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 behaviour. Therefore, fuel characterisation methods with a special focus on combustion related problems (gaseous HCl and SOx-emissions, ash-melting behaviour 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 utilisation of a new biomass fuel. Fuel indexes, which allow for accurate qualitative predictions are the molar 2S/Cl ratio and the molar ratio of (Si+P+K) / (Ca+Mg). The molar 2S/Cl ratio indicates the risk of high temperature corrosion. The molar (Si+P+K) / (Ca+Mg) ratio is an index which generally predicts the ash-sintering temperature and can also be used as first indicator for the K-release to the gas phase depending on the kind of biomass fuel (e.g. wood fuel, herbaceous biomass). Another index describing the ash-sintering temperature is the Si / (Ca+Mg) ratio, which can be applied for P-poor fuels (i.e. wood fuels). The sum of K, Na, Zn and Pb is an index predicting the range of aerosol emissions to be expected. The molar (K+Na) / [x*(2S+Cl)] ratio provides a first indication regarding the potential for gaseous HCl and SOx emissions, 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. Following, 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, as interactions of the bed material possible in fluidised-bed combustion systems are not considered.

Keywords: solid biomass fuel, characterization, fuel index
1 INTRODUCTION AND OBJECTIVES

The general increase in energy demand, higher costs and oncoming depletion of fossil fuels are the main reasons for the utilisation of “new” biomass fuels in medium and large-scale heating and CHP plants. Generally these “new” biomass fuels (e.g. short-rotation coppices (SRC) such as poplar and willow, energy crops such as Miscanthus, switchgrass, Arundo Donax and grasses, as well as wastes and residues from agriculture and the food industry) are not well defined yet regarding their combustion behaviour. For the introduction of these fuels, a fuel characterisation method with special focus on combustion related problems is a first important step for their introduction. Possible ash related problems (ash melting on grates, bed agglomeration in fluidised bed combustion systems, deposit formation and corrosion, particulate emissions) as well as problems regarding SOx and HCl emissions are thereby the main focus points. With state-of-the-art fuel characterisation methods these issues cannot be sufficiently covered and therefore, new and advanced fuel characterisation methods are needed. One option to gain quick first indications regarding the problems mentioned is the development, evaluation and application of fuel indexes.

The pre-evaluation step of this work consisted of testing existing empirical correlations for coals regarding their applicability for biomass fuels. It was seen that indexes developed for coal can not be applied for biomass. Depending on the biomass species the major elements responsible for the ash chemistry can roughly be categorised in low Si/ high Ca containing fuels (e.g. wood and woody biomass) and high Si/ low Ca containing fuels (e.g. herbaceous biomass) [1]. 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.

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 in order to predict combustion related problems for biomass fuels in fixed bed combustion systems. The work is based on data from lab-, pilot- and real-scale tests performed with a broad spectrum of biomass fuels.

2 METHODOLOGICAL APPROACH

2.1 General approach

Proximate and ultimate analysis of the fuels investigated (ash content, contents of N, S, Cl, major and minor ash forming elements) are applied as the basis for the work presented. The analytical methods are summarised in section 2.3. These analyses results were the basis for the calculation and evaluation of fuel indexes. The fuel indexes are defined by considering the physical behaviour 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 BIOENERGIESYSTEME GmbH, Graz, were considered.

2.2 Fuels investigated

Biomass fuels from five different biomass categories which are typical for different climate zones were used within this study:
(I) wood and woody biomass (WWB): (beech wood chips, spruce wood chips, softwood pellets, bark from softwood, waste wood and torrefied softwood); (II) short rotation coppice: (poplar chips, SRC poplar, SRC willow); (III) herbaceous and agricultural biomass (HAB): Miscanthus pellets, Arundo Donax, wheat straw, maize cob pellets (maize residues), grass pellets; (IV) others: i.e. sewage sludge; (V) industrial biomass residues: (decanter and rapeseed press cake and residues of starch production).

2.3 Chemical fuel analyses – The basis for the calculation of fuel indexes

General Aspects:
Since 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., since usually different parts of a plant show strongly deviating chemical compositions. The application of the following analyses 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 [2], 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.

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).

Fuel sample preparation
Sample preparation has been carried out according to CEN/TS 14780: the samples are homogenised, a cone is formed and subsequently divided into four portions. The two opposing portions are mixed in order 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:
(I) Drying of the sample at 105°C. (II) Milling of the whole sample in a cutting mill to a particle size <4 mm. (III) Sample division. (IV) Milling of the final analyses sample in an ultracentrifugal mill equipped with titanium rotor and screen to a particle size <0.2 mm.

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 due to the significantly higher combustion temperatures. Consequently, the ash content is overestimated compared with 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 CO₂ bound in carbonates.

Determination of the C, H, N and Cl content
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 Cl has been 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).
Major and minor elements and S concentrations
Major and minor elements in fuels have been determined by multi-step pressurised digestion of the fuel with HNO₃ (65%) / HF (40%) / H₃BO₃ (Multiwave 3000, Anton Paar), followed by measurement by inductively coupled plasma-optical emission spectroscopy (ICPOES) (Arcos, Spectro) or inductively coupled plasma-mass spectroscopy (ICPMS) (Agiland 7500, Agilent), depending on 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.

Ash sample preparation
The same sample preparation steps which are applied for the fuel sample are necessary for the bottom, furnace and boiler ash. 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 the digestion.

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

Determination of the ash-melting behaviour
The determination of the ash-melting behaviour has been done 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 moulds. These samples are then heated in an oven under oxidising conditions. The following temperatures are determined:
For the evaluation of the ash-melting behaviour, primarily the sintering temperature (start of ash melting) and the temperature window between the sintering and the melting temperature 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.

2.4 Pilot and real-scale combustion tests
All combustion plants from which test run data have been considered, are geometrically separated in 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 between 1.4-1.6. For furnace temperature control the plants are also equipped with flue gas recirculation.
The real-scale combustion plants investigated are also grate fired combustion systems with nominal thermal boiler capacities between 0.5 to 110 MW. Also these boilers are equipped with air staging technology and most of them with flue gas recirculation. Following, grate combustion plants representing the present state-of-the-art were chosen and only comparable combustion set-ups were considered within the evaluation.
Based on the analyses results and measurement data energy, mass and element balances over the plants 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.
2.5 Lab-scale reactor tests

In addition results from test runs with a lab-scale reactor especially designed for the investigation of the thermal decomposition behaviour 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 PID-controllers. 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 (SiC), which is inert under reducing and oxidising conditions; therefore, the walls do 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, with thermal oil. 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 pre-heated reactor and therefore, a rapid heating, which is well comparable with the one in real thermal conversion processes, can be achieved. A more detailed description of this reactor can be found in literature [3, 4].

3 DEFINITION OF FUEL INDEXES

Based on 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:

(I) Sum of K, Na, Zn and Pb as an indicator regarding aerosol emissions (fine particles smaller 1 µm) and deposit build-up. (II) The molar 2S/Cl ratio for the prediction of the risk of high temperature corrosion. (III) The prediction of the ash melting temperatures with the molar Si/(Ca+Mg) as well as the molar (Si+K+P)/(Ca+Mg) ratio. (IV) The molar (Si+K+P)/(Ca+Mg) ratio for an estimation of the K-release from the fuel to the gas phase. (V) The molar (K+Na)/[x*(2S+Cl)] ratio for the prediction of the gaseous emissions of SOx and HCl.

The definitions of the indexes mentioned above are based on theoretical considerations. With the exception of 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, due to the well defined conditions provided by this unit.

3.1 The sum of K, Na, Zn and Pb as an indicator regarding aerosol emissions (fine particles smaller 1 µm) and deposit build-up

This indicator can be used to evaluate if highly efficient dust precipitators (electrostatic precipitators - ESP, baghouse filter) will be needed to keep the particulate matter (PM) emission limits for a plant utilising a specific fuel. It is also an indicator for the deposit build-up on heat exchanger surfaces. This index is related to the formation of aerosols (particles with a diameter smaller 1 µm = 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 homogenous gas-phase reactions and later, due to supersaturation in the gas phase, these ash-forming vapours start to nucleate or condense on the surfaces of existing particles or heat exchanger tubes [5, 6].

Since 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.
From previous studies [7, 8] it is known 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 K₂SO₄ and K₂CO₃ in this temperature range. It is evident that there are a number of parameters influencing the K-release.

In [9] for instance it is reported that 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 constant temperature (900 and 1000°C). The main findings of these experiments are summarised 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 the K-Ca-P system. The K-Ca-Si system shows higher release rates at 1000°C compared to 900°C. Doubling of the molar Ca/Si ratio in K₂CO₃-CaO-SiO₂ mixtures increased the K-release 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 vapour because of the reaction to KOH.

Due to still existing uncertainties regarding the K-release, the indications made by this index must be handled with care especially for Si and P rich fuels (see also section 3.5).

As shown in Figure 1, the sum of K, Na, Zn and Pb in the fuel can be applied as an indicator regarding the potential for PM₁ emissions. The fuel and PM₁ emission data presented are taken from a considerable number of pilot-scale and real-scale test runs at grate fired combustion plants (see also section 2.4).

![Figure 1: PM₁ emissions in the flue gas downstream the boiler versus concentrations of aerosol-forming elements in the fuel](image)

**Explanation:** the correlation is statistically significant (p < 0.05)

It can be seen 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 categorised in a (I) low PM₁ emission range: index <1,000 mg/kg d.b. for softwood; (II) medium PM₁ emission range: index 1,000-10,000 mg/kg d.b. for poplar, hardwood, bark, waste wood and maize residues and a (III) high PM₁ emission range: index >10,000 mg/kg d.b. for grass pellets and straw pellets.

New biomass fuel assortments (e.g. poplar, Miscanthus, maize residues) are most commonly located in the medium to high PM₁ emission range.

Usually increasing aerosol emissions are associated with increased deposit formation on heat exchanger tubes (due to the fact that aerosol formation is always accompanied by direct condensation of ash vapours on cold heat exchanger surfaces), it can be concluded that, with
increased values of this index, also, deposit build-up 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.

3.2 The release of S and Cl to the gas phase
During combustion, S forms mainly gaseous SO₂ (to a certain extent, also SO₃) and alkali as well as earth-alkali sulphates [5, 6, 8, 15]. Therefore, the knowledge about the release of S is relevant for the gaseous SOₓ emissions as well as for aerosol emission and deposit formation. Cl contained in the biomass during combustion mainly forms gaseous HCl, Cl₂, or alkali chlorides, such as KCl and NaCl [5, 6, 8, 15]. The Cl-release is therefore of great relevance for aerosol and deposit formation, gaseous HCl emissions and regarding corrosion risks. In Figure 2, the absolute S- and Cl-release to the gas phase is plotted for the fuels investigated (results from lab-scale reactor tests).

![Figure 2: S- and Cl-release to the gas phase for the fuels investigated](image)

**Explanation:** If more than 2 test runs have been evaluated, error bars show the standard deviation, Tordis and Inger are two different willow clones, which were harvested in the 3rd year of the 1st growth.

As can be seen the S-release varies between 72 – 93 wt.%, with an average value of 87 wt.%. The results indicate that the S-release is almost constant and does not depend on the remaining fuel composition respectively ash matrix. Also Cl shows an almost constant release behaviour in the range of >90 wt.%, with an average value of 98 wt.%.

3.3 The molar 2S/Cl ratio as an indicator for high-temperature corrosion risks
With regard to high temperature corrosion in biomass-fired boilers, so called active oxidation is the most relevant mechanism. The sulfation of alkali metal or heavy metal chlorides in the ash deposition layer on tubes releases Cl, which subsequently attacks the tube surface [10, 11].

As already explained (section 3.2) S and Cl show almost constant release ratios for different biomass fuels. Both elements are relevant for aerosol and deposit formation since, in the gas phase, they form alkaline sulphates and alkaline chlorides, which subsequently form particles or condense on heat-exchanger surfaces. Therefore, a link between the molar 2S/Cl ratio in the fuel and the respective aerosol deposits formed prevails. In Figure 3, 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 sulphate layer is formed at the tube surfaces.
Figure 3: Dependency between the molar ratios of 2S/Cl in fuels and aerosol particles

According to literature [10], 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 3 shows that softwood and grass pellets show only minor corrosion risks. 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.

### 3.4 Indicators for ash-melting problems

It is generally well known that Ca and Mg increase the ash-melting temperatures, while Si in combination with K decreases the ash-melting temperatures [12, 13, 14]. The molar Si / (Ca+Mg) ratio [12] 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 4). As seen in Figure 4, the ash-sintering temperature drops below 1,100°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 and Arundo Donax. These two fuels show elevated P concentration which reduce the ash sintering temperature.

```latex
\begin{equation}
y = -162.96x + 1376.1
\end{equation}
R^2 = 0.9344
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Figure 4: Molar Si / (Ca+Mg) ratio versus ash-sintering temperature for different biomass fuels

Explanation: if grass pellets and Arundo Donax are excluded, the correlation is statistically significant (p<0.05); ash-sintering temperature according to prCEN/TS 15370-1

From the ternary phase diagrams for CaO–K₂O–P₂O₅ and MgO–K₂O–P₂O₅ [17] it can be derived that at constant K₂O/P₂O₅ 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 K₂O and P₂O₅ decrease the sintering temperature. In combination with Si, a modified index (Si+P+K) / (Ca+Mg) can be introduced (see Figure 5). With this index, also for P-rich fuels, a prediction regarding the ash-melting behaviour is possible. There is a linear correlation given between the molar (Si+P+K) / (Ca+Mg) ratio and the ash-sintering temperature.

\[ y = -102.71x + 1392.2 \]
\[ R^2 = 0.8449 \]

Figure 5: Molar (Si+P+K) / (Ca+Mg) ratio versus ash-sintering temperature for different biomass fuels

Explanation: the correlation is statistically significant (p<0.05)

3.5 The molar (Si+P+K) / (Ca+Mg) ratio as an indicator for the K-release

It is generally well known that a high molar Si/K ratio leads to a preferred formation of potassium silicates [8, 9, 15] which are bound in the bottom ash. This mechanism reduces the K-released to the gas phase. This is of relevance since, for instance, aerosol formation strongly depends on 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 SOₓ and HCl emissions may increase.

As already mentioned in section 3.1, also P may influence the K-release. P is able to bind K in the residual ash as potassium phosphates [16]. The formation of melted K-P-phases can also be explained with the ternary phase diagrams CaO–K₂O–P₂O₅ and MgO–K₂O–P₂O₅ [17]. From these phase diagrams, possible compounds with low melting temperature, (e.g. KPO₃, K₂O·4SiO₂) can be determined. Also, Ca and Mg may influence the K-release. A possible explanation for this behaviour is that Ca and Mg primarily bind Si as calcium silicates and not as potassium calcium silicates. Therefore, Ca and Mg may increase the K-release.

In Figure 6, data regarding the correlation between the molar (Si+P+K) / (Ca+Mg) ratio and the K-release, gained from lab- and real-scale test runs, are presented.
A trend can be seen, if the fuels bark, peat and sewage sludge are excluded. For woody biomass and short rotation coppice the values of the molar \((\text{Si}+\text{P}+\text{K})/\text{(Ca}+\text{Mg})\) ratio are <1.3, whereas the K-release varies between 14-51%.

For agricultural, herbaceous and other fuels the rather low K-release can be explained with the low ash melting temperatures. K is partly incorporated into compounds with low melting temperature (e.g. \(\text{KPO}_3\), \(\text{K}_2\text{O} \cdot 4\text{SiO}_2\)) and thus its release is reduced. In addition, other parameters, such as the fuel bed temperature, as well as the chemical occurrences of K in the fuel also seem to influence the K-release. For instance regarding sewage sludge and peat relevant fractions of water soluble K most likely have been leached due to the strong contact of the fuels with water. The reason for the low K release from bark may be due to high amounts of minerally bound K compounds in the fuel (e.g. bound in mineral impurities).

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

**Figure 6: Molar \((\text{Si}+\text{P}+\text{K})/\text{(Ca}+\text{Mg})\) ratio versus K-release for different biomass fuels**

Explanation: Error bars show the standard deviation, if more than one test run has been evaluated; RS… real scale combustion test; for the correlation the fuels bark, peat and sewage sludge have been excluded

### 3.6 The molar \((\text{K}+\text{Na})/ [x*(2\text{S}+\text{Cl})]\) ratio

This index can be used to estimate the gaseous emissions of \(\text{SO}_x\) and HCl. As seen from the previous sections, the S- and Cl-release show an almost constant ratio 72 – 93 wt.%, with an average value of 87 wt.% and >90 wt.%, with an average value of 98 wt.%, respectively. During combustion, S and Cl preferably form alkaline (K and Na) sulphates and chlorides. S also forms Ca and Mg sulphate 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 \(\text{SO}_x\). Due to 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 \((\text{K}+\text{Na})/ [x*(2\text{S}+\text{Cl})]\) 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 \(\text{SO}_x\) and HCl emissions associated with the combustion of a specific fuel.

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

Based on the results from pilot and lab-scale reactor combustion tests with different biomass fuels, the release rates for K have been determined.
With the release of K gained and the assumption that Na shows a comparable release behaviour to the gas phase, the values for the factor x used to calculate the molar \((K+Na)/(x*(2S+Cl))\) ratio, can be calculated (see Figure 7).

Figure 7: K-release and estimated factor x for different biomass fuels during combustion

Figure 8 shows the correlation of the molar \((K+Na)/(x*(2S+Cl))\) ratio versus the SO\(_x\) emissions and the conversion of fuel-S to S in SO\(_x\).

Figure 8: Molar \((K+Na)/(x*(2S+Cl))\) ratio versus SO\(_x\) emissions and the conversion of fuel-S to S in SO\(_x\).

Explanation: both correlations are statistically significant (p < 0.05)

From Figure 8, it can be seen that, with decreasing molar \((K+Na)/(x*(2S+Cl))\) ratio, SO\(_x\) emissions are increasing.

The SO\(_x\) emissions of the different fuels can be categorised into: (I) a low SO\(_x\) emission range (<50 mg SO\(_x\) / Nm\(^3\), dry flue gas, 13 vol.% O\(_2\)), e.g., wood chips, bark, mixtures of waste wood and bark, as well as maize residues; (II) a medium SO\(_x\) emissions range (50-200 mg SO\(_x\) / Nm\(^3\), dry flue gas, 13 vol.% O\(_2\)), e.g., waste wood, Arundo Donax and straw; (III) a high SO\(_x\) emission range (>500 mg SO\(_x\) / Nm\(^3\), dry flue gas, 13 vol.% O\(_2\)), e.g. grass pellets, a mixture of decanter and rapeseed press cake and residues of starch production with high S content.
In the right diagram of Figure 8, the molar \((K+Na) / [x*(2S+Cl)]\) 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. This index is suitable to estimate the SO\(_x\) emission range to be expected, SO\(_x\) emissions are negligible for a fuel molar \((K+Na) / [x*(2S+Cl)]\) ratio bigger or close to 0.5.

Figure 9 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.

Figure 9: Molar \((K+Na) / [x*(2S+Cl)]\) ratio versus HCl emissions and the conversion of fuel-Cl to Cl in HCl

Explanation: no statistical significance

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/Nm\(^3\), 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 9 that, with a molar ratio of \((K+Na) / [x*(2S+Cl)]\) 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 SUMMARY AND CONCLUSIONS

The application of fuel indexes as characterisation tool provides a good basis for a quick pre-evaluation of combustion-related problems that may arise. This characterisation 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 investigations 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 only.
Fuel indexes, which allow for accurate qualitative predictions are the molar $2S/Cl$ ratio and the molar $(Si+P+K)/(Ca+Mg)$ ratio regarding the prediction of the ash-sintering temperature. Indexes which can be applied with some restrictions regarding other constraints are the sum of K, Na, Zn and Pb, the molar ratios of $Si/(Ca+Mg)$, $(Si+P+K)/(Ca+Mg)$, as well as of $(K+Na)/[x*(2S+Cl)]$.

During combustion, easily 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 corrosions.

With a decreasing molar $2S/Cl$ ratio, for instance, the amount of alkaline chlorides in ash deposits on heat-exchanger surfaces increases. According to literature, a molar ratio of $2S/Cl < 8$ increases the risk of high temperature Cl corrosion.

The molar ratio of $(Si+P+K)/(Ca+Mg)$ is an indicator which can generally be applied regarding the pre-evaluation of ash-melting tendencies and is also valid for P-rich fuels. Moreover the molar $(Si+P+K)/(Ca+Mg)$ ratio may also be used as a first indicator for the K-release to the gas phase.

The sum of K, Na, Zn and Pb (in mg/kg dry fuel) describes the potential for aerosol and deposit formation, which increases with rising values of this index. The $Si/(Ca+Mg)$ ratio can provide first information about ash-melting tendencies for P-poor fuels.

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 HCl and SO$_x$ emissions expected. For values $> 0.5$, it is very likely that most of the S and Cl will be embedded in the ashes.

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 of possible Ca interactions are necessary. To investigate the K-release from biomass fuels in more detail, interactions of Si and P with K as well as of the combustion temperature and the mode of occurrence of K in biomass fuels need to be considered. However, more research on this special issue is needed and ongoing.

5 References


