

**BIOMASS AS AN ENERGY SOURCE:  
THE CHALLENGES AND THE PATH FORWARD**

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**ABSTRACT**

Modern society is highly dependent upon oil but world oil reserves are limited, corresponding to about 40 years, at the present consumption rate. Additionally, Europe is struggling to develop technologies for reducing CO<sub>2</sub> emissions. As a partial solution to these problems, in February 2003, Tony Blair and Göran Persson pledged to double the use of renewable energy sources in the European Union by 2010, so that 12 % of electricity production comes from renewable sources.

Beyond reducing the use of fossil fuels, Sweden has also made it its goal to replace nuclear energy with sustainable use of renewable resources. This goal is supposed to be implemented within an intermediate time period, mainly by the increased use of domestic biomass. Several estimates of present and future biomass fuel supplies have indicated that an expansion from the present 90 TWh/year to a maximum of about 150-210 TWh/year by the year 2025 could be feasible. However, as experience has already shown, switching from fossil fuels to using biomass and waste as fuels introduces some significant challenges that must be overcome. For example, biomass and waste can contain significant amounts of Na and K as well as trace elements such as Hg, P, Cu, Cr, As, Cd, Pb, Zn and Cl. The alkali metals together with P, Zn and Cl have a strong tendency to act as fluxing agents, decreasing the melting point of ashes to the point that, under combustion conditions, they form sticky, corrosive melts that are deposited on boiler surfaces. The deposits greatly reduce heat transfer in the furnace and corrode heat transfer surfaces. In addition, volatile metal chlorides are often formed, resulting in deposition on surfaces, with subsequent Cl-induced corrosion.

Simple measures to diminish these problems by using mixtures of fuels or inexpensive additives, thereby changing the melting and condensation temperatures and the specification of the ash system, have been proposed, but are primarily ad hoc and not guaranteed to work. At this point, solutions to these problems, which will allow biomass to be used sustainably, as desired by the politicians, can only come from increased knowledge of the underlying chemistry involving Na, K and the trace elements under combustion conditions. A survey of the literature quickly shows that there is very little available, especially of sufficient quality to allow models to be developed to allow the extent of fouling and corrosion problems to be identified and studied. The latter, of course, must be the outcome of any work in this area.

Work is currently underway at Umeå and Linköping Universities to determine and model the elementary, gas-phase, chemical reactions that occur when K, Na, Hg, Cd, etc., are released into a combustion environment, as during the burning of biomass. Specially designed reactors have been built and coupled to a molecular-beam, mass spectrometer (MBMS). The latter has seen virtually no use in this field and yet allows the possibility of identifying and quantifying the presence of reactive intermediate species hereto immeasurable. Experience and results from this novel technique will be presented along with the models developed.

## WASTE AND BIOMASS COMBUSTION

Technologies for combusting waste and biomass have existed for centuries and are today, to a large extent, in use in the Swedish district heating system. It was the oil crisis in the 1970s that initiated the desire to find a domestic source of energy and caused the ideas of implementing waste and biomass combustion to begin to grow. District heating contributes about 44 % [1] of the Swedish heat market and 17 % [2] of the total energy production arises from combustion of biomass. Even so, the dependency upon fossil fuels is still high, which is a problem since world reserves are limited. Additionally, fossil fuels are harmful for the environment and Europe is struggling to develop technologies for reducing CO<sub>2</sub> emissions. As a partial solution to this, in February 2003, Tony Blair and Göran Persson pledged to double the use of renewable energy sources in the European Union by 2010, so that 12% of electricity production comes from renewable sources [3]. Sweden has also made it a goal to replace nuclear power by increasing the usage of domestic biomass, within an intermediate time period.

While the politicians make grand statements about converting from fossil fuels to renewable energy sources, experience in the last 20 years has shown that switching from fossil fuels to using biomass and waste as fuels introduces some significant challenges which must be overcome. Table 1 shows the typical compositions of biomass and waste, and close inspection reveals the problems. First is the high content of volatile matter. As Table 1 shows, a typical biomass contains up to 70% volatile matter. By way of comparison, even a poor, low rank coal does not contain more than 30% volatiles and for a good anthracite, the figure will be as low as a couple of percent. The high volatility may be considered as a positive property (high reactivity) if the combustion technology is adjusted/optimized for these fuels. However, use in existing appliances and plants may result in severe problems. Volatile species are released quickly as a fuel heats up, in the early stages of its combustion, easily creating a fuel-rich cloud, which, if not quickly oxidized, produces significant amounts of heavy tars and soot, especially in small residential appliances. Additionally, if one is trying to use older, fossil fuel furnaces, the large amount of volatiles is likely to lead to combustion being displaced from where it was originally designed to be and, when they represent 70% of the mass of the fuel, it can be said that a significant part of the combustion is occurring in the "wrong" place, affecting the thermal efficiency of the boiler. Traditional technologies for biomass and waste combustion have involved direct oxidation to CO<sub>2</sub> and H<sub>2</sub>O, with the challenge being to ensure sufficient local oxygen supply. With the latter in mind, fixed bed systems were replaced by moving or vibrating grid furnaces: the constant motion of the solid particles assisted the heat and mass transfer. In the latter part of the 20<sup>th</sup> century, the fluidised bed (either bubbling or circulating) was developed; again with idea that the greatly improved heat and mass transfer would increase combustion and heat transfer efficiency. All of these, however, are sensitive to variations in the volatile content of the fuel.

Table 1: The composition of a typical biomass

	<b>Biomass</b> <sup>[4]</sup> [%]		<b>Biomass</b> [%]
Volatiles	70	MgO	0.012-0.177
Fixed Carbon	16	P <sub>2</sub> O <sub>5</sub>	0.012-0.360
Ash	0.5	Na <sub>2</sub> O	0.005-2.064
Moisture	10	K <sub>2</sub> O	0.104-3.049
Heating value [kJ/kg d.a.s.]	20000	<b>Trace elements and heavy metals</b> <sup>[6]</sup> [% d.a.s.]	
<b>Elements</b> [%]		Be	< 0.2
C	51	Cd	0.4-2.2
H	5	Cr	2.2-9.6
N	0.9	Co	< 0.4
S	0	Cu <sup>[7]</sup>	> 0.0062
O	42	Pb	0.01-0.15
Cl	0.01-2	Mn	0.005-0.02
<b>Ash forming elements</b> <sup>[5]</sup> [%, d.a.s]		Hg	0.1-0.44
SiO <sub>2</sub>	0.464 - 5	Ni	0.9-9
Al <sub>2</sub> O <sub>3</sub>	0.062-0.097	Ag	< 0.4
Fe <sub>2</sub> O <sub>3</sub>	0.058-0.092	Zn <sup>[7]</sup>	> 0.012
CaO	0.155-0.586		

More recent technologies aim to combat the latter problem by separating the combustion into two stages: first pyrolyze the biomass in a limited amount of air (just enough, to produce the required heat to do the pyrolysis), producing a gaseous fuel and a solid char (also combustible). The two can subsequently be burned separately in suitably designed furnaces. A modification of this process can be achieved by introducing steam to the pyrolysis stage, gasifying the biomass, producing what is referred to as syngas (a mixture of CO and H<sub>2</sub>). This can then be used in a Fischer-Tropsch synthesis to produce synthetic, liquid fuels.

The second problem facing biomass combustion and waste incineration (and perhaps the far more significant one), also appears from studying Table 1: biomass and waste can contain significant amounts of Na and K as well as trace elements such as Hg, P, Cu, Cr, As, Cd, Pb, Zn and Cl. Although fossil fuels, especially coal, can also contain inorganic components, such as potassium, there is a difference in how these components are bound within the fuel. With biomass and wastes the inorganic species are generally very loosely bound, organically or as simple salts, which means that they will vaporize as reactive gas components or affect the composition of the ash to a greater extent than the inorganic species in coal [8].

Chlorine, together with the alkali metals, can have a strong influence on the corrosion of boiler surfaces in several ways. Typically boiler tubes are made from Ni/Fe/Cr alloys and these are susceptible to accelerated, direct oxidation by Cl<sub>2</sub>, HCl, NaCl and KCl. Furthermore, the presence of sulphur compounds can lead to molten alkali sulfate corrosion. Finally, metal chlorides may be deposited on boiler tubes. The nature of the problem is best summarized in a stability diagram for Cr/Fe/Ni-O-Cl. An example is given in Fig. 1 for the Cr/Fe/Ni-O-Cl at 727 °C. Figure 1 shows that at low partial pressures of Cl<sub>2</sub> and O<sub>2</sub>, it is the oxides of the metals that will be formed. Oxides are generally very stable, have high melting points and low vapour pressures. As the Cl<sub>2</sub> content increases, however, the metal chlorides are what will be formed and are problematic because, even though they are likely to be solid at furnace surface temperatures, their vapour pressures can be high, leading to vaporization and metal loss. At higher temperatures, the chlorides become molten, causing further problems.

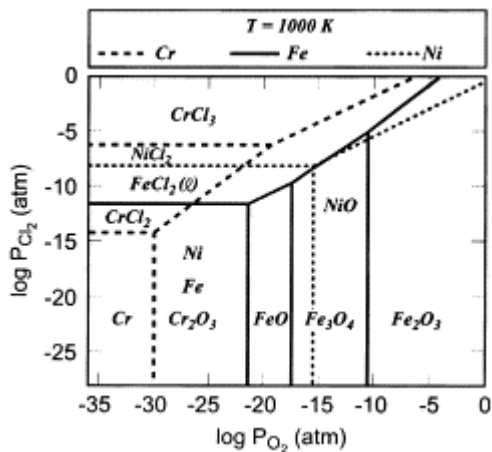


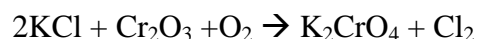
Fig. 2: Stability diagram of Cr/Fe/Ni–O–Cl at 727°C (from [9]).

As introduced above, the corrosion associated with Cl-species can result from gaseous or deposited compounds. Beginning with gaseous attacks on boiler surfaces, the most common culprits are HCl and Cl<sub>2</sub>. Under oxidizing conditions, if chlorine-species are absent, metal oxides form on the surface of boiler tubes. The oxides hinder further transfer of oxygen into the metal and the rate of oxidation is greatly reduced. Chlorine, however, can diffuse through the oxide layer to reach the metal surface below where it reacts to form chlorides, which diffuse outwards through the oxide layer. As they do so, however, the partial pressure of O<sub>2</sub> rises and, as shown in Fig. 1, the likelihood that they are oxidized increases. The difference, though, is that an oxide layer formed in this manner flakes off easily and does not protect the surface. During the cycle, the Cl<sub>2</sub> is released again and hence it becomes a catalytic cycle:



Under reducing conditions, the oxide layer on the metal surfaces will likely be non-existent and hence metal chlorides can form directly and subsequently vapourize.

Apart from the direct attack by chlorine-species, solid-phase reactions involving Cl-species in deposits also occur. Lead and zinc chlorides play a major role during waste combustion while potassium and sodium chlorides are the key species during biomass combustion. These species cause significant corrosion, even well below their melting points. The exact mechanisms are not clearly understood, but the two most common theories are (1) that high partial pressures of Cl are formed at the interface between the deposit and the metal, resulting in a mechanism similar to the direct gaseous oxidation described above and (2) that the chlorides form low-temperature melting eutectics which can flux the oxide layer. The high partial pressures of Cl that are formed in theory (1) when the alkali chlorides react with the metal oxide to release Cl<sub>2</sub>:



The formation of eutectics, as in theory (2), results in molten Cl-species allowing faster reactions, purely because of the liquid phase and also the liquid acts as an electrolyte for electrochemical attack.

Various solutions to these chlorine corrosion problems have been proposed, however, they generally involve mixing fuels or adding inexpensive additives in order to modify the

melting and condensation temperatures and the speciation of the gaseous species. Generally, extensive testing must be completed before these solutions can be judged reliable and, as such, they are not practical in the long run. At this point, solutions to these problems, which will allow biomass to be used sustainably, can only come from increased knowledge of the underlying chemistry involving Na, K and the trace elements under combustion conditions so that detailed chemical models can be built that allow the chemistry of chlorinated species to be predicted. A study of the literature reveals that surprisingly little information about even the basic gas-phase reactions is available.

The gas-phase combustion chemistry of light hydrocarbons is well described by chemical mechanisms from *e.g.* Bendsten *et al.* [10] or GRI [11]. Furthermore, the coupling with chlorine chemistry can be achieved with confidence using the additional reactions of, *e.g.*, references [12-14]. Recent tests conducted by Bolyos *et al.* [15] indicate that, for conditions typical for biomass combustion, the combination of the Bendsten *et al.* [10] mechanism with Roesler *et al.* [13] yields the most reliable results.

Beyond the "simple" case of combustion in the presence of chlorine, *i.e.* combustion including the presence of alkali and heavy metals, there has been relatively little published. There is a small amount of work available presenting chemical mechanisms for combustion temperatures involving sodium, oxygen and chlorine [16-20] with only one [19] giving a detailed chemical mechanism. The rest present some limited experimental measurements of a more global nature, not sufficient for extracting information on the elementary, chemical reactions that are occurring. For potassium, the number of papers is even more limited with virtually no specific reactions. Iisa and Lu [21] present some measurements and a global reaction mechanism. However, the latter is fraught with the usual problem of limited applicability. For the heavy metals, the detailed chemistry is mainly limited to mercury [22-24]. It is difficult to find anything for lead, zinc and other elements. The conclusion is that there has been relatively little published on the basic, detailed, gas-phase chemistry of the alkali and heavy metals found commonly in biomass and waste fuels in the presence of chlorine and sulphur.

Work is currently underway at Umeå and Linköping Universities to determine and model the elementary, gas-phase, chemical reactions that occur when K, Na, Hg, Cd, *etc.* are released into a combustion environment, as during the burning of biomass or waste. A major reason why little work has been done in this area is that it has been very difficult to measure enough chemical species in order to make precise comments about the details of the chemistry that are occurring. Unique in Sweden, The Thermal Process Chemistry group at Umeå University has acquired a molecular-beam, mass spectrometer (MBMS). Problems with traditional sampling techniques include the fact that either sample lines are required to connect an experimental set-up with the analyser and/or chemical components in the sampled gas must be dissolved in a solvent for subsequent analysis. It is never clear for these techniques what is being measured: reactions are likely to continue within the sample line to some degree and also backmixing will occur between the reactor and the analyser. The MBMS samples directly from a reactor and as such avoids the necessity for sampling lines. Additionally, as the sample enters the MBMS it undergoes a sudden temperature and pressure drop. Essentially, gas is drawn continuously through a fine nozzle (0.2  $\mu\text{m}$  in diameter), forming the beginning of a molecular beam. The rapid expansion of the gas effectively quenches any reactions instantaneously, providing an accurate representation of the composition of the gas at the sampling point. Additionally, the non-equilibrium nature of the jet expansion, together with the formation of the molecular beam allows reactive and condensable species to remain in the gas phase at temperatures far below their condensation point, for long periods of time relative to reaction rates. The MBMS is shown schematically in Fig. 2. A sample from a reactor is sucked through three nozzles, creating a molecular beam,

which enters a mass spectrometer (MS), where the gas is bombarded by electrons, ionising it. Because samples can be taken directly from a reaction and frozen rapidly, it is possible also to capture and detect reactive intermediates, which cannot be measured by other techniques. The MS allows species to be identified by comparing a produced spectrum of response as a function of atomic mass (the bombarding electrons fragment the compounds in the sample and the number and molecular weight of each fragment produced gives an indication of the original compound). To quantify the results, i.e. to measure a concentration, a specific molecular weight is used and the response to a given concentration of the original compound is noted. For stable species (e.g. HCl, O<sub>2</sub>, CH<sub>4</sub> *etc.*) a bottle of calibration gas suffices. For intermediate species, a more complicated process must be used. Taking as an example Cl, a key intermediate species in gas-phase chemistry of the alkali chlorides, one must produce it from a reliable source. HCl is one possibility. HCl in the presence of a small amount of H<sub>2</sub> decomposes to a small amount, producing some Cl. If one does this at a known temperature in a reactor long enough to ensure that equilibrium conditions are met, then the concentration of Cl can be calculated using standard equilibrium techniques (in this case the computer programme FACTSage [25] was used). A check also with a calculation including a detailed HCl chemical mechanism, in order to determine the length of time required for the equilibrium to be reached, showed that it was relatively quick (2 s). However, only a very small amount (< 0.001 %) of the HCl is decomposed at temperatures up to 1300 °C. A similar analysis of Cl<sub>2</sub> decomposition reveals that 80% decomposition to Cl can be achieved if equilibrium is reached, however at 1300 °C, 6 minutes is required: far too long to be practical. The final solution reached was to mix HCl and Cl<sub>2</sub> in He, giving concentrations of 1000 ppm, of each. In this case, an equilibrium concentration of 200 ppm Cl is reached in 100 s at 1300 °C.

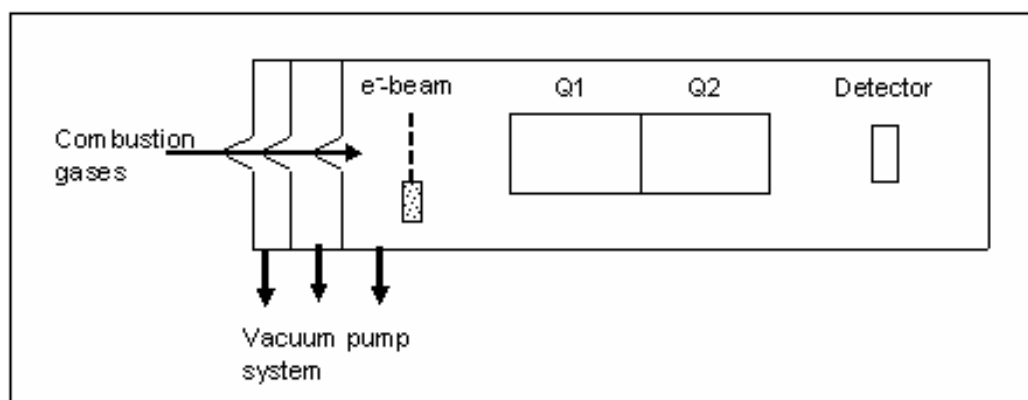


Fig. 2: Schematic diagram of the MBMS

## CONCLUSIONS

- Implementing waste and biomass as fuel in combustion processes to obtain energy and power is a challenge. The challenge being to obtain operational conditions that will sustain the thermal efficiency while limiting corrosion problems. The solution to this challenge starts with increasing the knowledge of the chemistry governing the problematic species, i.e. the alkali metals and trace elements.
- From a political view-point, the potential of waste and biomass is gaining interest, both in response to increasing environmental issues and since it is a domestic fuel.
- So far, no analytical technique has been sufficient for the requirements of measuring inorganic species at elevated temperatures. With the molecular-beam, mass spectrometer combustion species can be measured directly from the hot exhaust gases.

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