

ADDITIVATION GUIDELINE – HOW TO UTILISE INORGANIC ADDITIVES AS A MEASURE TO IMPROVE COMBUSTION RELATED PROPERTIES OF AGRICULTURAL BIOMASS FUELS

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ABSTRACT: Within a nationally funded Austrian research project an additivition guideline for agricultural biomass fuels has been developed. It aims at the targeted application of inorganic additives to overcome ash related problems (slagging, deposit formation, particulate emissions) usually associated to the combustion of agricultural fuels in fixed-bed combustion units. By the application of this guideline, these fuels shall be made applicable for conventional medium and large-scale wood combustion systems at economically and environmentally sound constraints. Thereby, advanced fuel characterisation tools such as fuel indexes, thermodynamic high temperature equilibrium calculations and lab-scale reactor tests as well as techno-economic considerations have formed the basis for the development of a strategy for the selection of technologically and economically optimised additives and additivition rates with respect to the specific compositions of the agricultural biomass fuels of interest. The strategy has been validated by combustion tests with additivited agricultural fuels at a 180 kW grate-fired combustion plant. The results of these test runs have shown that slagging, aerosol and deposit formation could significantly be reduced by additivition. As a conclusion an additivition guideline has been worked out which shall support interested stakeholders in the targeted and optimised selection of additives for problematic agricultural biomass fuels.

Keywords: combustion, fixed bed, additives, agricultural residues, agropellet, guidelines

1 INTRODUCTION AND OBJECTIVES

The demand for wood fuels for biomass heating and CHP plants is steadily increasing, thus the prices also rise accordingly, which results for more and more plant owners in economic problems. The utilisation of agricultural fuels (straw, Miscanthus, grasses) would be an alternative, however, an application of these fuels in conventional wood combustion plants is not possible due to their problematic chemical compositions (i.e. usually elevated N, S, Cl, alkaline metal and ash contents as well as comparably low ash melting properties) and due to their low energy densities.

Basic research [1-4] has already shown that by mixing straw with some percent of aluminosilicates such as kaolin or with Ca-compounds (CaO, CaCO₃), the ash melting temperatures could be increased by more than 500°C and in case of Kaolin the K-release from the fuel to the gas phase, which plays a dominant role in fine particulate matter and deposit formation, could be significantly reduced. The studies also show that the interactions between additive and fuel need to be carefully and scientifically analysed and considered within an additivition strategy. Exactly at this issue the demand for an additivition guideline comes into play. It shall allow the user to define for a specific fuel the best suitable additive based on a scientifically secured strategy.

Ash related problems, namely slagging, deposit formation as well as fine particulate emissions are the main reasons why agricultural fuels presently cannot be utilised in plants designed for wood combustion. Therefore, the aim of the work presented in this paper was to develop an additivition guideline for agricultural biomass fuels, which shall be applied to improve their combustion related properties in a way that they can be utilised in conventional fixed-bed wood combustion plants. Therefore, latest state-of-the-art biomass fuel characterisation tools should be further improved for an application on fuel/additive mixtures in order to study the interactions of additives and agricultural fuels in detail.

Based on this, an additivition strategy should be developed and validated via test runs at a pilot-scale combustion plant. Considering the results of these test runs as well as economic evaluations, finally an additivition guideline should be created.

Elevated N, S and Cl contents are also typical characteristics of agricultural biomass. Consequently, compared with wood combustion, for NO_x, HCl and SO_x higher emissions have to be expected since these parameters can most probably not be influenced by the utilisation of inorganic additives.

2 METHODOLOGY

2.1 General methodological approach

Within a first step, advanced fuel characterisation tools were further developed in order to characterise agricultural fuels regarding combustion related properties and to study the influence of specific inorganic additives. The advanced fuel characterisation tools applied cover the evaluation of combustion related fuel indexes, high temperature equilibrium calculations as well as the performance and evaluation of dedicated test runs at a specially designed lab-scale reactor. Based on this an additivition strategy has been worked out which was subsequently validated by pilot-scale test runs at a 180 kW grate-fired combustion unit. Finally, based on the evaluation of the test runs as well as on results of techno-economic assessments an additivition guideline has been worked out.

2.2 Chemical fuel analyses

Even if chemical fuel analyses are no advanced fuel characterisation methods they are one key element for the approach chosen since they deliver the basic data for all steps which follow. The chemical compositions of agricultural biomass fuels usually strongly deviate with respect to regional conditions regarding e.g. soil composition, fertilization, climate, rainfall as well as harvesting strategies. Therefore, representative fuel

sampling is a relevant basic issue. The performance of fuel analyses has become a standard business field of numerous laboratories but experience shows significant deviations between results from different laboratories. It is therefore worth to point out, that in order to gain reasonable data only analyses methods developed for biomass fuels shall be applied. Especially for the work presented in this paper, the application of analyses methods, which provide a high level of accuracy, is of relevance [5]. In the following, such analyses methods for relevant parameters are recommended.

The moisture content of fuel samples shall be determined according to EN 14774 (determination of the weight loss during drying at 105°C until a constant weight is reached). Sample preparation shall be done according to EN 14780. The ash content shall be determined according to EN 14775 by determination of the loss of ignition at 550°C. C, H and N contents shall be analyzed according to EN 15104 (combustion and subsequent gas-phase chromatographical separation and measurement in an elemental analyser). The determination of Cl shall be done according to EN 15289 applying a digestion step based on bomb combustion in oxygen and absorption in NaOH (0.05 molar) followed by a measurement by ion chromatography. For the determination of the contents of major and minor ash forming elements (excluding Cl) as well as S a multi-step pressurised digestion with HNO₃(65%)/HF(40%)/H₃BO₃ followed by measurement by inductively coupled plasma optical emission spectroscopy (ICPOES) or inductively coupled plasma mass emission spectroscopy (ICPMS) (depending on detection limits) is recommended.

2.2 Fuel indexes

Fuel indexes are defined in order to provide first qualitative indications regarding relevant combustion related properties of biomass fuels such as the potential for gaseous NO_x, SO_x and HCl emissions, the potential for the formation of fine particulate emissions and boiler tube deposits, high temperature corrosion risks as well as the ash melting behaviour. Thereby the physical behaviour, chemical reaction pathways as well as interactions between different elements respectively groups of elements during combustion are taken into account. Fuel indexes have firstly been developed and applied in coal combustion. It has been shown that these coal combustion indexes are not applicable for biomass combustion, mainly since the embedding of inorganic elements in coal and biomass significantly differs. Consequently, specific indexes, tailored to biomass fuels, have been developed [6].

For the work presented in this paper especially the following two fuel indexes are of major relevance. With an increasing value of the molar ratio of [Si+P+K]/[Ca+Mg+Al] the ash melting temperatures decrease and therefore this index is in the following referred to as "ash melting index". The molar ratio of Cl/Si indicates the K-release behaviour whereas increasing values result in increasing K-release. In the following this index is referred to as K-release index.

Besides these two indexes, also other indexes are of relevance for biomass combustion. The molar 2S/Cl ratio is used to estimate high temperature corrosion risks. While for values >8 no significant corrosion risks prevail, for values <2 severe corrosion risks are to be expected.

Additionally, the molar ratio of [K+Na]/[x*(2S+Cl)] can provide first estimations regarding gaseous HCl and

SO_x emissions since during combustion S and Cl released from the fuel to the gas phase are preferably bound by alkaline metals and therefore with an increasing value of the index an increased embedding of S and Cl in solid phases occurs. The factor x in this index was especially implemented to consider the ratio of the release of S and Cl to the release of K and Na for a certain fuel. In [6] x-values for different biomass fuels based on experimental release data are listed. As a rule of thumb for index values <0.5 elevated HCl and SO_x emissions have to be expected.

2.2 Thermodynamic high temperature equilibrium calculations

Thermodynamic equilibrium calculations (TEC) can be applied for the prediction of multi-phase equilibria and the identification and quantification of the liquid and solid phases, for a multi-component thermodynamic system in a pre-determined gas atmosphere as well as for the theoretical prediction of the characteristic ash melting temperatures. Therefore, the release behaviour of inorganic compounds as well as the ash melting behaviour in biomass combustion/gasification processes can be investigated under the assumption that chemical equilibrium is reached for the system investigated. For the TEC studies presented, the thermochemical software package FactSage 6.2 has been applied which consists of a series of calculation modules as well as databases and uses the image component method in Gibbs free energy minimisation concerning thermodynamic equilibrium. The "solution databases" FToxid (slags and other oxide mixtures) and FTsalt (liquid and solid salt phases) containing the optimized parameters for a wide range of solution phases and the "pure compound" database Fact 53 covering data for over 4,500 stoichiometric compounds have been used. Within the calculations, more than 1,000 components and 9 solutions (which have been shown to be stable and thermodynamically relevant) were considered. Their selection has been done application oriented for biomass fuels and ashes. More detailed information on the model applied is given in [7].

TEC can provide a deeper insight into ash formation processes, the interactions of certain elements as well as the formation of solid, liquid (molten) as well as gaseous phases. Therefore, they are an important tool to study the effects of different additives on ash transformation. However, their results should always be qualitatively evaluated and not quantitatively as it is not sure whether an equilibrium status can be reached and because there are also some weaknesses given in the thermodynamic databases available especially regarding P-chemistry but also to certain extent regarding Si-Al-compounds.

2.3 Lab-scale reactor tests

A purpose-built lab-scale reactor (see Fig.1) for the investigation of the pyrolysis/gasification/combustion behaviour of biomass fuels in packed beds has been applied to gain experimental data regarding the effects of certain additives. It 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 silicon 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 detailed description of the reactor setup, the measurement devices applied as well as the testing protocol is provided in [8]. With this reactor among others quantitative data regarding the release of inorganic elements from the fuel to the gas phase as well as indications regarding the slagging behaviour can be gained. Therefore, based on the lab-reactor results better interpretation of the qualitative results gained from fuel indexes as well as the TEC is possible.

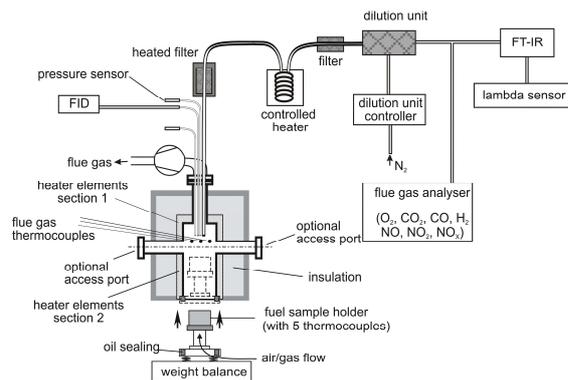


Figure 1: Scheme of the lab-scale reactor, including measurement setup

2.4 Pilot-scale combustion tests

To validate the additivisation strategy developed test runs at a grate-fired pilot-scale combustion plant have been performed. The plant is equipped with a screw feeder, a horizontally moving grate, an insulated furnace consisting of a primary and a secondary combustion zone with separately controllable primary and secondary combustion air supply as well as a fire tube hot water boiler. In order to control the combustion temperatures flue gas recirculation into the primary combustion zone was applied. The nominal plant capacity for the design fuel wood chips with a moisture content of 30 wt% w.b. amounts to 180 kW. To achieve an acceptable burnout of the ashes also for ash rich agricultural fuels the boiler capacity is limited to about 150 kW. In Fig. 2 a scheme of the combustion plant is presented.

Test runs with pure and additivated fuels lasted for at least 8 hours at stable high load conditions. During this period 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 boiler was continuously measured using standard flue gas analysers for O_2 (paramagnetic sensor), CO, NO (NDIR) and OGC (FID). Gaseous HCl and SO_x emissions have been determined downstream the boiler applying a discontinuous wet chemical absorption method. Furthermore, the total fly ash (TSP) concentrations (method according to VDI 2066) as well as the particle size distributions and concentrations of aerosols (particles $<1 \mu m$ aerodynamic diameter, measurement with 9-stage Berner-type low-pressure impactors - BLPI) have been determined discontinuously. Moreover, an air cooled deposit probe was applied in the furnace upstream the boiler to determine deposit formation regarding build-up and characterisation.

During the test runs fuel and ash samples have been collected and subsequently analysed regarding all relevant ash forming elements as well as carbonaceous species.

The data gained from the test runs have been evaluated regarding emissions, slagging tendencies and general aspects of plant operation. Additionally, mass, energy and element balances over the combustion plant have been calculated to evaluate release ratios for ash forming elements.

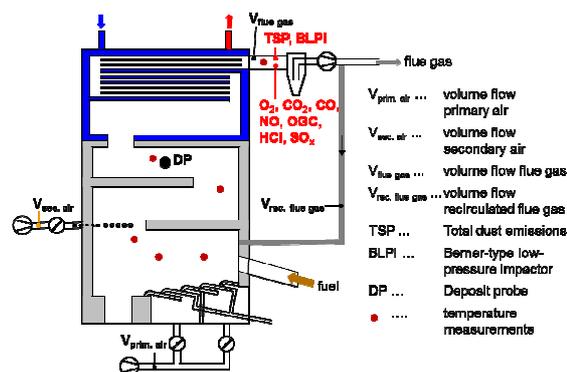


Figure 2: Scheme of the pilot-scale combustion plant and positions of sampling and measurement points

2.5 Techno-economic analyses

Techno-economic analyses were based on an additional costs method. With this method only additional costs arising from the implementation of fuel additives in comparison with basic scenarios are considered. The techno-economic analyses were conducted for pelletised and non-pelletised fuel/additive-mixtures. As a result, the annual additional or saved costs in comparison with the basic scenarios are gained. Wood pellet (according to EN ISO 17225-2-A1) as well as wood chip combustion represent the basic scenarios. The cost categories considered are

- consumption costs: fuel costs including costs for the raw fuel, additive, pelletising, drying and transport as well as costs for ash disposal
- operation costs: costs for additional maintenance work due to the increased ash contents of additivated agricultural fuels
- capital costs: additional costs for adaptations of the de-ashing system

3. ADVANCED FUEL CHARACTERISATION AS WELL AS IDENTIFICATION OF SUITABLE ADDITIVES AND ADDITIVATION RATES

Several agricultural biomass fuels have been screened and the advanced fuel characterisation tools mentioned have been applied to evaluate combustion related problems associated to these fuels. Three fuels, maize residues as well as wheat and rape straw have been selected for the further investigations. In Table I the chemical compositions of samples from these three assortments as well as values of selected fuel indexes are presented.

In comparison with conventional wood chips all three fuels distinguish themselves by elevated N, S, Cl and ash contents. The ash compositions, which can be estimated

from the fuel composition, indicate for maize residues and wheat straw K and Si dominated systems while rape straw ashes are rich in Ca and K.

Table I: Chemical compositions as well as relevant fuel indexes

Explanations: w.b. ... wet basis; d.b. ... dry basis

		maize residues	wheat straw	rape straw
moisture	wt% w.b.	8.5	7.9	11.0
ash content	wt% d.b.	2.1	6.5	7.9
C	wt% d.b.	47.2	45.0	43.9
H	wt% d.b.	6.2	5.8	5.9
N	wt% d.b.	0.5	0.5	0.4
S	mg/kg d.b.	475	926	3,420
Cl	mg/kg d.b.	1,870	1,730	6,790
Si	mg/kg d.b.	1,890	19,000	3,260
Ca	mg/kg d.b.	540	2,920	13,100
Mg	mg/kg d.b.	578	978	1,830
K	mg/kg d.b.	7,180	7,990	18,200
Na	mg/kg d.b.	42	84	956
P	mg/kg d.b.	774	510	650
Al	mg/kg d.b.	219	388	671
Fe	mg/kg d.b.	239	202	360
Mn	mg/kg d.b.	14	29	22
Zn	mg/kg d.b.	29	10	7
(Si+P+K)/ (Ca+Mg+Al)	mole/mole	6.08	7.04	1.41
Cl/Si	mole/mole	0.78	0.07	1.65
x	-	3.45	4.43	0.95
[K+Na]/ [x*(2S+Cl)]	mole/mole	0.65	0.44	0.84
2S/Cl	mole/mole	0.56	1.18	1.11

For an increasing value of the ash melting index decreasing ash melting temperatures are expected. Consequently, the high values for maize residues and wheat straw indicate very low melting temperatures. This can also be derived from Fig. 3, where the ash melting index and shrinkage starting temperatures determined with the standard ash melting test according to CEN/TS 15370-1 of the fuels investigated are compared with database values for herbaceous fuels and chemically untreated wood fuels. The very high K content of rape straw leads to an unexpectedly low shrinkage starting temperature, however, the next characteristic ash melting temperature, the deformation temperature, is with 900°C at the lower level of the database values for the other fuels in this index range.

The interpretation of the K-release index relies on the fact that high Cl contents support the release of K to the gas phase while high Si contents favor the embedding of K in K-silicates, thus with increasing index value also the release increases. Consequently, for maize residues elevated and for rape straw very high formation of particulate emissions as well as of boiler tube deposits have to be expected.

Moreover, it has to be noted that the low molar 2S/Cl ratios indicate high potential for high temperature Cl corrosion. Regarding gaseous HCl and SO₂ emissions especially for wheat straw increased values have to be expected.

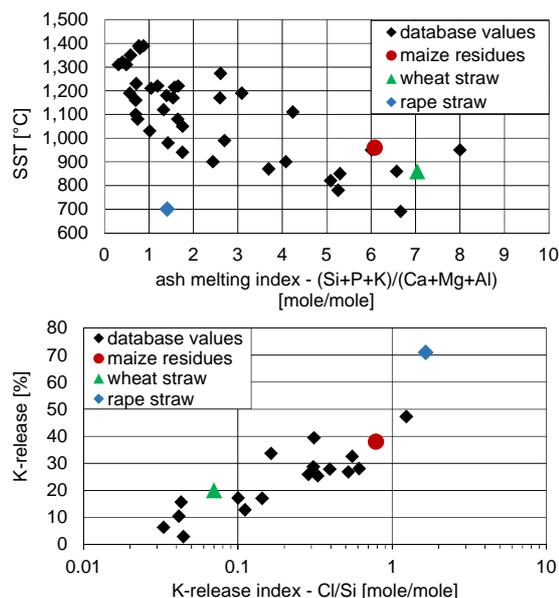


Figure 3: Qualitative evaluation of maize residues, wheat straw and rape straw based on the ash melting index and the K-release index

Explanations: SST ... shrinkage starting temperature according to CEN/TS 15370-1; database values taken from the biomass fuel database of BIOS BIOENERGIESYSTEME GmbH

According to the evaluation of fuel indexes, the following priorities regarding the definition of appropriate additives have been defined:

- Maize residues: main objective: to increase the ash melting temperatures; secondary objective: to further reduce the K-release.
- Wheat straw: main objective: to increase the ash melting temperatures and to reduce the K-release.
- Rape straw: main objective: to reduce K-release while not decreasing the ash melting temperatures.

In the following different options regarding additives and their impact on ash melting behaviour and K-release have been studied. In Table II some potential additives as well as their chemical compositions are listed.

Table II: Potential additives and their main constituents
Explanations: all data in wt% dry basis; n.d. ... no data available; data source: additive suppliers resp. in case of coal fly ashes own analyses (sample from a hard coal combustion plant)

Additiv	Si	K	Ca	Mg	Al
Kaolin	215,000	8,720	450	650	206,170
Bentonite	274,220	6,560	23,240	22,160	97,960
Bauxite	30,060	170	290	240	301,960
Limestone	1,870	n.d.	393,280	2,900	530
Dolomite	13,790	420	219,480	125,300	3,710
Coal fly ash	217,850	17,430	50,040	11,460	128,640

It is expected that aluminosilicates such as bentonite, kaolin as well as fly ashes from coal combustion increase the ash melting temperatures and foster the embedding of K in these solid phases. Ca-containing additives such as limestone or dolomite are also expected to increase ash melting temperatures. Therefore, the compositions of different mixtures of the fuels of interest with different additives have been determined by mixing calculations and the resulting mixtures have been evaluated applying again the ash melting index and the K-release index. As target values for appropriate additivation 2.5 for the ash melting index and 0.1 for the K-release index were defined. In addition, the upper additivation range was limited by the constraint, that the fuel/additive mixture should not exceed an ash content of 10 wt% d.b., which is an acceptable maximum value for conventional wood combustion systems.

Based on these evaluations, for maize residues bentonite, for wheat straw kaolin or dolomite and for rape straw bentonite as well as coal fly ash have been found as suitable additives.

To investigate the effects of different additives in detail, TEC have been performed. As an example for these calculations Fig. 4 and Fig 5 show results for wheat straw as well as mixtures of wheat straw with kaolin and dolomite (4 wt% additive in the mixture).

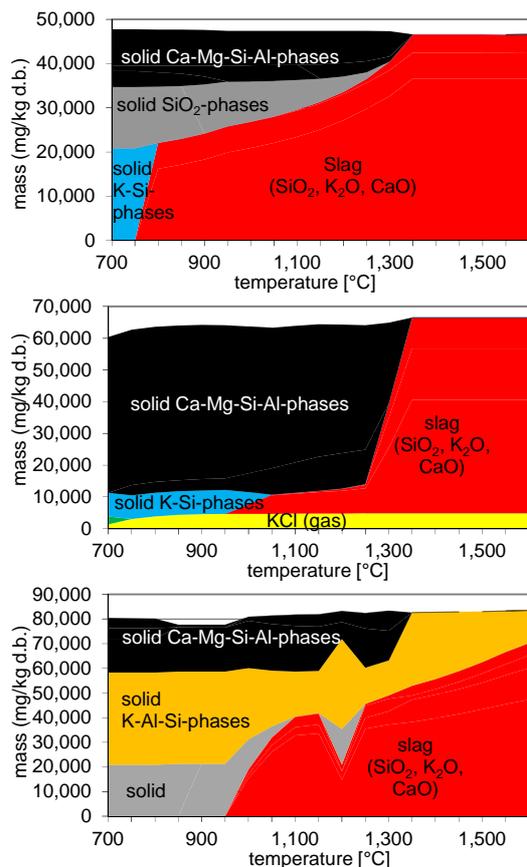


Figure 4: The effects of dolomite and kaolin addition to wheat straw on ash and slag formation – results from TEC

Explanations: from top to bottom: wheat straw, mixture of wheat straw with 4 wt% dolomite, mixture of wheat straw with 4% kaolin

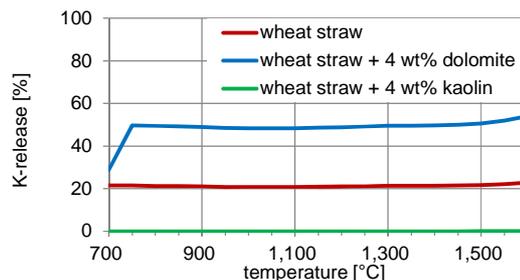


Figure 5: The effects of dolomite and kaolin addition to wheat straw on K-release – results from TEC

From the top diagram in Fig. 4, it can be revealed that at temperatures above 750°C an abrupt transformation of solid K-Si-Phases into slags takes place. With further increasing temperatures, these phases become more and more dominant. It has been found that the temperature at which TEC show that 30% of the ashes are molten (T_{30}), usually corresponds with the shrinkage starting temperature (SST) according to the CEN/TS 15370-1 ash melting test [7]. This is also confirmed by the data presented in Fig. 4, where for wheat straw a T_{30} of 786°C (SST: 790°C) could be identified. About 20 wt% of the K in the fuel is expected to be released to the gas phase (see Fig. 5).

When adding dolomite, the ash chemistry shifts into a more Ca-dominated system. The T_{30} increases due to the preferred formation of Ca-Si-Mg-Al-phases to 1,266°C. However, the less pronounced formation of K in K-silicates in this case leads to a substantial formation of gaseous KCl and thus increases the K-release to about 50 wt%. (see Fig. 5).

Also for kaolin addition an increase of the ash melting temperatures to 1,026°C (T_{30}) can be observed which is due to the formation K-aluminosilicates that melt at higher temperatures than K-silicates. The increase in melting temperatures is not that pronounced as with dolomite, but due to the embedding of K in the aluminosilicates, the K-release is significantly reduced in comparison to dolomite addition.

Based on the results of the evaluation of fuel indexes as well as the TEC, the following fuel/additive-mixtures have been proposed for lab-scale reactor test runs to gain quantitative experimental data, especially on the K-release:

- Maize residues / bentonite (6 wt% bentonite)
- Wheat straw / kaolin (4 wt% additive)
- Wheat straw / dolomite (4 wt% dolomite)
- Rape straw / bentonite (4 wt% bentonite)
- Rape straw / mixture of bentonite and fly ash from hardcoal combustion (2 wt% each)

Besides the mixtures also the pure fuels have been tested. For all fuels the aspired reduction of molten ash pieces in the residues from the test runs (ashes) could be observed. Moreover, for maize residues a reduction of the K release from 26 to 8 wt% could be achieved. For rape straw the K-release was reduced from 47 to 24 wt% (with bentonite) respectively 39 wt% (with the mixture of bentonite and coal fly ash). In case of wheat straw, the lab-scale reactor tests confirmed the trend gained from TEC that with dolomite an increase (from 6.3 to 7.2%) and with kaolin a decrease (to 4.0%) of the K-release can be achieved.

Since the lab-scale reactor tests confirmed the additivation strategy, the fuel/additive-mixtures proposed were also applied during pilot-scale test runs to validate

the effects achievable in real-life combustion environment.

4. RESULTS OF PILOT-SCALE TEST RUNS

From the original fuels and the additives pellets were produced at the facilities of Holzforschung Austria (Vienna, AT). Thereby special attention has been paid to achieving an even distribution of the additives. The ash content of the pellets has been used as a measure to identify the mixing quality. Generally, acceptable homogeneity of the different production batches could be achieved. The relative standard deviations calculated from at least 6 samples taken from each production batch amounted to less than 25%.

4.1 Test runs with maize residues

Test runs over a period of 8 hours at stable high-load operation have been performed with pure maize residues as well as a mixture of maize residues containing 6 wt% bentonite. During both test runs, only small amounts of sintered ash agglomerates, which did not disturb the plant operation, were found in the bottom ash. For the test runs with the additivated maize residues, these agglomerates were much more brittle and easy to break, which confirms the increased SST due to additivation as indicated in Fig. 9. During both sessions, a representative average load of 149 kW resp. 148 kW was achieved. The average oxygen content in the flue gas amounted to 7.2 resp. 7.3 vol% (dry flue gas) and with a primary combustion air ratio of 0.84 resp. 0.95 representative air staging could be achieved. The average adiabatic temperature of combustion under consideration of flue gas recirculation was 1,113°C for the pure maize residues and 1,126°C for the fuel-additive mixture. The average CO emissions of <10 mg/Nm³ (related to dry flue gas and 13 vol% O₂) indicate almost complete gas phase burnout. Regarding NO_x emissions (225.2 resp 256.1 mg/Nm³, as NO₂, related to dry flue gas and 13 vol% O₂) no significant differences occurred.

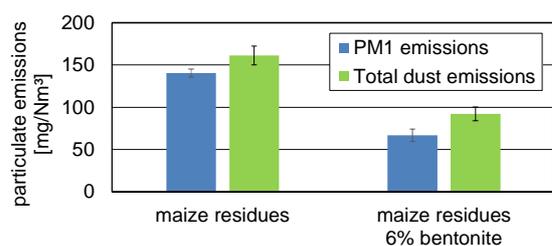


Figure 6: Particulate emissions measured during the test runs with maize residues

Explanations: mean value and standard deviation of at least 3 single measurements; data related to dry flue gas and 13 vol% O₂

The PM₁ emissions decreased from in average 140.4 mg/Nm³ during maize residues combustion to in average 66.8 mg/Nm³ for the utilisation of the additivated maize residues (see Fig. 6). The total dust emissions decreased from 161.2 to 82.1 mg/Nm³ (all data related to dry flue gas and 13 vol% O₂).

Element balances over the plant revealed that the K-release was reduced from 38 to 18 wt% when applying the additive which is the main reason for the decreased

particulate emissions. Due to this decreased K-release also the rates of deposit build-up, measured with a deposit probe, decreased from 39.9 to 22.5 g/m²/h. This is compared with wood fuels (usually <10 g/m²/h) still an elevated value.

While the additive had a positive effect on PM emissions and deposit formation as well as ash sintering, it on the other hand led to increased emissions regarding HCl (from 31.7 mg/Nm³ to 95.3 mg/Nm³) and SO_x (from 26.8 mg/Nm³ to 46.5 mg/Nm³, SO_x as SO₂, related to dry flue gas and 13 vol% O₂). This effect can be explained with the reduced K-release and therefore reduced potential for the formation of solid K-sulphate and K-chloride particles.

4.2 Test runs with wheat straw

Test runs with pure wheat straw as well as mixtures containing 2 and 4 wt% kaolin have been performed. During combustion of wheat straw a plate of sintered and partly molten ashes formed on the grate which at the end of the 8 hours test session covered almost the whole grate. A longer operation of the furnace would therefore not have been possible. Due to this ash plate, only an average load of 113 kW could be achieved. For the mixture with 2 wt% kaolin the situation did not improve significantly and therefore, this test is not discussed in the following. For the mixture with 4 wt% kaolin still the formation of sintered and partly molten ash particles was observed but they were much more porous and easier to break and therefore, also the targeted average plant load of about 150 kW could with 137 kW almost be reached (for related SSTs see Fig. 9). During the two sessions with pure wheat straw and the additivated straw (4% kaolin) the average oxygen content in the flue gas amounted to 7.7 respectively 7.6 vol% (dry flue gas). With a primary combustion air ratio of 0.70 resp. 0.94 representative air staging was achieved. The average adiabatic temperature of combustion under consideration of flue gas recirculation was about 943°C for the pure as well as the additivated wheat straw. The average CO emissions of <5 mg/Nm³ (related to dry flue gas and 13 vol% O₂) indicate almost complete gas phase burnout. Regarding NO_x emissions (275.3 resp 278.5 mg/Nm³, as NO₂, related to dry flue gas and 13 vol% O₂) no relevant differences occurred.

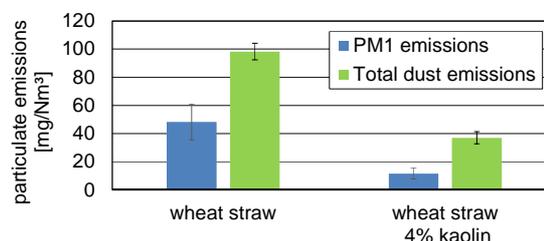


Figure 7: Particulate emissions measured during the test runs with wheat straw

Explanations: mean value and standard deviation of at least 3 single measurements; data related to dry flue gas and 13 vol% O₂

The average PM₁ emissions (see Fig. 7) decreased from 48.2 mg/Nm³ to 11.6 mg/Nm³ for the mixture with 4 wt% kaolin. The total dust emissions decreased from 93.3 to 37.1 mg/Nm³ (all data related to dry flue gas and 13 vol% O₂). Based on element balances over the plant a

reduction of the K-release from 20 to 5 wt% could be determined. Consequently, also the rates of deposit build-up, measured with a deposit probe, decreased from 14.9 to 7.3 g/m²/h.

Also for the wheat straw/kaolin-mixture an increase of the emissions regarding HCl (from 64.7 mg/Nm³ to 97.7 mg/Nm³) and SO_x (from 80.0 mg/Nm³ to 87.7 mg/Nm³, related to dry flue gas and 13 vol% O₂) was noticed.

4.3 Test runs with rape straw

Rape straw as well as mixtures of rape straw with 4 wt% bentonite as well as 2 wt% bentonite and 2 wt% coal fly ash have been tested. Generally, no obvious problems with slagging occurred. During operation with the additivated fuels, most probably due to the higher ash content, the formation of smaller ash agglomerates was observed, however, they had no negative impact on the combustion process. Information on the SST of the pure rape straw and rape straw-additive-mixtures can be taken from Fig. 9. Average plant loads of 144, 152 and 154 kW could be achieved. The average oxygen content in the flue gas amounted to 7.6, 7.5 and 7.1 vol% (dry flue gas) and with primary combustion air ratios of 0.64, 0.47 and 0.63 representative air staging could be achieved for all test runs. The average adiabatic temperature of combustion under consideration of flue gas recirculation was 944°C for the pure rape straw, 866°C for the 4 wt% bentonite additivated rape straw and 1,011°C for the rape straw with a mixture of bentonite and fly ash from hard coal combustion (2 wt% each). For the test run with pure rape straw average CO emissions of 3,370 mg/Nm³ (related to dry flue gas and 13 vol% O₂) were measured while during the test runs with additivated rape straw the average CO emissions decreased to 21 mg/Nm³ resp. <5 mg/Nm³. This result is probably due to the fact, that the low shrinkage starting temperature of rape straw led for pure rape straw to ash sintering, which resulted in channeling effects in the fuel bed and therefore CO strain formation. NO_x emissions are lower for pure rape straw combustion (283.9 compared with 361.4 and 318.0 mg/Nm³, as NO₂, related to dry flue gas and 13 vol% O₂) which is most probably due to NO reducing effects because of the high CO contents in the flue gas.

In terms of K content (see Table I) and K-release (see Fig 3) rape straw represents a worst case regarding fine particulate emissions and deposit formation. Therefore, the extremely high PM₁ emissions of 1,106 mg/Nm³ are no surprise. With additive utilisation they were reduced to 406 mg/Nm³ resp. 419 mg/Nm³ (see Fig. 8). The total dust emissions decreased even more pronounced from 1.437 mg/Nm³ to 513 mg/Nm³ and 521 mg/Nm³ (all data related to dry flue gas and 13 vol% O₂). The high coarse fly ash emissions (= total dust minus PM₁ emissions) of the test runs with the pure rape straw can be explained with channeling in the fuel bed and therefore increased coarse fly ash entrainment.

Based on element balances over the plant a reduction of the K-release from 71 wt% to 28 wt% resp. 29 wt% could be determined. Also the rates of deposit build-up, measured with the deposit probe, decreased from a remarkably high value of 164 g/m²/h to 79 g/m²/h resp. 139 g/m²/h, which are still unacceptably high values. The negative impact of these high deposit build-up rates clearly expressed itself in massive fouling and rapidly increasing flue gas temperatures at boiler outlet of more than 5 °C/hour.

Again, due to the significant reduction of the K-release, strongly increased emissions of HCl (from 63.9 mg/Nm³ to 140.7 resp. 171.6 mg/Nm³) and SO_x (from 33.3 mg/Nm³ to 256.6 resp. 175.3 mg/Nm³, SO_x as SO₂, related to dry flue gas and 13 vol% O₂) were noticed.

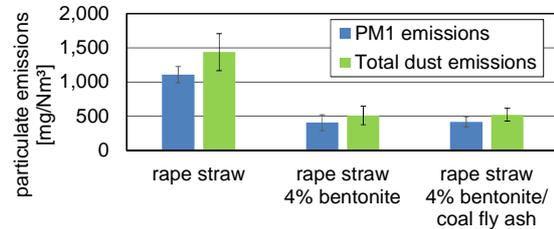


Figure 8: Particulate emissions measured during the test runs with rape straw

Explanations: mean value and standard deviation of at least 3 single measurements; data related to dry flue gas and 13 vol% O₂

4.4 Summary of the evaluation of the pilot-scale test runs

In general, the results of the pilot-scale test runs confirmed the expected effects of additive utilisation. Moreover, they also confirmed the methodological approach chosen.

For all fuels a positive impact of the additives on ash formation could be achieved. Ash agglomerates became more brittle (e.g. in case of maize residues and wheat straw) and in case of wheat straw a long-term plant operation without additive would not have been possible. For rape straw fuel bed channeling could be avoided and thus the CO and total dust emissions were considerably reduced. In Fig. 9 data regarding the pure fuels as well as the fuel/additive-mixtures are shown concerning the relation between melting index and SST. The comparison of the results gained from the test runs with the plot nicely underlines the high value of this fuel index for additive selection.

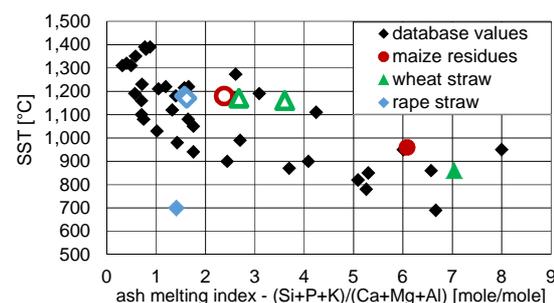


Figure 9: Ash melting temperatures vs. ash melting index for pure and additivated biomass fuels

Explanations: SST ... shrinkage starting temperature according to CEN/TS 15370-1; database values taken from the biomass fuel database of BIOS BIOENERGIESYSTEME GmbH; full symbols: pure fuels; open symbols: additivated fuels

The aim to reduce PM emissions could also be reached with all additives. The reduction is mainly a result of the decreased K-release from the fuel bed to the gas phase. In Fig. 10 the test run data are plotted in the diagram K-release index vs. K-release. Also in this case the applicability of the fuel index as an advanced

characterisation tool for the definition of fuel/additive mixtures is confirmed.

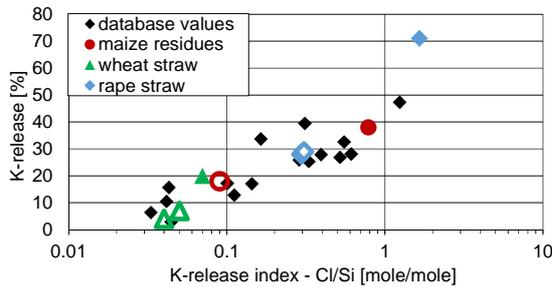


Figure 10: K-release versus K-release index for pure and additivated biomass fuels

Explanations: database values taken from the biomass fuel database of BIOS BIOENERGIESYSTEME GmbH; full symbols: pure fuels; open symbols: additivated fuels

With decreasing K-release also deposit formation could be reduced. In case of maize residues and wheat straw rates of deposit build-up (RBU) close to those usually determined during combustion of chemically untreated wood fuels could be achieved. For rape straw even with additive utilisation strongly elevated RBUs were measured (see Fig. 11).

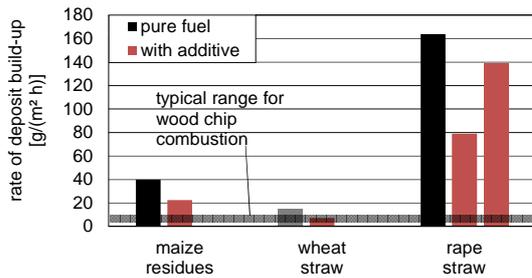


Figure 11: Effect of additivation on deposit formation

The additivation had no negative impact on the CO as well as the NO_x emissions, for rape straw even a significant improvement of the CO emissions could be observed.

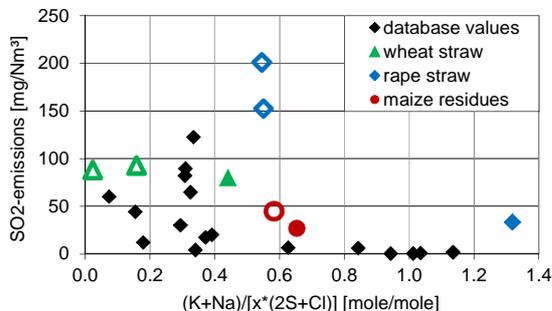


Figure 12: SO_x emissions vs. molar (K+Na)/(x(2S+Cl)) ratio

Explanations: database values taken from the biomass fuel database of BIOS BIOENERGIESYSTEME GmbH; full symbols: pure fuels; open symbols: additivated fuels; SO_x as SO₂, data related to dry flue gas and 13 vol% O₂

Due to the better embedding of K into the grate ashes, less reaction partners for Cl and S during aerosol

formation are available and consequently, gaseous HCl and SO_x emissions increase (Fig. 12). However, the SO₂ emission limit values presently applicable for Austrian conditions (350 mg/Nm³ related to 11 vol% O₂ resp. 280 mg/Nm³ related to 13 vol% O₂) were not exceeded. For HCl no emissions limits for agricultural fuels are defined.

Finally it has to be mentioned that the low molar 2S/Cl ratios (see Table I) were not influenced by the additivation and as expected chemical analyses of deposit probe samples revealed a strong dominance of KCl for all fuels and fuel/additive-mixtures. Therefore, aspects regarding high temperature corrosion have to be considered when utilising these fuels in CHP plants with live-steam temperatures exceeding 450°C.

5 ECONOMIC ASPECTS

In order to investigate the commercial performance of the utilisation of additivated agricultural fuels in a wood combustion plant, economic analyses following the methodology described in section 2.5 and based on Austrian framework conditions have been performed. Wood chips as well as softwood pellets according to EN 17225-2-A1 have been used as reference fuels. Two different scenarios have been considered:

- Production of pelletised additivated agricultural fuels at a pelletisation plant, purchase of the pellets by a plant operator and utilisation in a wood combustion plant. For this scenario, plant capacities of 350 and 2,000 kW_{th} have been considered.
- Direct mixing and utilisation of the chopped agricultural fuels and additives in a 350 kW combustion plant located in the region where the feedstock is harvested.

It has to be pointed out that according to the results of the pilot-scale test runs under Austrian framework conditions no additional secondary measures for emission reduction (emission limits: NO_x 500 mg/Nm³ for plants <1 MW and 400 mg/Nm³ for plants between 1 and 2 MW; SO₂ 350 mg/Nm³, PM 150 mg/Nm³ for plants <0,4 MW and 50 mg/Nm³ for plants between 0,4 and 2 MW; emissions related to dry flue gas, 11 vol% O₂) are needed for additivated maize residues as well as wheat straw. For additivated rape straw, at plant capacities >400 kW an ESP would be needed and for plants >1,000 kW a NO_x emission reduction by secondary measures (e.g. SNCR) is necessary. However, rape straw showed extremely high fouling tendencies, even when additives have been utilised, and cannot be recommended for utilisation. Therefore, in the following the results for maize residues and wheat straw are presented.

Regarding the fuel costs the following data have been applied. The costs for the feedstocks were derived from phone interviews with suppliers as well as from internet reviews. Costs of 80 EUR/ton for wheat straw and maize residues resulted. The additive costs of 345 EUR/ton for kaolin and 370 EUR/ton for bentonite are based on information from suppliers. Fuel transport costs of 20 EUR/ton have been considered. For maize residues additionally drying (due to their compared with wheat straw significantly higher moisture contents) was foreseen (15 EUR/ton). From that, fuel costs of 45.9 EUR/MWh (wheat straw) and 50.7 EUR/MWh (maize residues) resulted. For comparison the related costs for softwood pellets amount to 49.1 and for wood

chips to 35.0 EUR/MWh.

For the calculation of the consumption related costs the following framework conditions have been considered (data based on experience)

- Annual full load operation hours. 3,000 for the 350 kW plant and 4,000 for the 2,000 kW plant.
- Annual utilisation ratio: 85% for both capacity ranges.
- 85% of the ashes are grate ashes and 15% are filter ashes. The costs for ash utilisation/disposal have been considered to be 20 EUR/ton for grate ashes and 70 EUR/ton for filter ashes (average values available from Austrian wood-based heating plants).

Regarding operation costs for additional maintenance work due to the increased ash contents of additivated agricultural fuels 2,000 EUR/year for the 350 kW plant and 6,000 EUR/year for the 2,000 kW plant were considered.

Additional capital costs for adaptations of the de-ashing system were assumed with 5,000 EUR and 10,000 EUR for the 350 kW and the 2,000 kW plant, respectively.

In Table III the results for scenario 1 are summarised. Only in comparison to softwood pellets cost savings could be achieved.

Table III: Additional costs/savings in kEUR/year for the utilisation of additivated pelletised agricultural fuels in wood combustion plants

Explanations: negative values indicate additional costs

	Wheat straw	Maize res.	Wood pellets	Wood chips
350 kW plant				
Total additional costs	60.1	65.8	60.7	43.4
Costs/savings compared to wood chips	-16.8	-22.5	-17.3	
Costs/savings compared to wood pellets	0.5	-5.2		17.3
2,000 kW plant				
Total additional costs	446.0	89.6	462.3	330.3
Costs/savings compared to wood chips	-115.7	-159.3	-132.0	
Costs/savings compared to wood pellets	16.3	-27.3		132.0

Regarding scenario 2 the main differences are:

- Due to the direct utilisation no pelletising is needed and therefore the fuel costs decrease to 23.7 EUR/MWh for additivated wheat straw and 28.9 EUR/MWh for additivated maize residues.
- Additional capital costs of 20,000 EUR have been considered for the adaptation of the fuel feeding system.

In Table IV the results for scenario 2 are summarised which show that wheat straw and maize residues seem to be competitive in comparison to wood chips and wood pellets.

In all cases and scenarios the costs of the feedstock have turned out to be the most relevant influencing factor. The costs for the additives only play a minor role. At present Austrian conditions wheat straw seems to be an interesting alternative in general and maize residues in decentralized applications if no densification is needed. Of course these results always depend on the local

framework conditions given and are thus only indicative. It has to be mentioned that some other influencing factors such as a possible reduction of the plant availability as well as reduced lifetime of plant components due to corrosion problems can only be investigated during long-term operation and have therefore not been considered.

Table IV: Additional costs/savings in kEUR/year for the direct utilisation of additivated agricultural fuels in wood combustion plants

	Wheat straw	Maize res.	Wood pellets	Wood chips
350 kW plant				
Total additional costs	33.8	38.5	60.7	43.3
Costs/savings compared to wood chips	9.5	4.8	-17.4	
Costs/savings compared to wood pellets	26.9	22.2		17.4

6 ADDITIVATION GUIDELINE

Based on the findings and experiences made during the development of the basic strategy regarding additive selection and application, the results of the pilot-scale test runs as well as of the economic evaluation, an additivation guideline has been developed which is briefly summarised in the following. This guideline shall support the evaluation if a specific agricultural feedstock is suitable for additivation and shall provide recommendations regarding the definition of appropriate additives and additivation ratios.

The procedure, which is schematically presented in Fig. 13, is broken down into 6 steps with a number of intermediate evaluations (knock-out criteria).

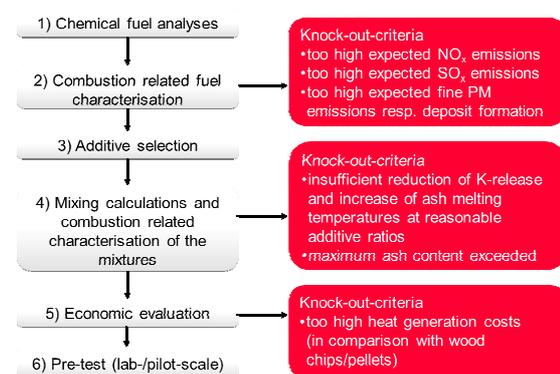


Figure 13: Procedure proposed within the additivation guideline

The first step represents the performance of chemical fuel analyses of the feedstock of interest. Thereby a detailed specification of the assortment, a representative sampling as well as the application of suitable fuel analyses methods (see section 2.1) have to be taken into account.

Step 2 shall then be a combustion related fuel characterisation based on fuel indexes (see section 2.2). Main parameters to be evaluated are the N-content of the fuel (regarding NO_x emissions), the ash melting index, the K-release index as well as the index molar ratio of (K+Na)/(x(2S+Cl)) regarding SO₂ emissions. Hereby the

factor x can be taken from literature [6] or, as a rule of thumb, be estimated from the K-release index. The aim of step 2 is to identify the specific need for additivition and to find out if criteria exist which make the specific feedstock generally not applicable in wood combustion systems. Such criteria would be significantly increased N-contents as well as too high expected SO₂ emissions which demand for the application of secondary emission reduction measures. Moreover, the application of fuels with high K-contents and high K-release index values is not recommended due to problems to be expected with high particulate emissions as well as deposit formation.

Within step 3 additive selection shall take place. Thereby the targets of the additivition must be considered. If mainly ash melting shall be influenced and a certain increase of the K-release can be accepted, Ca-based additives are a feasible option. If both, ash melting behaviour and K-release shall be positively influenced, aluminosilicates are recommended. Especially if additives are residues from other processes (e.g. fly ash from coal combustion), possible deviations in their composition must be considered during the evaluations, too.

Step 4 foresees the performance of mixing calculations based on the fuel analyses (step 1) as well as on the composition of selected additives. Additive composition data usually can be gained from suppliers. Based on the results of these mixing calculations again an evaluation of different mixtures based on the K-release index and the ash melting index shall be performed. During this step it is important to also consider possible variation ranges in fuel composition as they usually occur for agricultural fuels. Moreover, a reasonable compromise has to be achieved regarding the positive effects that can be reached with an additive and the increase of the ash content of the mixture. It is recommended not to exceed an ash content of 10 wt% d.b., otherwise this aspect represents a further knock-out-criterion.

Within step 5 preliminary cost analyses shall be performed. The most relevant cost category thereby are of course the feedstock costs.

Finally, if the steps 1 to 5 have led to positive results, it is recommended to perform test runs with the finally defined additive and additivition ratio in order to gain first practical experiences. Test runs can thereby be performed at lab-scale reactors (if available) or at pilot or real-scale combustion plants.

7 SUMMARY AND CONCLUSIONS

Agricultural fuels are commonly known as “difficult” in terms of ash melting behaviour, deposit formation and particulate emissions. Inorganic additives may provide an opportunity to make these fuels applicable in conventional wood combustion systems.

Therefore, basic research based on the application of advanced fuel characterisation tools such as the interpretation of fuel indexes, thermodynamic high temperature equilibrium calculations as well as lab-scale reactor tests has been performed in order to investigate interactions between agricultural fuels and different additives. Based on these investigations a strategy regarding a fuel composition related definition of suitable additives as well as reasonable mixing ratios has been worked out. Taking wheat straw (additive: kaolin), maize residues (additive: bentonite) and rape straw (additives:

bentonite and coal fly ash) as case studies, this strategy has been validated within pilot-scale combustion tests.

Generally, the results gained from these test runs confirmed the strategic approach chosen for additive selection and additive ratio. It was shown that in all cases slagging could be significantly reduced and that the particulate emissions as well as deposit formation could be reduced by 42% to 64%. No negative impact on CO and NO_x emissions could be observed. The SO₂ and HCl emissions increased when utilising additivited fuels, however, the Austrian limit value for SO₂ emissions could still be kept and HCl is not regulated for standardised biomass fuels. It should generally be mentioned, that the influence of elevated SO_x and HCl emissions on the acid dew point has to be considered regarding acid dew point corrosion in boilers.

Finally, based on the investigations and test runs performed, an additivition guideline has been worked out which shall help the user to identify suitable additives and additive ratios for a specific fuel in order to make this fuel suitable for combustion in conventional wood combustion plants with minor adaptations.

Economic evaluations revealed that the feedstock costs as well as the costs for pelletising are the most relevant parameters regarding the commercial performance of the utilisation of additivited agricultural fuels in slightly adapted wood combustion plants. Under current Austrian conditions, pelletised additivited wheat straw shows significant advantages compared with wood pellets. The direct application (without densification) of additivited wheat straw as well as of maize residues also results in savings compared with wood chips. In future, with the activation of further low-cost agricultural feedstock potentials and the development of a market for additivited agricultural fuels a better economic performance also for densified (pelletised) additivited agricultural fuels can be expected.

6 REFERENCES

- [1] L. Bäfver, M. Rönnbäck, Proceedings of the Central European Biomass Conference, 26-29 January 2011, Graz, Austria
- [2] L. Bäfver, M. Rönnbäck, B. Leckner, F. Claesson, C. Tullin, Fuel Processing Technology, 2009, 90 pp 353-359
- [3] S. Xiong, J. Burvall, H. Örborg, G. Kalen, M. Thyrel, M. Öhman, D. Boström, Energy and Fuels, 2008, 22 pp 3465-3470
- [4] M. Öhman, H. Hedman, D. Boström, A. Nordin, Energy and Fuels, 2004; 18 pp 1370-1376
- [5] G. Bärnthaler, M. Zischka, C. Haroldson, I. Obernberger, Biomass and Bioenergy, 2006, Vol. 30, pp 983-997
- [6] P. Sommersacher, T. Brunner, I. Obernberger, Energy&Fuels, 2012, 26 (1), p p 380-390
- [7] N. Ević, T. Brunner, I. Obernberger, 2012: Proceedings of the 20th European Biomass Conference & Exhibition, June 2012, Milano, Italy, 2012, pp 807-813; ISBN: 978-88-89407-54-7
- [8] T. Brunner, F. Biedermann, W. Kanzian, N. Ević, I. Obernberger, Energy Fuels, 2013, 27 (10), pp 5691–5698

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9 LOGO SPACE

