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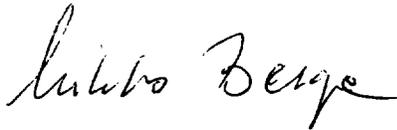
Projekthandläggare på NUTEK: Rolf Ingman

RELEASE OF CHLORINE FROM BIOMASS AT GASIFICATION CONDITIONS

SUMMARY

The objective of the project was to investigate the influence of different gasifying atmospheres on the release of chlorine from biomass during gasification conditions. Furthermore, the purpose was also to try and identify the formed chloro compounds. The results showed that O₂, H₂O and CO₂ had negligible effect on the chlorine release at temperatures under 700°C. At temperatures above 800°C the reactivity towards CO₂ increased and could be seen as higher chlorine release and less solid residue. NO chloro organic compounds (aliphatic one to six carbons or aromatic one to two rings) could be detected in the tar or the fuel gas produced during pyrolysis/gasifying. On the other hand, comparable amounts of chlorinated benzenes were found in the cooling section during combustion of lucerne and of synthetic waste, indicating that oxygen is essential for chlorination reactions.

Approved by:



Introduction

Emission of hydrogen chloride is the third most important contribution, after SO_2 and NO_x , to the global acidification from human activities. The HCl is a local pollutant, contrary to the other two, since it is easily dissolved in rain droplets and, therefore, usually falls down near the emission source. Furthermore, earlier work at Studsvik/TPS together with Umeå University on combustion of waste, have shown that HCl together with different carbon sources are the precursors for dioxin formation (1) and that the formation in the post-combustion zone is a significant contributor (2,3,4). Hydrogen chloride as an agent for high temperature corrosion have been extensively studied for waste combustion.

The increasing interest in using rapid growing biomass crops and straw as fuels for heat and power production, has led to concerns about the content of chlorine and alkali in these fuels. The level of the chlorine content for a biomass fuel varies between <100-7000 mg/kg (5), which can be compared to 50-2000 mg/kg for coal and 200-500 mg/kg for peat (6). The amount of chlorine in biomass is dependent on closeness to the sea, fertilisers and the leaching of the soil by the rain.

Well established theories from the field of combustion of waste is that chlorine are present in the fuel in two different forms, inorganic and organic chlorine. Furthermore, upon combustion or gasification of the waste, the inorganic chlorine will not leave below the melting point of the appropriate salt (around 800°C), while the organic chlorine leave at considerable lower temperatures. The same theories are not applicable on combustion/gasification of biomass, since we have shown that from a mixture of wood and KCl (s) 40% of the chlorine leave already at such low temperatures as 400°C (7), which makes it impossible to separate the bulk of the chlorine from biomass by simple thermal treatment. But anyway, the theories are valid in that respect that the chlorine, upon pyrolysis, will not leave a mixture of sand and KCl (s) at temperatures below 600°C.

Pyrolysing real fuels shows the same tendency that wood-KCl (s) mixture, i.e. the chlorine leaves at considerable lower temperatures than expected. When pyrolysing biomass 50% of the chlorine content evaporated at 300 to 400°C (7) and a coal emitted 90% of its chlorine content between 300 and 600°C (8). The origin of the chlorine in coal is mainly groundwater which has been incorporated in the fuel after the formation, and a smaller amount is from prehistoric vegetation. The main part of the chlorine can be found as chloride ions in the moisture within the pores of the coal particles, and which upon drying will form NaCl (6). In biomass the chlorine are most probably present as an inorganic salt, since 97% of the chlorine in switch grass are extractable in water (7).

To summarise, our earlier results showed that the hypothesis that the main part of the chlorine in biomass is in an inorganic form, and therefore should not vaporise below the melting point of the corresponding salt is too simplified and that the partial release of chlorine already at low temperatures does not make it possible to separate the bulk of the chlorine into either the char residue or to gas products by pyrolysis. In this report we report the results from the extended study in which we tried to identify the gaseous chlorine products and studied the effect of the gasifying media.

Experimental

The pyrolysis experiments were performed in a small fixed bed reactor (2 gr. fuel /test) at a heating of 50°C/min. The sample was kept at the desired final temperature for 30 minutes and thereafter cooled under nitrogen. The fuel was analysed for its chlorine content before and after gasification/pyrolysis.

When analysis of the tar was desired, the tar was collected in acetone in filled impinger bottles and the tar was then analysed with GC-MS.

The combustion experiments were carried out in a fluidised bed, which have been used for investigating dioxin formation from combustion of waste (2,3,4) and with a cooling section with ports for flue gas sampling. The fuel feeding rate was ≈ 1 kg/hour.

Results

The project started with a X-ray study which showed that the location of the chloro (green dots) and the potassium atoms (blue dots) seemed to correlate, but not the silica atoms (yellow dots), see Figure 1. The photo is the same for all figures and is shown in the bottom figure to the right. This indicates that the chlorine in biomass is most probably bonded to potassium in an inorganic salt (KCl).

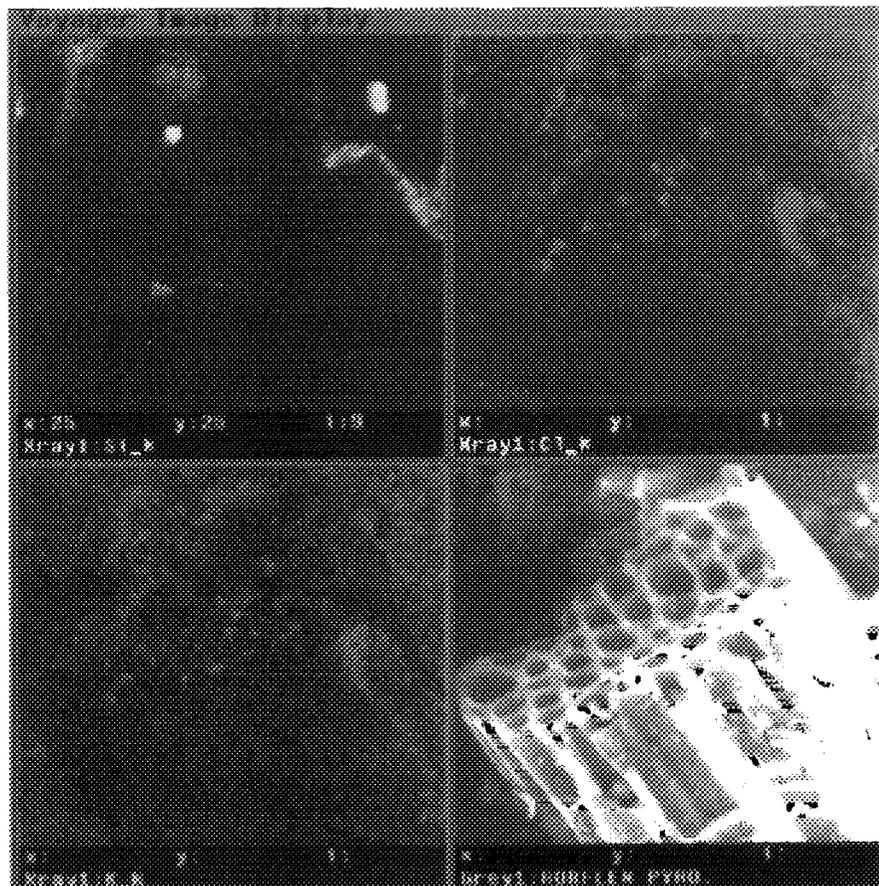


Figure 1. X-ray spectra of switch grass.

1996-10-28

The chlorine release from biomass was not significantly changed by different gasifying atmospheres as can be seen from Figure 2. The only exception was that CO₂ seemed to enhance the chlorine release at higher temperatures. This may be explained by increased gasifying reactivity towards CO₂ at 800°C and above, which is also indicated by the fact that 97% of fuel was consumed when sugar cane trash was gasified in CO₂ (in N₂ approximately 70% had left at 900°C). The tested gasifying media were CO₂, N₂ with 10% H₂O and N₂ with 2% O₂.

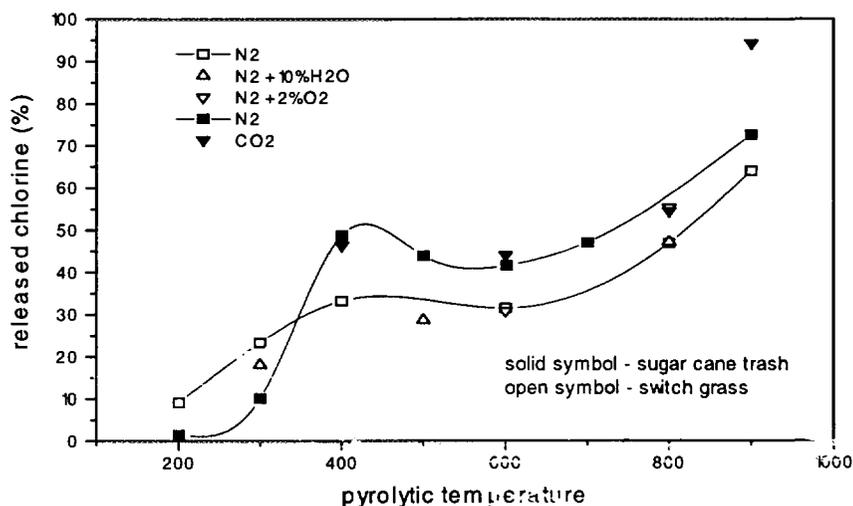


Figure 2 The percentage of released chlorine under different gasifying atmospheres.

We could not find any chloro-organic compounds such as aliphatic (one to six carbons) and aromatic (one to two rings) compounds, in the tar produced during pyrolysis of switch grass and sugar cane trash. The analyses were made by GC-MS, and the pyrolysing temperatures were chosen so that the dioxin formation should be at maximum (9). Nor could we see any influence from the gasifying media on the product composition of the tar, see Figure 3. The main identified compounds are the decomposition products from the lignin in the biomass fuel.

On the other hand, during combustion of biomass, chloro-organic compounds were formed in comparable amounts to that of the combustion of waste, see Table 1 and Figure 4. The experiments were carried out in a fluidised bed, which have been used for investigating dioxin formation from combustion of waste (2,3,4) and with a cooling section with ports for flue gas sampling. The cooling section was chosen since the optimal temperature for the dioxin formation is around 300°C, implying that dioxins are probably formed there. We did not analyse for dioxins but chlorinated benzenes, and have assumed that where there is a lot of chlorinated benzenes there will also be dioxins. Earlier results produced at TPS (9) and the present results are in agreement, and can be summarised as that the formation reactions are probably catalysed by metals in the fly ashes and that the presence of oxygen is very important for dioxin formation. Without oxygen, little or no chlorinated organic compounds are formed.

1996-10-28

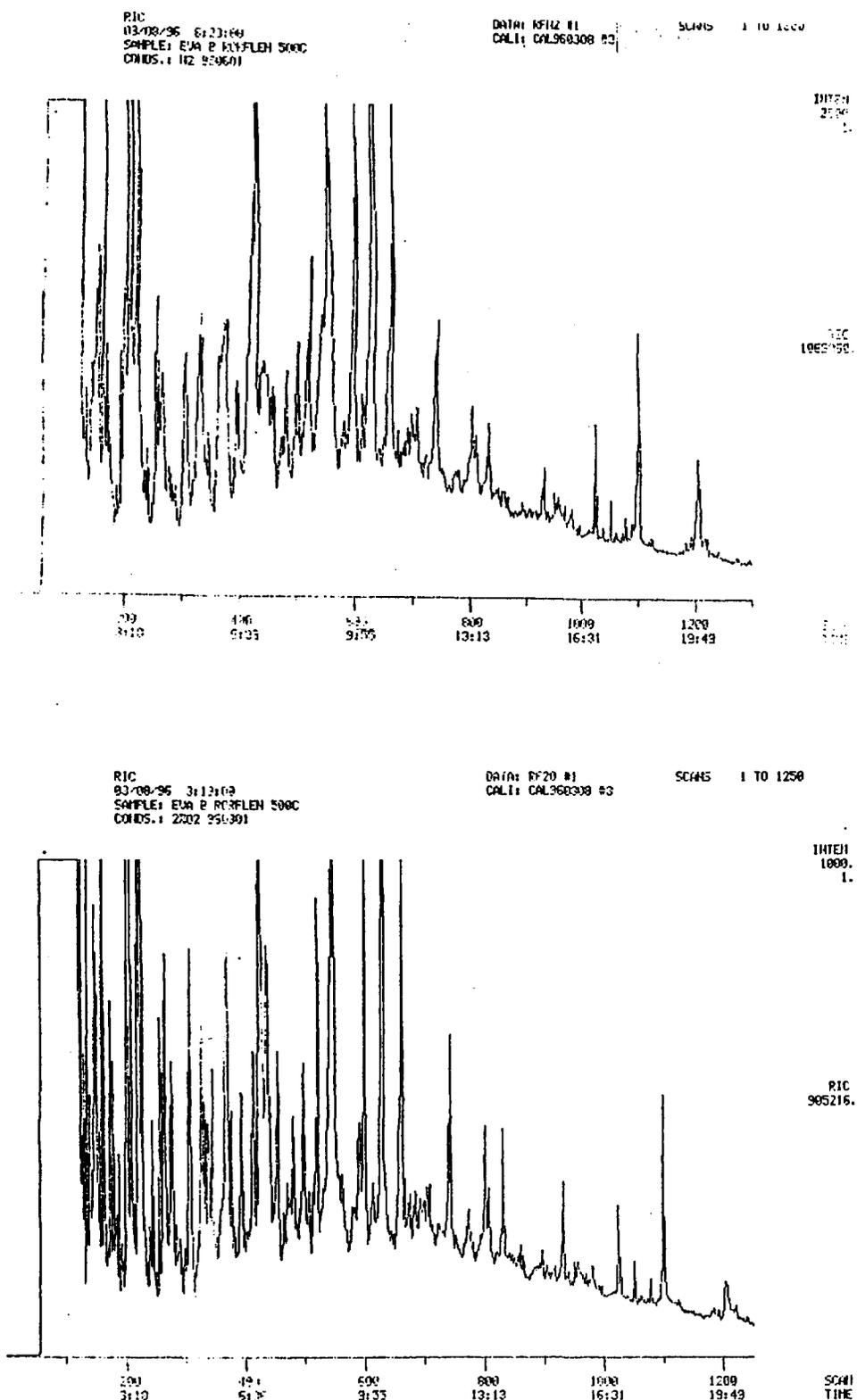


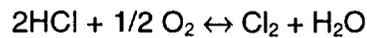
Figure 3 GC-MS chromatograms of the tars produced at different gasifying atmospheres (in the upper diagram N_2 , in the lower 2% O_2 in N_2). For identification of the peaks see reference 10

Further evidence for that the assumption above is too simplified can be found in reference 7.

The gasifying atmosphere is of minor importance for the chlorine release from biomass (Figure 2) and it did not significantly affect the tar composition (Figure 3).

So far we have only discussed results based on the disappearance of chlorine from the fuel, but we have also tried to identify the chloro compounds formed during thermal treatment of biomass. Attempts to measure amounts of HCl failed due to high levels of acetic acid in the product gas which led uncertainty in the analysis.

Since we could not observe any difference in chlorine release between biomass and waste (7), the problem with emissions of dioxins comes naturally. However, no precursors i.e. simply chlorinated organic compounds for dioxins was found in the tar produced when pyrolysing and gasifying biomass (Figure 3). On the other hand, combustion of lucerne produced similar amounts of organic chlorinated compounds as combustion of synthetic waste (Table 1), indicating that oxygen is an essential component in the formation of chlorinated organic compounds. The importance of oxygen may be explained by the theory that Cl_2 is a much more powerful agent for chlorination than HCl and that Cl_2 is formed in the flue gases via the Deacon process reaction from HCl and O_2 , according to:



The importance of fly ashes can be due to the fact that the Deacon process reaction is catalysed by copper (11).

Summarising the results from the total project shows that;

- during pyrolysis the chlorine release starts at 300°C
- there was no significant difference in the chlorine release between biomass and synthetic waste during pyrolysis
- 93% of the chlorine in switch grass was water soluble
- no chloro-organic compounds could be found in the tar produced when pyrolysing switch grass
- chlorine was released from a mixture of wood and KCl(s) but not from sand and KCl(s) at the same temperature
- combustion of biomass may give the same problem with emission of chloro-compounds as the combustion of waste
- the assumption that the inorganic chlorine in biomass does not evaporate below the appropriate melting point of the salt is too simplified
- the partial release of chlorine already at low temperatures does not make it possible to separate the bulk of the chlorine into either the char residue or to gas products by pyrolysis.

Future plans

Chlorine-containing energy crops is a fuel source expected to expand with the increasing demand for no net greenhouse emissions from heat and power production. To optimise those plants from a corrosion point of view and to be able to reduce the emission of chloro-compounds an increased knowledge of the fundamental chloro chemistry in fuel is essential. The main objective for the future is therefore to be able to explain and understand the detailed mechanism for the chloro release reactions. The problems are valid both for combustion and gasification conditions.

In order to achieve the objective we plan for the near future to investigate the influence of pressure on the release of chlorine from biomass, synthetic waste and coal. We will also try to correlate chlorine release with tar and char production, since it is known that chlorine is a chain terminator.

References

- 1 Eklund, G., Pedersen, J., Strömberg, B., *Nature* **320** (1986) 155-156
- 2 Fängmark, I., Strömberg, B., Berge, N., Rappe, C. *Environ. Science & Technology* **28** (1994) 624-629.
- 3 Fängmark, I., Strömberg, B., Berge, N., Rappe, C. *Chemosphere* **29** (1994) 1903-1909
- 4 Fängmark, I., Strömberg, B., Berge, N., Rappe, C. *Waste Management & Research* **13** (1995) 259-272
- 5 Gärdenäs, Vattenfall SV-UB-1991/40
- 6 Sloss, IEACR/45 (1992)
- 7 Björkman, E., Accepted for publication from "Development in Thermochemical Biomass Conversion" Banff, Canada, May 1996.
- 8 Shao, D., Hutchinson, E.J., Cao, H., Pan, W.P., *Energy & Fuels* **8** (1994) 399.
- 9 Strömberg, B., *Chemosphere* **23** (1991) 1515-1525
- 10 Björkman, E., Strömberg, B., TPS-Report, TPS-95/56 (1995)
- 11 Raghunathan, K., Gullett, B.K. *Environ. Sci. Techn.* **30** (1996) 1827



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