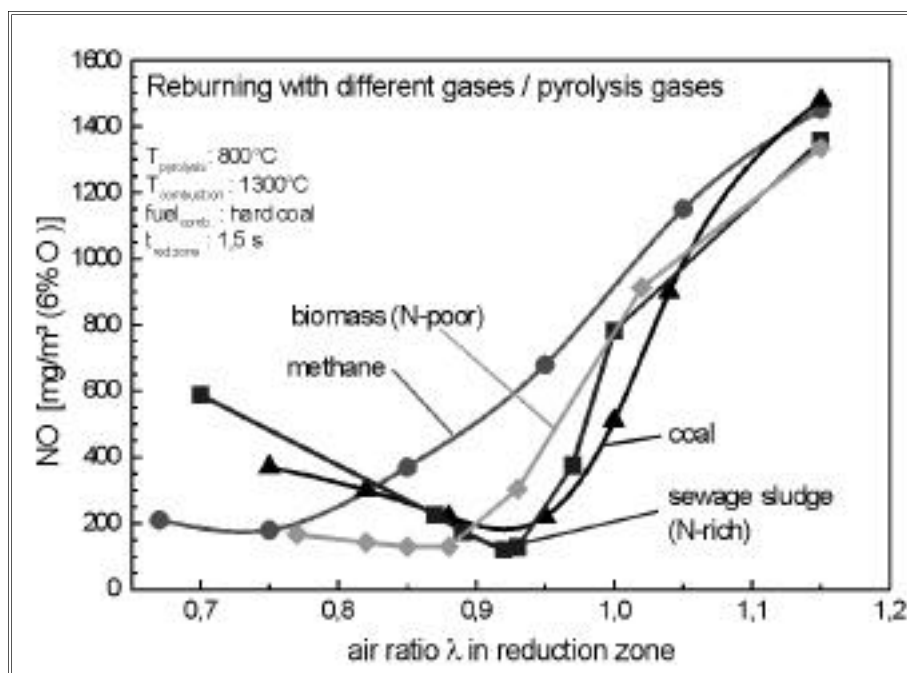


Figure 12 *Effect of reburn fuel on NO_x reduction*

The concept of using biomass derived gas as NO_x reburn fuel has been investigated by two partners, with a view to maximizing the potential of both coal and biomass utilization, whilst keeping the processing separate. The separate processing will permit the continued usage of bio-ash as a fertilizer and coal ash for construction, whilst removing the ash softening and corrosion problems normally associated with the direct addition of biomass to a coal flame.

In a series of experiments by IVD, University of Stuttgart, gases derived from the pyrolysis of coal, straw, miscanthus and sewage sludge have been compared with methane for reburning a PF coal flame. The biomass pyrolysis gases are seen, Figure 12, to be equally effective as pyrolysis gas from coal, and better than methane, with levels less than the desired 200 mg/m³ NO_x. Pyrolysis in an entrained flow reactor and a fluidized bed reactor has been tested; satisfactory reburning has been observed in every case.

Both reburning and NH₃ injection for NO_x reduction have been investigated by TPS at a pulverized coal fired 2 MW burner. The use of NH₃ injection addresses the logistical problem of supplying sufficient biomass for the full reburning of large coal fired power plants in many geographical locations. When using gasified biomass for reburning in semi-industrial scale NO_x emissions lower than 150 mg/m³ have been achieved in a wide range of stoichiometric conditions by addition of ammonia to the reburning zone.

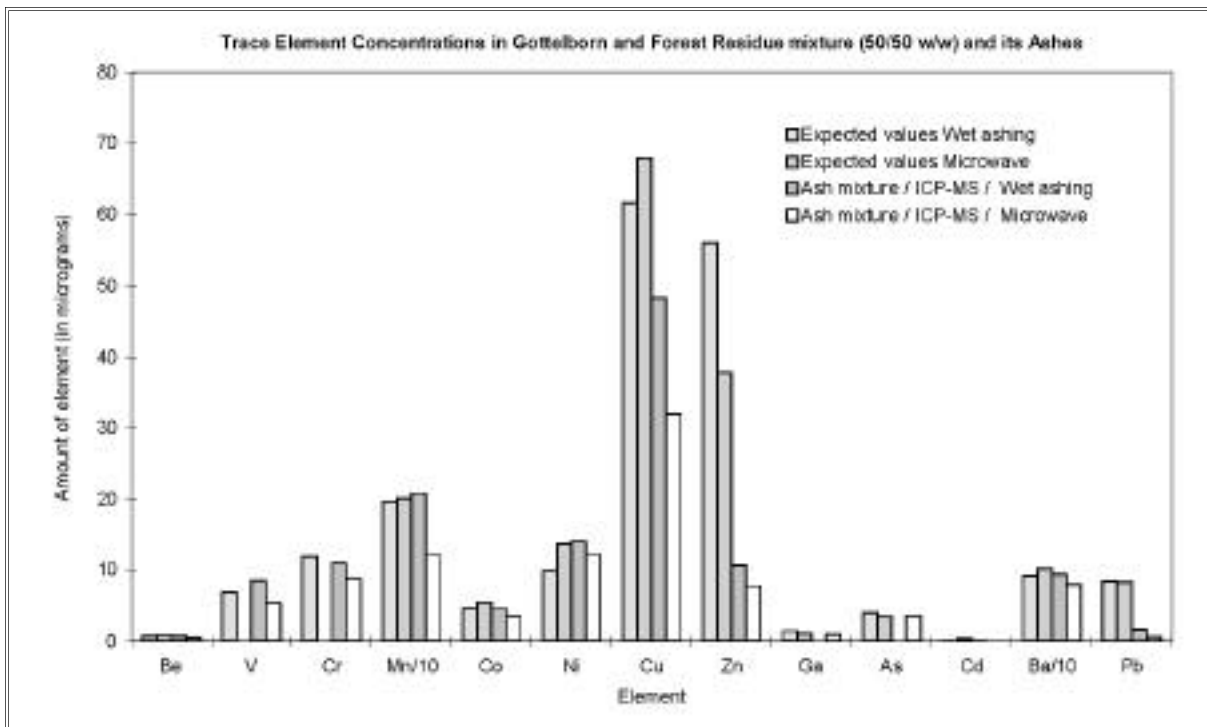
Significant effort has been expended on development of accurate trace element quantification procedures by Imperial College, Department of Chemical Engineering. Both wet ashing, using a series of four acids, and microwave digestion techniques have been refined to permit the introduction of samples, in dilute nitric acid solution, into the ICP-MS. Testing against validated standards has proved that solid samples as small as 10 mg can be analyzed for their trace element content (including 14 elements; As, Ba, Be, Cd, Co, Cr, Cu, Ga, Mn, Ni, Pb, V, Zn plus Hg by LECO analyzer). A wide range



of feed materials and their mixtures have been analyzed before and after combustion. Trace element contents of a 50:50 mixture of Götterborn plus Forest Residue are shown in Figure 13. Amounts of each element are given per gram of feed material before combustion, thus equal heights in all four bars represents no loss of the element from the combustor. Losses of Pb and Zn together with less losses of As, Cd and Ga are noted in almost all cases: in addition, some less volatile elements such as Ba or Cu show appreciable losses in the case of some biomass feeds and their mixtures.

The content of many trace elements is higher in coals than in biomass. Therefore co-combustion will tend to reduce the inventory of trace elements fed to the combustor. Furthermore, the behaviour of a coal/biomass mixture is predictable from the behaviour of its constituents, there being little evidence of synergy. Trace element emissions are thus not likely to increase by adding biomass to coal combustion.

Figure 13 Trace elements for mix of Götterborn / forest residues



The potential for the release of toxic hydrocarbons from co-combustion of biomass with coal has been investigated in several stages. In particular, evidence of any of the 75 PCDD's or 135 PCDF's has been sought, under the general label of dioxins. Firstly, an attempt to identify halogenated compounds in raw feed materials has been made by applying several mass spectrometry techniques to feed extracts in powerful solvents. No such compounds have been found suggesting the absence of pesticide or fungicide contamination. Similar attempts to identify halogenated materials from the condensed volatiles of high heating rate (1000 K/s) and high temperature pyrolysis (1000 °C) of biomass samples has produced negative results. The experiments suggest that dioxins and their direct precursors are not present in untreated biomass nor are they formed during the initial pre-combustion pyrolysis step. Rather such compounds are formed later in the combustion process as the reactant gas mixture cools down.

This hypothesis has been verified by mathematical modelling work by the University of Leeds, which has resulted in the development of two distinct models which may be used alone or in tandem. A



thermodynamic equilibrium model, based on Gibbs Free Energy minimization, works well at temperatures above about 1000 °C where the chemistry is sufficiently fast for equilibrium to be attained. At lower temperatures, the modelling of cooling combustion gases has required the development of a Perfectly Stirred Reactor model incorporating a complex scheme of 170 chemical species involved in 942 possible chemical reactions. The simulation of PF combustion over the range 1900 K down to 773 K, and FB combustion over the range 1573 K down to 673 K has been completed.

The models have been shown to predict general trends well, when compared to the data from experiments. Distinctly different patterns of behaviour emerge between the PF and the FB combustor. In the former case, high temperatures lead to the breakdown of fuel primary volatiles into light olefins, particularly ethyne, which subsequently recombine to create problematic hydrocarbon species as the burnt gases cool. Whereas, in the latter case, the primary volatiles dissociate into two ringed aromatic species such as naphthalene. However, the most important overall conclusion is that dioxins are the result of poor combustion conditions, i.e. with respect to air:fuel mixing, rather than a property of any particular fuel.

Measurements on a 43 MWth CFBC by CRE have confirmed, the above findings by showing little change in dioxin emission by the addition of 20 % bark or 15 % bark plus 5 % filter cake to the normal coal feed. In all three cases the dioxin emissions are well below the legal limit of 0.1 ng per m³. Similarly, PAH concentrations are not increased significantly by biomass addition. The same trials showed some reductions in both NO_x and SO_x, because of the reduced inventories of N and S added to the combustor and the high reactivity of biomass char (in the case of NO_x reduction).

4.5.1 Conclusions Regarding Emissions

No increase in trace element or dioxin emissions in biomass co-combustion could be observed.

4.6 Techno economic assessment

The Energy Research Centre of the University of Ulster carried out techno-economic assessment studies within the Industrial Biomass Co-combustion Project. The power generation systems studied included a PF boiler, a PFBC and a CFBC, with sizes ranging from 12MWe to 600MWe. The feedstocks included two different coals, straw, wood chips, woody material from pressed olive stones (WPOS) and sewage sludge.

In comparison to pure coal combustion both the additional investment costs for bio-mass co-combustion and the fuel costs itself consequently result in increased electricity production costs. However, in comparison with pure biomass combustion, co-combustion provides the most economic possibility for biomass utilization.

The economics of the pre-treatment process have been compared by DTU/ ELSAM-PROJEKT with other concepts for large-scale use of straw for power production. The alternatives are a) co-combustion of raw straw in coal-fired boilers, b) co-combustion of leached straw in coal-fired boilers and c) separate straw-fired boiler delivering steam to the turbine of a coal-fired boiler. A comparison of the electricity production cost is shown in Table 5. In all cases an annual straw consumption of 130,000 tons is applied. For co-combustion of raw straw it is assumed that 90 % of the produced fly ash has to be landfilled.



Table 5 *Economical comparison*

Straw combustion concept	Electricity cost
Pre-treatment by pyrolysis and char wash	71 EURO/MWh
Pre-treatment by straw leaching	73 EURO/MWh
Co-combustion of raw straw	67 EURO/MWh
Separate straw-fired boiler	89 EURO/MWh

Table 5 shows that the pre-treatment concepts are economically favourable compared with a separate boiler. The lowest cost is obtained for co-combustion of raw straw, but the high amount of ash for landfill disposal is a major drawback. It is expected that large scale landfill disposal will be prohibited in the future. Further development of straw pre-treatment is therefore recommended.

5 Summary of co-combustion technologies

The main new findings of the project are:

- The alkali content of biofuels may cause severe sintering, slagging, fouling and corrosion problems. The alkali chlorides are released during combustion and condense on the heat surfaces.
- The presence of alkali chlorides in the deposit is dependent on the boiler design, biomass type and coal/biomass ratio. In PF boilers, KCl is converted to potassium-silicates, K_2SO_4 and HCl, and no KCl is found in deposits, and corrosion rates are similar to coal combustion. In fluidized bed boilers, KCl is only partly converted and KCl is found in deposits leading to high corrosion rates. Design modifications are needed in fluidized bed boilers if the corrosion rate should be reduced to acceptable levels in plants.
- The OPTEB programme has identified process modifications, which can decrease high temperature corrosion co-fired coal and biomass plants. These measures include biomass pretreatment, modification of the CFB design, material optimisation and operational changes.
- The vaporization of potassium under PF conditions increases the melting temperature in the remaining ash, which reduces slagging problems in pulverized fuel combustion with dry ash removal. In slagging combustion, the slag flow may be negatively affected.
- In comparison to pure biomass combustion, the addition of coal considerably reduces operational problems
- Utilization of by-products plays a key role for further development of co-combustion. Residues from biomass co-combustion showed excellent properties of co-combustion ashes as potential construction materials. However, the European Norms consider only pulverized coal fly ash from pure combustion for utilization. A review of the European legislation on ash disposal and usage or national amendments are required.
- No increase in trace element or dioxin emissions in biomass co-combustion could be observed.



Co-combustion of biomass together with coal is the most economic way of biomass utilization, as long as there are no restrictions by operational problems.

Operational problems are dependent on fuel and firing system. Whereas wood can be considered as a less problematic fuel, especially the agricultural biomass like straw will cause severe operational problems due to its alkali and chlorine content. In fluidized bed systems the operational problems especially corrosion for such fuels are not yet solved, although some possible solutions are indicated in this project. For pulverized fuel systems operational problems seem to be manageable.

It has to be pointed out, that in every case co-combustion considerably reduces operational problems in comparison to pure biomass combustion. For pure biomass combustion even wood may cause corrosion.

For direct biomass co-combustion in PF boiler the utilization of residues is more complicated than for a separate biomass and coal combustion, as co-combustion residues are not considered in European norm for fly ash utilization in concrete and cement industry. However, i.e. in Germany a national amendment allows the addition of sewage sludge up to 5 % by weight. Although in general utilization of fluidized bed combustion residues from coal is considered to be less favorable than PF ash, the variety of different possibilities for utilization may give a better chance to use co-combustion residues.

Due to the above mentioned restrictions, the application of pretreatment technologies can be an economic solution.

Table 6 tries to summarize the investigations by indicating the main restrictions of the investigated firing systems and recommending suitable biomass types and ratios. It has to explicatively mentioned, that this can be only a rough indication.

For further RTD, two main problems are thought to be of major importance.

In order to promote the biomass co-utilisation in modern power plants, general prediction tools concerning the specific operational problems slagging, fouling and corrosion in pulverised fuel co-combustion of biomass in conventional and advanced power plants should be further developed.

Utilization of by-products plays a key role for further development of co-combustion. In order to promote a review of European legislation, to initiate national amendments and to indicate further utilization possibilities, a database should be established to provide sufficient data about the properties of co-combustion residues.



Table 6 *Comparison of biomass combustion systems*

System	Fluidized Bed	Pulverized Fuel	a) Pretreatment Facility b) Boiler System
plant scales (MW _{th})	10 - 600	100 - 2500	a) 1 - 250 b) 10 - 2000
typical biomass shares [% of energy input]	all	5 - 10	a) 100 b) 10
preparation requirements: milling/particle size water contents	low coarse (up to 1.00 mm) no specific restrictions, dispersion in bed required	high fine (mm-range) low (complete drying and combustion of particles during short flight)	dependent on technology (SP, FB)
main restrictions	corrosion	ash utilization catalyst deactivation	costs
manageable operational problems	fouling ash utilization bed sintering bed segregation	corrosion fouling slagging	air prevention/handling hot gas filtration handling and utilization of char and ash
phenomena	high chlorine fuels and in-situ desulphurization promotes potassium chloride formation	low chlorine/sulphur ratio prevents potassium chloride formation	

6 Deliverables

As an outcome of the project, the effects of different kinds of biomass on operation, emissions, residuals and the economics of the different co-combustion concepts have been shown. This allows a definition of the techniques best suited for co-combustion. The limits of co-combustion have been pointed out and measures to prevent operational problems and to reduce environmental effects have been outlined. The results are transferable to industrial application.

The deliverables of the overall project in detail are:

Direct co-combustion

- comparison of different co-combustion concepts with regard to operational and environmental issues
- development of combustion systems for biomass co-utilisation
- understanding of mineral ash behaviour, slagging and fouling phenomena and corrosion mechanisms as a function of the fuel
- slagging, fouling and corrosion evaluation in full-scale units
- measures to eliminate or control operational problems such as slagging, fouling and corrosion when using coal/biomass in PF/FB
- analysis of by-products and potential for utilisation of co-combustion residuals from co-combustion
- test methods for agglomeration in fluidised bed boilers and evaluation



- optimisation of fuel distribution and heat release for high volatile fuels in FB boilers
- material selection for superheater for coal/biomass co-combustion with high steam conditions or limitation of steam parameters
- identification of routes and mechanisms of formation of toxic organic compounds (TOCs) for co-combustion
- mathematical modelling for ash behaviour, TOCs

Pretreatment by pyrolysis and gasification

- technical feasibility of biomass pretreatment
- gas/char cleaning process for optimum removal of alkalis and chlorides
- combustion behaviour of gas/char
- evaluation of maximum NO_x reduction by using the gas as reburn fuel
- economics of pretreatment in comparison to direct co-combustion

The increase of detailed knowledge about the technical application allows development of strategies for the widespread use of biomass co-combustion in coal-fired boilers. Cost estimation and the limitation of technical risks allows a more economical use of biomass. The risks for potential operators and manufacturers of biofuel projects can be reduced. Hence, more combustion systems can be transformed to co-combustion operation.

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