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COMBUSTION PROPERTIES OF MAIZE COBS - RESULTS FROM LAB AND PILOT-SCALE TESTS

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ABSTRACT: In order to evaluate the fuel maize cobs regarding its combustion related properties a comprehensive fuel evaluation based on fuel analyses, lab-scale reactor tests as well as combustion trials at a pilot-scale grate-fired biomass combustion plant have been performed. The results and experiences gained from these investigations form an important basis for the development of combustion systems which are tailored to the demands of maize cob combustion. Maize cobs show a significantly lower energy density than wood fuels which has especially to be considered regarding fuel transport and storage as well as regarding the fuel feeding system and the grate design. Especially regarding their comparably high N, S and Cl contents as well as their unfavourable ash melting behaviour maize cobs distinguish themselves from conventional chemically untreated woody biomass fuels. Nevertheless, they could be utilised in the pilot-scale combustion plant at very low CO and OGC as well as acceptable NO_x, HCl and SO_x emissions which indicate that with the exception of HCl most probably no secondary emission control measures are needed for a real-scale plant. Fine PM emissions dominated the total dust emissions and due their high level (90.7 mg/Nm3, dry flue gas and 13 vol% O₂) advanced filter concepts such as ESP or baghouse filters will be needed for PM emission control. Special respect must be regarded to boiler tube deposits since they most probably will contain considerable amounts of KCl thus increasing corrosion risks. Moreover, K-Si-phases in the bottom ash with melting temperatures in the range of 1,050°C were found which underlines the need for an optimised fuel bed temperature control by appropriate combustion air settings as well as flue gas recirculation below the grate in order to avoid severe slagging problems. Summing up, it can be concluded that if all measures proposed in this paper are implemented in a medium sized combustion plant, maize cobs represent an interesting alternative to traditional wood fuels especially for decentralised systems where the fuel is available within short transport distances. Keywords: maize, agricultural residues, combustion

1 INTRODUCTION

Within recent years the utilisation of "new" biomass fuels (e.g. agricultural residues and energy crops) in biomass combustion processes has gained rising relevance. Unfortunately, most of these new biomass fuels are characterised by elevated contents of N, S, Cl as well as ash forming elements. Consequently, compared with the combustion of chemically untreated wood fuels, higher NO_x, HCl and SO₂ emissions as well as more severe ash related problems (aerosol formation, deposit formation, corrosion, slagging) must be expected. Therefore, combustion tests with new biomass fuels represent an important basis for the development and design of combustion systems which are tailored to the demands of these fuels. Within the broad variety of new biomass fuels maize cobs are an interesting material since they are a by-product of maize harvesting and therefore high potentials in many European regions are available. Worldwide, the potential of maize cobs is estimated to 25 billion litres heating oil equivalent per year. Fully utilising this potential for energy production would lead to a CO_2 emission saving of 77 million tons per year [1]. In this respect it is important to mention that maize cobs should be applied locally in decentralised biomass combustion systems since their transport over long distances is cost intensive and due to their low energy density not meaningful.

In order to investigate relevant combustion related characteristics of maize cobs, combustion tests at a labscale reactor as well as at a pilot-scale biomass combustion plant have been performed by the Institute for Process and Particle Engineering, Graz University of Technology (IPPT/TU Graz), in cooperation with BIOS BIOENERGIESYSTEME GmbH and Josef BINDER Maschinenbau und Handelsges.m.b.H.

2 METHODOLOGY

2.1 Lab-scale reactor

At IPPT/TU Graz a special lab-scale batch reactor has been designed in order to investigate the combustion behaviour of biomass fuels in grate-fired combustion systems. From test runs with this reactor information regarding the burnout behaviour of biomass fuels as well as the release of volatile compounds from the fuel during biomass gasification and combustion can be gained and it also provides first indications concerning the ash melting behaviour.

The lab-scale reactor consists of a cylindrical retort (height 35 cm, inner diameter 12 cm) which is heated electrically by two separated PID-controllers. The fuel is put in a cylindrical sample holder. Both parts are made of fibre-reinforced silica carbide (SiC)-ceramics to avoid reactions of CO, NO and ash with the walls and to avoid oxygen entering the reaction zone. The mounting and vessel for the fuel bed are placed on the plate of a scale. The scale is mechanically separated from the retort by a liquid sealing. The scale is used to determine the weight loss of the sample during the gasification and combustion process, respectively. A more detailed description of the lab-scale reactor setup as well as examples for its application can be found in [2].

With this setup it is possible to continuously measure the mass reduction of biomass fuel samples during the gasification/combustion process. The sample (between 100 and 400 g) is introduced into the pre-heated reactor and therefore, a rapid heating, which is well comparable with the one in real-scale thermal conversion processes, can be achieved. The composition of the gases produced can be measured by extraction of gas samples from the retort and application of conventional flue gas analyses (FT-IR, CLD, ND-IR). The initial sample as well as the residues (ashes) are analysed and therefore, also detailed information about the release of inorganic species from the fuel to the gas phase is obtained. Moreover, the visual evaluation of the ashes provides first indications regarding ash sintering and slag formation.

2.2 Pilot-scale combustion plant

The testing plant located at the company Binder (Austria) has specially been designed for the utilisation of dry biomass fuel assortments. It is equipped with a screw feeder, a horizontally moving grate, a partly water cooled and partly insulated furnace consisting of a primary and a secondary combustion zone, a 350 kW fire tube hot water boiler as well as a multi-cyclone for fly ash precipitation. In order to control the combustion temperatures flue gas recirculation below the grate can be applied. However, during the test runs performed the flue gas recirculation was not activated.

In Figure 1 a scheme of the pilot-scale combustion plant is presented. In this scheme also the measurement and sampling ports used during the test runs with maize cobs are denoted (see section 2.3).



Figure 1: Scheme of the pilot-scale combustion plant used and positions of sampling and measurement points <u>Explanations:</u> S ... sampling point, M ... measurement point; PA ... primary air; SA ... secondary air; FG ... flue gas; Rec ... recirculated flue gas; v ... velocity; BLPI ... Berner-type low-pressure impactor; TSP ... total suspended particulate matter

2.3 Performance of test runs, measurements and analyses

During the test runs the combustion plant has been operated with maize cobs right from the start-up. During the first operation phase the process control settings were adjusted to the special needs of maize cob combustion. After stable representative combustion conditions had been achieved, a comprehensive measurement and sampling program was started lasting for the remaining testing period.

Each 2 hours fuel samples were taken and an aggregate sample produced from these samples has been forwarded to analyses regarding the following parameters: bulk density (CEN/TS 15103), moisture content (ÖNORM CEN/TS 14774), ash content (ÖNORM CEN/TS 14775), contents of C, H and N (ÖNORM CEN/TS 15104), Cl (ÖNORM CEN/TS 15289) as well as contents of Ca, Cu, K, Mg, Na, P, Pb, S, Si and Zn (ÖNORM CEN/TS 15290 respectively 15297). Moreover, the gross calorific value (ÖNORM CEN/TS 14918) as well as the ash melting behaviour (ÖNORM CEN/TS 15370-1) have been determined.

At the end of the test run representative samples from the grate ash and from the cyclone fly ash have been taken and analysed regarding the parameters total organic carbon (TOC), total inorganic carbon (TIC) (ÖNORM EN 13137) as well as Ca, Cu, K, Mg, Na, P, Pb, S, Si and Zn (ÖNORM CEN/TS 15290 respectively 15297).

During the whole test run relevant plant operation data such as flue gas temperatures, combustion chamber temperatures, boiler load, combustion air and flue gas flows were recorded and subsequently evaluated. Moreover, the flue gas composition downstream the multi-cyclone was continuously measured using standard flue gas analysers for O2 (paramagnetic sensor), CO (NDIR), NO_x (CLD) and OGC (FID). Gaseous HCl and SO_x emissions have been determined downstream the boiler applying a discontinuous wet chemical absorption method. Also based on discontinuous methods, the total fly ash (TSP) concentrations (method according to VDI 2066) as well as the particle size distributions and concentrations of aerosols (particles <1 µm aerodynamic diameter, measurement with 9-stage Berner-type lowpressure impactors - BLPI) have been determined in the flue gas downstream the multi-cyclone.

The data gained from the test runs have been evaluated focusing on combustion related issues such as emissions, slagging tendencies and general aspects of plant operation. Additionally, mass, energy and element balances over the combustion plant have been calculated to provide a broader basis for the evaluations. Finally the results of the pilot-scale test runs have also been compared with the results of the lab-scale reactor tests in order to gain a detailed overall assessment of the combustion behaviour of maize cobs.

3 RESULTS AND DISCUSSION

3.1 Combustion related characterisation of maize cobs

In Table I the results of the fuel analyses performed with the samples taken during the pilot-scale test run are summarised.

The analyses data clearly show the differences of maize cobs compared to more commonly used wood fuels such as wood chips from softwood. Maize cobs show for instance a lower energy density. Their ash content is higher than the one usually determined for wood chips. Moreover, also the N content as well as the S content are higher while the Cl content is significantly higher (about 10 times compared with wood chips). Regarding the ash forming elements Si and K dominate which is rather typical for agricultural fuels. The high Si and K as well as the comparably low Ca concentrations lead to a fuel ash composition with a rather low sintering temperature of 950°C.

Based on the evaluation of the fuel indexes mentioned in Table I the following general assumptions regarding the combustion behaviour of maize cobs can be made. The low molar 2S/Cl ratio (0.54) indicates a high risk concerning high temperature corrosion while based on the molar ratio of (K+Na)/[3*(2S+Cl)] (0.73) it can be expected that not all S and Cl is bound by the alkali metals thus leading to elevated HCl and SO_x emissions. The molar ratio of Si/K is also comparably low and therefore only a moderate embedding of K in Si-rich bottom ashes is to be expected. Since additionally the sum of aerosol forming elements in the fuel (K+Na+Zn+Pb) is rather high, elevated fine particulate matter emissions have to be expected. Due to the fact that the molar (Si+P+K)/(Ca+Mg) ratio is with 5.37 rather high, low ash melting temperatures have to be expected which is also confirmed by the results of the ash melting test which shows a sintering temperature of 950°C.

Table I: Fuel characterisation of maize cobsExplanations:w.b....wet basis;d.b....dry basis;

moisture content	wt% w.b.	17.56
ash content	wt% d.b.	2.98
С	wt% d.b.	47.14
Н	wt% d.b.	5.86
Ν	wt% d.b.	0.39
S	mg/kg d.b.	338
CI	mg/kg d.b.	1,390
Si	mg/kg d.b.	5,135
Ca	mg/kg d.b.	1,575
Mg	mg/kg d.b.	505
Р	mg/kg d.b.	503
К	mg/kg d.b.	4,820
Na	mg/kg d.b.	199
Zn	mg/kg d.b.	19.50
Pb	mg/kg d.b.	0.51
Cu	mg/kg d.b.	11.83
gross calorific value (GCV)	MJ/kg d.b.	18.90
net calorific value (NCV)	MJ/kg w.b.	14.09
bulk density	kg w.b./m³	132.4
energy density	kWh/m³	518.2
sintering temperature	°C	950
deformation temperature	°C	1,030
hemisphere temperature:	°C	1,100
flow temperature	°C	1,190
fuel indexes		
2S/CI	mol/mol	0.54
(K+Na)/[3*(2S+CI)]	mol/mol	0.73
Si/K	mol/mol	1.48
(Si+P+K)/(Ca+Mg)	mol/mol	5.37
K+Na+Zn+Pb	mg/kg d.b.	5,039

3.2 Plant operation - general aspects

During the test runs the plant has been operated at 70 to 85% of its nominal capacity (350 kW_{th}). The average flue gas temperatures in the secondary combustion zone were in the range of 1,040°C (measured with a suction pyrometer). After a short phase of about 1 hour needed to adjust the control system settings, a stable fuel bed with no optically noticeable problems regarding bed development as well as bed and flame stability could be reached and maintained during the remaining test run period of 6 hours.

Some minor ash sintering as well as the formation of small slag pieces could be observed, however, these phenomena had no noticeable effect on the combustion process. The slag pieces (only some cm in diameter, see Figure 2) did not cause any problems with blocking the primary combustion air flow through the fuel bed and were removed by the de-ashing system. Nevertheless it has to be taken into account that regarding long-term operation the formation of large ash agglomerates and slag pieces can not be generally excluded. Therefore, an advanced air staging concept (low primary air ratios to keep the fuel bed temperatures low) as well as appropriate measures for fuel bed temperature control (e.g. flue gas recirculation below the grate) should be considered for an appropriate real-scale plant design.



Figure 2: Pictures of the fuel applied and different ash fractions

Explanations: upper row: fuel and grate ash; lower row: slag pieces in the bottom ash (left picture, picture width: 10 cm) and cyclone fly ash (right picture)

In Figure 2 images of the fuel, the grate ash, the cyclone fly ash as well as of small slag pieces and mineral impurities found in the grate ashes are presented. That the maize cobs may bare a certain risk for slagging could already be derived from the low ash sintering temperatures (950°C). However, as mentioned above, no negative effects on the combustion process occurred.

From an optical evaluation of the ashes it can be derived that the burnout quality of the grate ash seems to be good (grey colour) while the dark colour of the cyclone fly ash indicates elevated amounts of organic carbon. This is also confirmed by the ash analyses (see Table IV in section 3.5).

The implementation of advanced air staging is a very important prerequisite for a plant operation at low emissions. To gain detailed information about the air staging finally achieved during the test runs, the mass flows of the primary and the secondary combustion air as well as of the flue gas downstream the boiler have been determined by continuously measuring the air respectively flue gas velocities (see Figure 1). In order to check the measurement results, mass and energy balances over the furnace have been calculated by using the O_2 content and temperature of the flue gas downstream the boiler, the results of the load measurements, the fuel composition regarding C, H, ash and moisture content as well as the GCV as input data. The comparison of the measured and calculated mass flow data for the combustion air (primary and secondary air) as well as the flue gas showed only small deviations of less than 8% for the flue gas mass flow and less than 11% for the combustion air mass flow. Since the measured air flow was lower than the balanced one, a small amount of leakage air intake, most likely over the fuel supply and the de-ashing system, are assumed to be the reason for the deviation.

Based on the measured air flow data and oxygen concentrations in the flue gas downstream the boiler, an average overall combustion air ratio (λ_{total}) of 1.74 can be calculated. The average primary combustion air ratio (λ_{prim}) amounted to 0.9. These combustion conditions can be evaluated as acceptable however, regarding the primary air ratio also slightly lower values could be recommended in order to keep the bed temperatures on a low level and to optimally utilise the potential of air staging for NO_x emission reduction.

3.3 Gaseous emissions

A short phase of about 1 hour was needed to adjust the process control settings to the combustion of maize cobs. Afterwards, stable gas phase burnout conditions could be achieved for the remaining testing period. In Table II the results of the flue gas analyses performed downstream the boiler are summarised.

Table II: Results of the flue gas analyses

Explanations: continuous flue gas analyses: mean ... 6 hr. mean value; s ... 6 hr. standard deviation; discontinuous flue gas analyses: mean values and standard deviations of 3 single measurements; all data related to dry flue gas; emissions related to 13 vol% O2; NOx as NO2; SOx as SO2

Continuous flue	das analyses
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			-		
	O ₂	CO	OGC	NO _x	NO ₂
	VOI.%	mg/inm³	mg/inm³	mg/inm³	mg/inm [.]
mean	8.9	15.6	1.3	246.8	5.4
S	1.2	28.2	1.1	38.3	3.0
Discontinuous flue gas analyses SO _x HCI mg/Nm ³ mg/Nm ³					

	mg/Nm³	mg/Nm³
mean	30.0	34.1
S	2.7	3.7

The average O₂ concentrations in the flue gas downstream the multi-cyclone during these 6 hours amounted to 8.9 vol% (dry flue gas), while the CO and OGC emissions were in the range of 15.6 respectively 1.3 mg/Nm³ (related to dry flue gas and 13 vol% O₂). The average NO_x emissions amounted to 246.8 mg/Nm³ (NO_x as NO₂; related to dry flue gas and 13 vol% O₂) and the average NO2 emissions to 5.4 mg/Nm3 (related to dry flue gas and 13 vol% O_2). Thus the share of the NO_2 emissions on the NO_x emissions was in average 2.2% which is in accordance with former experiences from biomass combustion.

As these data show, the plant could be operated with maize cobs at very low CO and OGC emissions. Regarding NO_x the elevated emission levels compared to the combustion of chemically untreated wood chips had to be expected due to the higher N content of maize cobs (0.39 wt% d.b.).

To compare NO_x emissions measured during the combustion of different fuels with different fuel-N contents, the conversion factor of fuel-N into N bound in the NO_x emissions is a suitable parameter. In Figure 3 this conversion factor derived from the test runs is compared with conversion factors gained from other test runs at modern grate-fired combustion plants equipped with air staging technology. Moreover, the fuel-N content is compared with the NO_x emissions. As the diagrams show, the data regarding maize cob combustion generally fit well with the database values. A certain potential regarding NO_x emission reduction exists which could be achieved mainly by an optimisation of the air staging strategy (lower primary air ratio) as well as by geometric optimisations of the furnace geometry to gain a better mixing of the flue gases in the primary combustion zone before secondary air injection. By utilising these emission reduction potentials it should be possible to operate a maize cob combustion plant in the capacity range of up to 10 MW_{th} in most European countries without a need for secondary measures for NO_x emissions reduction (e.g.: SNCR systems). This of course

also depends on national and regional emission limits.



Figure 3: Relation between N content of the fuel and NO_x emissions for different biomass fuels burned in modern fixed-bed combustion systems equipped with air staging technology

Explanations: d.b. ... dry basis; source [3]

The discontinuously measured HCl emissions were in a range of 34.1 mg/Nm³ and the SO₂ emissions amounted to in average 30.0 mg/Nm3 (mean values of 3 single measurements; data related to dry flue gas and 13 vol% O₂). These elevated HCl and SO₂ emissions are also in line with the expectations based on the evaluation of the fuel analyses as well as of the fuel indexes.

3.4 Particulate emissions

In Table III the results of the particulate emission measurements performed downstream the multi-cyclone are presented.

Table III: Results of the PM emission measurements downstream the multi-cyclone

Explanations: TSP ... total suspended particulate matter; PM₁ ... particles smaller 1 µm aerodynamic diameter; mean values and standard deviations of 3 single measurements; all data related to dry flue gas and 13 vol% O2

	TSP mg/Nm³	PM ₁ mg/Nm ³
mean	92.3	90.7
S	5.5	10.6

The particle size distributions and concentrations of fine particulate matter emissions (aerosols) have been determined in the flue gas downstream the multi-cyclone (measurement port M6 in Figure 2) with Berner-type low-pressure impactors (BLPI). 3 single measurements have been performed showing a very good reproducibility. The emissions of the particle size fraction

<1 um (aerodynamic diameter) amounted in average to 90.7 mg/Nm³ (related to dry flue has and 13 vol% O₂) which is a significantly higher value than usually determined during the combustion of chemically untreated softwood or hardwood. These elevated PM1 emissions are due to the increased contents of inorganic aerosol forming species in the maize cobs (mainly K). Figure 4 shows a correlation between the concentrations of the most relevant aerosol forming elements in the fuel (i.e. K, Na, Zn and Pb) with the PM₁ emissions derived from database data as well as a comparison with the current test run results for maize cobs. As it can be seen from the diagram, the data gained from maize cob combustion nicely fit with the general trend of increasing aerosol emissions with increasing contents of aerosol forming elements in the fuel.



Figure 4: Correlation between the concentrations of aerosol forming elements in the fuel (K, Na, Zn, and Pb) and aerosol emissions downstream the boiler <u>Explanations:</u> d.b. ... dry basis; aerosol emissions related to dry flue gas and 13 vol% O_2 ; source for database values: [4]

In Figure 5 the particle size distributions of the aerosol emissions are presented. They show a typical unimodal particle size distribution with a distinct peak located on the second impactor stage (0.125 to 0.25 µm).



Figure 5: Particle size distributions of the fine particulate emissions measured downstream the multi-cyclone <u>Explanations:</u> all data related to dry flue gas and 13 vol% O₂; dp (ae.d.) ... aerodynamic particle diameter

The TSP (total suspended particulate matter) emissions have also been determined downstream the multi-cyclone (measurement port M6 in Figure 2). They amounted to in average 92.3 mg/Nm³ (related to dry flue gas and 13 vol% O₂). A comparison with the aerosol emissions shows that only minor amounts of coarse fly ashes have passed the multi-cyclone (about 2% of the particles are >1 μ m). In the pilot-scale combustion plant used the multi-cyclone is mounted directly downstream

the boiler and consequently it has not been possible to install an appropriate measurement port between boiler outlet and multi-cyclone. Therefore, in order to gain an indication regarding the TSP emissions downstream the boiler, the multi-cyclone ashes have been weighed after the test run and based on these data, the average flue gas flow and the TSP emissions downstream the multicyclone, the dust load in the flue gas at boiler outlet was calculated. A TSP concentration of about 190 mg/Nm³ (related to dry flue gas and 13 vol% O₂) could be determined by that way.

3.5 Ash and aerosol analyses

In Table IV the results of the wet chemical analyses of the grate ash, the cyclone fly ash as well as of an impactor sample (aerosols) are presented.

An appropriate measure for an acceptable charcoal burnout are TOC concentrations below 50.000 mg/kg d.b. (= 5.0 wt% d.b.). As it can be derived from Table IV the grate ash shows an almost complete burnout (TOC <500 mg/kg d.b.) while the cyclone fly ash still contains 11.6 wt% TOC. This insufficient burnout is most probably due to the comparably low temperatures in the secondary combustion zone. As suction pyrometer measurements have shown the temperatures there quickly drop from around 1.050°C after secondary air injection to values around 830°C due to an intensive cooling by the surrounding water cooled furnace walls. The TIC concentrations are, as expected, rather low, since carbonates are not stable at the combustion temperatures prevailing.

Table IV: Results of the wet chemical analyses of the grate ash, the cyclone fly ash and of an aerosol samples <u>Explanations</u>: TOC ... total organic carbon; TIC ... total inorganic carbon; aerosols: analyses of the pooled impactor stages 1 to 4 (particles <1 μ m); d.b. ... dry basis; n.a. ... not analysed

		grate ash	cyclone fly ash	aerosols
S	mg/kg d.b.	1,300	7,010	18,400
CI	mg/kg d.b.	3	45,500	284,000
Si	mg/kg d.b.	267,000	121,000	<10,000
Ca	mg/kg d.b.	61,000	166,000	11,900
Mg	mg/kg d.b.	16,900	14,800	2,900
Р	mg/kg d.b.	11,500	9,390	38,300
К	mg/kg d.b.	92,600	61,200	346,000
Na	mg/kg d.b.	8,990	5,880	14,100
Zn	mg/kg d.b.	44,6	1,150	7,400
Pb	mg/kg d.b.	<30	38,4	n.a.
Cu	mg/kg d.b.	72,6	103	744
TOC	mg/kg d.b.	<500	116,000	n.a.
TIC	mg/kg d.b.	<500	6,000	n.a.

In general the composition of the grate ash reflects the characteristics of the fuel maize cobs. The grate ash is Si-dominated. As expected, the Si contents decrease from the grate over the cyclone fly ash to the aerosol emissions. Ca and P on the other side show higher concentrations in the cyclone fly ash than in the grate ash which indicates that these elements, contrary to silicates, are higher concentrated in small ash particles which can more easily be entrained from the fuel bed with the flue gases. The concentrations of the semivolatile K as well as of the volatile elements S and Cl increase from the grate ash over the cyclone ash to the aerosol emissions which is also a typical behaviour for ash formation in biomass combustion. The same trend also prevails for the easily volatile heavy metal Zn and the semivolatile Cu.

Regarding options for ash utilisation it has to be mentioned that the grate ash is comparably rich in P and K which are essential plant nutrients while the heavy metal concentrations (Zn, Cu and Pb) are very low. Therefore, an utilisation of the ashes as fertilising material on the maize fields is recommended in order to widely close the natural cycles of relevant plant nutrients with the exception of N. For Austrian framework conditions, where this utilisation of ashes from biomass combustion on agricultural soils is regulated by a guideline [5], the ashes from maize combustion are clearly below the limit values for the heavy metal concentrations investigated (Zn, Pb, Cu) and also for other heavy metals, which have not been analysed, no problems are expected. The same also applies for a mixture of the grate ash with the cyclone fly ash.

From the results of mass and energy balances calculated over the combustion plant it has been revealed that 64 wt% of the ashes were found as grate ash, 32 wt% as cyclone fly ash and 4 wt% left the plant as fly ash emissions (mainly aerosol emissions). In Figure 6 element balances for the most relevant ash forming elements as well as for S and Cl, calculated over the combustion process, are summarised. The diagram shows the percentage of each element found in the single fractions (grate ash, cyclone fly ash, aerosol emissions and in case of S and Cl gaseous emissions) related to the input mass flow of the respective element with the fuel. As a measure for the quality of these element balances also the recovery rate for each element was determined. The recovery rate is calculated by dividing all outgoing element flows by the ingoing element flow and for most elements investigated an acceptable closure of these balances (recovery rates in the range between 70 and 130%) could be achieved. Only Si was overbalanced due to the inhomogeneous distribution of Si in the fuel (distribution of mineral impurities) and K was slightly underbalanced which could be due to the fact that K is one of the main elements involved in deposit formation in the boiler and on cooled furnace surfaces.

From Figure 6 it can be derived that the major part of the non volatile elements (Si, Ca, Mg) is mainly found in the grate ash. Also the semivolatile element Na is well embedded in the grate ash which is mainly due to its reactions with silicates (sintered and molten phases). The same is also true for K.



Figure 6: Element flow analyses of ash forming elements <u>Explanations:</u> GA ... grate ash, CFA ... cyclone fly ash; share of the elements in the respective ash fraction and the gaseous emissions in % of the element input flow with the fuel

Based on these data the release of ash forming elements from the fuel to the gas phase can be calculated. As an approximation it can be assumed that the element mass found in the gas phase and in the aerosols downstream the boiler respectively multi-cyclone have been released from the fuel to the gas phase during the combustion process. The most relevant elements concerned are K, Na, S, Cl, Pb und Zn. By dividing their mass flows related to the gas phase and the aerosol fraction by their input mass flow with the fuel a release rate can be calculated. This release rate of course does not consider the portion of these elements which has formed deposits on boiler tubes and cold surfaces in the furnaces, however, due to the comparably small amount of these element losses it is still a good approximation. Based on this method release rates of 18% for K, 8% for Na, 78% for Zn, 86% for S and 93% for Cl can be calculated. These results are in good agreement with the lab-scale reactor tests performed, where release rates of 14% for K, 12% for Na, 98% for Zn, 86 for S and 99% for Cl have been found.

Based on the chemical composition of the aerosols mentioned in Table IV also an estimation of the most relevant compounds in this fraction can be made. This estimate is based on the fact that all S and Cl present in the aerosol fraction is bound to K and Na. If there is a surplus of S and Cl, as it sometimes happens with aerosols from the combustion of chemically treated waste wood assortments, heavy metal chlorides are formed. In the case of maize cob combustion a surplus of alkaline metals exists and therefore, the remaining alkaline metals are most probably bound as carbonates. Heavy metals as well as refractory species are usually present as oxides. Applying this approach on the aerosol compositions from Table IV leads to the result that KCl is with 59.7 wt% the dominating compound in aerosols followed by alkaline metal sulphates (in total 8.9 wt%) and Ca, Mg, P and Si oxides (in total 13 wt%) as well as minor amounts of heavy metal oxides. Carbonaceous aerosols (organic particles and soot) could not be determined, which is, due to the very good burnout quality (low CO and OGC emissions), an expected result.

Regarding boiler tube corrosion it is important to consider that the TSP emissions downstream the boiler consist of about 50% aerosols. Especially the high KCl concentrations in the aerosols are thereby of relevance. At the high temperatures at boiler inlet KCl is still in the gas phase and as soon as the flue gas starts to cool down gas to particle conversion is initiated. This process can either result in the formation of new aerosol particles (nucleation) or in the condensation of KCl on surfaces such as already existing fly ash particles and boiler tube surfaces. Direct condensation of KCl on boiler tube surfaces can thereby cause increased fouling and, especially at high tube surface temperatures, as they prevail in steam boilers, severe corrosion problems. Therefore it is essential to equip a maize cob combustion plant with a well working automated heat exchanger cleaning system, which periodically removes these deposits from the tube surfaces.

Figure 7 shows the results of SEM/EDX analyses of a selected slag piece sampled from the grate ash. From the optical evaluation of the image it can be derived that area 1 represents a molten phase. When plotting the chemical composition of this phase into a ternary melting diagram of the system SiO₂-K₂O-CaO it can be derived that this specific composition shows a melting

temperature of around 1,050°C which is in good agreement with the ash melting tests performed with the ashed fuel (see Table I). However, only a slight increase of the K-concentration in the ashes, which could be caused by variations of the K content of the fuel, leads, according to the phase diagram, to melting temperatures below 1,000°C. Consequently, maize cobs have the potential to cause more severe slagging problems than observed during the test run.



		1	2	3
Mg	wt%	1.5		2.2
Si	wt%	29.9	24.9	15.5
Ca	wt%	2.6	27.1	14.1
Mn	wt%			1.4
Fe	wt%	4.0		22.7
Na	wt%	2.5		
AI	wt%	4.4	1.8	2.3
Ti	wt%			1.4
к	wt%	7.7		
0	wt%	45.8	42.8	39.2

Figure 7: SEM image and results of EDX analyses of a selected slag piece

 $\underline{\text{Explanations:}}$ the compositions in the table are related to the areas marked in the SEM image

4 SUMMARY AND CONCLUSIONS

In order to evaluate the fuel maize cobs regarding its combustion related properties a comprehensive fuel evaluation based on fuel analyses, lab-scale reactor tests as well as on combustion trials in a pilot-scale grate-fired biomass combustion plant have been performed. The results and experiences gained from these investigations form an important basis for the development of combustion systems which are tailored to the demands of maize cobs.

Due to their low bulk density the energy density of maize cobs amounts with 518 kWh/m³ to about 55% of the energy density of wood chips with comparable moisture content. This very low energy density has to be considered regarding fuel transport, fuel storage, design of the fuel feeding system as well as regarding the grate design.

Maize cobs typically show a N content which is

higher than the one of chemically untreated wood chips (comparable with bark) and therefore also increased NO_x emissions have to be expected. Moreover, a high Cl content and a comparably low molar 2S/Cl ratio are typical for this fuel assortment which can lead to problems with high temperature corrosion in case of boiler designs with elevated tube surface temperatures (e.g. steam boilers). Elevated SO₂ and HCl emissions have to be expected since the molar ratio of (K+Na)/[3*(2S+Cl)] is with 0.7 comparably low.

During the pilot-scale test runs the combustion plant has been operated at 70 to 85% of its nominal boiler capacity (350 kW_{th}). The average total excess air ratio amounted to 1.74 while the average primary combustion air ratio was in the range of 0.9 which is an acceptable value for the application of air staging as a primary measure for NO_x emission reduction.

The formation of small slag pieces in the grate ash could be observed which was mainly due to the formation of K and Na-enriched silicates with melting temperatures in the range of 1,050°C. The possible formation of these phases was already expected from the fuel analyses due to the rather high molar (Si+P+K)/(Ca+Mg) ratio. Moreover, the investigation of the fuel ash melting behaviour also indicated a softening temperature of about 950°C. Although this slag formation had no negative impact on the plant performance (no problems with an uneven combustion air distribution over the fuel bed was observed) it may lead to problems during long term operation, especially since slag analyses by SEM/EDX have shown, that only a small increase of the K concentration could significantly lower the ash melting temperatures of the K-Si-phases concerned. Therefore, measures to reduce and control the fuel bed temperatures such as low primary air ratios, flue gas recirculation below the grate and/or cooled furnace sections are strongly recommended.

Regarding gaseous emissions it can be stated that with CO and OGC emissions of in average 15.6 respectively 1.3 mg/Nm³ (dry flue gas, 13 vol% O₂) a very good gas phase burnout could be achieved. The average NO_x emissions amounted to 247 mg/Nm³ (NO_x as NO₂ related to dry flue gas and 13 vol% O_2). Comparisons with database values indicate that a further NO_x emission reduction potential of about 30% could be achieved by the optimised application of primary measures. These primary measures mainly involve an optimisation of the residence time of the flue gases in a reduction zone in the primary combustion chamber. By achieving this aim it should be possible to operate a maize cob combustion plant in the medium-scale capacity range (<10 MW_{th}) in most European countries without the need for secondary measures for NO_x emission control (e.g.: SNCR systems).

As already expected from the evaluation of the wet chemical fuel analyses elevated HCl and SO_x emissions had to be recognised amounting to in average 34 mg/Nm³ respectively 30 mg/Nm³ (related to dry flue gas and 13 vol% O_2). Concerning HCl this could result, depending on the plant capacity and the national/regional emission limits, in a need for secondary measures for emission control such as dry sorption in combination with a baghouse filter. Regarding SO_x emissions no secondary emission control measures are to be expected.

The TSP emissions (downstream the multi-cyclone) were clearly dominated by fine particulate emissions, which amounted to in average 91 mg/Nm³ (dry flue gas

and 13 vol% O_2). Consequently, especially for larger scale applications, the installation of a baghouse filter or an ESP for fine particulate emission control will be necessary.

As analyses have revealed, the aerosols formed are predominantly composed of KCl. This also allows the assumption that the deposit layers formed directly on heat exchanger surfaces will also be dominated by KCl thus increasing the corrosion risk especially in boilers with increased tube surface temperatures (e.g. steam boilers). Consequently, an efficient automated heat exchanger cleaning system should be foreseen. For hot water boilers the return temperatures should be kept as high as possible to avoid H_2SO_4 dew point corrosion.

Analyses of the grate and cyclone fly ashes have shown that these fractions contain comparably high concentrations of plant nutrients such as P and K while their heavy metal concentrations are low. Therefore, by recycling the grate ashes or a mixture of the grate and the cyclone fly ashes to the maize fields, the cycle of relevant plant nutrients (except N) could be almost closed.

Summing up it can be concluded that, if all recommendations stated are considered, maize cobs can be utilised in biomass combustion plants equipped with state-of-the-art components at comparably low emissions. The plant of course has to be tailored to the special demands of this fuel and therefore, combustion in conventional wood chip or pellet combustion systems cannot be recommended. Consequently, maize cobs represent a meaningful option for renewable energy production especially in regions dominated by maize production. However, due to the comparably low energy density of maize cobs long transport distances must definitely be avoided.

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7 LOGO SPACE

