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Fuel Indexes: A Novel Method for the Evaluation of Relevant Combustion Properties of New Biomass Fuels

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ABSTRACT: The increasing demand for biomass fuels leads to the introduction of new biomass fuels into the market. These new biomass fuels (e.g., wastes and residues from agriculture and the food industry, short rotation coppices, and energy crops) are usually not well-defined regarding their combustion behavior. Therefore, fuel characterization methods with a special focus on combustion-related problems (gaseous $NO_{x'}$ HCl, and SO_x emissions, ash-melting behavior, and PM emissions) have to be developed. For this purpose, fuel indexes are an interesting option. Fuel indexes are derived from chemical fuel analyses and are checked and evaluated regarding their applicability by measurements performed at lab- and real-scale combustion plants for a large variety of fuels. They provide the possibilities for a pre-evaluation of combustion-relevant problems that may arise from the use of a new biomass fuel. A possible relation to describe the corrosion risk is, for instance, the molar 2S/Cl ratio. The N content in the fuel is an indicator for NO_x emissions, and the sum of the concentrations of K, Na, Zn, and Pb in the fuel can give a prediction of the aerosol emissions, whereas the molar (K + Na)/[x(2S + Cl)] ratio provides a first indication regarding the potential for gaseous HCl and SO_x emissions. The molar Si/K ratio can supply information about the K release from the fuel to the gas phase. The molar Si/(Ca + Mg) ratio can give indications regarding the ash-melting temperatures for P-poor fuels. For Prich fuels, the (Si + P + K)/(Ca + Mg) ratio can be used for the same purpose. The fuel indexes mentioned can provide a first pre-evaluation of combustion-relevant properties of biomass fuels. Therefore, time-consuming and expensive combustion tests can partly be saved. The indexes mentioned are especially developed for grate combustion plants, because interactions of the bed material possible in fluidized-bed combustion systems are not considered.

1. INTRODUCTION, BACKGROUND, AND SCOPE

The general increase in energy demand, higher costs, and oncoming depletion of fossil fuels are reasons for considerable research on renewable energies and raw material resources. Biomass energy can be an important factor in reducing greenhouse gas emissions and energy source independence.¹

To increase the biomass use in the energy sector, products such as wastes and residues from agriculture and the food industry, as well as short-rotation plants, such as poplar, and energy crops, such as *Miscanthus*, *Arundo donax*, and grasses, can be used. These new biomass fuels gain rising interest for use in biomass combustion systems. As a result, new biomass fuels are of relevance for furnace and boiler manufacturers as well as utilities. According to the increasing prices for conventional biomass fuels (e.g., wood), new options for heat and power generation from cheap feedstocks have to be identified to increase the economic efficiency of biomass heating and combined heat and power (CHP) plants. The introduction of new biomass fuels may also create new employment opportunities in rural areas and, therefore, also contribute to the social aspect of sustainability.^{2,3}

For the past decade, agricultural studies throughout Europe have been focusing on introducing new nonfeed crops with a perspective for industrial applications. Perennial rhizomatous grasses, such as switchgrass (*Panicum virgatum*), *Miscanthus* spp., giant reed (*A. donax*), and red canarygrass (*Phalaris arundinacea*), have been considered as the most promising energy crops for Europe. The employment of such raw materials contributes to reduce anthropogenic CO_2 emissions. Also, the situation of the agricultural sector in the European Union (EU) can be improved. This sector is characterized by food surplus, which has led to a policy of setting land aside. Therefore, introducing alternative nonfood crops as energy crops can represent a new opportunity for the population of rural areas. Perennial grasses, such as *Miscanthus* and giant reed, show some ecological advantages. They require limited soil management and a low demand for nutrient inputs. Also, further restoration of degraded land may be possible.⁴

Short-rotation coppices (SRCs) are fast-growing tree species, which are used to produce biomass as a renewable energy source. The most common SRCs are willow and poplar, which have been shown to be viable alternatives to fossil fuels.²

Agricultural residues, such as olive stones, are already used as fuels for combustion processes; however, a great further potential of these fuels exist, which is presently not used but disposed.⁵

However, because new biomass fuels are not well-defined yet regarding their combustion behavior, fuel characterization with a special focus on combustion-related fuel properties is a first important step for their introduction. Possible ash-related problems (ash melting on grates, bed agglomeration in fluidized-bed combustion systems, deposit formation and

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corrosion, and particulate emissions) as well as problems regarding NO_{xy} SO_{xy} and HCl emissions are thereby the main focus points. With state-of-the-art fuel characterization methods, these issues cannot be sufficiently covered, and therefore, new and advanced fuel characterization methods are needed. One option to gain quick first indications regarding the problems mentioned is the development, evaluation, and application of fuel indexes as one advanced biomass fuel characterization tool.

1.1. Background and Scope. The fireside behavior of minerals in coal was first investigated more than 100 years ago. After the beginning of burning high-sulfur coals rich in pyrites (FeS_2) on grates, it was quickly recognized that pyrite was responsible for the formation of clinkers. For the first time, a combustion-related problem was directly related to a specific mineral species. It was understood that iron occurring in high-sulfur coals acted as a fluxing agent, lowering the melting temperature of quartz and clays found in coal. These early problems associated with slagging were the trigger for the development of empirical correlations for the prediction of slagging tendencies. The correlations describe the relationship between the melting temperature of slag and the proportional distribution between basic and acidic constituents.⁶

Afterward, the increasing electricity demand since the 1950s as well as the ambition to increase the electric efficiency resulted in continuously increasing steam temperatures. Also, the use of more problematic coals resulted in further fireside problems, such as ash sintering or slagging, fouling of convective heat recovery surfaces, and high-temperature corrosion. Therefore, various empirical correlations especially to predict the ash-sintering behavior of coal have been developed.⁶

In a pre-evaluation step of this work, existing empirical correlations for coals were tested regarding their applicability for biomass fuels. It was seen that indexes developed for coal cannot be applied for biomass. Because coal is a type of sedimentary rock, minerals can occur disposed as tiny inclusions within macerals, layers, nodules, fissures, and rock fragments. Thick layers and abundant nodules are removed by standard preparation facilities. The thinner layers and nodules stay in the coal and typically consist of aluminum silicates (clay, illite, kaolinite, feldspar) and silicon oxide (quartz). The alkali metals (typically Na) are bound in this aluminum silicate structure and occur in minor concentrations. In biomass fuels, in contrast, K exists in high concentrations, and its chemical binding in the fuel matrix is different from coal. K occurs as highly mobile ion in biomass fuels. Si as a further example is introduced in the plants by absorption of silicate acid from the soil. Si is deposited as a hydrated oxide usually in an amorphous form but occasionally in crystalline form. Dependent upon the biomass species, the major elements responsible for the ash chemistry can roughly be categorized in low-Si-/high-Cacontaining fuels, e.g., wood and woody biomass and high-Si-/ low-Ca-containing fuels, e.g., herbaceous biomass. It can generally be said that coals contain higher amounts of S mostly in the form of FeS2. In biomass plants, S exists as sulfates or organic sulfur. The amount of Cl in coal depends upon the coal type and exists predominantly as inorganic alkali chlorides and a smaller amount of unspecific organic chlorides. In biomass, Cl appears as a chloride ion, where its concentration is closely related to the nutrient composition of the soil.⁶ The difference in occurrence and in chemical binding of certain elements explains the non-applicability of empirical coal correlations for

sintering or slagging, fouling, and high-temperature corrosion on biomass fuels.

Far less empirical correlations or fuel indexes predicting combustion-related problems have thus far been found in the literature for biomass. For fluidized-bed systems, the indexes (K + Na)/(2S + Cl), (K + Na + Si)/(Ca + P + Mg), and K/Si have been investigated.⁷ The index (Na + K)/(2S + Cl) is based on the general observation that the initial gas-phase alkali concentration is attributable to the alkali concentration in the fuel. A molar (Na + K)/(2S + Cl) ratio in the fuel >1 reflects the chance that the excess alkali over the sum of S and Cl would stay in the bed and may react with silicates. The formation of alkali silicates is often observed and leads to sintering or defluidization. The index (K + Na + Si)/(Ca + P + Mg) is applied to describe the probability of the formation of a nonsticky outer coating on a bed material particle. For a ratio smaller than 1, the refractory outer coating is likely to form and prevent the sintering of coatings. Also, a third agglomeration indicator, the molar K/Si ratio, was introduced, where values >1 indicate that the occurrence of agglomeration is more likely a result of melt-induced sintering than the sintering of coating.

On the basis of results of test runs in a residential biomass pellet boiler with 12 different fuels, which were combusted, the slagging tendencies and the K retention have been investigated. The molar amounts of Si-(Cl + Ca + Mg) in the fuel should describe the K retention in residual ash (slag and bottom ash). The second correlation, the molar amounts of Si-(Cl + Ca + Mg) in the residual ash, should describe the K retention in the slag and the slagging tendency. There is a trend reported for the second correlation, where with increasing value of this index, the K retention in the slag and the slagging tendency increase.⁸ It is assumed that the elements Cl, Ca, and Mg may increase the K retention in the ash and slag.

The molar Si/(Ca + Mg) ratio has been reported to predict the slagging tendency for residential heating appliances, where with rising value, slagging increases.⁹

Although the indexes of (K + Na)/(2S + Cl), (K + Na + Si)/(Ca + P + Mg), and K/Si were developed for fluidized-bed systems, where interactions of the bed material influence the combustion behavior, some fundamental considerations may also be used within this work focusing on fixed-bed systems.

The aim of this work was the evaluation of the applicability of already defined fuel indexes as well as the development of new fuel indexes, which can be applied to predict combustionrelated problems. This work is based on data from lab, pilot, and field tests performed with a broad spectrum of biomass fuels at fixed-bed combustion systems.

2. METHODOLOGICAL APPROACH

2.1. Fuels Investigated. Biomass fuels from five different biomass categories, which are typical for different climate zones, were used within this study: (1) wood and woody biomass (WWB): (i) beech woodchips from Austria, (ii) spruce wood chips from Austria, (iii) spruce pellets from Austria, (iv) bark of softwood, (v) waste wood, and (vi) torrefied softwood; (2) SRC: (i) poplar from Austria; (3) herbaceous and agricultural biomass (HAB): (i) *Miscanthus* pellets from Germany, (ii) wheat straw from Austria, (iii) olive kernels from Greece, (iv) maize spindel pellets (maize residues) from Austria, and (v) grass pellets; (4) others: (i) sewage sludge from Austria; and (5) industrial biomass residues: (i) decanter and rapeseed press cake and (ii) residues of starch production.

The group WWB represents the conventional biomass fuels, whereas the remaining groups represent new biomass fuels.



Figure 1. Scheme of the lab-scale reactor, including measurement setup (left), definition of common test conditions for all experiments (middle), and projection of the lab-scale reactor fuel bed to the fuel layer in a grate furnace (right).^{10,11}

2.2. Methodology. Proximate and ultimate analyses of the fuels investigated (ash content, contents of N, S, Cl, and major and minor ash-forming elements) are applied as the basis for the work presented. The analytical methods are described in section 3. From the results of these analyses, fuel indexes are calculated and evaluated. They are defined by considering the physical behavior and chemical reactions of dedicated elements during biomass combustion, known interactions of different ash-forming elements during thermal biomass conversion, and correlations and experiences gained from pilot- and real-scale combustion as well as lab-scale combustion tests with conventional and new biomass fuels. Data derived from combustion tests performed at BIOENERGY 2020+, the Institute for Process and Particle Engineering, Graz University of Technology, and BIOS BIOEN-ERGIESYSTEME GmbH, Graz, Austria, were considered.

2.3. Pilot- and Real-Scale Combustion Tests. All combustion plants have geometrically separated primary and secondary combustion zones and, thus, enable an efficient air staging. The primary air ratio (amount of primary air/stoichiometric amount of air) is typically below 1 (0.6-0.9), and the overall air ratio applied is between 1.4 and 1.6. The plants are also equipped with flue gas recirculation, which ensures that the bed temperature is kept in a range of 900–1100 °C.

The real-scale combustion plants investigated are also grate-fired combustion systems with nominal thermal boiler capacities between 0.5 and 110 MW. Also, these boilers are equipped with air-staging technology, and most of them are equipped with flue gas recirculation. Grate combustion plants representing the present state-of-the-art were chosen, and only comparable combustion setups were considered within the evaluation.

During the pilot- and real-scale combustion tests, the following data were collected: (1) Fuel sampling and subsequent analyses: (i) moisture content, ash content, and chemical composition. (2) Aerosol and fly ash sampling: (i) For aerosol emissions, low-pressure-cascade impactors (Berner-type low-pressure impactors) were used. (ii) For total fly ash emissions, the gravimetric method according to VDI 2066 was used. (3) Deposit sampling with deposit probes. (4) Emission measurements concerning CO, CO₂, NO, NO_x, O₂, SO_x, and HCl: (i) CO, CO₂, and O₂ were measured with a multi-component gas analyzer (Rosemount NGA 2000). This device uses non-dispersive infrared measurement technique (NDIR) for CO and CO₂ analyses and paramagnetism as a measurement principle for O2 detection. (ii) A nitric oxide analyzer (ECO Physis CLD 700 El ht), which uses the principle of chemiluminescence, has been used for NO and NO_x detection. (iii) The SO_x and HCl emissions were performed by discontinuous measurements according to VDI 3480, Sheet 1. (5) Determination of the furnace temperatures. (6) Sampling of all relevant ash fractions (bottom ash, furnace ash, cyclone ash, filter fly ash, and aerosols) and subsequent analyses: (i) chemical composition. (7) Recording of all relevant operating parameters (O_2 content in the flue gas, furnace temperature, load, combustion air supply, etc.)

The methods used for fuel and ash analyses are described in section 3. On the basis of the analysis results and measurement data, energy, mass, and element balances over the plant were calculated. Moreover, recovery rates for all ash-forming elements considered were evaluated to ensure the quality of the data. Only test runs with recovery rates >90% were used for further evaluation.

2.4. Lab-Scale Reactor Tests. In addition, results from test runs with a lab-scale reactor especially designed for the investigation of the thermal decomposition behavior of biomass fuels have been considered.

This lab-scale reactor consists of a cylindrical retort (height, 35 cm; inner diameter, 12 cm), which is heated electrically and controlled by two separated proportional—integral—derivative (PID) controllers (see Figure 1, left). The fuel is put in a cylindrical holder of 100 mm height and 95 mm inner diameter. The material of the reactor wall and sample holder is silicon carbide, which is inert under reducing and oxidizing conditions; therefore, the wall does not react with the fuel, ash, and flue gas. The mounting and vessel for the fuel bed are placed on the plate of a scale. The scale is mechanically separated from the retort by a liquid sealing (synthetic thermal oil: Therminol 66). The scale is used to determine the weight loss of the sample.

With this setup, it is possible to continuously measure the mass reduction of the sample during drying, pyrolysis, gasification, and charcoal combustion. The sample is introduced into the preheated reactor, and therefore, a rapid heating, which is well-comparable to the heating in real thermal conversion processes, can be achieved. The test conditions for all test runs performed with the lab-scale reactor are defined in Figure 1.

The following measurements/analyses were performed during each of the combustion test runs: (1) Mass decrease of the fuel over time (balance). (2) Concentrations of flue gas species over time: (i) Determination of CO₂, H₂O, CO, CH₄, NH₃, HCN, N₂O, and basic hydrocarbons was performed with a multi-component Fourier transform infrared (FTIR) spectroscopy device (Ansyco Series 447). (ii) The O₂ and H₂ concentrations were measured with a multicomponent gas analyzer (Rosemount NGA 2000). This device uses paramagnetism as a measurement principle for O2 detection and a thermal conductivity detector (TCD) for H₂ detection. (iii) The amount of total hydrocarbons (C_xH_y) was determined with a flame ionization detector (FID, Bernath Atomic 3005), which detects organic compounds by ionization in a burning H₂ flame. (iv) Wideband λ sensor (O₂). (v) A nitric oxide analyzer (ECO Physis CLD 700 El ht), which uses the principle of chemiluminescence, has been used for NO and NO₂ detection. (3) Temperature measurements over time: (i) Five thermocouples in the fuel bed (three different heights NiCr-Ni). (ii) Thermocouples in the gas phase (NiCr-Ni). (4) Analysis of the biomass fuel used and residual ash produced (see section 3).

The data of the fuel analysis and the residual ash analysis as well as the weight measurements of the fuel sample and the ash sample can be

used to calculate the elemental release to the gas phase. This is performed by calculating the mass balance for every relevant element as well as the total ash.

The lab-scale reactor has been designed to represent the burning conditions of a biomass fuel layer on a grate as well as possible (Figure 1, right). This approach is valid if diffusional transport and mixing effects on the grate can be neglected in comparison to the transport of the fuel along the grate. The validation has been achieved in previous research, which has shown that the fuel transport along the grate can be fluidically characterized by a plug flow in good approximation.^{10,11}

2.5. Definition of Fuel Indexes. On the basis of the evaluation of the fuel analysis and test runs as well as a theoretical evaluation, the following fuel indexes have been investigated and are presented in the following: (1) N concentration in the fuel as an indicator for NO_x emissions, (2) sum of K, Na, Zn, and Pb as an indicator regarding aerosol emissions (fine particles smaller than 1 μ m) and deposit buildup, (3) molar Si/K ratio for an estimation of the K release from the fuel to the gas phase, (4) molar 2S/Cl ratio for the prediction of the risk of high-temperature corrosion, (5) molar (K + Na)/[x(2S + Cl)] ratio for the prediction of the ash-melting temperatures with the molar Si/(Ca + Mg) and molar (Si + K + P)/(Ca + Mg) ratios.

The definitions of the above-mentioned indexes are based on theoretical considerations. With the exception of the molar Si/K ratio and the factor x occurring in the index (K + Na)/[x(2S + Cl)], all indexes were validated using results of pilot- and real-scale combustion tests. The factor x is a function of the release of K, Na, S, and Cl from the fuel to the gas phase, which has been derived from lab-scale reactor tests (see Figure 1), because of the well-defined conditions provided by this unit. To evaluate the index of the molar Si/K ratio, data from the lab-scale reactor have also been used.

3. CHEMICAL FUEL ANALYSES: THE BASIS FOR THE CALCULATION OF FUEL INDEXES

3.1. General Aspects. Because the quality of the fuel analyses applied forms the most important basis for the evaluation of fuel indexes, only highly accurate methods, which have already proven their applicability for biomass fuels, should be applied. Moreover, it has to be taken into consideration that the fuel sample investigated is representative for the biomass fuel of interest. Especially when new agricultural biomass fuels are evaluated, it must always be clearly defined if the fuel contains, for instance, leaves, stalks, grains, whole fruits, etc., because usually different parts of a plant show strongly deviating chemical compositions. The application of the following analysis methods, which have also been used by the authors, is strongly recommended. The recommendation of the methods is a result of the FP6 project BioNorm,¹² which among other aspects also dealt with the definition of standards and best practice guidelines for biomass fuel analyses. Recommendations of this project also resulted in new European standards implemented by CEN/TC 335.

3.2. Moisture Content. The moisture content of fuel samples has been determined according to ÖNORM CEN/TS 14774 (determination of the weight loss during drying at 105 °C until a constant weight is reached).

3.3. Fuel Sample Preparation. Sample preparation has been carried out according to CEN/TS 14780: the samples are homogenized, and a cone is formed and subsequently divided into four portions. The two opposing portions are mixed to receive two sub-samples. One of the two sub-samples is stored as a retain sample. The other sub-sample is handled as follows: (1) drying of the sample at 105 °C, (2) milling of the whole sample in a cutting mill to a particle size <4 mm, (3) sample division, and (4) milling of the final analysis sample in an

ultracentrifugal mill equipped with a titanium rotor and screen to a particle size <0.2 mm.

3.4. Determination of the Ash Content. The ash content has been determined according to CEN/TS 14775 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 systems, on the other side, almost no carbonates and preferably oxides are formed because of the significantly higher combustion temperatures. Consequently, the ash content is overestimated in comparison to the amount of ashes formed in a real process. Therefore, in deviation from CEN/TS 14775, it is recommended to determine the inorganic carbon content of the ashed fuel sample additionally and to correct the ash content by subtracting the CO_2 bound in carbonates.

3.5. Determination of C, H, N, and Cl Contents. The determination of C, H, and N contents of biomass fuels has been carried out according to ÖNORM CEN/TS 15104 by combustion and subsequent gas-phase chromatographical separation and measurement in an elemental analyzer (Vario EL 3, Elementar). The determination of chlorine should be carried out according to ÖNORM CEN/TS 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 (ISC 90, Dionex).

3.6. Major and Minor Elements and S Concentrations. Major and minor elements in fuels have been determined by multi-step pressurized digestion of the fuel with HNO₃ (65%)/HF (40%)/H₃BO₃ (Multiwave 3000, Anton Paar), followed by measurement by inductively coupled plasma–optical emission spectroscopy (ICP–OES, Arcos, Spectro) or inductively coupled plasma–mass emission spectroscopy (ICP–MS, Argiland 7500, Agilent), depending upon detection limits. This digestion method is of great importance to ensure a complete dissolution of the ash matrix, which is a basic requirement for correct element detection.

3.7. Ash Sample Preparation. The same sample preparation steps that are applied for the fuel sample are necessary for the bottom, furnace, and boiler ash (see section 3.3).

For fly ash samples, a vaporization of the silica wool used for sampling is necessary with HF (40%).

The aerosol samples are dissolved from the impactor foils in the respective fluid, which is used for digestion.

3.8. Determination of the Concentrations of Major and Minor Elements in the Ash. For the determination of major and minor elements, expect Cl, the same methods as described for the fuel analysis have been applied (see section 3.6).

The Cl content was measured by ion chromatography (ISC 90, Dionex) after elution for 24 h with deionized water.

3.9. Determination of the Ash-Melting Behavior. The determination of the ash-melting behavior has been performed according to prCEN/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. The following temperatures are determined: (1) sintering temperature, corners of the mold first become round; (2) sphere temperature, top of the mold takes a spherical shape; (3) hemisphere temperature, entire mold takes a hemispherical shape; and (4) melting temperature, molten ash collapses to a flattened button.

For the evaluation of the ash-melting behavior, primarily the sintering temperature (start of ash melting) and the temperature window between the sintering and melting temperatures are of relevance. It has to be considered that the characteristic ash-melting temperatures are valid for the total ash (fuel ash). In real-scale applications, the distribution of certain elements in different ash fractions may influence the melting temperatures of the individual fractions.

4. SELECTED RELEVANT FUEL INDEXES AND THEIR APPLICATION

4.1. N Content as an Indicator for the NO_x **Emission Potential.** In biomass combustion processes, NO_x emissions mainly result from the fuel N, while their formation from the combustion air (prompt and thermal NO_x formation) plays only a minor role. ^{13–15} For the pre-evaluation of a new biomass fuel, it is important to know if problems with NO_x emissions exceeding the emission limits have to be expected, which cannot be overcome by primary measures and make secondary measures for NO_x emission control [e.g., selective non-catalytic reduction (SNCR)] affordable.

On the basis of results of test runs at modern state-of-the-art grate combustion plants (see section 2.3) equipped with airstaging technology, a correlation between the conversion rate of fuel N to N in NO_x emissions has been derived (see Figure 2),



Figure 2. NO_x emissions and fuel N converted to N in NO_x dependent upon the N content. Explanation: both correlations are statically significant (p < 0.05).

which can be applied to estimate the NO_x emissions formed during the combustion of a certain fuel in grate combustion systems. Because combustion plants investigated are equipped with air-staging technology, the index is only valid for state-ofthe-art grate-fired combustion units with air-staging technology.

As seen in Figure 2, the NO_x emissions increase with the N content of the fuel. However, there is no linear correlation

because, as the second diagram shows, with an increasing N content of the fuel, the conversion of fuel N to NO_x decreases.

The N concentrations in the biomass fuels can be categorized into (1) low-N fuels (<0.4 wt %, db), e.g., wood fuels; (2) medium-N fuels (0.4–1 wt %, db), e.g., SRCs, kernels, and straw; and (3) high-N fuels (1–10 wt %, db), e.g., cereals and waste wood.

Experience shows that many new biomass fuels are mediumor high-N fuels (e.g., SRCs, cereals, energy grass); thus, NO_x emissions >200 mg N⁻¹ m⁻³ (related to dry flue gas and 13 vol % O₂) have to be expected.

4.2. Sum of K, Na, Zn, and Pb as an Indicator Regarding Aerosol Emissions (Fine Particles Smaller than 1 μ m) and Deposit Buildup. This indicator can be used to evaluate if highly efficient dust precipitators [electrostatic precipitators (ESPs) and baghouse filter] will be needed to keep the particulate matter (PM) emission limits for a plant using a specific fuel. It is also an indicator for the deposit buildup on heat-exchanger surfaces. This index is related to the formation of aerosols (particles with a diameter smaller than 1 μ m = PM₁) during the combustion process and does not include coarse fly ashes.

A part of the semi-volatile and volatile ash-forming elements, such as K, Na, S, Cl, Zn, and Pb, is released from the fuel to the gas phase during combustion. In the gas phase, these elements undergo homogeneous gas-phase reactions, and later, because of supersaturation in the gas phase, these ash-forming vapors start to nucleate or condense on the surfaces of existing particles or heat-exchanger tubes.^{16,17}

Because for most biomass fuels K usually shows significantly higher concentrations than other aerosol-forming elements (e.g., Na, Zn, and Pb), the release of K is most relevant for the formation of aerosol emissions.

It is reported in previous studies^{18,19} that the main part of K released to the gas phase consists of KOH and KCl in the entire temperature range of 500–1150 °C. Smaller amounts of K are released as K_2SO_4 and K_2CO_3 in this temperature range. It is evident that there is a number of parameters influencing the K release.

It has also been reported²⁰ that ash-forming elements, such as Ca, Si, and P, may influence the K release to the gas phase to a certain degree. Therefore, well-defined mixtures of K, Ca, and Si (or P) species were heat-treated in a reactor at a constant temperature (900 and 1000 °C). The main findings of these experiments are summarized as follows. The presence of water in the gas flow was found to significantly enhance the K-release rate in both the K-Ca-Si and K-Ca-P systems. The K-Ca-Si system shows higher release rates at 1000 °C than at 900 °C. Doubling of the molar Ca/Si ratio in K₂CO₃-CaO-SiO₂ mixtures increased the K-release rate about 2 times. This suggests that it is more likely that SiO₂ reacts with CaO and K is being released to the gas phase instead of being incorporated into silicate structures. For the K-Ca-P system, where K₂CO₃ was used as the K source, it has been observed that, with a decreasing molar Ca/P ratio, the K-release rate significantly decreases. In the case of K-Ca-P mixtures, with KCl as the K source, the Ca/P ratio had no effect on the K-release rate. It has been proven that the sublimation of KCl is less influenced by other elements, whereas the release of K₂CO₃ is enhanced in the presence of water vapor because of the reaction to KOH.

Straw, *Miscanthus*, and maize residues are typical fuels with increased Si and slightly increased P concentrations. Because of still existing uncertainties regarding the K release, the indications made by this index must be handled with care for Si- and P-rich fuels (see also section 4.3).

As presented in Figure 3, the sum of K, Na, Zn and Pb in the fuel can be applied as an indicator regarding the potential for



Figure 3. PM_1 emissions in the flue gas downstream of the boiler versus concentrations of aerosol-forming elements in the fuel. Explanation: the correlation is statistically significant (p < 0.05).

 PM_1 emissions. The fuel and PM_1 emission data presented are taken from a considerable number of pilot- and real-scale test runs at grate-fired combustion plants (see also section 2).

It can be seen in Figure 3 that, with an increasing sum of K, Na, Zn, and Pb in the fuel, the aerosol emissions increase. According to this index regarding aerosol emissions, biomass fuels may be categorized in (1) low PM_1 emission range, index <1000 mg/kg dry basis (db) for softwood; (2) medium PM_1 emission range, index 1000–10 000 mg/kg db for poplar, hardwood, bark, waste wood, and maize residues; and a (3) high PM_1 emission range, index >10 000 mg/kg db for grass pellets and straw.

New biomass fuel assortments (e.g., poplar, *Miscanthus*, and maize residues) are most commonly located in the medium to high PM_1 emission range.

Because increasing aerosol emissions are usually associated with increased deposit formation on heat-exchanger tubes (because of the fact that aerosol formation is always accompanied by direct condensation of ash vapors on cold heat-exchanger surfaces), with increased values of this index, also, deposit buildup usually increases. In future work, the influence of Si and P on the K release and, thus, aerosol formation will be investigated in more detail, especially for new biomass fuels.

4.3. Molar Si/K Ratio as an Indicator for the K Release. A high molar Si/K ratio leads to a preferred formation of potassium silicates,^{19–21} which are bound in the bottom ash. Therefore, the K release is reduced. This is of relevance because, for instance, aerosol formation strongly depends upon the amount of K released from the fuel. Moreover, if less K is available in the gas phase for reactions with S and Cl, the gaseous SO_x and HCl emissions may increase.

In Figure 4, data regarding the correlation between the molar Si/K ratio and the K release, gained from lab-scale test runs, are presented.

For very high Si/K ratios (i.e., for sewage sludge), a good embedding of K in the bottom ash and, consequently, a very low K release prevails. However, for low Si/K ratios (<2.5), no clear conclusion can be made concerning the dependency of the K release upon the Si/K ratio. Other parameters, such as



Figure 4. Molar Si/K ratio versus K release for different biomass fuels. Explanations: no statistical significance.

the fuel bed temperatures, as well as the association of K in the fuel, seem to have a strong influence on the K release.

As already mentioned in section 4.2, also, P may influence the K release. P is able to bind K in the residual ash as potassium phosphates.²² The formation of melted K–P phases can also be explained with the ternary-phase diagrams CaO– $K_2O-P_2O_5$ and MgO– $K_2O-P_2O_5$.²³ From these phase diagrams, possible low melting molecules, e.g., KPO₃, can be determined. Also, Ca and Mg may influence the K release. A possible explanation for this behavior is that Ca primary binds Si as calcium silicates and not as potassium calcium silicates; therefore, Ca may increase the K release as well.²⁴

This complex system as well as its influencing parameters still have to be investigated further.

4.4. Release of S to the Gas Phase. During combustion, S forms mainly gaseous SO₂ (to a certain extent, also SO₃) and alkali and alkaline earth sulfates.^{16,17,19,21} Therefore, the knowledge about the release of S is relevant for the gaseous SO_x emissions as well as aerosol emissions and deposit formation.

In Figure 5, the absolute S release is plotted over the S content of the fuel (results from lab-scale reactor tests). As



Figure 5. S concentration of the fuel versus S release to the gas phase. Explanation: the trend is statistically significant (p < 0.05).

seen, an almost linear correlation exists, which indicates that the S release is almost constant (around 80–90 wt %) and does not depend upon the remaining fuel composition or the ash matrix.

4.5. Release of Cl to the Gas Phase. Similar to S, Cl contained in the biomass during combustion mainly forms gaseous HCl, Cl_2 , or alkali chlorides, such as KCl and NaCl.^{16,17,19,21} The Cl release is therefore of great relevance

for aerosol and deposit formation, gaseous HCl emissions, and regarding corrosion risks.

In Figure 6, data from lab-scale reactor tests are presented that clearly show that there is an almost linear increase of the



Figure 6. Cl concentration of the fuel versus Cl release to the gas phase. Explanation: the trend is statistically significant (p < 0.05).

amount of Cl released from the fuel to the gas phase and the Cl concentration in the fuel. As for S, this indicates that the Cl release does not strongly depend upon other fuel properties and is usually in the range of >90 wt %.

4.6. Molar 2S/Cl Ratio as an Indicator for High-Temperature Corrosion Risks. With regard to corrosion in biomass-fired boilers, in particular, three mechanisms are relevant:^{25,26} (1) the direct attack of gaseous HCl or Cl_2 to heat-exchanger surfaces, (2) the formation of alkali sulfate and/ or alkali chloride melts, which dissolve the protective oxide layer of the heat-exchanger surface, and (3) the sulfation of alkali metal or heavy metal chlorides in the tube near the deposition layer. From this mechanism, Cl is released, which subsequently attacks the tube surface (so-called active oxidation).

Among the three mechanisms mentioned, active oxidation is the most relevant mechanism regarding high-temperature corrosion in boilers.²⁵

As already explained in sections 4.4 and 4.5, S and Cl show almost constant release ratios for different biomass fuels. Both elements are relevant for aerosol and deposit formation because, in the gas phase, they form alkaline sulfates and alkaline chlorides, which subsequently form particles or condense on heat-exchanger surfaces. Therefore, a link between the 2S/Cl ratio in the fuel and the respective aerosol deposits formed prevails. In Figure 7, data regarding the 2S/Cl ratio in aerosol emissions are plotted over the respective index related to the fuel. A clear correlation can be derived. For fuels with high 2S/Cl ratios, a protective sulfate layer is formed at the tube surfaces. According to the literature,²⁵ therefore, only minor corrosion risks have to be expected for 2S/Cl ratios in the fuel of >4. It is additionally suggested that the molar 2S/Cl ratio in the fuel should be at least 8 to achieve negligible chlorine levels in boiler deposits and thereby eliminate corrosion from this source. Figure 7 shows that softwood and grass pellets show only minor corrosion risks.

According to Figure 7, the Cl concentrations in aerosols increase with decreasing 2S/Cl ratios in the fuel, while the sulfate concentrations decrease. For 2S/Cl ratios in the fuel <2, even a Cl surplus in aerosols prevails, indicating that severe corrosion risks have to be taken into account. Accordingly, corrosion risks increase from bark over waste wood and straw to maize residues.

The corrosion risk is additionally enforced by the fact that, with increasing concentrations of chlorides, also, the melting temperatures of deposits decrease.

4.7. Molar (K + Na)/[x(2S + Cl)] Ratio. This index can be used to predict the gaseous emissions of SO_x and HCl. As seen from the previous sections, the S and Cl release show an almost constant ratio of 80–90% and >90%, respectively. During combustion, S and Cl preferably form alkaline (K and Na) sulfates and chlorides. S also forms Ca and Mg sulfate, and to a smaller extent, Ca and Mg chlorides can be formed. Cl and S, which are not bound by these elements to the solid phase, form gaseous emissions, namely, HCl and SO_x . Because of the fact that in biomass fuels usually the K concentration is much higher than the Na concentration, the K release to the gas phase is of great relevance for the reaction schemes explained above.

The factor x in the molar (K + Na)/[x(2S + Cl)] ratio describes the average release rates of K and Na in relation to the average release rates of S and Cl. When considering the reaction schemes mentioned above, this index can be defined to predict the potential for SO_x and HCl emissions associated with the combustion of a specific fuel.

A molar ratio (K + Na)/[x(2S + Cl)] > 1 indicates a surplus of released alkaline metals. Therefore, for a value clearly >1, very small HCl and SO_x emissions have to be expected, because most S and Cl will be bound in the ash. If the value of the index is clearly <1, elevated HCl and SO_x emissions are to be expected.



Figure 7. Dependency between the molar ratios of 2S/Cl in fuels and aerosol particles. Explanations: no statistical significance.

On the basis of the results from pilot, real, and lab reactor combustion tests with different biomass fuels, the release rates for K were calculated. The release was quantified by a mass balance based on weight measurements and chemical analysis of the fuel and ash obtained. The formula of the release rate for pilot- and real-scale combustion tests is shown in eq 1, and the formula of the release rate for lab-scale combustion tests is shown in eq 2.

release_{K,wt %} =
$$(1 - (c_{K,bottom ash(db)})$$

 $(m_{bottom ash(db)} + m_{furnace ash(db)})$
 $+ m_{boiler ash(db)}))$
 $/(c_{K,fuel(db)}m_{fuel(db)})) \times 100$ (1)

The incoming mass flow of fuel is $m_{\text{fuel(db)}}$. The mass flow that is not released to the gas phase is the sum of the remaining ash fraction on the grate $m_{\text{bottom ash}(db)}$ (kg/h, db) and the mass of entrained particles from the fuel bed. The mass flows (kg/h, db) that are entrained from the fuel bed and separated in the boiler are $m_{\text{furnace ash}(db)}$ and $m_{\text{boiler ash}(db)}$. The chemical composition of the fuel is $c_{K,\text{fuel}(db)}$ (mg/kg, db), and the chemical composition for the ash sample is $c_{K,\text{bottom ash}(db)}$. It is assumed that the entrained ash particles $[m_{\text{furnace ash}(\text{db})}]$ and $m_{\text{boiler ash}(\text{db})}$] have the same composition as the bottom ash. This of course neglects the mass of ash-forming vapors, which end up on the surface of coarse fly ash particles (e.g., by condensation or surface reactions) in the boiler (e.g., K₂SO₄ and KCl). However, these processes have only a minor influence on the total mass of entrained particles.

release_{K,wt %} =
$$\left(1 - (c_{K,output(db)}m_{output(db)}) / (c_{K,input(db)}m_{input(db)})\right) \times 100$$
 (2)

In equation (2) $m_{input(db)}$ is the mass (g, db) of the sample fed to the reactor, $c_{K,input(db)}$ is the concentration of K in the fuel (mg/kg, db), $m_{output(db)}$ is the mass (g, db) of the ash residual after the experiment in the reactor and $c_{K,output(db)}$ is the concentration of K in the ash residual (mg/kg, db). The mass of entrained fly ash particle is negligible because of the much lower air velocities in the fuel bed compared to pilot- or realscale applications.

The determined release rates are shown in Figure 8.

45

20

15

10

5

20d chipe

softwood chips

waste wood

K release [wt.%]



xundo Donat

bait

and anesed persone

residues of stored product

It can be assumed that Na shows a comparable release behavior to the gas phase as K. Therefore, the values of K release can be used for calculating the factor x of the molar (K (+ Na)/[x(2S + Cl)] ratio. An averaged release for S and Cl (90) wt %) is divided by the average K release to obtain the factor x. The calculated values are summarized in Table 1.

Table 1. Experimentally Determined K-Release Rates for Different Biomass Fuels and the Resulting Factor x

	average K release (wt %)	standard deviation (wt %)	factor <i>x</i>
hardwood chips	32.8	12.0	2.7
softwood chips	24.9	8.1	3.6
waste wood	18.5	3.2	4.9
bark	6.8	1.3	13.2
A. donax	18.5	4.6	4.9
straw	20.1	2.6	4.5
maize residues	12.1	1.7	7.4
grass pellets	13.5	1.3	6.7
decanter and rapeseed press cake	8.6	1.6	10.5
residues of starch production	10.8	2.5	8.4

For biomass fuels for which the release behavior has not been investigated thus far, the release can be determined with a labscale reactor experiment, such as, for instance, described in section 2.4. On the basis of the results of such an experiment, a meaningful assumption for the K release can be made and, thus, the factor x can be calculated.

The estimated values from Table 1 can be used for the calculation of the index (K + Na)/[x(2S + Cl)]. Figure 9 shows the correlation of the molar (K + Na)/[x(2S + Cl)] ratio versus the SO_r emissions and the conversion of fuel S to S in SO_r .

From Figure 9, it can be seen that, with a decreasing molar (K + Na)/[x(2S + Cl)] ratio, SO_x emissions are increasing.

The SO_x emissions of the different fuels can be categorized into (1) a low SO_x emission range (<50 mg of SO_x N⁻¹ m⁻³, with dry flue gas, at 13 vol % O2), e.g., wood chips, bark, mixtures of waste wood and bark, as well as maize residues; (2) a medium SO_x emission range (50–200 mg of SO_x N^{-1} m⁻³, with dry flue gas, at 13 vol % O₂), e.g., waste wood, A. donax, and straw; and (3) a high SO_x emission range (>500 mg of SO_x) N^{-1} m⁻³, with dry flue gas, at 13 vol % O₂), e.g., grass pellets, a mixture of decanter and rapeseed press cake, and residues of starch production with high S content.

In the second diagram of Figure 9, the molar (K + Na)/[x(2S + CI)] ratio is plotted against the conversion of fuel S to S in SO_x. The same trend of the molar (K + Na)/[x(2S + Cl)]ratio and the conversion of fuel S to SO_x can be observed. SO_x emissions are negligible for a fuel molar (K + Na)/[x(2S + Cl)]ratio bigger or close to 0.5. This index is suitable to estimate the SO_x emission range to be expected.

Figure 10 shows the correlation of the molar (K + Na)/[x(2S + Cl)] ratio versus HCl emissions and the conversion of fuel Cl to Cl in HCl.

No clear correlation between the molar (K + Na)/[x(2S +Cl)] ratio and the HCl emissions can be seen. For a molar ratio of (K + Na)/[x(2S + Cl)] < 0.5, the HCl emissions are varied from 0 to 110 mg N⁻¹ m⁻³, with dry flue gas, at 13 vol % O_2 . The reason for this strong scattering in comparison to S is not yet understood. Further investigations are needed. In our case, it can be seen from Figure 10 that, with a molar ratio of (K +



Figure 9. Molar (K + Na)/[x(2S + Cl)] ratio versus SO_x emissions and the conversion of fuel S to SO_x. Explanation: both correlations are statistically significant (p < 0.05).

Na)/[x(2S + Cl)] bigger or close to 0.5, the HCl emissions are very low. Therefore, this index can also be used to make a first estimation of the gaseous HCl emissions to be expected.

When using this index, it has to be noted that the factor x is based on first estimations regarding the release of K and Na. Further investigations are recommended to ensure the alkali metal release described.

4.9. Indicators for Ash-Melting Problems. It is generally well known that Ca and Mg increases the ash-melting temperature, while Si in combination with K decreases the ash-melting temperature.^{9,27,28} The molar Si/(Ca + Mg) ratio⁹ can therefore provide first information about ash-melting tendencies in ash systems dominated by Si, Ca, Mg, and K. However, for P-rich systems (e.g., grass pellets), this correlation is not valid (see Figure 11).

As seen in Figure 11, the ash-sintering temperature drops below 1100 °C as soon as the Si/(Ca + Mg) ratio exceeds 1. It can also be seen that there is a linear correlation of the molar Si/(Ca + Mg) ratio with the ash-sintering temperature, except for grass pellets that show a low ash-sintering temperature because of the high P concentration.

From the ternary-phase diagrams for CaO- $K_2O-P_2O_5$ and MgO- $K_2O-P_2O_5$ ²³ it can be derived that, at constant K_2O/P_2O_5 ratios, the melting point increases with increasing CaO and MgO concentrations. It can be concluded that CaO and MgO increase the ash-sintering temperature, whereas K_2O and P_2O_5 decrease the sintering temperature. In combination with Si, a modified index (Si + P + K)/(Ca + Mg) can be introduced (see Figure 12). With this index, also for P-rich fuels, a prediction regarding the ash-melting behavior is possible. There

is a linear correlation given between the molar (Si + P + K)/(Ca + Mg) ratio and the ash-sintering temperature.

5. SUMMARY AND CONCLUSION

The application of fuel indexes as a characterization tool provides a good basis for a quick pre-evaluation of combustionrelated problems that may arise. This new and advanced fuel characterization method can therefore be applied to support decision making concerning the application of new biomass fuels or fuel blends in existing combustion plants, as well as for the preliminary design and engineering of new combustion plants, which should be tailored to the needs of a specific fuel or fuel mixture. During this first decision phase regarding the applicability of a certain fuel, time-consuming and expensive combustion tests can therefore be saved.

The investigation of the fuel indexes has been performed for a broad spectrum of biomass fuels ranging from different types of wood to herbaceous and agricultural biomass, as well as industrial biomass residues. The data for the investigation are based on test runs from fixed-bed lab-, pilot-, and real-scale combustion systems, and therefore, the indexes derived in this work are applicable for grate combustion plants.

Fuel indexes, which allow for accurate qualitative predictions, are the N content, the molar 2S/Cl ratio, and the molar ratio of (Si + P + K)/(Ca + Mg). Indexes that can be applied with some restrictions regarding other constraints are the sum of K, Na, Zn, and Pb and the molar ratios of (K + Na)/[x(2S + Cl)]) and Si/(Ca + Mg).

The N content generally determines the potential for NO_x emission formation. A correlation between the conversion rates



Figure 10. Molar (K + Na)/[x(2S + Cl)] ratio versus HCl emissions and the conversion of fuel Cl to HCl. Explanation: both correlations are not statistically significant.



Figure 11. Molar Si/(Ca + Mg) ratio versus ash-sintering temperature for different biomass fuels. Explanation: if grass pellets are excluded, the correlation is statistically significant (p < 0.05); ash-sintering temperature according to prCEN/TS 15370-1.

of fuel N to NO_x emissions has been derived, showing a nonlinear correlation of the NO_x emissions with rising fuel N content. When this correlation is applied, a first estimation of the NO_x emissions can be made. During combustion, easily volatile and semi-volatile elements (K, Na, S, Cl, Zn, and Pb) are partly released from the fuel to the gas phase, where they undergo chemical reactions and finally contribute to problems concerning emissions, deposit formation, and corrosion. With a decreasing molar 2S/Cl ratio, for instance, the amount of alkaline chlorides in ash deposits on heat-exchanger surfaces increases. According to the literature,²⁵ a molar ratio of 2S/Cl < 8 increases the risk of high-temperature Cl corrosion. The sum of K, Na, Zn, and Pb (in mg/kg of dry fuel) describes the



Figure 12. Molar (Si + P + K)/(Ca + Mg) ratio versus ash-sintering temperature for different biomass fuels. Explanation: the correlation is statistically significant (p < 0.05).

potential for aerosol and deposit formation, which increases with rising values of this index. Moreover, the molar ratio of (K + Na)/[x(2S + Cl)], where x represents the ratio of the average K and Na release in relation to the average S and Cl release from the fuel to the gas phase, provides a first prediction concerning the expected HCl and SO_x emissions. For values >0.5, it is very likely that most S and Cl will be embedded in the ashes. The molar ratio of Si/(Ca + Mg) can provide first information about ash-melting tendencies in systems dominated by Si, Ca, Mg, and K (decreasing melting temperatures with an increasing value). The molar ratio of (Si + P + K)/(Ca + Mg) is also valid for P-rich fuels and is therefore an index that can generally be applied regarding the pre-evaluation of ashmelting tendencies.

Presently, ongoing work is focusing on the further improvement of existing fuel indexes. For the prediction of HCl and SO_x emissions, a more detailed investigation of the K release to the gas phase and also possible Ca interactions is necessary. To investigate the K release from biomass fuels in more detail, interactions of Si and P with K as well as the combustion temperature need to be considered. However, more research on this special issue is needed.

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An addition sign was added between Ca and Mg in the fourth to last paragraph of the Background and Scope section of the version of this paper published December 16, 2011. The correct version published December 20, 2011.