

Strategy for the Application of Novel Characterization Methods for Biomass Fuels: Case Study of Straw

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ABSTRACT: Because of an increasing interest in the utilization of new and in terms of combustion-related properties rather unknown biomass fuels in heat and power production, advanced fuel characterization tools are gaining rising interest. Currently, ongoing research and development (R&D) focuses on a better and more precise description of the combustion properties of specific biomass fuels by applying new/advanced analysis methods and modeling tools. These novel characterization methods cover combustion tests in specially designed lab reactors, special fuel indices for biomass fuels, and the dedicated application of high-temperature equilibrium calculations. In this paper, a strategy is presented how the information gained from different advanced fuel characterization methods can be combined to characterize a fuel regarding its combustion behavior in a novel way. By means of this strategy, relevant qualitative and quantitative information regarding the ash-melting behavior, aerosol, SO_x, HCl, and NO_x emissions to be expected, and high-temperature corrosion risks can be gained. In addition, the approach can also be used for the evaluation of additives and fuel blending as measures to improve specific combustion properties. The results show that a much better and clearer picture about the combustion properties of a specific biomass fuel can be provided than by conventional approaches (such as wet chemical analysis or other standardized methods). The results can be used for the preliminary design of plants as well as for evaluation of the applicability of a specific technology for a certain biomass fuel or fuel spectrum. Moreover, they can be applied in combination with computational fluid dynamics (CFD) simulations for the detailed design and evaluation of furnaces and boilers.

1. INTRODUCTION AND OBJECTIVES

In recent years, the thermal utilization of solid biomass for heat and electricity production has gained great importance. Within the European Union (EU), in particular, biomass is seen as the most relevant renewable energy source besides hydropower and is, thus, expected to substantially contribute to the CO₂ emission reduction targets defined. Additionally, there is a broad international consensus that the utilization of renewable energy sources should be globally further enforced to reduce greenhouse gas emissions. Moreover, the increase of fossil fuel prices because of increasing energy demand and limited resources is also a major driving force toward renewable energy.

On the basis of market data for 2008,^{1–4} the primary energy consumption and total turnover of biomass combustion plants (small-, medium-, and large-capacity ranges) in the EU was estimated to about 3711 petajoule/year and 6423 million €/a, respectively. In the EU, several political measures have been initiated with the aim of supporting the utilization of renewable energies, including, for instance, the Res-e Directive (2001), the EU Biomass Action Plan (2005), the Energy and Climate Change Package (March 2007), and the Renewable Energy Directive (June 2009). Against the background of these targets, a compound annual market growth rate of approximately 8.3% is expected. The market volume should grow up to 260% (of the 2008 data), and the primary energy consumption from biomass should be more than doubled until 2020.

Consequently, also, the demand for biomass feedstocks is increasing accordingly, and therefore, the number and diversity of different biomass sources applied in combustion systems will

also increase. Typical examples for fuels with remarkable future market potentials are (i) fuels from short-rotation forestry (e.g., poplar and willow), (ii) agricultural biomass fuels (*Miscanthus*, grasses, and maize cobs), (iii) residues from food production and agricultural industries, (iv) residues from new biomass conversion technologies, and (v) second-generation biomass fuels (e.g., torrefied biomass, pyrolysis char, and hydrolytic lignin).

Generally, most of these “new” biomass fuels are not yet well-explored regarding their combustion-related properties. Therefore, the development of new and advanced fuel characterization tools is presently gaining rising relevance, and related research and development (R&D) already shows the first promising results. These novel characterization methods cover special fuel indices for biomass fuels, combustion tests in specially designed lab-scale reactors equipped with innovative measurement equipment, and the dedicated application of high-temperature equilibrium calculations. Moreover, they provide basic input data for the application of new computational fluid dynamics (CFD) models for detailed NO_x and aerosol formation simulations, which can be applied for plant design. To evaluate and validate these new methods, a comparison to measurement data from real-scale plants is of great relevance.

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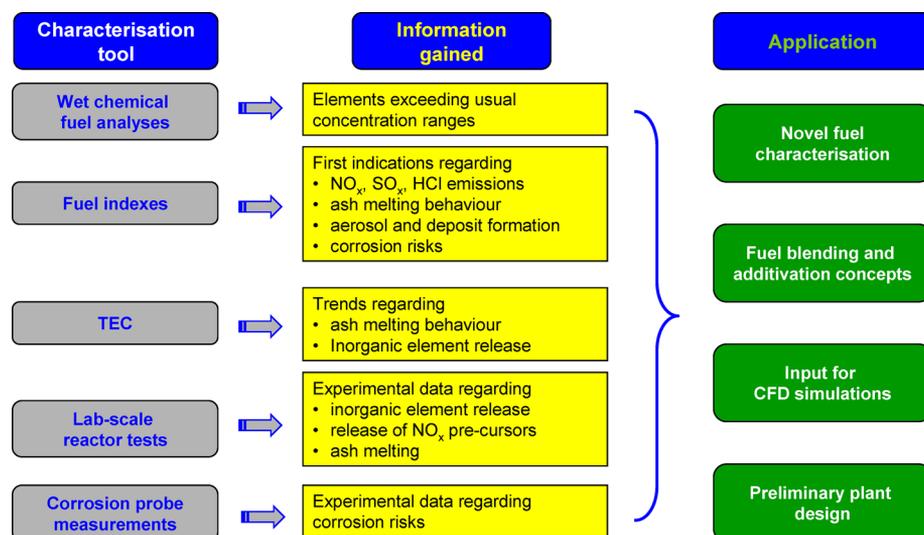


Figure 1. Strategy for the application of fuel characterization tools and their application: overview.

Because most of the new biomass fuels mentioned above are suspected and already known to be rather difficult in combustion processes, also, comprehensive R&D work regarding fuel blending as well as the utilization of additives to influence relevant combustion-related fuel properties is ongoing.^{5–8} The reduction of the release of inorganic elements, especially K, from the fuel to the gas phase during combustion as well as influencing the ash-melting behavior are the main aims of this research. In this respect, the new and advanced characterization tools mentioned above can also be applied as a basis for a better understanding and evaluation of the effects of fuel blending and additive utilization on the fuel properties.

Moreover, R&D trends concerning biomass combustion technologies focus on next-generation systems with ultralow emissions and increased efficiencies. In addition, CFD model development for overall biomass combustion plants, including emission formation and ash-related problems, is ongoing. Especially for these models, advanced combustion-related fuel characterization data, such as the release of NO_x precursors as well as aerosol-forming species from the fuel to the gas phase, represent essential input data. An enhanced fuel characterization, therefore, also supports these R&D trends considerably.

Traditional fuel characterization methods are mainly based on the evaluation of ultimate and proximate fuel analyses as well as thermogravimetric methods. Plant design is often based on the experience of the manufacturers with comparable fuels and not on a scientifically developed fuel evaluation-related design strategy. Especially for new biomass fuels with rather unknown behavior regarding the formation of NO_x, HCl, SO_x, and particulate emissions as well as deposit formation, slagging, and corrosion, this strategy may fail. This may lead to not optimally designed flue-gas-cleaning measures causing increased operation costs as well as increased ash-related problems, which reduce the availability of the plants and may also result in reconstructions.

Against this background, this paper aims at the presentation and discussion of a target-oriented application strategy for novel fuel characterization methods, taking the combustion of straw in fixed-bed systems as an example. It should be demonstrated how these new methods with their different information depths can be applied and combined to gain estimations and predictions of the ash-melting behavior,

aerosol, SO_x, HCl, and NO_x emission formation as well as high-temperature corrosion risks. This evaluation of combustion-related fuel properties can subsequently support the preliminary design of an appropriate combustion plant. Moreover, the utilization of data gained (e.g., release profiles) in CFD simulation models can additionally support the detailed furnace and boiler design phase.

Because most of the fuel characterization tools applied have been developed for fixed-bed combustion systems, the case study is also restricted to this combustion technology. However, the general approach presented may, in principle, also be applied for fluidized-bed combustion systems. However, because of the different time–temperature profile of the flue gas in a fluidized-bed combustion plant, the different bed behavior, and the influence of the bed material on ash formation, the indices as well as the lab-scale reactor design will have to be adapted.

2. EXPERIMENTAL SECTION

Within this paper, a strategy for the application of novel and advanced fuel characterization tools for combustion-related fuel characterization is presented. In Figure 1, an overview is given. The diagram shows the different characterization tools presented and discussed in the following, the kind of information that can be gained from each specific tool as well as proposals of how this information can be used within the fuel characterization strategy presented for practical applications, such as preliminary plant design. In the following, first, the methods applied within the different characterization tools are described, and then their application is discussed by means of the characterization of wheat straw as a case study.

2.1. Wet Chemical Fuel Analyses. Wet chemical fuel analyses always represent the first step of fuel characterization. They provide the basic data for all subsequent methods, and therefore, only well-proven fuel analysis methods should be applied. It is strongly recommended to generally follow the best practice guidelines worked out within the EU project BIONORM^{9,10} and subsequently implemented in various European Committee for Standardization (CEN) standards for biomass fuels. In the following, the methods applied for the analyses presented in this paper are listed and relevant issues are highlighted.

2.1.1. Moisture Content. The moisture content of fuel samples has been determined according to EN 14774-1 (2009) (determination of the weight loss during drying at 105 °C until a constant weight is reached).

2.1.2. Fuel Sampling and Fuel Sample Preparation. It is of relevance that a representative fuel sample is analyzed. This is especially crucial if agricultural fuels are investigated, where the shares of, e.g., stems and leaves can vary substantially. Therefore, sampling has been performed according to EN 14778 (2011 06). Sample preparation has been carried out according to EN 14780 (2011 06): the samples are homogenized and milled in a cutting mill to a particle size of <4 mm. Then, the sample size is reduced and milled in an ultracentrifugal mill equipped with a titanium rotor and screen to a particle size of <0.2 mm to obtain the analysis sample.

2.1.3. Determination of the Ash Content. The ash content is determined according to EN 14775 (2009 11) by determination of the loss of ignition at 550 °C. With this method, it has to be taken into account that especially Ca-rich fuels form considerable amounts of carbonates at the proposed treatment temperature. In real-scale applications, on the other side, almost no carbonates and preferably oxides are formed because of the significantly higher process temperatures. Consequently, the ash content is overestimated in comparison to the amount of ashes formed in a real process. Therefore, in deviation from EN 14775 (2009 11), it is recommended to determine the inorganic carbon content of the ashed fuel sample additionally and to correct the ash content by subtracting CO₂ bound in carbonates to gain an ash content that is based on oxide formation.

2.1.4. Determination of C, H, N, and Cl Contents. The determination of C, H, and N contents of biomass fuels is carried out according to EN 15104 (2011 02) by combustion and subsequent gas-phase chromatographical separation and measurement in an elemental analyzer. The determination of Cl is performed according to EN 15289 (2011 02), applying a digestion step based on bomb combustion in oxygen and absorption in NaOH (0.05 M), followed by ion chromatography measurements.

2.1.5. Determination of Major and Minor Ash-Forming Elements and S. It is recommended to perform these analyses by digesting the fuel and not by analyzing ashed fuel samples to minimize losses during pretreatment. Following this approach, multi-step pressurized digestion of the fuel with HNO₃ (65%)/HF (40%)/H₃BO₃, followed by measurement by inductively coupled plasma–optical emission spectroscopy (ICP–OES) or inductively coupled plasma–mass emission spectroscopy (ICP–MS), is performed. The digestion method is of great importance to ensure a complete dissolution of the ash matrix, which is a basic requirement for correct element detection.

2.1.6. Determination of the Ash-Melting Behavior. The determination of the ash-melting behavior has been performed according to CEN/TS 15370-1. The fuel samples are ashed at a temperature of 550 °C, and the remaining ash is pressed into cylindrical molds. These samples are then heated in an oven under oxidizing conditions, and characteristic melting temperatures (shrinkage starting temperature, deformation temperature, hemisphere temperature, and flow temperature) are determined. This method of course is questionable because it does not take the fractionation of elements in the different ash fractions occurring in a real combustion process into account. However, it provides good indications, and because there is no better standard method presently available, most data sets available rely on this method.

2.2. Fuel Indices. Fuel indices are calculated from the biomass fuel analysis data. Thereby, the physical behavior, chemical reaction pathways, and interactions between different elements and groups of elements during combustion are taken into account. In recent years, some groups have developed different fuel indices, especially for the prediction of corrosion-related risks as well as the slagging behavior of biomass fuels.^{11–15} The sum of K, Na, Zn, and Pb, which are the most relevant aerosol-forming species in biomass combustion, for instance, can be used to estimate the potential for aerosol formation.¹⁵ Moreover, the molar 2S/Cl ratio has been proven as an appropriate index to assess the risk for high-temperature Cl corrosion.^{11,15} The molar ratio of (K + Na)/(2S + Cl) has been reported to be a useful index for the evaluation of gaseous HCl and SO_x emissions, because during biomass combustion, S and Cl are preferably bound by alkaline metals.¹² In ref 15, this index has been further developed to (K + Na)/

[x(2S + Cl)], where the newly introduced parameter *x* allows for a consideration of the differing release ratios of S, Cl, K, and Na from the fuel to the gas phase during combustion. Finally, the molar ratio of Si/(Ca + Mg) can provide information about slagging tendencies.¹⁴ In ref 15, this index has been modified to (Si + K + P)/(Ca + Mg), which led to an increased prediction preciseness. Besides literature data, correlations and experiences gained from pilot- and real-scale combustion tests have been used to validate the fuel indices mentioned. More detailed information concerning fuel indices for biomass fuels as well as their evaluation is provided in ref 15.

The fuel indices mentioned above are designed to provide first indications regarding relevant combustion-related properties of biomass fuels. However, the results of these evaluations must be regarded as qualitative and not quantitative.

2.3. Lab-Scale Reactor Tests. At the Institute for Process and Particle Engineering, Graz University of Technology, a special lab-scale reactor for the investigation of the combustion behavior of biomass fuels in packed beds has been developed. This lab-scale reactor consists of a cylindrical electrically heated retort made of silicon carbide. The fuel (100–400 g depending upon the fuel density) is put in a cylindrical sample holder, which is placed on a balance and inserted into the preheated reactor. Preheating is usually set to 450 °C in the lower part (which surrounds the sample holder) and 750 °C in the upper part (above the sample holder). Combustion air and reaction gas are then injected through the fuel bed. During fuel decomposition, the sample mass loss and the temperatures in and above the fuel bed are recorded online. Moreover, downstream of the reactor, the composition of the flue gases produced is measured using analysers based on Fourier transform infrared (FTIR) spectroscopy (Ansysco, CO₂, H₂O, CO, CH₄, NO, NH₃, HCN, NO₂, N₂O, and basic hydrocarbons), paramagnetism (Emerson NGA 2000, O₂), non-dispersive infrared (NDIR) analysis (Emerson NGA 2000, CO₂ and CO), heat conductivity (Emerson NGA 2000, H₂), flame ionization detection (FID) (Bernath Atomic 3005, OGC), and chemiluminescence detection (CLD) (ECO Physics CLD 700 EL ht, NO and NO_x). A more detailed description of the reactor setup is provided in ref 16.

For the performance of tests with this reactor, the fuel is first dried to a moisture content of about 10 wt %, wet basis. Then, it is placed in the sample holder and inserted into the preheated reactor, and a combustion air flow of typically 30 L/min (at 20 °C) is initiated, which is kept constant during the whole test run. First, a drying phase prevails, during which the fuel temperature slowly increases and the moisture is released. After this phase, a rapid heating of the upper fuel layer (about 1000 K/min) accompanied by volatile release under reducing conditions takes place. With increasing test run duration, this reaction front moves downward in the fuel bed. After the release of volatiles, char coal combustion takes place (hyperstoichiometric conditions prevail).

When the mass decrease of the fuel, the temperatures at different positions in the fuel bed and the concentrations of the main flue gas species and N species are continuously measured, comprehensive information about the thermal decomposition process, and the release of NO_x precursors can be gained. Moreover, when the fuel and the residual ash are analyzed, information about the release of ash-forming elements can be achieved. Test runs with this reactor also provide first indications regarding the slagging behavior of a fuel (by visual observation).

Because the sample is introduced into the preheated reactor, rapid heating conditions, which are well-comparable to the heating in real combustion/gasification processes, can be achieved. The arrangement of the heating elements and the air/gas flow through the fuel bed provides that, under the consideration that the fuel transport along the grate can be compared to 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. Consequently, the utilization of the results gained is restricted to fixed-bed systems and cannot be directly applied to fluidized-bed systems. It should also be mentioned that other groups have already applied different reactor setups, such as single-particle or wire-mesh reactors, for the investigation of the release of inorganic

elements and NO_x formation-related issues.^{17,18} In principle, also, results from these studies may be implemented into the strategy presented.

2.4. Thermodynamic Equilibrium Calculations (TECs). TECs 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 predetermined gas atmosphere. In several previous studies, TECs have been successfully used for the prediction of different coal and biomass ash properties.^{19–22} Therefore, TECs provide the possibility to investigate the release behavior of inorganic compounds as well as the ash-melting behavior in biomass combustion/gasification processes under the assumption that chemical equilibrium can be achieved for the system investigated. With regard to 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 minimization 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 containing the data for over 4500 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 1000 components and nine solutions (which have been shown to be stable and thermodynamically relevant) were considered; the selection has been performed application-oriented for biomass fuels and ashes. More detailed information on the model applied is given in ref 22.

2.5. Online Corrosion Probe Measurements. The application of online corrosion probes is well-known regarding the investigation of corrosion processes in coal and waste combustion.^{23,24} Recently performed R&D and further development of the probes have made this technology also applicable for biomass combustion processes, where in comparison to, e.g., waste combustion, rather low corrosion rates occur.²⁵ Therefore, online corrosion probes can now also be applied in lab- and real-scale reactors to investigate corrosion potentials of different biomass fuels.

In the studies from which the data presented in this paper are taken, a corrosion probe manufactured by the German company Cormoran has been applied. The system is designed to simulate a superheater tube in the flue gas of a combustion system. A temperature-controlled air-cooled sensor is placed on the top of a water-cooled carrier lance. When exposed to the flue gas, a layer consisting of deposits and corrosion products is formed on the sensor surface. This layer represents an electrolyte and allows for the measurement of the corrosion rate. The system is based on the measurement of a linear polarization resistance. After completion of the measurement, the probe rings themselves can be investigated by scanning electron microscopy (SEM)/energy-dispersive X-ray (EDX) analysis to evaluate the structure and chemical composition of the corrosion front in the deposit layer. A more detailed description of this probe, its application, and the evaluation of measurement results is provided in refs 26 and 27.

2.6. Real-Scale Test Runs. To validate the fuel characterization methods presented, results from real-scale test runs are needed. In this paper, several results from combustion tests at grate-fired combustion plants in the fuel capacity range between 200 and 100 000 kW_{NCV} are presented. These test runs have been performed by BIOS BIOENERGIESYSTEME GmbH, the Institute for Process and Particle Engineering, Graz University of Technology, and BIOENERGY 2020+ GmbH, all located in Graz, Austria.

All test runs were designed in a way that, besides gaseous and particulate emission measurements and also mass, energy, and element balances (regarding relevant ash-forming elements), could be performed. Only data from elements that showed a reasonable closure of the element balances have been used for the evaluations. Recovery rates between 70 and 130% have therefore been used as a criterion that is in a reasonable range when taking measurement and analysis error ranges, the inhomogeneity of the fuel, and ash losses by furnace and

boiler depositions into account. Moreover, it must be mentioned that, during all tests, stable representative combustion conditions (with respect to load, furnace temperatures, excess air ratios, and air-staging settings) prevailed, which is also an important basic prerequisite to gain representative data.

3. APPLICATION OF ADVANCED FUEL CHARACTERIZATION TOOLS FOR WHEAT STRAW: AN EXEMPLARY CASE STUDY

In this section, the strategy regarding the application of advanced fuel characterization methods for preliminary plant design is presented, taking wheat straw as a case study. The strategy can generally be structured into two main steps. The first step covers the evaluation of wet chemical fuel analyses as well as fuel indices. From these evaluations, a general categorization of a biomass fuel as well as first indications regarding combustion-related issues, such as HCl, SO_x, NO_x, and particulate emissions, ash-melting properties, and corrosion risks, can be gained. The second step demands for further tests (lab-scale reactor tests) as well as thermodynamic equilibrium calculations. By applying these tools, deeper insight regarding the parameters mentioned above can be gained and more precise predictions can be made, which can also be applied for plant design.

3.1. Wet Chemical Fuel Analyses. In Table 1, the chemical composition of the straw sample investigated is

Table 1. Chemical Composition of the Straw Investigated and Comparison to Database Values^a

		wheat straw	straw database values		
			mean	s	number
ash content	wt %	5.2	6.6	1.47	19
ash content corrected	wt %	4.7	na		
C	wt %	46.6	44.9	2.7	15
H	wt %	5.9	5.6	0.36	15
N	wt %	0.53	0.58	0.16	15
S	mg/kg	1000	1485	527	19
Cl	mg/kg	1900	3046	1859	19
Si	mg/kg	12400	17618	4917	19
Ca	mg/kg	3930	3785	1614	19
Mg	mg/kg	787	945	662	19
K	mg/kg	9010	6629	4149	19
Na	mg/kg	126	282	228	19
P	mg/kg	857	442.0	148.2	19
Al	mg/kg	42.8	237.9	244.9	18
Fe	mg/kg	74.7	250.3	205.5	18
Mn	mg/kg	22.1	16.0	6.2	5
Cu	mg/kg	2.1	na		
Zn	mg/kg	5.6	9.9	3.4	6
Pb	mg/kg	0.17	0.32	0.20	6

^aData were on dry basis. Database values were taken from ref 28 and the internal fuel database of BIOS BIOENERGIESYSTEME GmbH. Ash content corrected, ash content without total inorganic carbon (TIC); s, standard deviation; and na, no data available.

summarized and compared to database values for wheat straw gained from the IEA Task 32 biomass fuel database²⁸ as well as from the internal database of BIOS BIOENERGIESYSTEME GmbH.

As a first step within a comprehensive fuel evaluation, it should be checked whether the fuel composition generally

complies with the typical ranges of element concentrations of a certain fuel category (if such data are available). For the actual example, this is the case for all elements, except P (above the range of the database values). In general, the straw investigated can be categorized as a typical wheat straw.

Table 1 also shows that straw fuels typically are comparably rich in ash, N, S, and Cl as well as K and Si, while the heavy metal contents are rather low (in comparison to wood fuels). Consequently, gaseous NO_x , SO_x , and HCl emissions, fine particulate emissions (because of the high K and ash contents), corrosion (because of the high Cl content), and ash melting (because of the high Si and K contents) might be issues that demand more detailed investigations.

3.2. Evaluation of Fuel Indices. The evaluation of fuel indices can provide first important indications regarding combustion-related issues. The big advantage of a fuel-index-based evaluation is that, besides the fuel analyses, no additional tests are needed, and therefore, a quick first estimation of combustion-related fuel properties can be achieved. In Table 2,

Table 2. Fuel Indices of the Straw Sample Investigated^a

wheat straw		
K + Na + Zn + Pb	mg/kg, db	9142
2S/Cl	mol/mol	1.16
$(K + \text{Na})/[x(2S + \text{Cl})]$	mol/mol	0.45
$(\text{Si} + \text{P} + \text{K})/(\text{Ca} + \text{Mg})$	mol/mol	5.36

^adb = dry basis.

relevant fuel indices, which have been calculated on the basis of the analyses listed in Table 1, are presented. In Figure 2, database values for the fuel indices mentioned in Table 2 for the biomass fuel categories, wood chips, bark, straw, and waste wood, are compared. Detailed information regarding the definition and calculation of fuel indices can be taken from ref 15.

The fuel index $K + \text{Na} + \text{Zn} + \text{Pb}$ indicates the potential for the formation of fine particulate emissions. Figure 2 shows that this potential generally increases from chemically untreated wood fuels over bark and waste wood to straw fuels. Increased particulate emissions typically also result in enhanced deposit formation tendencies. A more detailed discussion is given in section 3.4.

The molar ratio of $(K + \text{Na})/x(2S + \text{Cl})$ is an indicator to which extent S and Cl will be embedded in the ashes and, thus, concerning HCl and SO_x emissions. In this index, the factor x considers the different average release ratios of K, Na, S, and Cl from the fuel to the gas phase. Lower values of this index indicate rising HCl and SO_x emissions. More detailed information concerning this index is provided in section 3.6.

The molar ratio of $2S/\text{Cl}$ is used as an indicator for high-temperature corrosion risks. With decreasing values, corrosion risks increase, from chemically untreated wood chips over bark and waste wood to straw. Straw shows high risks for high-temperature chlorine corrosion (see also section 3.5).

Finally, the molar ratio of $(\text{Si} + \text{P} + \text{K})/(\text{Ca} + \text{Mg})$ can be used as an indicator for ash-melting properties. Increasing values mean decreasing ash-melting temperatures. As a rule of thumb, the shrinkage-starting temperature drops below 1200 °C at values above 1. Figure 2 clearly shows decreasing ash-melting temperatures from wood chips over bark and waste wood to straw. For straw, very low ash-melting temperatures can be expected; for more details, also see section 3.3.

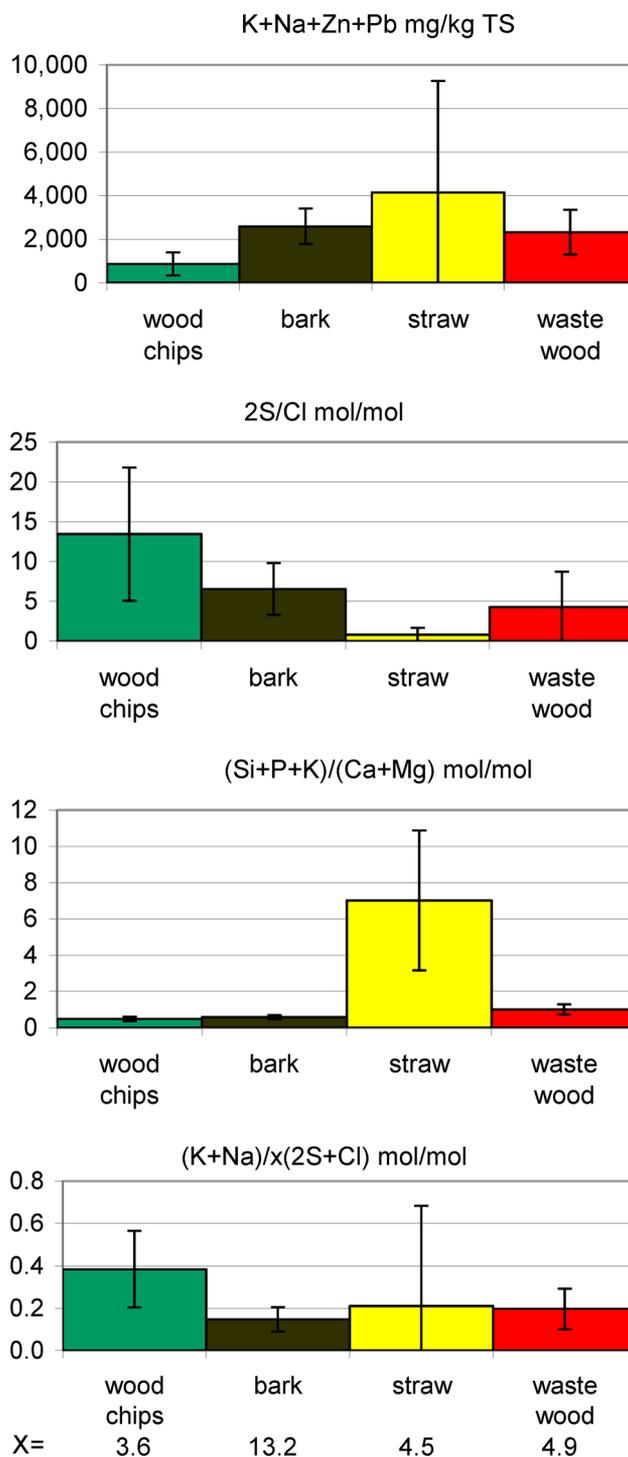


Figure 2. Relevant fuel indices for the fuel categories, straw, wood chips, bark, and waste wood. Waste wood of the classes A1 and A2 is according to German regulations, and waste wood of the classes Q1–Q4 is according to Austrian regulations. db, dry basis; factor x , see also section 3.6.

In summary, the pre-evaluation of the straw sample investigated shows that, when burning this fuel, special care has to be taken regarding fine particulate emissions and deposit formation, high-temperature corrosion, and low ash-melting temperatures. For all of these parameters, the fuel sample investigated shows disadvantageous properties compared to conventional chemically untreated wood fuels and bark. This

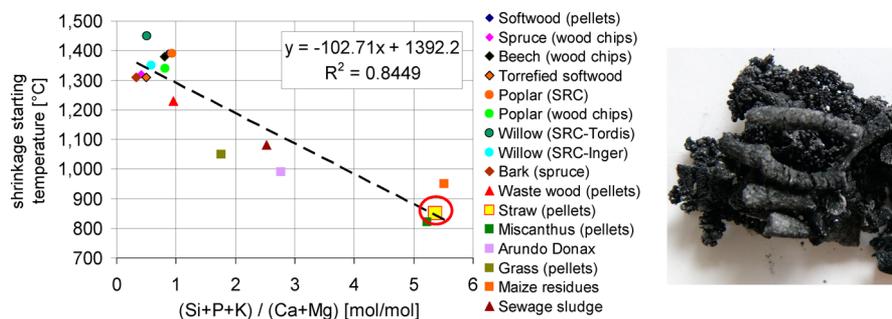


Figure 3. Shrinkage-starting temperature (SST) versus the molar ratio of $(\text{Si} + \text{P} + \text{K}) / (\text{Ca} + \text{Mg})$ and a picture of sintered ash particles from lab-reactor test runs with straw pellets. Straw is marked with a red cycle.

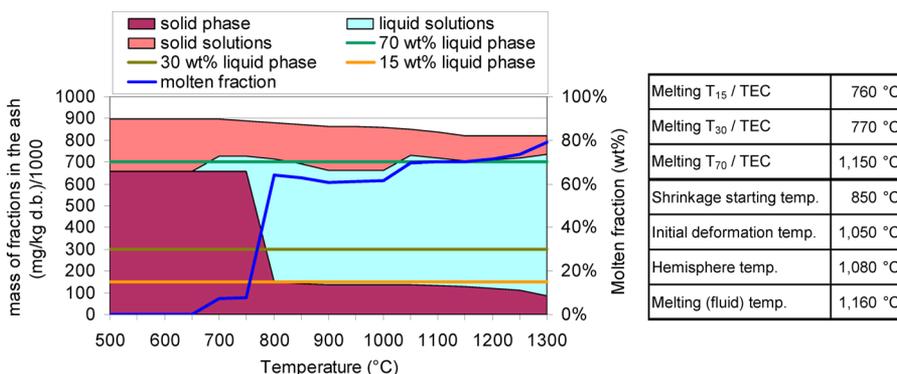


Figure 4. Ash-melting behavior of straw determined by TECs. Characteristic ash-melting temperatures are according to CEN/TS 15370-1. db, dry basis; TEC, thermodynamic equilibrium calculation; and temp, temperature.

basic information can, for instance, be used to support initial decisions if a specific fuel could be of interest for a certain application or not. To gain more detailed information, additional evaluations and fuel characterization tools as presented in the following sections can be applied.

3.3. Evaluation of the Ash-Melting Behavior. Low ash-melting temperatures can significantly affect the operation of grate combustion systems because ash melting on grates disturbs the combustion air flow through the fuel bed and can also cause problems in the de-ashing system. Moreover, increased risks regarding the formation of hard deposits on furnace walls and heat exchanger surfaces may occur. Therefore, knowledge about the ash-melting behavior is of great relevance for the design and operation of biomass combustion systems.

As a first evaluation tool, as already mentioned, the fuel index $(\text{Si} + \text{P} + \text{K}) / (\text{Ca} + \text{Mg})$ can be applied. In Figure 3, this index is plotted against the shrinkage-starting temperature determined with the standard ash-melting test according to CEN/TS 15370-1. The correlation presented is statistically significant. As already mentioned, the high value of the index (5.36) for the straw sample investigated is associated with a very low shrinkage-starting temperature of about 850 °C. This is also confirmed by the results of lab-scale reactor tests, which show considerable amounts of sintered and molten particles in the ash residue.

A deeper insight into the ash-melting behavior can be achieved by the application of high-temperature TECs. In Figure 4, results from TECs based on the chemical composition of an ashed straw sample (ashed at 550 °C) under oxidizing conditions are presented. In the figure, the phases resulting from TECs are summarized into three categories, i.e., solid

phases, solid solutions, and liquid solutions. Moreover, the trend of the share of the liquid solutions on the total ash over time is indicated as the molten fraction. T_{15} , T_{30} , and T_{70} indicate characteristic temperatures at which 15, 30, and 70 wt % of the molten fraction occur, respectively. T_{30} (770 °C) can be used as an indicator for the shrinkage-starting temperature. A good agreement with the standard ash-melting test is achieved (850 °C). Moreover, the T_{70} temperature calculated (1150 °C) is a good indicator for the fluid temperature (1160 °C). Furthermore, additional valuable information can be gained from TECs. The diagram in Figure 4, for instance, shows that the share of molten phases on the whole ash rapidly increases between 750 and 800 °C, which underlines the need for an efficient temperature control of the fuel bed to avoid severe ash-melting problems. Moreover, from detailed analyses of the compositions of the molten phases, trends regarding the influence of deviations of the fuel composition on the ash-melting behavior can be derived (also see section 3.7). Finally, TECs allow for the evaluation of ash-melting trends for different ash fractions, which makes this method even more attractive.

3.4. Fine Particulate Emissions and Release of Ash-Forming Elements from the Fuel to the Gas Phase. In section 3.2, the fuel index $\text{K} + \text{Na} + \text{Zn} + \text{Pb}$ has been introduced as an indicator regarding the potential for the formation of fine particulate emissions and the potential for deposit buildup. Figure 5 clearly shows a trend of increasing aerosol emissions with increasing values of this index, whereas straw is located at the upper end of the data. However, the error bars are remarkably high, and therefore, a more precise prediction tool would be of advantage. The trend displayed is mainly influenced by the K concentration in the fuel or, more

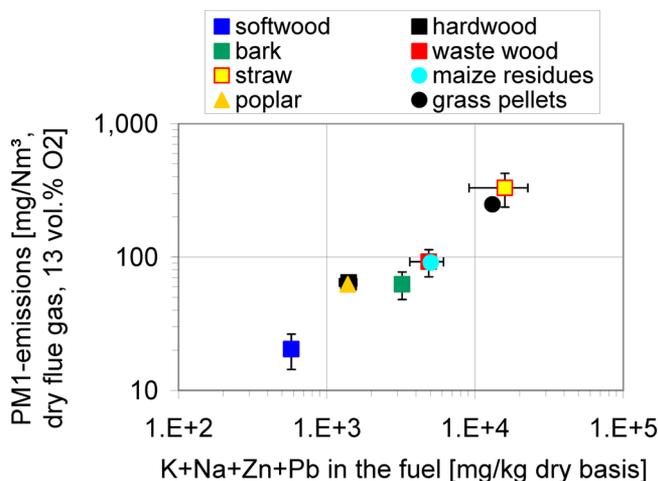


Figure 5. PM₁ emissions versus the concentration of aerosol-forming species (K + Na + Zn + Pb) in the fuel.

precisely, the K release from the fuel to the gas phase, and therefore, various attempts have been made to gain a universal fuel index that is able to describe the K release as a function of, for instance, the Si/K ratio. However, thus far, no satisfactorily good predictions could be achieved.

Therefore, other advanced fuel characterization methods have to be applied to gain more detailed information on the potential for aerosol formation. Two feasible options are the performance of TECs and the performance of lab-scale reactor tests. In Figure 6, results regarding the release of relevant ash-

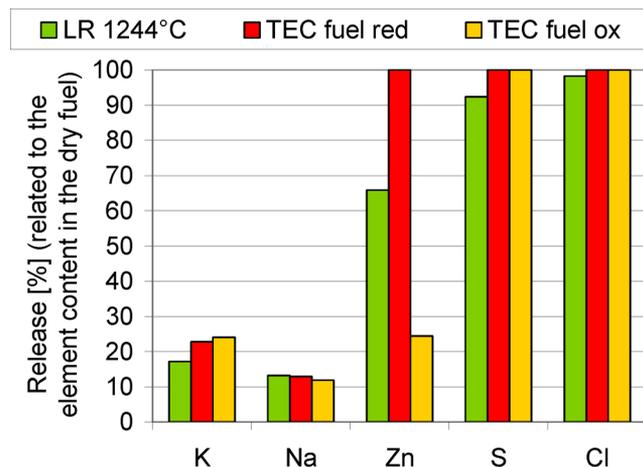


Figure 6. Inorganic element release during straw combustion: results from TEC and lab-scale reactor tests. TEC evaluations were performed for the maximum fuel-bed temperature during the lab-scale reactor test of 1244 °C. TEC fuel red and TEC fuel ox, TECs performed based on the fuel composition and oxidizing and reducing conditions, respectively.

forming elements (K, Na, Zn, S, and Cl) achieved with these two methods are presented. The results from TECs presented have been achieved by calculations for reducing conditions (gasification mode) and oxidizing conditions because they prevail at different sections of a biomass grate. Obviously, a good agreement for K, Na, S, and Cl could be achieved. For Zn, the gas atmosphere prevailing has a dominating influence on the release behavior, and the comparison of TEC and lab-scale reactor results indicate that Zn release takes place partly under

reducing and oxidizing conditions. However, it has to be mentioned that, with the models presently available, good agreement for Si- and K-rich fuels is achieved, while the model still needs some improvements for an application to wood fuels regarding the K release.

Assuming that K and Na form sulfates and chlorides and Zn forms ZnO, a maximum potential for aerosol emissions of about 300 mg/Nm³ (related to dry flue gas and 13 vol % O₂) can be calculated from the data presented in Figure 6. This maximum potential does not consider particle losses as a result of deposit formation on heat exchanger tubes because of direct condensation and thermophoresis, which are expected to amount to 10–20 wt %. However, these data are in good agreement with aerosol emissions of, on average, 323 mg/Nm³ (standard deviation of 74.6 mg/Nm³) measured downstream from a large-scale boiler using straw with comparable chemical composition.

A possibility to also consider deposit formation in these calculations can be provided by CFD simulations. Thereby, the release data gained from TEC or lab-scale reactor tests are used as input data for a specially developed CFD-based model. The model, which has been developed at BIOENERGY 2020+ GmbH in cooperation with the Institute for Process and Particle Engineering, Graz University of Technology, considers thermodynamic equilibrium of ash-forming species, particle formation and growth mechanisms, such as nucleation and condensation, a special kinetic approach for SO₃ formation, and different mechanisms describing particle deposition on heat exchanger surfaces and furnace walls.²⁹ The present version of this model thereby considers K, Na, S, and Cl as aerosol-forming elements, 220 gas species and 382 solid and liquid phases, and alkaline metal chlorides, sulfates, and carbonates as possible aerosol-forming vapors. Results from simulations performed with this model for a small-scale residential biomass boiler fired with wood pellets showed PM₁ emissions of 9.9 mg/Nm³ (related to dry flue gas and 13 vol % O₂). Measurements during test runs at the boiler simulated showed an average aerosol emission of 7.7 mg/Nm³, which indicates a reasonably good agreement. The aerosols formed are dominated by K₂SO₄ and KCl.

3.5. High-Temperature Corrosion. As already mentioned in section 3.2, the molar ratio of 2S/Cl can be applied as an indicator for high-temperature corrosion risks. As Figure 6 indicates, during straw combustion, more than 90% of S and Cl are released from the fuel to the gas phase. Database values available show about the same release rates for S and Cl for a great majority of other biomass fuels.¹⁵ Assuming comparable time–temperature profiles in furnaces and boilers, which are relevant for the sulfation of chlorides (mainly of KCl), a dependency of the molar 2S/Cl ratio of the aerosol particles formed and the fuel prevails. Moreover, deposits on boiler tube surfaces tend to show compositions, which are well-comparable to the aerosol compositions. Consequently, the fuel index 2S/Cl directly affects the composition of the boiler tube deposits and, therefore, can be used to describe their potential for high-temperature corrosion. It can generally be stated that, for 2S/Cl ratios of more than 8, no significant corrosion risks exist.³⁰ With decreasing values of the index, corrosion risks increase, and for values below 4, significant corrosion risks have to be expected. In Figure 7, the molar 2S/Cl ratios of different biomass fuels are plotted against the same index related to the aerosol emissions, and moreover, the areas for high, medium,

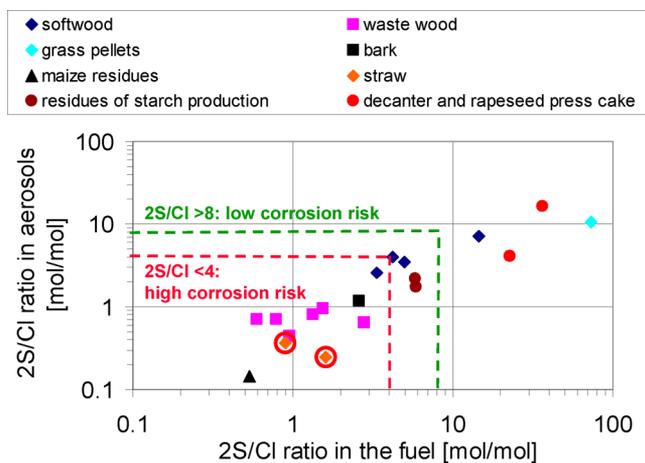


Figure 7. Relation between the molar 2S/Cl ratio in the fuel and aerosol emissions for different biomass fuels.

and low corrosion risks are indicated. Straw is situated in the area indicating high corrosion risks.

More detailed information concerning high-temperature corrosion risks can be gained from dedicated test runs with online corrosion probes. Thereby, the influence of parameters, such as flue gas temperature, probe surface temperature (i.e., surface temperature of the heat exchanger simulated), flue gas and deposit compositions, and the material used on the corrosion risk, can be investigated. Of course, long-term measurements at real-scale applications provide the most complete picture; however, as Figure 8 shows, also short-term tests at lab-scale installations already provide first relevant information. In the left-hand diagram, the increase of the corrosion signal with a rising flue gas temperature at a constant probe surface temperature is presented. The right-hand diagram shows the variation of the corrosion signal during changing probe surface temperatures at a constant flue gas temperature.

The results can be used to support the choice of the material as well as the definition of permissible surface temperatures of superheaters (which also influences the steam parameters and, therefore, the electric efficiency that can be achieved) for real-scale applications against the background of corrosion risks.

3.6. HCl, SO_x, and NO_x Emissions. As already mentioned in section 3.2, the molar ratio of $(K + Na)/x(2S + Cl)$ can be used as an indicator for the embedding of S and Cl into the ashes and, thus, as an indicator for HCl and SO_x emissions. The background of this fuel index can be explained as follows.

During combustion, major parts of S and Cl as well as varying shares of K and Na contained in the fuel are released to the gas phase. At the high temperatures, prevailing K and Na form sulfates and chlorides. If there is a surplus of K and Na available in the gas phase, almost all S and Cl can be bound and only minor gaseous S and Cl emissions, i.e., SO_x and HCl emissions, have to be expected. Consequently, not the concentration of these key elements in the fuel but their release to the gas phase plays an important role in this mechanism, which is considered by the factor x . The factor x represents the ratio of the K and Na release to the S and Cl release. Former studies¹⁵ have shown that the S and Cl release ratios are almost constant for biomass fuels (at comparable combustion temperatures), while the Na and K release strongly depends upon possible reactions with other ash-forming elements, such as Si. Therefore, this factor x has to be defined on a fuel-specific basis from, e.g., lab-scale reactor tests.

In Figure 9, SO_x and HCl emissions determined during real-scale tests are plotted over the molar $(K + Na)/x(2S + Cl)$ ratio of the fuel. Both diagrams show a strong decrease of the emissions in the range of >0.5 . In the range below 0.5, a significant increase of the emissions has to be expected. This increase can presently only be qualitatively evaluated because a number of additional parameters influence HCl and SO_x emissions (reactions of S and Cl with Ca and Mg as well as the kinetics of SO₃ formation, which is essential for reactions of S with alkaline metals).

With respect to the interactions of S and Cl with alkaline metals mentioned above, the K release from the fuel to the gas phase is the most relevant parameter influencing the formation of solid sulfates and chlorides. This also means that an increased embedding of K in the bottom ash (i.e., a lower K release) positively influences all issues related to deposit formation and fine particulate emissions (see sections 3.2 and 3.4) but, in turn, leads to increased gaseous HCl and SO_x emissions. Especially when applying fuel blending or additives to reduce the K release (as discussed later on in section 3.7), this effect has to be considered and a meaningful compromise between K release reduction and increased gaseous emissions has to be found.

Another relevant gaseous pollutant is NO_x. A good prediction of the NO_x emission potential of a fuel is needed to be able to evaluate the necessity for secondary measures regarding emission reduction [e.g., selective non-catalytic reduction (SNCR)]. Generally, as Figure 10 shows, NO_x emissions increase with increasing fuel N content even if the

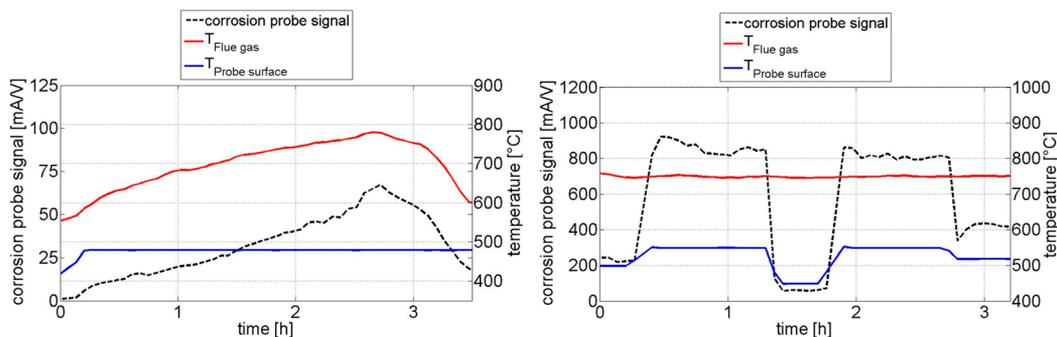


Figure 8. Corrosion signal as a function of the flue gas and probe surface temperature. Results from test runs with straw pellets at a 50 kW biomass furnace which was connected with an electrically heated drop tube (see ref 26). $T_{\text{flue gas}}$, flue gas temperature at the measurement position; $T_{\text{probe surface}}$, surface temperature of the corrosion probe; and probe material, 13CrMo4-5.

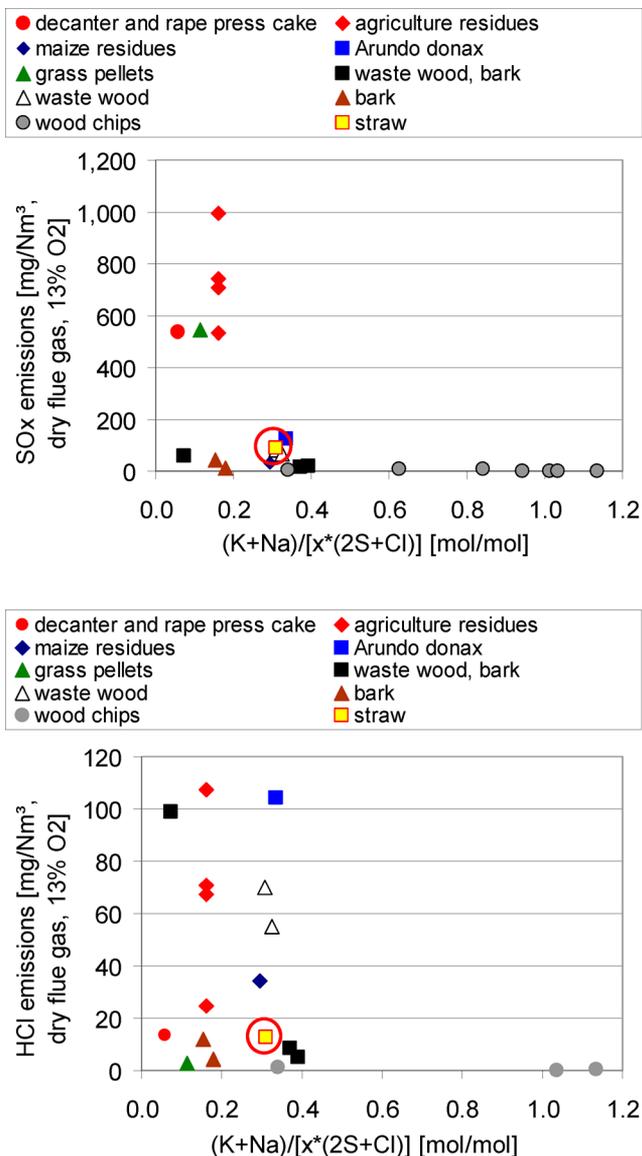


Figure 9. SO_x and HCl emissions versus the molar (K + Na)/x(2S + Cl) ratio. Results from test runs are at real-scale plants. Results for straw combustion are marked.

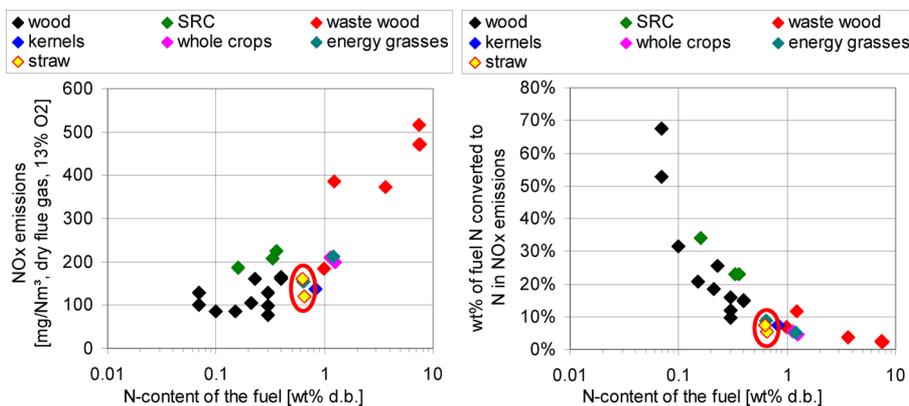


Figure 10. NO_x emissions and N conversion related to the N content of the fuel. Results from test runs are at real-scale plants equipped with air-staging technology. Results for straw combustion are marked. NO_x is calculated as NO₂.

conversion of fuel N to NO_x decreases. These graphs allow for a good approximation of the NO_x emissions to be expected for a certain fuel, if grate combustion equipped with air staging is applied. Air staging means that the stoichiometric air ratio in the primary combustion zone is kept slightly below 1 and that appropriate residence time (at least 0.5 s) of the flue gas in the primary combustion zone at temperatures above 800 °C is achieved before secondary air injection takes place. The potential for NO_x emission reduction by primary measures (air staging) is thereby in the range of 30–60%.^{31,32}

A deeper insight into NO_x formation is achieved by lab-scale reactor tests, which provide information about the release of certain NO_x precursors during the combustion process. In Figure 11, the respective results of test runs with straw as well

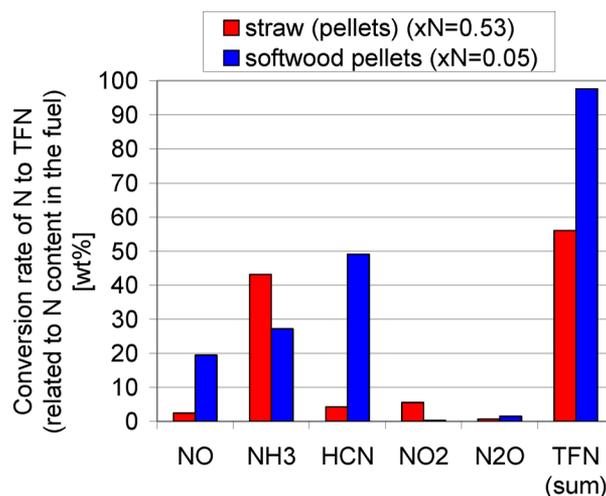


Figure 11. Release of NO_x precursors during straw and softwood pellet combustion according to lab-scale test runs. TFN, total fixed nitrogen (species NO, NH₃, HCN, NO₂, and N₂O); xN, N content of the fuel (wt %, db).

as a comparison to results from test runs with softwood pellets are presented. During straw combustion, NH₃ is the dominating NO_x precursor, while during wood combustion, HCN, NH₃, and NO play a relevant role. The conversion of N in the fuel to N in total fixed nitrogen (TFN) considerably decreases with an increasing N content (which means that more fuel N is converted into N₂).

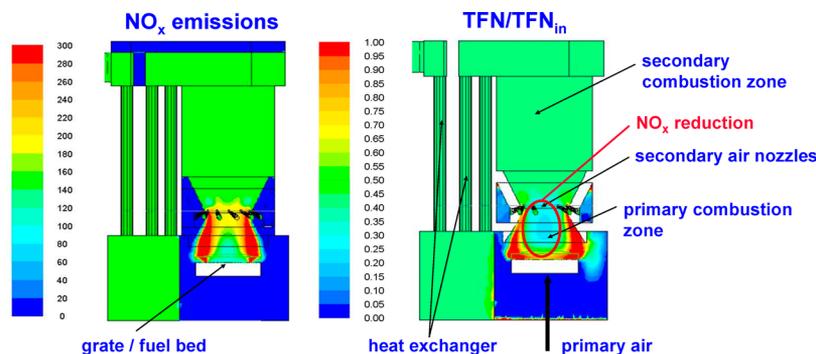


Figure 12. Isosurfaces of NO_x emissions (ppmv, wb) (left) and the ratio $\text{TFN}/\text{TFN}_{\text{in}}$ (right) in a vertical cross-section through the combustion chamber of a 20 kW underfeed multi-fuel boiler. TFN, sum of N moles in NO , NH_3 , NO_2 , HCN , and N_2O ; TFN_{in} , sum of N moles in NO , NH_3 , and HCN released from the fuel bed; and $\text{TFN}/\text{TFN}_{\text{in}}$, local TFN conversion rate in the furnace.

This information about the release of NO_x precursors can further be used as an input for CFD simulations of NO_x formation. In Figure 12, results of such calculations for a 20 kW underfed boiler burning straw pellets are presented. The simulations have been performed with the software ANSYS-FLUENT applying a self-developed empirical packed-bed combustion model as well as detailed NO_x reaction kinetics. It has been validated for various fixed-bed combustion systems and allows for a qualitative as well as semi-quantitative prediction of NO_x emissions. In the empirical packed-bed combustion model for biomass grate furnaces, the release profiles of NO_x precursors are implemented. For the simulation of the gas-phase combustion, the realizable $k-\epsilon$ model (regarding turbulence), the discrete ordinates model (regarding radiation), and the eddy dissipation model (regarding the interaction of turbulence and chemistry) were used. The distribution of flue gas residence times was simulated by scalar transport equations. For NO_x formation calculations, an extension of the empirical packed-bed combustion model by the most relevant NO_x precursors NO , NH_3 , and HCN was performed. The simulation of NO_x formation in the combustion chamber has been performed with detailed reaction kinetics (Kilpinen 97-skeletal) and the eddy dissipation concept (interaction of turbulence and chemistry). Moreover, modes for the reduction of calculation time have been applied [*in situ* adaptive tabulation (ISAT) and chemical agglomeration algorithm].^{33,34}

From Figure 12, it can be evaluated where the major parts of the NO_x emission formation but also the NO_x emission reduction reactions take place. Therefore, such CFD simulations can be used (i) to investigate the NO_x emissions of a new fuel when using it in an existing plant and derive recommendations for the adaptation of the air-staging settings and (ii) to optimize the combustion chamber design and air-staging concept for a new plant that should be tailored to the demands of a specific fuel type.

3.7. Application of Additives and Fuel Blending. Thus far, the evaluation of straw has shown that considerable problems concerning low ash-melting temperatures as well as increased aerosol and, consequently, deposit formation have to be expected. The application of additives (e.g., kaolin) or blending with peat could be options to improve the melting properties and achieve a higher embedding of K in the bottom ash. The evaluation of fuel indices, lab-scale reactor tests, and TECs are also appropriate characterization tools for the

prediction of the effects of additives and fuel blending on the fuel properties.

Tests have been performed with kaolin additions of 1, 4, and 7 wt % related to the dry fuel mass. The 4% kaolin case was, according to TECs, assumed to be the optimum addition because TEC results indicated that the K release could be reduced to a very low level and a considerable increase of the ash-melting temperatures could be reached. Higher kaolin addition would not have resulted in a significant further improvement in terms of increased ash-melting temperatures and reduced K release. The kaolin and straw were milled, mixed, and then pelletized. Chemical analyses were performed to investigate the mixing quality. Then, ash-melting tests as well as lab-scale reactor tests have been performed with the different straw-kaolin mixtures. Moreover, on the basis of the fuel analysis data, TECs were carried out applying a two-step model (step 1, pyrolysis/gasification at reducing conditions and 700 °C; step 2, char coal combustion at oxidizing conditions and evaluation of the results at the maximum temperature achieved during the lab-scale reactor tests).

In Figure 13, the effect of kaolin addition to straw on the ash-melting behavior is shown. The ash-sintering temperatures gained from the standard ash-melting test (experimental) as well as the results gained from TECs are plotted over the fuel index $(\text{Si} + \text{P} + \text{K})/(\text{Ca} + \text{Mg} + \text{Al})$, which represents a

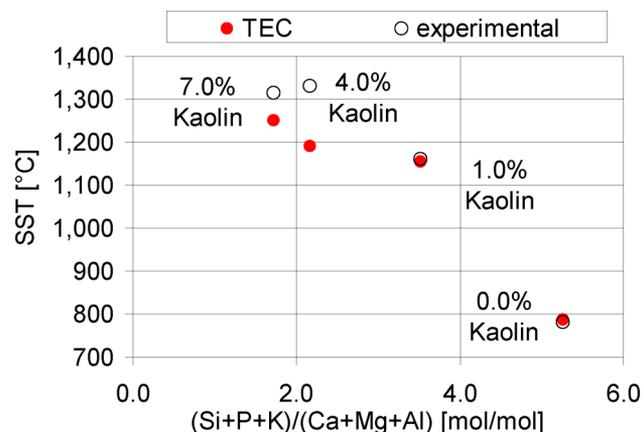


Figure 13. Evaluation of the effect of kaolin addition to straw as a function of the fuel index $(\text{Si} + \text{P} + \text{K})/(\text{Ca} + \text{Mg} + \text{Al})$: comparison of experimental and TEC results. The shrinkage-starting temperatures (SSTs) from TECs were estimated at 30 wt % molten fraction. TEC, results from thermodynamic equilibrium calculations.

modification of the fuel index $(Si + P + K)/(Ca + Mg)$ taking the high Al content of kaolin into account. The diagram clearly shows the increasing melting temperatures with increasing kaolin addition. Overall, the trend fits well with the data presented in Figure 3. Moreover, a good agreement between TEC and experimental data exists.

Figure 14 shows results regarding the K release gained from TEC and lab-scale reactor test runs. The data nicely

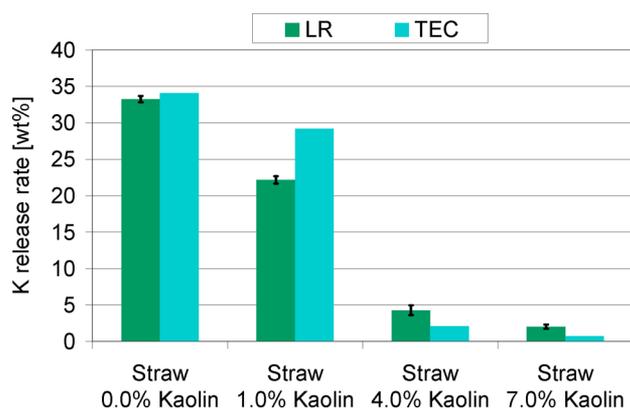


Figure 14. Effect of kaolin addition on the K release. The TEC release is calculated at 1250 °C, which was the maximum fuel-bed temperature during the lab-scale reactor tests. LR, results from lab-scale reactor tests; TEC, results from thermodynamic equilibrium calculations.

demonstrate how kaolin addition can reduce the K release considerably. Again, a good agreement between lab-scale reactor tests and TECs exists. Concluding, for straw, the addition of 4% kaolin can result in considerably reduced aerosol and deposit formation as well as an increase of the shrinkage-starting temperature by about 500 °C.

4. CONCLUSION

New and advanced methods for biomass fuel characterization are available, which are fuel indices, dedicated lab-scale reactor tests, and TECs, specially adapted for biomass fuels and ashes. If appropriately applied and combined, they can provide relevant information regarding fuel application and plant design, with special focus on some of the most crucial combustion-related issues, which are (i) the release of ash-forming species, (ii) fine particle formation and emissions, (iii) ash-melting behavior, (iv) expected NO_x , SO_x and HCl emissions, and (v) corrosion behavior prediction.

Moreover, the new and advanced fuel characterization methods can also be used as a basis for the evaluation of the effects of additive utilization and fuel blending on the fuel characteristics, especially regarding ash-related problems.

As the case study of straw shows, the results achievable with these advanced fuel characterization tools are verifiable in practice, and therefore, a fuel evaluation strategy based on these tools can provide valuable information for preliminary plant design. Moreover, the integration of results concerning the release of ash vapors and NO_x precursors into CFD simulation routines enables a detailed evaluation as well as prediction of influencing parameters on aerosol and deposit formation as well as NO_x emissions, which can support the detailed design of furnaces and boilers.

New biomass fuel databases considering the results of advanced fuel characterization methods are under development. Additionally, R&D is ongoing regarding the further improve-

ment of these methods to enhance their prediction preciseness. In conclusion, the new fuel evaluation strategy presented can be a powerful tool in future plant design.

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Notes

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