

Advanced biomass fuel characterisation methods and their application for creating designer fuels

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Abstract

The utilisation of fuel additives such as Ca- or clay-based minerals offers the opportunity to produce designer fuels with improved combustion properties which is especially of relevance for difficult to burn fuels such as agricultural residues. Thereby mainly the ash melting as well as the K-release behaviour can be positively influenced. In this paper a systematic and targeted 3-step approach for the creation of such designer fuels is presented. First, by the application of fuel indexes which are formed based on chemical analyses of the fuel of interest as well as of possible mixtures of this fuel with different additives, a qualitative combustion related fuel evaluation and pre-selection of suitable additives is done. Then, within a second step, thermodynamic equilibrium calculations (TEC) are applied in order to gain deeper insights into ash transformation processes. Based on TEC it is possible to identify relevant fuel specific mechanisms responsible for ash melting and to evaluate the expected influence of additives. Finally, to gain quantitative data on additive ratios and effects of the additive on the combustion behaviour of a certain fuel, lab-scale reactor tests with defined fuel/additive-mixtures resulting from the prior steps are conducted. This systematic 3-step approach presented can generally be applied for improving the ash melting and K-release behaviour of so-called difficult biomass fuels by additives or fuel blending in a targeted and time efficient way. In this paper the application of this method is shown for the case study wheat straw and kaolin as an additive.

Keywords

Biomass combustion, straw, fuel index, lab-scale reactor, emissions, slagging, additives

Introduction and objectives

To widen the available biomass feedstock potential for heat and power production, agricultural biomasses as well as biogenic residues gain rising interest on the fuel market. These feedstocks typically contain increased contents of ash forming elements, S, Cl and N in comparison to wood fuels which makes them more difficult to combust in conventional grate-fired combustion plants. To overcome or reduce these problems fuel pre-treatment (e.g. leaching, torrefication), fuel blending as well as the utilisation of fuel additives are interesting options. Especially regarding ash related problems, i.e. slagging, deposit formation and fine particulate emissions, the utilisation of inorganic additives provides the possibility to create from problematic feedstocks designer fuels with significantly improved combustion properties. Inorganic additives (e.g. Ca or clay-based minerals) are thereby utilised in order to increase ash melting temperatures and to decrease the release of alkaline metals (especially of K) to the gas phase which helps to reduce deposit formation as well as fine particulate emissions [1, 2, 3]. The objective of this paper is to present a systematic approach, how new and advanced fuel characterisation methods can support the targeted creation of such designer fuels for grate-fired combustion plants taking the specific compositions of the biomass fuel of interest as well as of potential inorganic fuel additives and their interactions into consideration.

Methodology

General approach

The general approach relies on three evaluation steps which are performed in sequence. With each step the information depth gained is gradually improved by applying increasingly complex methods. In the following, first the whole evaluation strategy is described and then the different methods applied within the three steps are briefly outlined. Finally an example how to apply this strategy is presented taking wheat straw as a case study. Wheat straw has been chosen since it is a typical representative of "difficult" biomass fuels, whereas the specific problems of pure wheat straw combustion are well known. Therefore, a great potential for improving the fuel quality by the application of appropriate additives is given.

The approach starts with the performance of chemical fuel analyses of the original fuels. Fuel indexes formed from the results of the fuel analyses as well as of calculated mixtures of the fuel and potential additives are then applied in order to gain first estimates how combustion relevant ash related properties can be influenced by the application of different additives. By the evaluation of this first step the number of meaningful additives can be narrowed and reasonable additive/fuel mixing ratios can be identified.

Fuel indexes can provide first trends regarding the influences of additives on ash related issues, however, in order to gain more detailed insights into the problems concerned, thermodynamic equilibrium calculations (TEC) are applied within a second step of the approach. Within this step the information quality especially regarding the influence of different additives on the amounts, compositions and melting temperatures of relevant ash compounds formed as well as on inorganic element release are evaluated and therefore, a better understanding of the underlying mechanisms can be achieved. This again supports the selection of appropriate additives.

With the results gained from step 1 and step 2, appropriate additives to be mixed with the specific fuel can be identified and based on the trends regarding their influence on combustion relevant parameters gained reasonable additive/fuel mixing ratios can be identified. However, the information gained is still qualitative. Therefore, within step 3 test runs with selected fuel/additive mixtures at a specially designed lab-scale reactor shall provide quantitative results in order to finally define suitable additive/fuel ratios.

Step 1 – Fuel sampling, fuel analyses and evaluation of fuel indexes

Agricultural biomasses as well as biogenic residues usually show a wide range of compositions which may strongly deviate with respect to regional conditions regarding e.g. soil composition, fertilisation, climate, rainfall as well as harvesting strategies. Therefore, representative fuel sampling represent a relevant initial issue in biomass fuel characterisation. Chemical analyses of fuels represent then the first

step to provide basic information regarding the biomass composition and the contents of relevant key elements. The performance of such analyses has become a standard business field of numerous laboratories. However, experience shows significant deviations between results from different laboratories and therefore it is worth to point out, that in order to gain reasonable data only analyses methods specially developed for biomass fuels shall be used. Especially for the evaluation procedure presented, the application of analyses methods, which provide a high level of accuracy, is of relevance [1]. In the following, appropriate methods are briefly introduced.

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). For further analyses, sample preparation according to EN 14780 shall be performed. The ash content shall be determined according to EN 14775 by determination of the loss of ignition at 550°C.

The determination of the C, H and N contents shall be carried out according to EN 15104 by 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) shall be applied.

With the methods mentioned highly accurate data on the composition of biomass fuels can be achieved which are then used for a combustion related fuel evaluation as well as a basis for the calculation of fuel indexes. Fuel indexes are defined in order to provide first 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 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 first been developed and applied in coal combustion [e.g. 5]. 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 and their applicability has been proven [6].

For the work presented in this paper especially the following two fuel indexes, which have especially been developed for fixed-bed biomass combustion systems, are of major relevance. With an increasing value of the molar ratio of $[\text{Si}+\text{P}+\text{K}]/[\text{Ca}+\text{Mg}+\text{Al}]$ 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 fixed-bed biomass combustion. The molar 2S/Cl ratio is used to estimate high temperature corrosion risks. Additionally, the molar ratio of $[\text{K}+\text{Na}]/[\text{x}^*(2\text{S}+\text{Cl})]$ can provide first estimations regarding gaseous HCl and SO_x emissions since during biomass 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.

Step 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 of interest, 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, TEC provide the possibility to investigate the

release behaviour of inorganic compounds as well as the ash melting behaviour in biomass combustion/gasification processes under the assumption that chemical equilibrium can be reached for the system investigated. Regarding TEC studies presented in this paper, the thermochemical software package FactSage 6.2 has been applied. This package 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 currently accessed databases are "solution databases" containing the optimized parameters for a wide range of solution phases and "pure compound" databases covering data for over 4,500 stoichiometric compounds. For the work presented the component database Fact 53 as well as the solution databases FToxid (slags and other oxide mixtures) and FTsalt (liquid and solid salt phases) have been applied. More than 1,000 components and 9 solutions (which have been shown to be stable and thermodynamically relevant) were considered – the selection has been done application oriented for biomass fuels and ashes. More detailed information on the model applied is given in [8].

For the calculations presented in this paper a two-step calculation procedure has been applied which shall simulate the two main phases of biomass combustion namely the devolatilisation and the charcoal combustion phase. For step 1 the input data consist of the complete elemental fuel composition under consideration of a sub-stoichiometric combustion air ratio ($\lambda < 1$) and atmospheric pressure during the devolatilisation phase. The results of the calculations are evaluated for a temperature of 700°C which is assumed to be a realistic fuel bed temperature during biomass devolatilisation in fixed-bed combustion systems. For the subsequent simulation of the charcoal combustion phase (step 2), the input consists of the solid residues from the evaluation of step 1 (ash forming matter and charcoal), whereby the charcoal is assumed to consist of pure C and amounts to 15 wt% of the initial organic dry matter. Moreover, an oxidizing gas atmosphere ($\lambda > 1$) and atmospheric pressure are applied. The calculations concerning step 2 are carried out in a temperature range from 700-1,600°C. Regarding element release studies the release gained for both steps is considered whereby the evaluation of the element release ratios for step 2 have been conducted at 1,250°C (typical charcoal bed temperature for fixed-bed combustion systems). Regarding ash melting, only step 2 is evaluated.

It has been shown that a realistic prediction of the ash melting and K-release behaviour primarily depends on a reliable quantification of the molten solution phases SLAGH and SALTF over the temperature range of interest. Previous work showed that the assessment of these two phases is strongly influenced by the amounts of Al, Si and K. By means of empirically estimated limits for the characteristic molar ratios of K/(Si+P) and Al/Si, an optimisation method for TEC has been developed in [8] and later on further improved. When assessing pure fuels (without Al-containing additives) Al_2O_3 is excluded from SLAGH in calculation cases with a molar Al/Si ratio < 0.45 in order to avoid an unrealistic prediction of slag formation which is attributed to a strong influence of minor amounts of Al_2O_3 on slag formation and may be explained with the current inaccuracy of thermodynamic data for Al in slag solutions. The molar ratio K/(Si+P) is the determining criterion if the molten salt solution SALTF shall be used in the TEC model. For molar ratios larger than 1 SALTF is eliminated from the TEC model, otherwise it causes an over-prediction of the SALTF phase (mainly composed of K-carbonates/sulphates) connected with an unrealistic drop of the melting temperatures estimated.

Step 3 - Lab-scale reactor experiments

A special lab-scale reactor for the investigation of the combustion behaviour of biomass fuels in packed beds has been applied. It consists of a cylindrical electrically heated retort made of silicon carbide. The fuel (100 to 400 g depending on the fuel density) is put in a cylindrical sample holder which is placed on a balance and inserted into the pre-heated reactor. Combustion air respectively reaction gas is then injected through the fuel bed. Downstream the reactor a comprehensive number of various analysers is applied in order to determine the composition of the flue gases produced during the thermal decomposition of the fuel sample. A more detailed description of the reactor setup, the measurement devices applied as well as the testing protocol is provided in [9].

The sample is introduced into the pre-heated reactor, and therefore, a rapid heating, which is well comparable to the heating in real combustion/gasification processes, can be achieved. The arrangement of the heating elements and of the air/gas flow through the fuel bed provides that under the consideration that the fuel transport along the grate can be compared with a plug flow, the time dependent results of the lab-scale reactor can be correlated to the local burning conditions on a grate, i.e. drying phase,

pyrolysis/gasification and charcoal burnout. By continuously measuring the mass decrease of the fuel, the temperatures at different positions (heights) in the fuel bed and the concentrations of the main flue gas species comprehensive information about the thermal decomposition process can be gained. Moreover, by analysing the fuel as well as the residual ash information regarding the release of ash forming elements can be achieved. Test runs with this reactor also provide first indications regarding the slagging behaviour of a fuel (by visual observation of the combustion residues).

Results - improving the combustion related properties of wheat straw

Combustion related properties of wheat straw – problems to be expected

Wheat straw is a typical representative of agricultural fuels which show a high potential for energetic utilisation but disadvantageous combustion related properties. In the following these properties and the main problems associated to the combustion of wheat straw are briefly discussed. In Table 1 database values for wheat straw compositions as well as selected fuel indexes derived from these data are presented and compared with data for softwood chips with bark which is a well known and rather unproblematic biomass fuel. In Figure 1 comparisons of different fuel indexes with data from pilot and real-scale test runs regarding NO_x, SO₂ and HCl emissions, K-release as well as ash melting behaviour are presented in order to support the discussion of the different fuel indexes.

Table 1: Chemical composition and selected fuel indexes for wheat straw in comparison with softwood chips with bark

Explanations: data taken from the internal biomass fuel database of BIOS BIOENERGIESYSTEME GmbH; d.b. ... dry basis; # ... number of analysis considered in the database; mean ... mean value; s ... standard deviation; the fuel indexes are calculated for each sample separately; based on these data mean values and standard deviations have been calculated

		wheat straw			wood chips (softwood with bark)		
		#	mean	s	#	mean	s
ash content	wt% d.b.	19	6.57	1.5	39	0.82	0.5
C	wt% d.b.	15	44.91	2.73	24	49.60	1.35
H	wt% d.b.	15	5.61	0.36	24	6.24	0.52
N	wt% d.b.	15	0.58	0.16	27	0.17	0.10
S	mg/kg d.b.	19	1,485	527	36	120	48
Cl	mg/kg d.b.	19	3,046	1,859	38	49	31
Si	mg/kg d.b.	19	17,618	4,917	33	570	495
Ca	mg/kg d.b.	19	3,785	1,614	39	2,105	1,158
Mg	mg/kg d.b.	19	945	662	39	256	198
Al	mg/kg d.b.	18	238	245	10	134	132
Fe	mg/kg d.b.	18	250	205	14	82	56
Mn	mg/kg d.b.	5	16	6	7	95	43
P	mg/kg d.b.	19	442	148	11	85	87
K	mg/kg d.b.	19	6,629	4,149	39	812	381
Na	mg/kg d.b.	19	283	228	39	25	23
Zn	mg/kg d.b.	6	9.92	3.41	35	11.68	5.46
Pb	mg/kg d.b.	6	0.32	0.20	35	0.72	0.89
2S/Cl	mol/mol		0.80	0.87		13.44	8.38
(K+Na)/x(2S+Cl)	mol/mol		0.21	0.47		0.38	0.18
(Si+P+K)/(Ca+Mg+Al)	mol/mol		6.45	3.51		0.47	0.1
Cl/Si	mol/mol		0.16	0.10		0.05	0.04

With respect to gaseous emissions the higher N-contents of straw indicate slightly higher NO_x emissions compared with softwood combustion (see Figure 1). Regarding the calculation of the index (K+Na)/[x(2S+Cl)] according to [6] x-values for straw and wood chips of 4.5 and 3.6 respectively have been applied. The resulting values for the index indicate increased gaseous HCl and SO_x emissions for straw compared with softwood. The very high molar [Si+P+K]/[Ca+Mg+Al] ratio (6.5) implies very low

ash melting temperatures in comparison with wood fuels (0.5) which is confirmed by trend of this index vs. the shrinkage starting temperature (according to CEN/TS 15370-1 - see Figure 1).

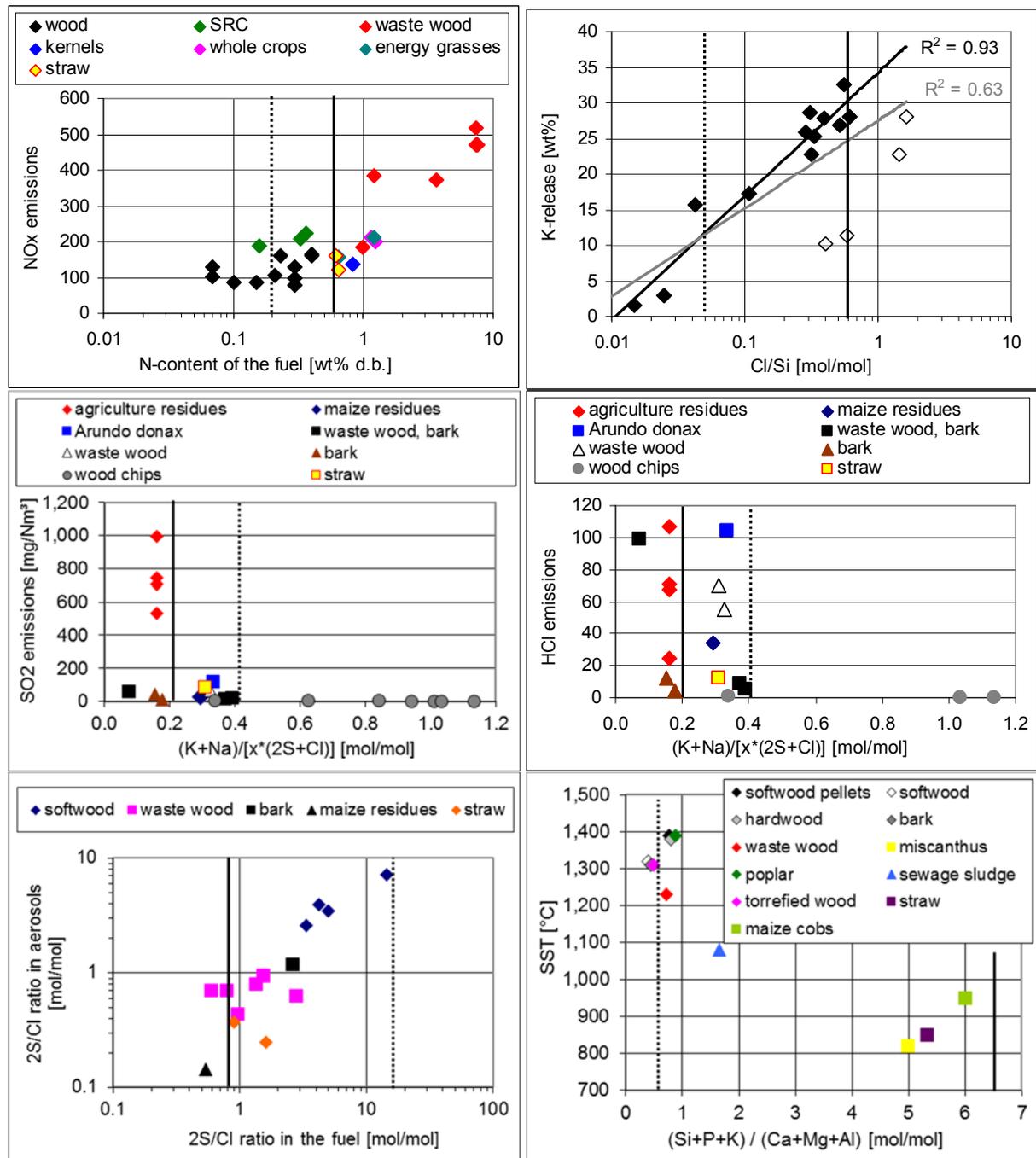


Figure 1: Comparisons of different fuel indexes with data from pilot and real-scale test runs regarding NO_x, SO₂ and HCl emissions, K-release as well as ash melting behaviour

Explanations: data for wheat straw (solid line) and softwood with bark (dashed line) according to Table 1 are highlighted; all emission related to dry flue gas and 13 vol% O₂; NO_x calculated as NO₂; SST ... shrinkage starting temperature determined according to CEN/TS 15370-1; R² values regarding K-release: grey value related to all data; black value related to the full symbols only

Moreover, the very low molar 2S/Cl ratio (0.8) indicates increased corrosion risks for wheat straw in comparison with wood chips (13.4). In [7] it is stated that corrosion risks increase with decreasing value of this index whereas no corrosion risks can be expected with a value of >8 while severe corrosion must

be expected for values <2 which is also confirmed by real-scale experiences. Finally, Figure 1 displays a clear trend of increasing K-release with increasing molar Cl/Si ratio, especially when the 4 outliers which show a comparably low K-release (open symbols) are not considered. The high molar ratio of Cl/Si of wheat straw (0.16) indicates a rather high K-release which gains relevance when taking the high K contents of wheat straw into consideration.

Step 1 - Selection of suitable additives for wheat straw based on fuel indexes

When considering the ash transformation processes prevailing during biomass combustion different additives could be applicable to influence the ash melting properties as well as the K-release behaviour of wheat straw. Generally, clay-based minerals (such as kaolin or bentonite but also fly ashes from coal combustion) as well as Ca-containing additives (e.g. dolomite or limestone) would be possible options. In Table 2 typical chemical compositions of selected minerals as well as coal fly ash are presented.

Table 2: Chemical composition of selected potential inorganic fuel additives

Explanations: data represent mean values of compositions taken from product datasheets provided by different suppliers of the materials; coal fly ash: analyses data of coal fly ash sample from a hard coal fired power plant; d.b. ... dry basis; n.d. ... no data available

	Si	K	P	Ca	Mg	Al
	[mg/kg d.b.]					
kaolin	215,000	8,720	n.d.	450	650	206,170
bentonite	260,000	10,400	196	24,600	13,200	74,300
limestone	1,870	n.d.	n.d.	393,280	2,900	530
dolomite	13,790	420	n.d.	219,480	125,300	3,710
coal fly ash	232,500	14,100	1,780	25,200	15,300	114,000

In Figure 2 the trends of the ash melting index and the K-release index for mixtures with different additives vs. the additive contents of the mixtures are presented. From [6] it has been evaluated that with a value of the melting index of <2.4 melting temperatures in the range of 1,100°C should be achievable (see respective diagram in Figure 1). Regarding the Cl/Si ratio a value of below 0.1 should be achieved by the mixing with the additive in order to decrease this index significantly and to reduce the K-release by more than 50% (see respective diagram in Figure 1) which is of great relevance for straw combustion due to the comparably high K content of this fuel. These benchmarks, which are assessed as reasonable aims to be achieved for combustion in a conventional fixed-bed combustion plant designed for wood fuels are also embedded in Figure 2. As the left hand diagram shows, the addition of dolomite would result in the lowest additive ratios needed for increasing the ash melting temperatures below the benchmark value. On the other side dolomite shows almost no effect on the K release (right hand diagram) since only Ca and Mg are added in relevant amounts and therefore the Cl/Si remains unchanged. Limestone addition shows about the same effects as dolomite addition and is therefore not considered in Figure 2. For coal fly ash rather high amounts of additive are needed to meet the benchmark regarding the ash melting index which is with respect to the costs as well as the design of common de-ashing systems not desirable. With reasonable amounts of bentonite addition it is not possible to reach the benchmark of the ash melting index. Kaolin however, shows a significant reduction of the ash melting index at rather low additive ratios (the benchmark is reached at a kaolin content of about 4.0 wt% d.b.) and additionally reduces the K release index significantly. It has to be mentioned that due to the desired reduction of the K-release the factor x in the fuel index $(K+Na)/[x(2S+Cl)]$ will increase and therefore, the value of this fuel index will decrease. Consequently, somewhat increased gaseous HCl and SO_x emissions are expected to result from additive utilisation. As a result of step 1 of the strategy presented, kaolin and dolomite are pre-selected as the most suitable additives.

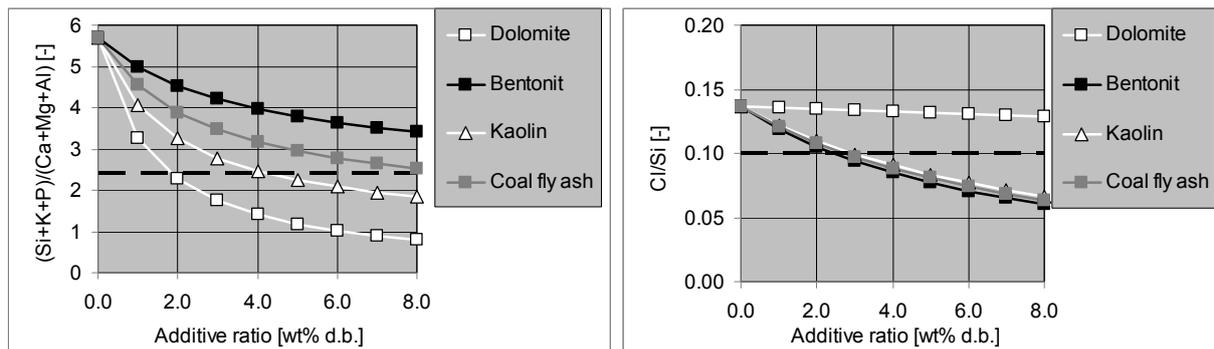


Figure 2: Influence of different additives mixed with wheat straw on the ash melting and the K-release index

Explanations: basis for the calculations: straw data: mean values from Table 1; additive compositions taken from Table 2; additive ratio ... additive content of the mixture calculated on dry basis; dashed line: benchmark

Step 2 - Selection of suitable additives for wheat straw based on TEC

As a consequence from step 1, the application of dolomite and kaolin as additives has been further evaluated by means of TEC. The 2-step approach and the methodology explained were therefore applied during the calculations. The temperature at which 30 wt% of molten phases result from the calculations (T_{30}) is taken as an indicator for the shrinkage starting temperature (according to the CEN/TS 15370-1 standard ash melting test). It is assumed that above this temperature problems with slagging significantly increase [4].

In Figure 3 results of the TEC performed regarding the effect of 4 wt% dolomite addition (related to the dolomite content of the final fuel/additive mixture) and 4 wt% kaolin addition on the ash melting temperatures as well as the K-release are shown. For both additives T_{30} shows the increase which was expected from the evaluation of the fuel indexes. Regarding the K-release only kaolin addition shows a positive effect while for dolomite addition the K-release unexpectedly increases. Applying an in depth analyses of the TEC results, these effects can be explained as follows.

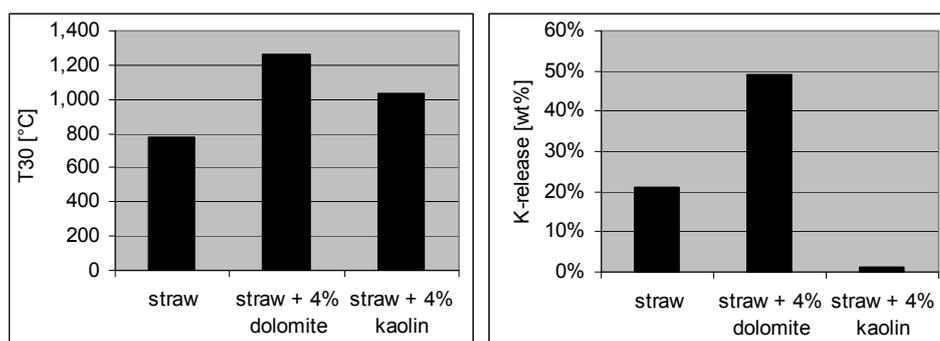


Figure 3: Influence of dolomite and kaolin addition on the ash melting temperatures (left) as well as the K-release (right) – results from TEC

Explanations: T_{30} temperatures according to TEC results at which 30 wt% of the ashes occur in molten phases; K-release at 1,250°C in wt% of the mass of K in the initial material; fuel/additive mixing ratios: 4 wt% dolomite respectively kaolin in the final fuel/additive mixture.

In Figure 4 more detailed results from TEC are presented. As it can be revealed from the diagrams, K-silicate compounds (mainly $K_2Si_4O_9(s)$, which is the dominant compound in the blue marked phase) are relevant for the low ash melting temperatures during wheat straw combustion. They are transformed into molten phases (slags) at temperatures above 750°C. When adding dolomite the formation of solid phases containing Ca, Si, Mg and Al is preferred compared to the K-silicate compounds and therefore,

also the formation of the molten phases originating from the K-Si-compounds at 750°C is hindered. Consequently, T_{30} increases to above 1,200°C where a steep increase of the amount of molten phases occurs. The addition of kaolin on the other side results in an enforced formation of K-Al-Si-phases which remain stable in the solid phase also above 750°C and start to form molten phases at temperatures above 950°C. In this case the T_{30} could be increased to above 1,000°C.

The formation of Ca-Si-phases (dolomite) as well as K-Al-Si-phases (kaolin) also provides an explanation for the strongly differing K-release behaviour. During dolomite addition the formation of Ca-silicates instead of K-silicates leads to an increased release of K (see KCl in Figure 4) while during the addition of kaolin, a stronger embedding of K in the K-Al-Si-phases prevails resulting in a significantly reduced K-release.

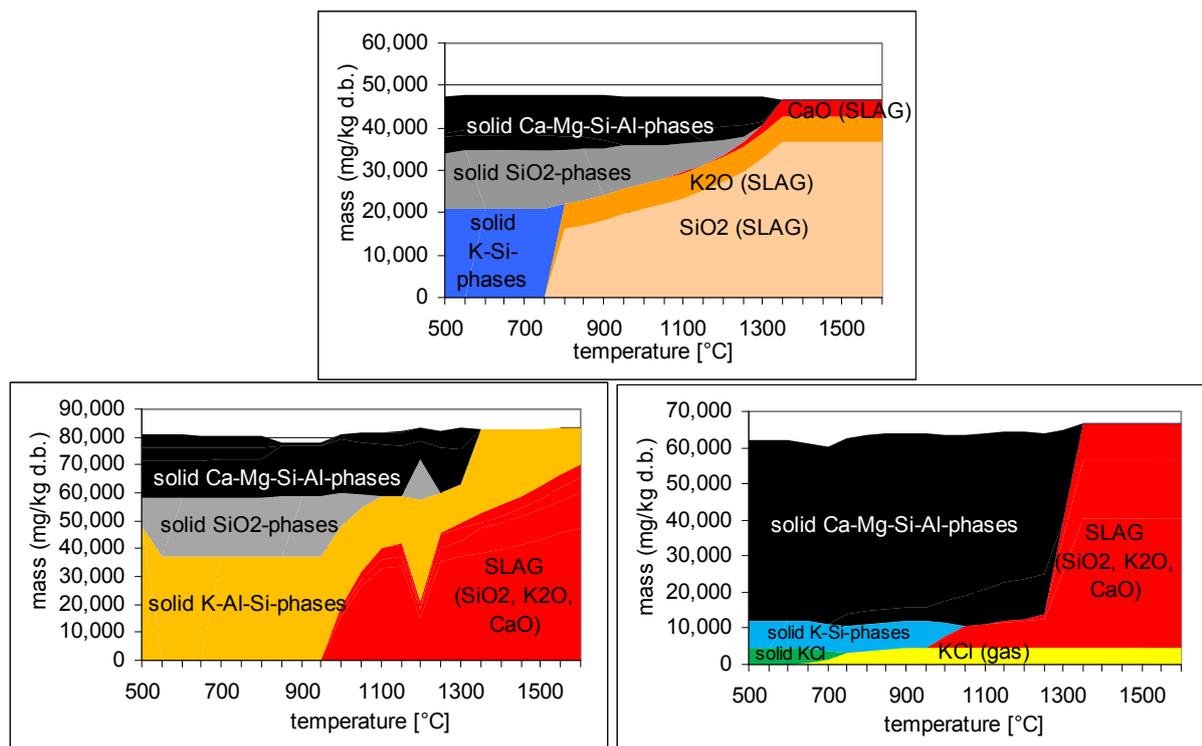


Figure 4: TEC results for pure wheat straw as well as mixtures of wheat straw with 4 wt% kaolin respectively 4 wt% dolomite

Explanations: Summary of relevant Si, Ca, K and Al-rich phases; top: wheat straw; bottom left: wheat straw + kaolin; bottom right: wheat straw + dolomite

The results from TEC are in good agreement with the preliminary conclusions regarding ash melting based on the evaluation of fuel indexes. They provide a deeper insight into the ash chemistry and can also supply relevant information about the mechanisms responsible for the effects of certain additives on ash melting and K release. The increased K-release caused by dolomite addition can for instance only be identified by TEC since the K-release index applied does not consider the underlying mechanism appropriately. However, insecurities in the thermodynamic databases applied as well as the uncertainty to which extent thermodynamic equilibria can be reached in a real system, still make lab-scale reactor tests as a third and final step of the strategy introduced affordable to obtain quantitative results.

Step 3 - Selection of suitable additives for wheat straw based on lab-scale reactor tests

Based on the results of step 1 and step 2 finally kaolin has been selected as most suitable additive for wheat straw since it shows both effects, a considerable increase of the ash melting temperatures and a considerable reduction of the K-release. 3 mixtures of wheat straw and kaolin (with 1, 3 and 7 wt% kaolin in the final mixture) were prepared and pelletised for lab-scale reactor tests. In Table 3 the chemical compositions, shrinkage starting temperatures as well as the ash melting and the K-release index of the

pure wheat straw applied and the straw/kaolin mixtures are presented. The data for the wheat straw utilised presented in Table 3 are within the standard deviation ranges of the database values presented in Table 1 and therefore, the wheat straw applied can be assessed as representative.

Based on the data in Table 3, straw-kaolin-mixtures with melting indexes of around 1.7 (7 wt% kaolin addition), 2.2 (about 4 wt% kaolin addition) as well as 3.5 (1 wt% kaolin addition) have been produced. Moreover, the K-release index decreases from 0.45 (no kaolin) to 0.2 (7 wt% kaolin).

Table 3: Chemical composition, ash melting temperatures and selected fuel indexes for wheat straw and straw/kaolin mixtures investigated in the lab-scale reactor

Explanations: d.b. ... dry basis; shrinkage starting temperature ... determined according to CEN/TS 15370-1

Kaolin ratio wt.%		0%	1%	4%	7%
ash content (550°C)	wt.% d.b.	4.5	5.0	7.1	9.5
C	wt.% d.b.	46.6	46.5	45.3	43.7
H	wt.% d.b.	6.0	6.0	5.9	5.8
N	wt.% d.b.	0.40	0.38	0.34	0.37
S	mg/kg d.b.	913	849	857	874
Cl	mg/kg d.b.	2,300	2,210	2,240	2,240
Ca	mg/kg d.b.	3,010	2,820	2,790	2,800
Si	mg/kg d.b.	11,100	12,000	17,000	22,400
Mg	mg/kg d.b.	688	649	636	651
K	mg/kg d.b.	6,970	6,430	6,430	6,370
Na	mg/kg d.b.	201	204	244	287
P	mg/kg d.b.	385	358	357	372
Al	mg/kg d.b.	217	2,010	7,160	12,600
Zn	mg/kg d.b.	6.6	5.9	6.1	7.5
Pb	mg/kg d.b.	0.23	0.37	0.7	1.2
Shrinkage starting temperature	°C	780	1,160	1,330	1,310
(Si+K+P)/(Ca+Mg+Al)	mol/mol	5.26	3.52	2.16	1.73
Cl/Si	mol/mol	0.16	0.15	0.10	0.08

Visual evaluations (see Figure 5) of the ashes remaining in the reactor after the test runs show a significant reduction of molten ash pieces with increasing kaolin addition. As an example on the left hand picture in Figure 5 for the test runs with wheat straw molten ash pieces at the fuel bed thermocouples can be identified while the thermocouples after the test run with a mixture with 4 wt% kaolin are free of slag and also in the ash bed only minor amounts of sintered particles could be found. In Figure 6 the shrinkage starting temperatures gained from ash melting tests according to CEN/TS 15370-1 (see also Table 3) are plotted against the ash melting index. As expected a significant increase of the ash melting temperature with increasing kaolin additions has been observed which confirms the optical evaluation of the ashes. Moreover, the results of TEC regarding T_{30} plotted into the diagram display a trend which is well comparable with the experimental data. However, due to the reasons already indicated during the discussion of step 2, a direct quantitative comparison is not permissible.



Figure 5: Pictures of the residues (ashes) after the test runs with wheat straw (left) and with a wheat straw/kaolin mixture containing 4 wt% kaolin (right)

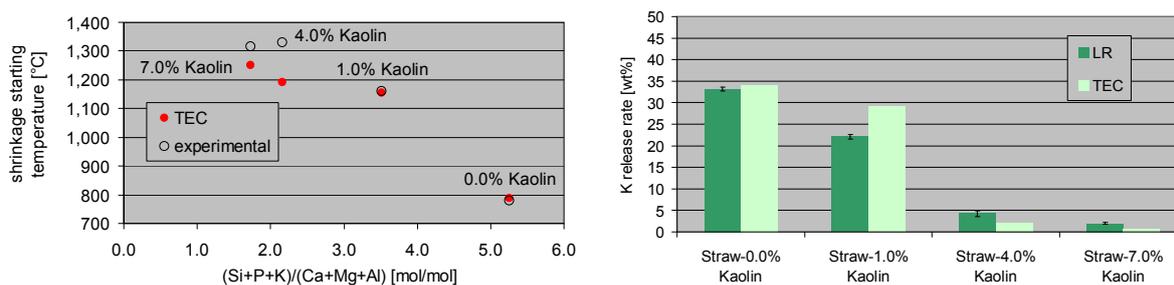


Figure 6: Experimental evaluation of the effect of kaolin addition to straw on ash melting and K-release

Explanations: left diagram: ash melting behaviour: TEC ... results from thermodynamic equilibrium calculations; the shrinkage starting temperatures from TEC were estimated at 30 wt% molten fraction; experimental ... results of the standard ash melting test according to CEN/TS 153701-1; right diagram: K release; kaolin addition related to the wt% of kaolin in the final straw-kaolin-mixture; LR ... results from the lab-scale reactor tests

Regarding K-release, the desired decrease with increasing kaolin addition results. Also in this case TEC can reproduce the general trend but some deviations regarding the absolute values gained from the experiments exist. When taking into account that K released during combustion is preferably bound in aerosols as sulphate or chloride a maximum (sulphate dominated) and minimum (Cl-dominated) aerosol formation potential can be calculated [9]. Due to the reduced K-release the maximum and minimum aerosol formation potentials decrease from about 380 mg/Nm³ respectively 340 mg/Nm³ (related to dry flue gas and 13 vol% O₂) for pure straw combustion to 50 mg/Nm³ respectively 45 mg/Nm³ for the mixture containing 4 wt% kaolin which represents a significant improvement regarding deposit formation tendencies and fine particulate emissions. However, in turn it also causes an increase in the gaseous HCl and SO₂ emissions which has to be considered when applying this additivation strategy.

Summary and conclusions

A new systematic and targeted approach based on advanced fuel characterisation methods for the creation of biomass designer fuels with improved combustion properties in terms of ash related issues by utilisation of inorganic additives has been presented based on the example of wheat straw. The approach is structured into three relevant characterisation steps.

The first step comprises representative chemical analyses of the fuel of interest as well as the calculation and evaluation of specific fuel indexes for the pure fuel as well as potential fuel/additive mixtures. By this measure a quick and valuable pre-evaluation of relevant combustion related properties such as the ash melting behaviour, the K-release, gaseous (NO_x, SO₂, HCl) and fine particulate emission as well as of the expected influence of additives on these parameters can be achieved and the range of meaningful additives can be narrowed.

In a second step thermodynamic equilibrium calculations (TEC) are applied to gain more detailed information about ash transformation, ash melting and K-release. The results gained from TEC are still on a qualitative level but they can support the understanding of the underlying processes and thereby help to select an appropriate additive which can influence both, the ash melting as well as the K-release.

Finally, lab-scale reactor tests with selected fuel/additive mixtures which have been derived from the pre-evaluations within step 1 and 2 are applied in order to gain quantitative experimental results. They act as a basis for the elaboration of recommendations regarding the definition of appropriate fuel/additive mixing ratios in order to reduce problems with ash melting and K-release.

The successful application of this 3-step approach has been shown for the case study wheat straw. This example underlines that the new method opens the possibility for a quick and targeted assessment of

combustion related fuel properties as well as additive selection at rather low efforts and risks compared with real-scale combustion tests. However, some relevant restrictions have to be considered when applying the new approach.

In any case the evaluation has to be done fuel specific. At least during the third step representative samples of the fuel of interest shall be utilised.

So-called problematic biomass fuels often show considerable variation ranges regarding their chemical composition (especially regarding ash forming elements, S and Cl). This aspect has to be appropriately considered during the definition of the additive ratio to be finally applied.

As a side effect of the reduction of the K-release increased HCl and SO₂ emissions result which is especially relevant for S and Cl-rich fuels and has to be considered regarding eventually needed emission reduction measures.

The targeted application of additives can in future facilitate the utilisation of agricultural fuels in conventional wood combustion plants with moderate adaptations of the flue gas cleaning systems. Since the most efficient mixing of fuel and additive is realised during a compaction step which also significantly increases the energy density of the final fuel, pelletising or briquetting is recommended. Besides the combustion technology related aspects discussed in this paper, also economic aspects have to be considered for a real-scale application, among them the costs for the additive (typically low), the increased ash content as well as the lower fuel costs in comparison to wood fuels.

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