

# ASH TRANSFORMATION CHEMISTRY DURING ENERGY CONVERSION OF BIOMASS

Dan Boström<sup>1\*</sup>, Markus Broström<sup>1</sup>, Nils Skoglund<sup>1</sup>, Christoffer Boman<sup>1</sup>, Rainer Backman<sup>1</sup>,  
Marcus Öhman<sup>2</sup>, Alejandro Grimm<sup>2</sup>

<sup>1</sup> Energy Technology and Thermal Process Chemistry  
Umeå University  
SE-901 87  
Sweden

\* dan.bostrom@chem.umu.se  
markus.brostrom@chem.umu.se  
christoffer.boman@chem.umu.se  
rainer.backman@chem.umu.se

<sup>2</sup> Division of Energy Engineering  
Luleå University of Technology  
SE-971 87 Luleå  
Sweden  
marcus.ohman@ltu.se  
alejandro.grimm@ltu.se

## ABSTRACT

There is relatively extensive knowledge available concerning ash transformation reactions during energy conversion of woody biomass. Traditionally, these assortments have constituted the main resources for heating in Sweden. In recent decades the utilization of these energy carriers has increased, from a low technology residential small scale level to industrial scale (*e.g.* CHP plants). Along this evolution ash-chemical related phenomena for woody biomass has been observed and studied. So, presently the understanding for these are, if not complete, fairly good. Briefly, from a chemical point of view the ash from woody biomass could be characterized as a silicate dominated systems with varying content of basic oxides and with relatively high degree of volatilization of alkali sulfates and chlorides. Thus, the main ash transformation mechanisms in these systems have been outlined. Here, an attempt to give a general description of the ash transformation reactions of biomass fuels is presented, with the intention to provide guidance in the understanding of ash matter behavior in the utilization of any biomass fuel, primarily from knowledge of the concentrations of ash forming elements but also by considering the physical condition in the specific combustion appliance and the physical characteristic of the biomass fuel. Furthermore, since the demand for CO<sub>2</sub>-neutral energy resources has increased the last years and will continue to do so in the foreseeable future, other biomasses as for instance agricultural crops has become highly interesting. Globally, the availability of these shows large variation. In Sweden, for instance, which is a relatively spare populated country with large forests, these bio-masses will play a secondary role, although not insignificant. In other parts of the world, more densely populated and with a large agricultural sector,

such bio-masses may constitute the main energy bio-mass resource in the future. However, the content of ash forming matter in agricultural bio-mass is rather different in comparison to woody biomass. Firstly, the content is much higher; from being about 0.3 – 0.5% (wt) in stem wood, it can amount to between 2 and 10 % (wt) in agricultural biomass. In addition, the composition of the ash forming matter is different. Shortly, the main difference is due to a much higher content of phosphorus (occasionally also silicon) which has major consequences on the ash-transformation reactions. In many crops, the concentration of phosphorus and silicon is equivalent, which (depending on the concentration levels of basic oxides) may result in a phosphate dominated ash. The properties of this ash are in several aspects different from the silicate dominated woody biomass ash and will consequently behave differently in various types of energy conversion systems. The knowledge about phosphate dominated ash systems has so far been scarce. We have been working with these systems, both with basic and applied research, for about a decade now. Some general experiences and conclusions as well as some specific examples of our research will be presented.

## 1. INTRODUCTION

The inorganic content in biomass comprises many metals but also some non metals. For instance Si, Ca, Mg, K, Na, P, S, Cl, Al, Fe, Mn, N, Cu, Zn, Co, Mo, As, Ni, Cr, Pb, Cd, V, Hg are present in varying amounts [1]. Most of these elements act as nutrients and have essential biological functions for the living plant.

Biomass as a concept embraces a wide range of material and is of course heterogeneous with widely varying properties. This applies also to the content and concentration of ash-forming matter. Large variations depending on type of plant biomass but also within specific part of a species are observed. Woody biomass contains in general relatively low levels of inorganic matter. For instance, stem wood of pine, spruce, birch and aspen contain about 0.3 – 0.4 wt-% “ash-forming” matter, *i.e.* non-combustible inorganic matter [2]. Other parts of the tree as for instance branches, twigs, bark, needles and shoots, contains increasing levels of inorganic matter, up to approximately 7 wt-% for aspen shoots.

Energy crops, agricultural crops or waste products from the agricultural sector are another group of biomass material that is receiving increased interest as the demand for renewable energy is increasing. Compared to wood there are a number of distinct differences related to the content of ash forming elements. In general the concentration of these elements is higher in crops than in wood [3]. The overall ash content generally varies between 2 wt-% up to 10 wt-%. Concerning the composition of the ash-forming matter a general trend of higher levels of phosphorus can be seen. For some crops the phosphorus concentration is even higher than the silicon content, a condition that has a major impact on the ash transformation reactions.

The most significant ash forming elements are Si, Ca, Mg, K, Na, P, S, Cl, Al, Fe and Mn, normally making up for more than 95 wt-% of the ash forming elements. Still this list of elements is long, their possible interaction are many and can be too complex to have a full comprehension of. Considering the most important ash transformation

reactions and the ones responsible for ash related operational problems during combustion and gasification of biomass, the list can be further reduced to; Si, Ca, Mg, K, Na, P, S, Al and Cl. The reason for excluding Fe and Mn is that these metals often turn up as individual oxides, with limited interaction with other ash forming elements. Sometimes interactions in terms of solid and especially liquid solutions will take place, though. A further simplification can be made by excluding or approximating Na as K, since the concentration of Na in biomass (plants) in general is substantially lower than K and their functions and roles in the ash transformation reactions are similar. Al has no known biological function and is considered to originate from external mineral matter as for instance feldspars and clay minerals that have “polluted” the plant during its living cycle or during the harvesting process. Subsequently Al could be present at significant levels and can play an important role in the ash transformation mechanisms, which will be described later. Thus, with a certain degree of simplification, the main ash-forming elements in bio-mass can be said to comprise the following list: Si, Ca, Mg, K, P, S, Cl and Al.

A relatively comprehensive literature exists that deals with the behavior of the volatile fraction of ash forming matter in biomass. For instance, several mechanisms are suggested for release of alkali, S and Cl .e.g. [4-8]. Further, it has been concluded that the association of the inorganic elements in the fuel is important for the release behavior [9-12]. Also bottom ash behavior and problems with slagging have been addressed in a number of investigations [13-19].

However, detailed experimental knowledge about all coupled ash transformation reactions taking place simultaneously in a real combustion situation is not available and may be difficult to predict with high accuracy. It can be concluded, though, that burning fuel particles at all different stages coexists simultaneously in many combustion conditions, implying that all sequences of ash transformation reaction stages described for the single burning particle will take place in parallel. Thus a steady state is likely to occur, which more or less realistically depending on the prevailing *chemical and physical conditions*, could be described or at least interpreted with global and/or local chemical equilibrium calculations:

The relative concentrations of the ash forming elements along with the total amount of ash forming matter are circumstances of major impact on the ash transformation reactions. The ash transformation sequences and the properties of the formed ash will differ substantially within the concentration variations of ash forming elements displayed in biomass. In this respect, it is not only the relative mutual stability, but also the kinetic properties and the aggregation states of the ash forming elements, intermediate and final products that have a decisive effect on the ash transformation scenario. In general, as for the reactivity in terms of reaction rate, it decreases along the sequence;

$(g)+(g) \gg (g)+(l) > (g)+(s) \gg (l)+(l) > (l)+(s) \gg (s)+(s)$ .

In addition, the temperature and residence time of the combustion process has to be taken into account which very much are related to principle and design of the specific combustion facility together with employed operational parameters. Finally, many

physical properties of the fuel have impact on the features of the ash transformation reactions.

To conclude, taking into account all possible influencing factors a rather complex and seemingly incalculable situation is at hand that may appear to resist any predictions.

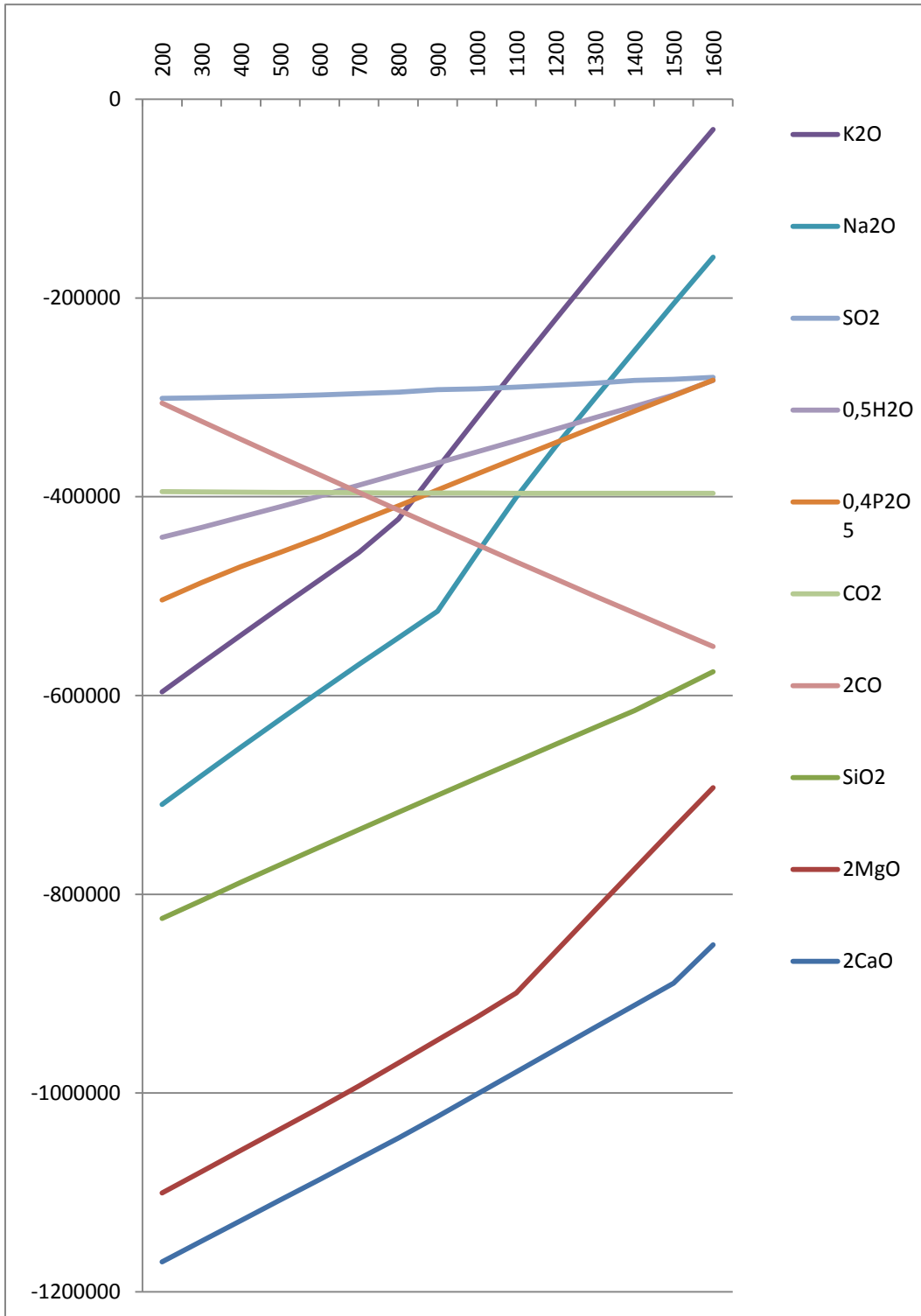
Still, a huge amount of empirical observations from a large number of different combustion facilities are available in the literature that may be interpreted and rationalized in terms of the conditions and factors briefly given above.

By use of GEA (global equilibrium analysis) or LEA (local equilibrium analysis) and making simple stoichiometric considerations based on the ash elemental concentrations analysis and also paying attention to the reactivity limitations as outlined above and including empirical observations from experimental combustion experiments, at least rough quantitative predictions of real ash transformation and ash fractionation scenarios should be plausible. For instance, it should be possible to decide which formation reactions, under the prevailing physical and chemical conditions, that are close to equilibrium, which reactions are correspondingly far from equilibrium and which are "intermediate".

The present approach is intended to provide guidance in the understanding of ash matter behavior in the utilization of any biomass fuel, primarily from knowledge of the concentrations of ash forming elements but also by considering the physical condition in the specific combustion appliance and the physical characteristic of the biomass fuel.

## **2. PRIMARY ASH TRANSFORMATION REACTIONS**

Considering the thermodynamic stability of the corresponding oxides of the major ash forming elements in the successive stages of combustion of a biomass particle, the following schematic description is plausible (see Figure 1):



**Figure 1: An Ellingdiagram showing the thermodynamic stability (the vertical axis:  $\Delta G^\circ$  (J)) of the main combustion products together with the major ash forming oxides, as the function of temperature (the horizontal axis:  $C^\circ$ ). Thermodynamic data for the calculation of the diagram were taken from the FACT database [20].**

Due to the high stability of oxidized Ca it is assumingly present in various oxide configurations already in the biomass. During the breakdown of the biomass as a consequence of the fuel oxidizing processes the oxide will probably be liberated as very small particles. CaO(s) is refractory to its character and will stay solid at all combustion temperatures, provided no reaction takes place. The same accounts for Mg and MgO(s).

Si is also present, either organically integrated in the cellular structure, as amorphous  $\text{SiO}_2 \cdot \text{H}_2\text{O}(\text{s})$ , or as dissolved  $\text{Si}(\text{OH})_4(\text{aq})$  in biomass fluids [21]. Again, this element shows stronger affinity to oxygen than the carbo-hydrogen matrix. During combustion, Si will therefore initially probably be released as small silica ( $\text{SiO}_2(\text{s})$ ) particles. As for earth alkali oxides, silica is also a refractory, which in pure form will be solid at all combustion temperatures. At really high temperatures and reduced atmospheres, e.g. in the char burning stage, silica may be reduced to gaseous silicon mono oxide,  $\text{SiO}(\text{g})$ , that however, will be very susceptible to oxidation as it released and enters the flue gas. P is present in oxidized form (V) as various phosphates in the biomass. Upon the combustion breakdown of the biomass, it is initially probably released as  $\text{P}_2\text{O}_5$  *i.e.* as the relatively volatile ( $\text{P}_2\text{O}_5(\text{g})$  or  $\text{P}_4\text{O}_{10}(\text{g})$ ) at the combustion temperatures. The phosphate may also be reduced to  $\text{P}_2\text{O}_3(\text{g})$  or even further under the gasification conditions. Under all such circumstances the volatility of the phosphoric components is assumed to be high. The alkali metals, K and Na, form less stable oxides than all the previous ash-forming elements. In fact at higher combustion temperatures these may even be reduced by the carbo-hydrogen fuel matrix to metal vapor (see the Ellingham diagram above). These alkali species will initially readily react with the ubiquitous water vapor, to stable and relatively volatile hydroxides,  $\text{KOH}(\text{g})$  and  $\text{NaOH}(\text{g})$ . Depending on the temperature, part of the hydroxides may condense as liquids.

Sulfur has lower affinity to oxygen than the carbo-hydrogen matrix. Subsequently it will be released as elemental and gaseous sulfur ( $\text{S}_2(\text{g})$ ), that will oxidize to gaseous sulfur dioxide ( $\text{SO}_2(\text{g})$ ) and later to sulfur trioxide ( $\text{SO}_3(\text{g})$ ) depending on the  $\text{O}_2$  concentration in the combustion atmosphere.

Chlorine, in general, forms relatively weak oxides that not are stable at combustion conditions. Thus it will be liberated as  $\text{Cl}_2(\text{g})$  that will react with the water vapor to  $\text{HCl}(\text{g})$ .

In the present approach high reactivity for P, S and Cl are assumed due to the high volatility of their initially formed host phases. Provided no further interaction with other ash element are taking place resulting in formation of thermal stable condensed phases, these elements will to a large extent evaporate.

The alkali metals can be assumed to be less reactive considering the lower volatility of their initially formed host compounds. Still, hydroxides and especially chlorides are relatively volatile which imply comparable high reactivity.

The earth alkali metals and Si must be considered the least reactive inherent ash forming matter in bio-fuel, due to the refractive character of these components. It must be

remembered, though, that the solid particles that initially formed, probably are nano-sized, and upon encountering other reactive ash forming constituents (gaseous or liquidus) comparable fast reactions will still take place.

Concerning external minerals as for instance sand (mainly quartz and feldspars), clay minerals and carbonate minerals, these matters are generally much less reactive compared to the inherent bio mass ash forming matter. The sand minerals mainly provide interaction with their solid particle surfaces and will not be in equilibrium with other ash matter unless long residence times and high temperatures prevails as for instance on a hot grate. The situations for clay type minerals and minerals that will be calcined under combustion conditions are somewhat different. Upon the brake down of their minerals structures, their surfaces may increase dramatically, with a substantial increase of reactivity as the result.

### 3. SECONDARY ASH TRANSFORMATION REACTIONS

To facilitate the description of the second step of ash transformation reaction, i.e. the essential ash forming reaction, the primary products of ash forming elements from the initial stages of combustion could be divided into two categories; basic and acid compounds:

Table 1

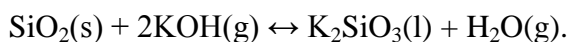
Basic compounds	Acid compounds
KOH(l,g) (K <sub>2</sub> O)	P <sub>2</sub> O <sub>5</sub> (g)
NaOH(l,g) (Na <sub>2</sub> O)	SO <sub>2</sub> (g)/SO <sub>3</sub> (g)
CaO(s)	SiO <sub>2</sub> (s)
MgO(s)	HCl(g) (Cl <sub>2</sub> )
H <sub>2</sub> O(g)	CO <sub>2</sub> (g)
	H <sub>2</sub> O(g)

Roughly, the compounds are arranged according to reactivity that descends from the top downwards. This is not a completely strict order, since for instance varying temperature may change it in some case. However, despite its schematic character, this arrangement is a useful tool that will serve the purpose of organizing and rationalizing the complex ash transformation reactions. The order is solely based on thermodynamical considerations, i.e. reflecting a pure equilibrium condition. Thus, in a situation where there is a competition for P<sub>2</sub>O<sub>5</sub>(g) among the base cat-ions, primarily K-phosphates will form. If K is consumed the turn comes to Na, and so on. In a reversed case, if there is a competition for K among the acid components, a K-phosphate would be the first compound to form. If P<sub>2</sub>O<sub>5</sub>(g) is consumed, the turn comes to SO<sub>2</sub>(g)/SO<sub>3</sub>(g) , and so on. As pointed out, this is a simplification and in a realistic situation, mixed compounds as for instance K-Ca-phosphates and K-Mg-phosphates may form due to the even lower formation energies for such phases. However, the table could be said to constitute a description of the order in which the various ash forming components are consumed.

As pointed out above, this thermodynamic approach, although very important, is only one of several other factors that have to be considered. The reactivity, as briefly outlined above, can sometimes also be formulated as *availability of the ash forming species for reaction*. For example, CaO is, as mentioned earlier, refractory in its character and will be solid at any combustion conditions. K<sub>2</sub>O on the other hand is assumed to instantly combine with water vapor to volatile KOH(g). Thus, even if the initially formed CaO can be assumed to be dispersed as relatively reactive nano-or sub micron sized solid particles, the availability of KOH for reaction is several orders of magnitude higher due to its gaseous state. This implies that although CaO forms ash compounds that are almost as stable as corresponding potassium compounds, the former are frequently formed in proportions considerably larger than motivated from the difference in thermodynamical stability. As indicated above, another effect of different aggregation states of the components is a strong fractionation of the ash compounds along the flue gas path, causing a significant deviation from a global equilibrium condition for the ash forming matter.

Schematically, the scenario is believed to be started by the successive formation of certain amounts of K-phosphates, sulfates, chlorides, silicates and carbonates, depending on the relative concentrations of these ash elements (see Table 1).

The initially formed K-phosphates are molten and probably rather volatile as well. Upon encounters with alkali earth oxides, condensed, preferably solid ternary phosphates are formed that will remain in the bottom ash environment. The sulfates are condensed under lower temperature conditions, while at higher temperatures they are released to the flue gas and later precipitated. The chlorides are almost invariably released to the flue gas and precipitated at lower temperatures. The situation concerning the silicates is different. A plausible course of events would be started by the formation of preferably molten K-silicate particles due to the high availability of KOH(g), *e.g* according to the following reaction;



There are eutectic temperatures in the K- silicate system as low as at 600 C°. Due to the high availability of KOH(g) the density of molten K-silicates particles rapidly will become rather high. However, as the fuel particle is burning out it shrinks and the ash particles will successively approach each other with increased opportunities for contact. Eventually the molten K-silicate particles will aggregate forming larger droplets that may initiate slag formation. Since these molten silicate droplets also will encounter the earth alkali oxide particles, reactions will take place where the latter will dissolve into the melt. The high thermodynamic affinity of silicate melts for earth alkali metal oxides supports the assumption that these reactions actually take place. It is even so that K to some extent can be out concurred by Ca and Mg in the melt with evaporation of K as a result [22]. The physical effect in terms of melting temperatures on the silicate melt by these processes can be studied in for instance ternary phase diagram. A general trend is that, as the content of Ca and Mg is increasing the melting temperatures is also increasing, possibly reducing the tendency for slag formation. The binary and ternary silicates in the system CaO-MgO-SiO<sub>2</sub> frequently observed in bio fuel bottom ashes are probably the



result of precipitations from such silicate melts. Often, as mentioned before, woody biomass is contaminated with sand and/or clay. Since these minerals often contain Al, a possibility of alkali alumino-silicate formation is provided for. These compounds, which have high thermodynamic stability and high melting temperature, will also contribute to a reduction of the slagging tendencies. For instance leucite ( $\text{KAlSi}_2\text{O}_6$ ) and kalsilite ( $\text{KAlSiO}_4$ ) have been frequently identified in woody biomass ashes.

Finally, the formation of carbonates will take place, depending on the overall stoichiometry of the ash forming elements. If there is a general surplus of basic oxides over the acidic component, carbonates will form as the result of reaction of the former with the  $\text{CO}_2$  in the combustion atmosphere.  $\text{K}_2\text{CO}_3(\text{s})$  is rarely observed whereas  $\text{CaCO}_3$  and/or  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  (occasionally also  $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ ) are common phases identified in bio fuel ashes deficient in acidic components.

So far, the reasoning has been pursued on a principal level, where basic inorganic chemical trends and mechanisms have been considered. To transfer these general concepts to a realistic situation, the physical characteristics of the specific energy conversion facility such as combustion temperature, residence time, air supply and flue gas velocities, have to be taken in account. Thus, the practical consequences of the ash transformation reactions for a certain fuel may be quite different depending on if the fuel is fired in a fluidized bed, on a grate or with a powder burner.

Table 2 A survey of the major ash forming reactions (simplified)

Reaction	comments
$\text{P}_2\text{O}_5(\text{g}) + 2\text{KOH}(\text{g}) \leftrightarrow 2\text{KPO}_3(\text{l,g}) + \text{H}_2\text{O}(\text{g})$	fast reaction*, product molten and partially volatile in r.a.**
$\text{SO}_3(\text{g}) + 2\text{KOH}(\text{g}) \leftrightarrow \text{K}_2\text{SO}_4(\text{l,g}) + \text{H}_2\text{O}(\text{g})$	fast reaction, product molten or not stable in r.a.
$\text{HCl}(\text{g}) + \text{KOH}(\text{g}) \leftrightarrow \text{KCl}(\text{g,l}) + \text{H}_2\text{O}(\text{g})$	fast reaction, product not stable in r.a.
$\text{SiO}_2(\text{s}) + 2\text{KOH}(\text{g}) \leftrightarrow \text{K}_2\text{SiO}_3(\text{l}) + \text{H}_2\text{O}(\text{g})$	intermediately fast reaction, product stable and molten in r.a.
$\text{CO}_2(\text{g}) + 2\text{KOH}(\text{g}) \leftrightarrow \text{K}_2\text{CO}_3(\text{l,g}) + \text{H}_2\text{O}(\text{g})$	fast reaction, product not stable in r.a.
$\text{P}_2\text{O}_5(\text{g}) + 3\text{CaO}(\text{s}) \leftrightarrow \text{Ca}_3\text{P}_2\text{O}_8(\text{s})$	intermediately fast reaction, product stable and solid in r.a.
$\text{SO}_3(\text{g}) + \text{CaO}(\text{s}) \leftrightarrow \text{CaSO}_4(\text{s,l})$	intermediately fast reaction, product (not) stable and solid in r.a.
$2\text{HCl}(\text{g}) + \text{CaO}(\text{s}) \leftrightarrow \text{CaCl}_2(\text{g,l}) + \text{H}_2\text{O}(\text{g})$	intermediately fast reaction, product not stable in r.a.
$\text{SiO}_2(\text{s}) + \text{CaO}(\text{s}) \leftrightarrow \text{CaSiO}_3(\text{s})$	slow reaction***, product stable and solid in r.a.
$\text{K}_2\text{SiO}_3(\text{l}) + \text{CaO}(\text{s}) \leftrightarrow \text{K-Ca-silicate}(\text{l})$	rather slow reaction***, product stable and molten in r.a.
*	The reaction rates are classified in four categories on an arbitrarily scale.
**	The stability in r.a. (residual ash) varies according to the thermal condition of the specific appliance.
***	These reaction rates are also highly dependent on the dispersion of fuel and reactant particles.

The Table 2 gives a schematic and simplified overview over the main ash forming reactions taking place at energy conversion of biomass. It is obvious that these reactions to varying extent will be effected by the inherently different physical conditions concerning temperature profile, residence time, flue gas speed and demand on physical fuel characteristics exhibited in different combustion facilities.

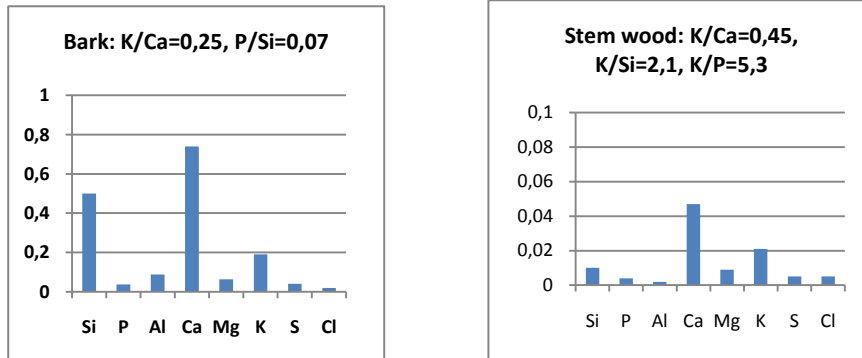
By comparing powder combustion with fluidized bed and grate combustion techniques, some of these effects can be made apparent. The principle of the former technique involves high temperatures and short fuel conversion time and in order to obtain complete

conversion of the fuel it has to be comminuted. This implies that the bottom ash environments typical for grates and fluidized beds that provide relative good opportunities for contact between gaseous and solid initial formed ash matter, are not present. On grate and in fluidized bed environments the density of the ash forming compounds is considerable higher and together with longer residence times, conditions are created where the ash transformation reactions could approach equilibrium. In the flame of a powder burner the fuel particles are dispersed. This implicates that the already limited mutual ash interaction and encounters due to the small fuel particles will be even more limited as a consequence of the extensive fuel dispersion. Under such combustion environment fast reactions involving gaseous ash compounds is favored at the expense of reactions where condensed components participate. Accordingly, the conditions promote gas phase reactions resulting in the formation of chlorides, sulfate and carbonates whereas reactions involving condensed reactants are suppressed. However, reactions between condensed and gaseous components as for instance between KOH(g) or KCl(g) and SiO<sub>2</sub>(s) will occur to some extent, since silica particles will encounter a flue gas containing gaseous potassium (although diluted) and molten K-silicates will form. The frequently observed positive influence of CaO on low melting K-silicates in for instance fluidized bed and in grate combustion will probably not occur in the flame and flue gas during powder combustion. If these condensed components are settled on the bottom and on the walls of the boiler, conditions for obtaining equilibrium are more favorable and reactions may take place. In general it can be concluded that under powder combustion conditions equilibrium are approached selectively and that the ash matter will be strongly fractionated [23].

For practical utilization of the present approach a remaining major challenge is to determine the extent of the deviation a specific energy conversion process (and a specific appliance) exhibits from a multi step local equilibrium analyses (LEA) model. If this could be appreciated for the schematic reactions in Table 2, the effects on the ash fractionation behavior could be estimated as well.

#### **4. WOODY BIOMASS**

In general, the content of ash-forming elements in woody biomass is characterized by a high Si/P ratio and a rather low K/Ca ratio.



**Figure 2: The concentration profile (mole %) of major ash forming elements in a typical spruce bark (left) and stem wood (right). Note that the concentration scale of the bark profile is one order of magnitude higher than the one of stem wood.**

**Table 3. Ash minerals in woody biomass ashes identified by XRD.**

Residual ash	Fine particles (sub-micron)
SiO <sub>2</sub> (quartz)	
(K,Na)AlSi <sub>3</sub> O <sub>8</sub> (feldspars)	
CaO (lime)	
MgO (periclase)	
CaCO <sub>3</sub> (calcite)	
K <sub>2</sub> Ca(CO <sub>3</sub> ) <sub>2</sub> (fairchildite)	
K <sub>2</sub> Ca <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	
K <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>
K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> (aphthitalite)	K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> (aphthitalite)
	KCl(sylvite)
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH (apatite)	
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (whitlockite)	
CaSiO <sub>3</sub> (wollastonite)	
CaMg(SiO <sub>3</sub> ) <sub>2</sub> (diopside)	
Ca <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub> (åkermanite)	
Ca <sub>7</sub> Mg(SiO <sub>4</sub> ) <sub>4</sub> (bredigite)	
Fe <sub>2</sub> O <sub>3</sub> (maghemite, hematite)	
SiO <sub>2</sub> (cristobalite, tridymite)	
Amorphous matter (silicate slag)	

In Table 3, a compilation of common mineral observed in woody fuel ashes, is given. The two first mineral in the residual ash column, quartz and feldspars, are principally always present in residual ash, reflecting the contamination of sandy material in woody biomass. Depending on the bottom ash conditions these minerals could be considered as rather un-reactive or at other conditions to participate heavily in slag formation. The presence of the minerals in the second category, the alkali earth oxides and the carbonates, is a consequence of either a stoichiometric surplus of the basic over the acid constituents, or of non-equilibrium conditions. The carbonates indicate moderately temperatures in the bottom ash environment. The latter goes also for the presence of the sulfates, which more often are found in fly ash fractions and as fine particulate matter. The phosphates, apatite and whitlockite are the two most commonly observed host phases for P in residual ashes of woody biomass. The relation between them is probably related to the

temperature and water vapor pressure. The whitlockite structure admits incorporation of several other elements and very often varieties with for instance Fe, Mg and K are observed. As long as the ratio of basic components over the P content in the fuel is high, the major part of the phosphates are contained in the bottom ash, despite the volatile character of the initial release form of P. The next category of phases in Table 3, the alkali earth silicates, is practically always present in residual ashes of woody fuels. These are believed to form as the result of either occasional encounters of solid oxide and silica particles but perhaps rather from incorporation these oxides into K rich silicate melts and a subsequent precipitation due to saturation or temperature drop. The earth alkali silicates are relatively refractory and are supposed to contribute to decreased slagging tendencies. Remarkably often Fe is found as an oxide in the residual ash thus apparently not as attractive as the acidic components for combining with the basic oxides. Interaction with silicate melt/slag is anticipated though (see below). The observation of high temperature modifications of silica, cristobalite (occasionally tridymite) in the residual ash are indications on either a surplus of Si over the basic components or on non-equilibrium conditions. These phases are believed to form from the reactive Si present in the fuel structure. The cristobalite modification also implicate on comparable high temperatures at least under some stages of the burn-out of the fuel particle. Finally, in Table 3 the amorphous part of the residual ash is given, which not directly could be observed by XRD but is indirectly seen as a heavily enhanced background in the XRD patterns. This is believed to originate from the formation of molten K-silicates in which other components such as the earth alkali oxides subsequently are dissolved. We have never with certainty identified Ca-K-silicates in residual ash of woody fuels, with XRD. Still, SEM analyses, on apparently previously molten residual ash, have shown on silicate material containing K along with Ca and Mg (and together with P and Fe as well). The amount of K in the residual ash present as silicate thus depends on the amount of reactive Si in the fuel, and on if the physical combustion conditions admits equilibrium to be approached. In addition, as described above, K can also be “captured” by reaction with thermally decomposed clay type minerals and of course the feldspar “contamination”.

The sub micron particulate matter in the flue gas of woody biomass combustion mainly consists of alkali sulfates and KCl, The proportions reflects the composition of the fuel concerning Cl and S, with respect paid to bottom ash temperature conditions and to the retention properties (to bottom ash) of the fuel ash in form of reactive Si.

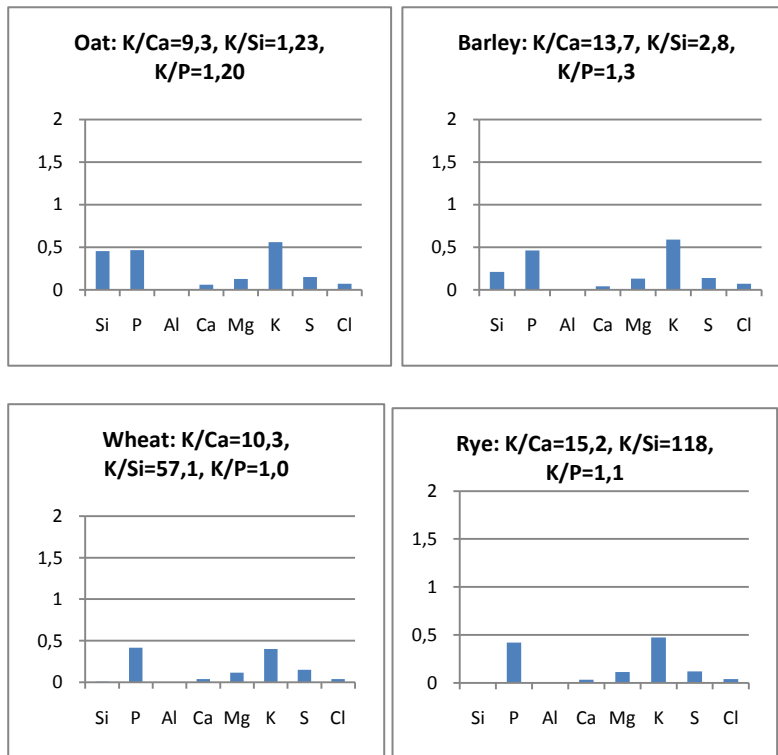
## 5. ENERGY AND AGRICULTURAL CROPS

Much less is known concerning detailed ash transformation reactions during combustion of crops. Since the absolute amount of ash in these materials often is 5 – 20 times higher, the ash related problems in general are also larger in comparison to woody biomass. Furthermore, the relative concentration of the ash forming elements in crops often shows more heterogeneity and often differs in some crucial aspects from the corresponding in woody biomass. Thus, quite different ash transformation reaction behavior can be expected during combustion of crops and consequently also other ash related problems. A general model or description of the ash chemistry for crops is out of the scope for the present paper. However, work aiming at a general description of the ash-chemistry of P-rich biomass has been performed during the last decade in our group (Energy Technology

and Thermal Process Chemistry, Umeå University, Sweden) and will be presented in a near future. Here results from some selected experimental investigations of different crops and with different combustion principles will be presented and discussed. The results will be interpreted according to the scheme outlined above.

*Combustion of cereal grains in a 20kW fixed residential cereal burner (simulating a grate combustion process)*

Oat grains were combusted, without and with additives (calcite and kaolin) in order to study the behavior of bottom ash and slag, fly ash and precipitated particulate matter in the flue gas channel [24]. Oat has a reputation of being the most suitable cereal for combustion of the four common cereals in Sweden (oat, barley, wheat and rye). A closer look at the ash element compositional profile reveals that the ratios K/Ca is high and P/Si is rather low compared to the other three cereals (see figure 3).



**Figure 3: The concentration profile of major ash forming elements of the four cereals; oat, barley, wheat and rye.**

The latter condition is probably one of the reasons behind the relative low slagging tendency reported for oat. According to the reactivity order in given in table 1 the base cations primarily reacts with the phosphorus oxide to phosphates and the main part of the silica remains unreacted and forms tridymite or cristobalite depending on the reaction temperatures. These silica modifications are true refractory compounds with melting temperatures above 1700C (cristobalite). Although the K/Ca ratio appears high there is enough Ca and Mg to form relatively high melting K-Mg/Ca-phosphates and avoid the low melting K-phosphates. Rather high particulate emissions has been observed, though, during combustion of oat caused by the high concentration of K in the fuel and the study was undertaken in order investigate the effects of calcite and kaolin additives on these phenomena. Without additives, the fine particulate matter consisted of K-phosphates, K-sulphate and KCl. The calcite additive was observed to bind more phosphate in the bottom ash and slag, resulting in a higher degree of sulfates and chlorides in the fine particles. Since no increased capture of K in the bottom ash could be expected with the calcite additive, no reduction of precipitated particulate matter was anticipated. A total reduction of the particles compared to the pure oat case was observed though and was attributed an earlier precipitation of K-sulfate, ahead of the low-pressure impactor particle collector.

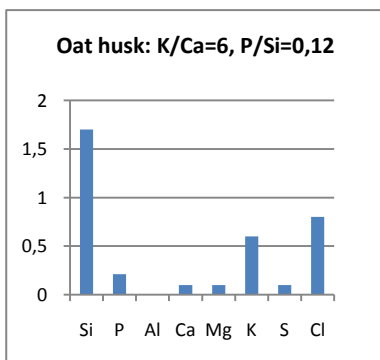
The kaolin additive on the other hand is known to be an effective K adsorbent [25]. The kaolinite mineral ( $Al_2Si_2O_5(OH)_4$ ) converts to meta-kaolinite ( $Al_2O_3 \cdot 2SiO_2$ ) at combustion temperatures and reacts presumably with some K-species, plausibly  $KOH(g)$  to kalsilite ( $KAlSiO_4$ ) and leucite ( $KAlSi_2O_6$ ) (in the last case a silica ( $SiO_2$ ) is also

required in order to balance the reaction). A substantial reduction of particulate matter was observed that was attributed the K-binding property of kaolin. In addition the slagging tendencies was completely eliminated which at least to some extent could be explained by the refractory character of kalsilite and leucite.

In another study, the slagging tendencies during combustion of all four cereals were investigated [26]. According to the ash-elemental concentration profiles and indices for wheat, barley and rye (see figure 3), the slagging tendencies for all these cereals should be worse. Decreasing K/Ca ratio generally lowers the melting temperatures in these phosphate systems. Furthermore the much higher P/Si ratios for these cereals also imply much less amounts of free refractory silica that can contribute to higher melting temperatures and reduce the slagging tendency.

*Combustion of oat husk in a 5MW grate fired boiler*

Presently we are investigating ash related issues in connection to combustion of oat husk in a 5MW grate fired boiler. Compared to the grain, the husk contains dramatically higher levels of Si but also higher levels of Cl (see figure 4). One expected consequence was even higher content of refractory silica in the different ash fractions which also was experimentally verified. Due to high primary air velocities through the grate the residence time for volatiles is relatively short. Thus comparatively high concentrations of gaseous ash forming matter, including P<sub>2</sub>O<sub>5</sub>(g), KOH(g) together with SO<sub>2</sub>(g)/SO<sub>3</sub>(g) and HCl are expected to escape with the flue gases. High amounts of deposits was also observed on the boiler walls, the heat transferring surfaces, together with large amounts of cyclone and EPS filter ash. The speciation of that ash was found to be, beside silica, (cristobalite and tridymite), various amounts of K-phosphates, K-sulfate and KCl. This is according to the reaction order in given in table 1; that is, primarily K-phosphate should form, followed by K-sulfate and KCl.

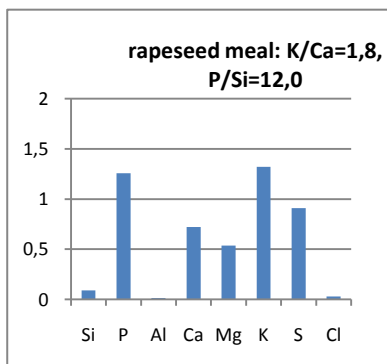


**Figure 4: The concentration profile of major ash forming elements for oat husk.**

Since the deposits imposed serious problems in terms of reduced availability use of additives to bind more P in the bottom ash, alternatively to bind more K in the bottom ash, thereby reducing one important prerequisite for the formation of deposits, is planned.

*Combustion of rapeseed meal in a small scale (5kW) fluidized bed*

Rapeseed meal is the residue from rape oil production. It has mainly been used for cattle feeding but since the heating value is relatively high, it has a potential as a bio-energy resource. In a combustion experiment where rapeseed meal was fired in a 5kW bench-scale fluidized bed the interaction of the ash forming matter with the quartz bed material was studied [27]. The total ash content of the utilized rapeseed meal was 7.5 wt-%. The ash element concentration profile is shown in figure 5. Since the Si concentration is very low, the bottom ash from combustion of rapeseed meal can be expected to consist almost entirely of phosphates. A quite different interaction between the residual ash and the quartz bed grains was observed for rapeseed meal compared to woody fuels. In the latter case, continues K-Ca-silicate rich coatings are always present which occasionally is sticky and causes bed agglomeration. In this case, no or only thin and discontinues coatings was observed. Instead partly or completely melted lumps of residual ash was distributed between the bed grains or attached to the grains. Again, the interpretation according to the reaction order in table 1, becomes that the rich abundance of phosphorus prevented potassium from attacking the surface of the quartz bed grains. The elemental analysis of the melted residual ash showed that it contained various amounts of P, Ca, Mg, K and also some amounts of Si.



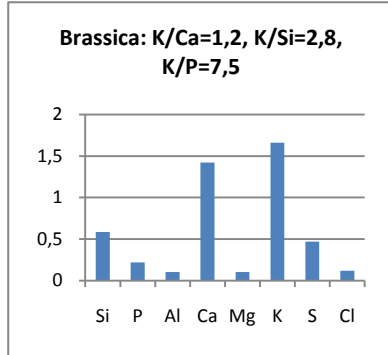
**Figure 5: The concentration profile of major ash forming elements rapeseed meal.**

*Combustion of “Brassica carinata” in a residential 20kW pellets burner*

*Brassica carinata*, a common energy crop in the Mediterranean parts of Europe, was combusted in a horizontal pellets burner (20kW) to elucidate the combustibility and environmental performance [28].

The ash content is high, 8.5 wt-%, implying that the composition is crucial if severe ash related problems are to be avoided and the bottom ash could be handled with available equipment. The elemental ash concentration profile is given in figure 6.



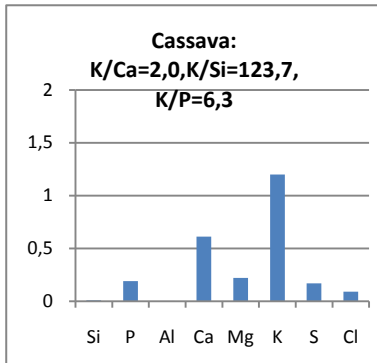


**Figure 6: The concentration profile of major ash forming elements for *brassica carinata*.**

The K/Si ratio is high but as the Ca/Si ratio is comparable, a bottom ash with a high element of refractory Ca-silicates could be expected. An examination of the residual ash revealed a material that only partly was slightly sintered and no real fused material could be observed. The XRD-speciation analyses showed on the presence of  $\text{Ca}_2\text{SiO}_4$ ,  $\text{KCaPO}_4$  and  $\text{CaO}$ , which in principle is according to reactivity order given in table 1. Significant amounts of  $\text{K}_2\text{SO}_4$  was also found in the bottom ash, indicating on lower temperatures in some parts of the boiler. It was speculated that the formation of this sulfate in the bottom ash was responsible for the mild sintering effect. The fine particulate matter of the fly ash was dominated by  $\text{K}_2\text{SO}_4$  lesser amounts of  $\text{KCl}$ , which was expected.

#### *Combustion of harvesting waste of Cassava in a residential 20kW pellets burner*

In an ongoing project the harvesting waste of Cassava (that was obtained from China), was combusted in a horizontal pellets burner (20kW) to investigate the combustibility in terms of bottom ash behavior and the extent of particulate emissions. The material has an ash elemental concentration profile that is quite different from most other bio-fuel we have studied previously (see fig 7). There is a huge surplus of base cations in comparison with the acid oxide elements Si and P. Almost no Si but some amounts of P are present in the fuel. The total ash content was 4.5 wt-%. According to the reactivity order (see table 1), some phosphate could be expected in the bottom ash and low slagging tendencies due to the refractory character of these. Since the surplus of K, Ca and Mg is so large compared to the acid oxide formers, Si, P and S, and Cl, a significant formation of carbonates in some part of the appliance was also expected. An XRD-analysis showed that the ash in various parts of the boiler was dominated by phosphates and carbonates along with minor amounts of sulfates and earth alkali oxides. The ash was only light sintered. The fine particulate matter in the fly ash was dominated by sulfates and  $\text{KCl}$  together with minor amounts of carbonates and phosphates. Due to the high concentrations of K in the fuel, high amounts ( $> 1000 \text{ mg/Nm}^3$ ) of emitted particulate matter was observed.

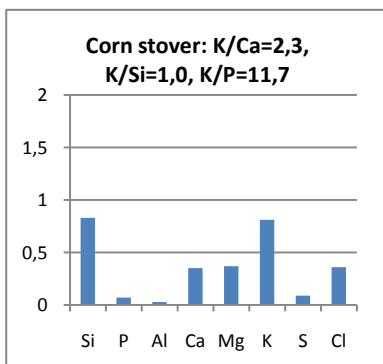


**Figure 7: The concentration profile of major ash forming elements for cassava harvesting waste.**

As long as techniques for handling the bottom ash and some efficient equipment for fly ash capture are at hand, this could be a suitable fuel.

*Combustion of corn stover pellets in a small scale (50kW) pellet burner*

Corn stover materials, (originating from Jilin, northeast China), was combusted in a small-scale underfed pellet burner (50kW) to study the combustibility in terms of slagging tendencies [29]. By considering the elemental concentration profile (see figure 8); a high K/Ca ratio in an ash dominated by equivalent amounts of K and Si together with the reactivity order, severe slagging tendencies are to be expected. This was also observed as about 40% of the residual ash formed slag. To improve these conditions the corn stover pellets were fired with two different additives, calcite ( $\text{CaCO}_3$ ) and kaolin (kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ )). The idea with the calcite additive was to change the ash elemental concentration profile by decreasing the K/Ca ratio, thus providing a measure to increase the melting temperature of the (initially) K rich silicate melt that is supposed to form in this kind of ash. The kaolin additive is previously known to be able to capture K into thermodynamically very stable and refractory K-Al-silicate phases. In fact the formation of one of these refractory silicates (leucite,  $\text{KAlSi}_2\text{O}_6$ ) requires equal amounts of both a K-species and silica. Thus, the ash elemental profile is in practice “improved” by lowering both the concentration of K and Si.



**Figure 8: The concentration profile of major ash forming elements for corn stover**

The addition of 3 wt-% kaolin and 3 wt-% calcite was observed to lower the amount of formed slag (of the residual ash) to 20 wt-% and 13 wt-%, respectively.

## 6. REFERENCES

- [1] I. Obernberger, F. Biedermann, W. Widmann, R. Riedel, *Biomass and Bioenergy*, 12 (1997) 211-224.
- [2] J. Werkelin, B.J. Skrifvars, M. Hupa, Ash-forming elements in four Scandinavian wood species. Part 1: Summer harvest, *BIOMASS BIOENERG*, 29 (2005) 451-466.
- [3] A. Monti, N. Di Virgilio, G. Ventura, *Biomass and Bioenergy*, 32 (2008) 216-223.
- [4] S.C. van Lith, V. Alonso-Ramirez, P.A. Jensen, F.J. Frandsen, P. Glarborg, Release to the gas phase of inorganic elements during wood combustion. Part 1: Development and evaluation of quantification methods, *ENERG FUEL*, 20 (2006) 964-978.
- [5] F.J. Frandsen, S.C. van Lith, R. Korbee, R. Backman, P. Yrjas, I. Obernberger, T. Brunner, Quantification of the Release of Inorganic Elements from Biofuels, in: *Impacts of Fuel Quality on Power Production*, Snowbird, Utah, USA, 2006.
- [6] S.Q. Turn, C.M. Kinoshita, D.M. Ishimura, J.C. Zhou, The fate of inorganic constituents of biomass in fluidized bed gasification, *Fuel*, 77 (1998) 135-146.
- [7] J.G. Olsson, U. Jäglid, J.B.C. Pettersson, Alkali metal emission during pyrolysis of biomass, *ENERG FUEL*, (1997) 779-784.
- [8] T. Kowalski, C. Ludwig, A. Wokaun, Qualitative Evaluation of Alkali Release during the Pyrolysis of Biomass, *Energy & Fuels*, 21 (2007) 3017-3022.
- [9] J.N. Knudsen, P.A. Jensen, K. Dam-Johansen, Transformation and release to the gas phase of Cl, K and S during combustion of annual biomass, *ENERG FUEL*, (2004).
- [10] D.C. Dayton, B.M. Jenkins, S.Q. Turn, R.R. Bakker, R.B. Williams, D. Belle-Oudry, L.M. Hill, Release of inorganic constituents from leached biomass during thermal conversion, *ENERG FUEL*, (1999) 860-870.
- [11] P.A. Jensen, F.J. Frandsen, K. Dam-Johansen, B. Sander, Experimental investigation of the transformation and release to gas phase of potassium and chlorine during straw pyrolysis, *ENERG FUEL*, 14 (2000) 1280-1285.
- [12] H.M. Westberg, M. Bystrom, B. Leckner, Distribution of potassium, chlorine, and sulfur between solid and vapor phases during combustion of wood chips and coal, *ENERG FUEL*, 17 (2003) 18-28.
- [13] D. Vamvuka, D. Zografos, G. Alevizo, Control methods for mitigating biomass ash-related problems in fluidized beds, *Bioresource Technology*, 99 (2008) 3534-3544.
- [14] M. Zevenhoven-Onderwater, J.P. Blomquist, B.J. Skrifvars, R. Backman, M. Hupa, The prediction of behaviour of ashes from five different solid fuels in fluidised bed combustion, *Fuel*, 79 (2000) 1353-1361.
- [15] M. Ohman, C. Boman, H. Hedman, A. Nordin, D. Bostrom, Slagging tendencies of wood pellet ash during combustion in residential pellet burners, *BIOMASS BIOENERG*, 27 (2004) 585-596.
- [16] E. Lindstrom, M. Ohman, R. Backman, D. Bostrom, Influence of sand contamination on slag formation during combustion of wood derived fuels, *ENERG FUEL*, 22 (2008) 2216-2220.
- [17] C. Gilbe, M. Ohman, E. Lindstrom, D. Bostrom, R. Backman, R. Samuelsson, J. Burvall, Slagging Characteristics during Residential Combustion of Biomass Pellets, in: 2008, pp. 3536-3543.

- [18] C. Gilbe, E. Lindstrom, R. Backman, R. Samuelsson, J. Burvall, M. Ohman, Predicting Slagging Tendencies for Biomass Pellets Fired in Residential Appliances: A Comparison of Different Prediction Methods, in, 2008, pp. 3680-3686.
- [19] E. Lindstrom, M. Sandstrom, D. Bostrom, M. Ohman, Slagging Characteristics during Combustion of Cereal Grains Rich in Phosphorus, in, 2007, pp. 710-717.
- [20] C. Bale, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, R. Ben Mahfoud, J. Melancon, A.D. Pelton, S. Petersen, FactSage thermochemical software and databases, *Calphad*, 26 (2002) 189-228.
- [21] J.C.C. Freitas, F.G. Emmerich, T.J. Bonagamba, High-Resolution Solid-State NMR Study of the Occurrence and Thermal Transformations of Silicon-Containing Species in Biomass Materials, *Chem. Mater.*, 12 (2000) 711-718.
- [22] P. Thy, B.M. Jenkins, C.E. Leshner, *ENERG FUEL*, 13 (1999) 839-850.
- [23] D. Nordgren, H. Hedman, N. Padban, D. Bostrom, M. Öhman, Ash transformations in pulverised fuel co-combustion of straw and woody biomass. Unpublished work.,
- [24] D. Boström, A. Grimm, C. Boman, E. Björnbom, M. Öhman, Accepted for publication in *Energy & Fuels*, in, 2010.
- [25] K.Q. Tran, K. Iisa, B.M. Steenari, O. Lindqvist, A kinetic study of gaseous alkali capture by kaolin in the fixed bed reactor equipped with an alkali detector, *Fuel*, 84 (2005) 169-175.
- [26] E. Lindström, M. Sandström, D. Boström, M. Öhman, *Energy & Fuels*, 21 (2007) 710-717.
- [27] D. Boström, G. Eriksson, C. Boman, M. Öhman, *ENERG FUEL*, 23 (2009) 2700-2706.
- [28] M. Diaz, D. Bostrom, C. Boman, J. Royo, in: 17th European Biomass Conference and Exhibition, Hamburg, Germany, 2009.
- [29] S. Xiong, J. Burvall, H. Örberg, G. Kalen, M. Thyrell, D. Bostrom, *Energy & Fuels*, 22 (2008) 3465-3470.

## 7. ACKNOWLEDGEMENTS

The financial support from the Botnia-Atlantica program; Enhanced Forest Biomass Production, the Swedish Farmers Foundation for Agricultural Research (SLF), the Thermal Engineering Research Foundation (Värmeforsk), the Swedish Energy Agency (STEM) and the national (Swedish) strategic research program Bio4Energy are gratefully acknowledged.