Combustion related characterisation of Miscanthus peat blends applying novel fuel characterisation tools

Peter Sommersacher a,⇑, Thomas Brunner b,c, Ingwald Obernberger b,c, Norbert Kienzl a, Werner Kanzian b,c

a BIOENERGY 2020+ GmbH, Inffeldgasse 21b, 8010 Graz, Austria
b Institute for Process and Particle Engineering, Graz University of Technology, Inffeldgasse 13, 8010 Graz, Austria
c BIOS BIOENERGIESYSTEME GmbH, Inffeldgasse 21b, 8010 Graz, Austria

HIGHLIGHTS

• Laboratory methods presented regarding the combustion related characterisation.
• Peat addition to Miscanthus increases the ash melting temperatures.
• Decreased aerosol emissions with increasing peat shares.
• Increased NOx and SOx emissions can be expected with increasing peat shares.
• New evaluation method for the prediction of optimum fuel blends for biomass fuels.

ARTICLE INFO

Article history:
Received 4 March 2015
Received in revised form 15 May 2015
Accepted 18 May 2015
Available online 28 May 2015

Keywords:
Fuel blends
Miscanthus
Peat
Solid biomass characterisation

ABSTRACT

A continuously increasing demand for energy from biomass encourages utilisation of new biomass fuels which usually cause ash related problems in conventional wood combustion systems. One approach to make these biomass fuels applicable in such systems is to prepare blends with other fuels such as peat, which positively influence the behaviour of ash-forming elements. Usually the application of fuel blends has been evaluated experimentally, but in this study novel and advanced fuel characterisation tools (developed for fixed bed/grate combustion systems) are applied to Miscanthus/peat blends. In a first step the pure fuels and the Miscanthus/peat blends were chemically analysed. Fuel indexes provide primary information on ash-melting behaviour and a first estimation of the K release, indications of aerosol emissions, risk of high-temperature chlorine corrosion and the NOx emission potential. Thermodynamic equilibrium calculations were used for a qualitative and semi-quantitative prediction of the release of volatile and semi-volatile elements (K, Na, S, Cl, Zn, Pb) and the ash-melting behaviour. To quantitatively determine the release behaviour of ash-forming elements, lab-scale reactor experiments for the pure fuels and blends were conducted and a comparison with the theoretical calculations was performed. This work shows that the new approach of applying novel and advanced fuel characterisation tools to characterise Miscanthus/peat blends works well and meaningful blends can be recommended. The advantage of this characterisation method is that the influence of varying peat compositions (since the composition of peat strongly depends on its origin) can be considered. Additionally this approach helps to significantly reduce time-consuming and expensive testing programs.

1. Introduction and objectives

The relevance of biomass for energy production will most probably increase during the coming years. To cover the future demand for feedstocks besides traditional biomass fuels (e.g. wood chips, bark, etc.) also so-called new biomass fuels have to be introduced into the market. In this respect fast growing non-food crops which are not competing with the food industry like perennial grasses such as Miscanthus and giant reed [1,2] and fast growing wood species (so-called short-rotation coppices (SRC) such as willow and poplar [3,4]) as well as herbaceous and agricultural residues (straw, press cake from oil production, kernels, etc.) show promising potential. Due to the high growth rates of these plants the nutrient uptake is increased which generally leads to higher N, S, Cl and ash contents in comparison to conventional wood fuels (wood pellets, wood chips, bark) [5]. Therefore, the combustion of these fuels is often associated to increased ash related problems
and HCl), which in most cases formed emissions may increase due to the increasing and HCl emissions, peat with a relatively high Ca/Si ratio. In Ref. [10] forest residues publication. In Ref. [9] the effect of peat addition to wood pellets on slagging characteristics, especially the ash-melting behaviour and the K release. Peat is an often mentioned candidate for the preparation of such fuel blends.

Peat is an accumulation of partially decayed vegetation. One of the most common components is Sphagnum moss, although many other plants can contribute. Soils that contain mostly peat are known as a histosol. Peat forms in wetland conditions, where flooding obstructs flows of oxygen from the atmosphere, which reduces rates of decomposition [7].

The composition of peat [8] depends on the geological surroundings, historical topography as well as hydrology and meteorology, why peat lands give different peat compositions. For this reason it is important to consider the elemental composition, since it has a strong influence on the application of fuel blending.

From Ref. [8] it can also be concluded that peat usually contains higher amounts of N, S, Al and Ca and lower concentrations of K compared to virgin wood fuels without chemical treatments or coatings and painting. The Si concentration in peat may vary, depending on the type of peat, values of 0.55 ± 1.3 wt.% d.b. have been reported. Typically they are considerably higher than in wood fuels. For blending peat with new biomass fuels higher ash-melting temperatures are expected, since peat typically elevates the Ca and Al concentration of the blend, whereby Si in combination with K decreases the ash melting temperatures. A reduced K release may result due to better embedding of K in the ash due to K-alumo-silicate formation. In case of an elevated Si content in the peat a lower K release can also result from the formation of silica melts. A reduced K release may result mainly due to better embedding of K in the ash due to K-alumo-silicate formation. The increasing S content in the blend may lead to decreased high-temperature chlorine corrosion problems. On the other side gaseous NO, and SOx emissions may increase due to the increasing concentrations of S and N in the blend.

A few studies regarding biomass/peat blends have already been published. In Ref. [9] the effect of peat addition to wood pellets on slagging characteristics during combustion in residential pellet burners has been investigated. It has been reported that the addition of a Si rich peat increased the slagging tendency, whereas the slagging tendency was significantly lower when adding ash poor peat with a relatively high Ca/Si ratio. In Ref. [10] forest residues and wheat straw were co-combusted with peat (15 respectively 40 wt.% d.b.) in a small scale (15 kW) grate-fired boiler. Peat addition led to a reduction of the release of fine particle and deposit forming alkali metals of up to 74% for forest residues and to 45% for wheat straw. In Ref. [11] it is reported that the addition of peat prevented agglomeration in a fluidised bed, where bark from pine and spruce were used as fuels. This study reports that even 5% peat was found to have a significant effect on preventing bed agglomeration. Another study Ref. [12] investigated the combustion of forest residues and peat mixtures in controlled experiments in a bench-scale fluidised bed reactor. The main results are an increased bed agglomeration temperature, a decreased concentration of K and an increased concentration of Ca in the inner bed particle layers, a reduced amount of fine particle but an increased amount of coarse particle emissions. The mechanisms for the positive effects were the transfer and/or removal of K in the gas phase to a less reactive solid form via sorption and/or the reaction with the reactive peat ash (SiO2 and CaO), which in most cases formed larger particles (>1 μm) containing Ca, Si and K.

All previous investigations were based on experimental (fixed bed and fluidised bed combustion) evaluations of biomass peat blends. Within this work however advanced fuel characterisation tools shall be used for an evaluation of the combustion related effects of peat blends during fixed bed/grate combustion. Advanced fuel characterisation tools such as fuel indexes, thermodynamic equilibrium calculations and lab-scale reactor experiments have already proven their general applicability for the evaluation of pure fuels [6,17] as well as fuel/additive mixtures [13]. Compared with combustion experiments they are rather quick, need significantly less amounts of fuel and are less cost intensive. The aim of this work was to investigate the influence of peat addition to Miscanthus and to identify a meaningful blending ratio.

2. Methods

For a combustion related characterisation of Miscanthus and peat blends the following methods were used. Wet chemical fuel analyses provide the chemical compositions of the pure fuels and the fuel blends. Fuel indexes were calculated which delivers first information about the ash-melting tendency and the K release (by using the molar [Si + P + K]/[Ca + Mg] ratio), a first estimation of the aerosol emissions to be expected (by using the sum of K, Na, Zn and Pb) and an indicator for the high-temperature chlorine corrosion risk (by using the molar 2S/Cl ratio). Thermodynamic equilibrium calculations (TEC) were used for a prediction of the release of volatile and semi-volatile elements (K, Na, S, Cl, Zn, Pb) as well as of the ash-melting behaviour. Additionally lab-scale reactor combustion tests as well as ash-melting analysis according to CEN/TS 15370-1 have been conducted with selected Miscanthus/peat blends in order to gain experimental data and to compare the results to theoretical calculations.

2.1. Wet chemical analysis

Wet chemical fuel analyses form the basis for the fuel characterisation methods used in this study. Well proven fuel analysis methods were applied [6,14,15]. Fuel analysis have been performed according to ÖNORM CEN/TS 15104 (C, H, N), ÖNORM CEN/TS 15289 (Cl), ÖNORM EN 14775 (ash content). The concentrations of major and minor elements as well as of S have been determined by multi-step pressurised digestion of the fuel, followed by detection applying inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Arcos, Spectro) or inductively coupled plasma-mass spectrometry (ICP-MS) (Agiland 7500), depending on the detection limits.

2.2. Fuel indexes

Fuel indexes are calculated based on results of wet chemical fuel analysis and can be used to provide indications regarding relevant combustion related properties for biomass fuels. These are for instance the potentials for gaseous NOx, SOx and HCl emissions, the potentials for fine particulate emissions and deposit formation, high-temperature chlorine corrosion risks as well as the ash-melting behaviour. The indexes are derived under the consideration of the physical behaviour and chemical reactions of biomass fuels. Detailed background information regarding the definition and evaluation of fuel indexes can be found in Ref. [6].

Fuel indexes which were used within this study are the molar (Si + P + K)/(Ca + Mg) ratio as indicator for the ash-melting tendency and for a first estimation of the K release. The sum of K, Na, Zn and Pb can be applied for an estimation of the aerosol emission potential, the molar 2S/Cl ratio as indicator for
high-temperature chlorine corrosion risks and the N content of the fuel as indicator for the NOx emission potential.

2.3. Thermodynamic equilibrium calculations

Thermodynamic equilibrium calculations (TEC) provide the possibility to predict multi-phase equilibria, whereby gaseous, liquid and solid phases of interest can be identified and quantified. These calculations are conducted for a multi-component thermodynamic system in a pre-determined gas atmosphere, under the assumption that chemical equilibrium can be achieved for the system investigated. In this study TEC were used to qualitatively investigate the release behaviour of inorganic compounds (K, Na, S, Cl, Zn, Pb) and the ash-melting behaviour. The thermochemical software package FactSage 6.3 has been applied, which uses the image component method in Gibbs free energy minimisation concerning thermodynamic equilibrium. In FactSage a series of calculation modules as well as databases are included. The currently accessed databases are “solution databases” including the optimised 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, the solution databases FToxid (slags and other oxide mixtures) and FTSalt (liquid and solid salt phases) have been applied. More than 1000 components and 9 solutions (which have been shown to be stable and thermodynamically relevant) were considered. The selection has been done application oriented for biomass fuels, peat and biomass/peat blends as well as their ashes.

Previous work showed that a realistic prediction of the characteristic ash-melting temperatures and the release behaviour primarily depends on a reliable quantification of the molten solution phases SLAGH and SALTF over the temperature range of interest. Experience shows that the assessment of these two phases was strongly influenced by the amounts of Al, Si and K. Therefore, based on empirically estimated limits for the characteristic molar ratios of (Si + K + P)/(Ca + Mg), K/(Si + P) and Al/Si, an optimisation method [16] for TEC has been developed which is briefly discussed in the following.

1. The fraction of reactive Si considered in the calculation is related to the molar ratio (Si + K + P)/(Ca + Mg), whereby for fuels with a value lower than 0.94 a Si-reactivity of only 10% is assumed. Especially for pure wood ashes the inclusion of typically sand-like contaminants combined with the low ash content of the corresponding fuels causes a significant share of the Si to be less or almost not reactive. It can be assumed that this inert Si-fraction (approx. 90%) does not take place in the ash-melting processes and thus by limiting the reactive fraction an overestimation of slag formation can be avoided. For non-wood ashes the Si-reactivity is defined to be 100%, because the corresponding fuels usually contain high Si amounts in the ash, making the Si fraction coming from external contaminants (e.g. sand, stones) of minor relevance.

2. To avoid an unrealistic prediction of slag formation Al2O3 is excluded from SLAGH in calculation cases with a molar Al/Si ratio <0.1. Al2O3 has a strong influence on slag formation and the currently available thermodynamic data for Al in slag solutions seem inaccurate, therefore this reduction has been defined.

3. The molar ratio K/(Si + P) determines whether the molten salt solution SALTF is used in the TEC model. SALTF is eliminated from the TEC model for molar ratios larger than 1, otherwise SALTF phases (mainly composed of K-carbonates/sulphates) are over-predicted which results in an unrealistic drop of the melting temperatures estimated.

To gain a better prediction of the inorganic element release from the fuel to the gas phase (especially regarding K and Na), the calculations have been performed following a 2 step procedure, which separately considers the devolatilisation and charcoal combustion phase. For the calculation step 1 the input data consist of the complete elemental fuel composition, under consideration of a sub-stoichiometric combustion air ratio (lambda typically 0.7) and atmospheric pressure. The evaluation of step 1 has been performed for a temperature of 700 °C which is assumed to be a realistic fuel bed temperature during volatilisation. Furthermore, this evaluation temperature has proven its applicability in a previous study [13]. For calculation step 2 which simulates the charcoal combustion phase, the input consists of the solid residues from step 1 (ash forming matter and charcoal), whereby the charcoal is assumed to consist of pure C and amounts to 15 wt.% of the initial organic dry matter. For this step an oxidising atmosphere (lambda > 1) and atmospheric pressure are applied, whereby the calculations are carried out in a temperature range from 700 to 1500 °C. The release resulting from this calculation stage has been evaluated for a temperature of 1250 °C, since this is a typical charcoal bed temperature for fixed bed combustion systems. The total release of the elements considered is calculated as the sum of the release from step 1 and step 2. The calculated release ratios are compared with experimentally determined release ratios from lab-scale experiments (see Section 4.3).

The calculations of the ash melting temperatures are performed in a 1–step approach using the results of chemical analysis of the laboratory ashed fuel (ashed at 550 °C) as input data. The ashed fuel has been used to gain a better comparability with the standard ash melting test according to CEN/TS 15370-1. The calculations have been performed under oxidising gas atmospheres as well as atmospheric pressure in a temperature range of 500–1600 °C. The calculated ash-melting temperatures have been compared with the results of the standard ash-melting test (see Section 4.2). In [13,16] additional information regarding the software, the applied models and the evaluation procedure can be found.

2.4. Lab-scale reactor experiments

Defined Miscanthus/peat blends (see Section 3.2) as well as the pure fuels have been investigated with a lab-scale reactor. The basic idea behind this reactor is to provide a tool which is capable for the simulation of the fuel decomposition behaviour in real-scale fixed-bed biomass combustion systems. The experiment delivers information regarding the release of NOx, precursor species, the release of ash-forming elements and a first indication regarding the ash melting behaviour. The setup, design and evaluation procedure of this reactor has already been described in Refs. [13,17–19].

3. Materials

3.1. Fuels investigated

Within the ERA-NET Bioenergy project FutureBioTec [20] different blends of Miscanthus and peat were prepared. Miscanthus was provided from Teagasc (the Irish agriculture and food development authority) from the research farm Oak Park Carlow and was harvested in March 2011. The peat used originated from Ireland and was a Spagnum type peat.

In Fig. 1, the chemical composition of the Miscanthus investigated is compared with Miscanthus samples from previous in-house investigations.

The database values shows a high standard deviations for the Si, Ca, K, Mg, S and Cl concentrations indicating the broad range of

3.2. Fuel blends prepared

For the investigations 3 different blends of Miscanthus and peat were prepared: 75 wt.% Miscanthus with 25 wt.% peat (P25), 50/50 (P50) and 25/75 (P75) related to dry basis. A pure Miscanthus sample (M100) and a pure peat sample (P100) have been used as reference points. The harvesting and the treatment of the fuels as well as the pelleting (Greenforce MZLP 400 series flat pellet die) was done by Teagasc (the Irish agriculture and food development authority) in cooperation with Umeå University Sweden, Institute for Applied Physics and Electronics.

Based on results of the chemical analysis of the pure fuels, mixing calculations were conducted. To check the quality of the blends these theoretically calculated concentrations were compared with results of analyses of the mixtures (see Table 1).

It can be seen from Table 1, that generally the results of chemical analyses are in good agreement with the calculated blend compositions indicating a good mixing quality. Only for P50 and P75 for Pb deviations exist which can be explained with the low concentrations of this element in the fuel, which are close to the detection limit of the analysis method applied.

It can also be seen from Table 1 that with increasing amounts of peat in the blend the concentrations of C and N increase whereas the H content decreases. The ash content remains rather constant for the peat ratios higher than 90%. The concentrations of Ca, Mg, Na, Al and Pb increase whereas the concentrations of Si, K, P and Zn decrease with increasing amount of peat in the blend, whereas the concentrations of Ca, Mg, Na, Al and Pb increase.

Regarding the ash-melting behaviour, peat shows a considerably lower shrinkage starting temperature in comparison to Miscanthus whereas the flow temperatures are rather similar.

4. Results and discussion

4.1. Evaluation of fuel indexes

In Table 2, the values of relevant fuel indexes are summarised.
emissions mainly result from a decreased formation of low melting K-silicates and decreasing molar (Si + P + K)/(Ca + Mg) ratios. This behaviour is expected for values >4 and for values over 8 negligible Cl emissions are expected, since the amount of K in the fuel decreases with an increasing amount of peat in the blend. It has to be mentioned that this index only works if comparable release ratios for the different blends prevail. Due to the trend of the molar (Si + P + K)/(Ca + Mg) ratio the K release is supposed to increase with increasing peat shares and therefore a less pronounced decrease of aerosol emissions with increasing peat shares may be expected.

### 4.1.5. NOx emissions

In biomass combustion processes NOx emissions mainly result from the fuel N, while their formation from combustion air (prompt and thermal NOx formation) typically plays only a minor role. In the case of peat blends, the conversion of NO into NO2 is expected to be much lower than in the case of wood fuels (softwood, hardwood, bark) [6]. Therefore, the high-temperature chlorine corrosion risks can be expected for values >4 and for values over 8 negligible Cl emissions are expected, since the amount of K in the fuel decreases with an increasing amount of peat in the blend. It has to be mentioned that this index only works if comparable release ratios for the different blends prevail. Due to the trend of the molar (Si + P + K)/(Ca + Mg) ratio the K release is supposed to increase with increasing peat shares and therefore a less pronounced decrease of aerosol emissions with increasing peat shares may be expected.
role [27,28]. In Ref. [6] a correlation between the N content in the fuel and the NOx emissions has been presented for fixed-bed biomass combustion, whereby with increasing fuel N content higher NOx-emissions have to be expected.

It can be seen from Table 2, that with increasing share of peat also the N-content increases and consequently also higher NOx emissions have to be expected.

4.2. Evaluation of the ash-melting behaviour predicted by TEC in comparison to experimental results

To investigate the ash-melting behaviour the standard ash-melting test (CEN/TS 15370-1) and TEC have been used. Based on TEC the amount of molten fractions can be calculated, whereby T30 is defined as the temperature at which 30 wt.% liquid phases occur. Previous work [13,16] has shown that this temperature is an appropriate indicator for the shrinkage starting temperature (SST) (according to CEN/TS 15370-1).

In Fig. 3, for comparison the SST and the T30 values are plotted against the molar (Si + P + K)/(Ca + Mg) ratio (see Section 4.1.1).

An index of 3.9 for M100 indicates a very low SST which is confirmed by the ash melting test and the TEC results (see Fig. 3). With increasing amount of peat the index decreases and the SST increases, which is also confirmed by TEC.

4.2.1. Optical evaluation of selected ashes after lab-scale reactor experiments

Lab-scale reactor experiments (see Section 2.4) have also been used for an optical evaluation of the ash sintering tendencies. From the residual ashes of tests with M100 and P25 (see Fig. 4 middle) slightly sintered ash particles with a brittle structure have been obtained, whereby for P25 a decreasing amount of sintered particles compared to M100 has been observed. This is also in agreement with the SST determined for M100 (870 °C) and for P25 (1120 °C). For higher amounts of peat P50 (see Fig. 4 right), P75 as well as for P100 a loose ash residue has been noticed.

4.3. Comparison of the release behaviour of ash-forming elements calculated by thermodynamic equilibrium calculation with the experimentally determination by lab-scale reactor experiments

TEC has also been applied for the prediction of the release behaviour of ash-forming elements for the samples investigated. The calculated results have been compared with experimental results from lab-scale reactor tests. From these tests release ratios are derived by mass and element balances based on analyses taken of the initial fuel as well as the residues (ashes) remains after the test runs. In Refs. [13,17] a detailed description of the release calculations and the evaluation of the lab-scale reactor experiments can be found.

The chemical compositions of the residual ashes of the test runs performed (in duplicate) are summarised in Table 3. In general it can be seen (Table 3) that with increasing peat share the ash chemistry shifts from a K–Si dominated system to a Ca–Si dominated system. Also the Al and Mg contents increase with increasing peat addition.

In Fig. 5, the experimentally determined inorganic element release ratios from the fuel to the gas phase from lab-scale reactor experiments are compared with results from TEC.

The release behaviour of S and Cl, which is of major relevance regarding the high temperature corrosion risk, is well predicted with TEC (see Fig. 5). For S TEC slightly overestimates the release ratios compared with lab-scale reactor experiments (84–89 wt.% respectively 95–99 wt.%). The release ratios determined for S are also in good agreement with a former work [23], where for a broad variety of fuels S release ratios between 72 and 93 wt.% with an average value of 87 wt.% were reported. The K release is the most relevant parameter regarding fine particulate matter emissions as well as deposit build-up. The trend of increasing K release with increasing peat shares, identified during the lab-scale reactor tests, is also predicted by TEC, whereby a detailed discussion regarding the K release is provided at the end of this chapter. The release prediction for Pb is in very good agreement with experimental results.

For Na and Zn strong deviations between TEC and experimental results can be observed. While the lab-scale reactor experiments indicate an increased Na release with increasing peat content of the blend, TEC predicts a Na release <5% which results from an almost complete embedding in solid phases (Na–Ca–Si phases for M100 to P75; Na–Al–Si phases for P100) for calculation step 1 (devolatilisation phase) at 700 °C. Also the second calculation step predicts small amounts (<5%) of Na to be stable in the gas phase. Generally for Na the formation of solid phases is overestimated by TEC. For Zn TEC predicts a non-systematic variation of the release between 7 and 55 wt.% while the experimental results show release ratios of about 80–90 wt%.

Zn shows strongly differing release behaviours under oxidising and reducing conditions. Generally from TEC it can be revealed that the main part of Zn is released during calculation step 1 where reducing conditions prevail. A steep increase of the Zn release can be observed for calculation step 1 in the temperature window between 700 and 900 °C, whereas the release ratios for the remaining ash-forming elements (S, Cl, K, Na, Pb) stay rather constant. Reducing atmospheres inside char particles, which are not considered by TEC, are most probably responsible for the high Zn release ratios. Therefore, TEC-based release predictions for Zn have to be evaluated as problematic.

In Section 4.1.2 the molar (Si + P + K)/(Ca + Mg) ratio has been used for a first prediction regarding the K release. In Ref. [23] a correlation between the molar (Si + P + K)/(Ca + Mg) ratio and the K release has been presented where increasing K release ratios with decreasing values of this index have been found. In Fig. 6, the molar (Si + P + K)/(Ca + Mg) ratio versus the experimentally determined K release and the predicted K release ratios from TEC as well as the correlation presented in Ref. [23] are plotted.

From Fig. 6, it can be revealed that with decreasing molar (Si + P + K)/(Ca + Mg) ratio the K release increases. Also a qualitatively good agreement of the data presented in comparison with the correlation from Ref. [23] can be observed. For TEC an underestimation of the K release for M100, whereas for P100 an overestimation and a good agreement for the blends in comparison with experimental results exists. A detailed evaluation of TEC has
shown, that almost the complete release takes place during the devolatilisation phase (calculation step 1). Therefore, the evaluation temperature of this step influences the results of the release prediction. Furthermore, it has been shown that the gaseous atmosphere has a strong influence on the K release behaviour. In a fuel bed the conditions can switch between reducing and oxidising zones and thus equilibrium conditions might not be reached. This and the definition of the evaluation temperature of step 1 can be the reason for the quantitative differences observed regarding the K release. Generally, it can be concluded that TEC is able to describe the K release qualitatively but for quantitative evaluations lab-scale reactor tests are needed.

4.4. Aerosol as well as SO2 and HCl emission potentials

Based on the release data gained from the lab-scale reactor experiments, the potential for aerosol formation can be estimated. The released amounts of K, Na, Zn and P were considered to form K$_2$SO$_4$, KCl, Na$_2$SO$_4$, NaCl, ZnO and P$_2$O$_5$. Concerning the alkali metals K$_2$SO$_4$ and Na$_2$SO$_4$ also K$_2$Na(SO$_4$)$_2$ may be formed, whereby the formation of K$_2$Na(SO$_4$)$_2$ has almost no influence on the amount of aerosols. Regarding P it has been suggested in Ref. [29] that the release occurs in form of P$_2$O$_5$ to the gas phase and from Ref. [30] it can be concluded that P remains in its phosphate form in the aerosol fraction. It has to be noted that for P50, P75 and P100 the P release was rather low (<3%) and for M100 and P25 a P release of 4.2% and 3.2% has been determined. Since for P50, P75 and P100 the P concentration in the fuel is low, the contribution to the amount of aerosols is not significant, while for M100 and P25 P showed a considerable (~10%) contribution to the amount of aerosols due to higher P concentrations in the fuel. In Ref. [6] it is shown that data from test runs performed at real-scale grate fired combustion plants show a correlation between the 2S/Cl ratio in biomass fuels and the 2S/Cl ratio found in the aerosols sampled.

### Table 3

<table>
<thead>
<tr>
<th></th>
<th>M100</th>
<th>Test 1</th>
<th>Test 2</th>
<th>P25</th>
<th>Test 1</th>
<th>Test 2</th>
<th>P50</th>
<th>Test 1</th>
<th>Test 2</th>
<th>P75</th>
<th>Test 1</th>
<th>Test 2</th>
<th>P100</th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>S mg/kg d.b.</td>
<td>1740</td>
<td>2180</td>
<td>5730</td>
<td>5310</td>
<td>10,900</td>
<td>11,700</td>
<td>15,800</td>
<td>16,700</td>
<td>21,000</td>
<td>21,500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl mg/kg d.b.</td>
<td>171</td>
<td>193</td>
<td>516</td>
<td>442</td>
<td>771</td>
<td>916</td>
<td>1270</td>
<td>1160</td>
<td>726</td>
<td>976</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca mg/kg d.b.</td>
<td>96,500</td>
<td>95,700</td>
<td>121,000</td>
<td>118,000</td>
<td>143,000</td>
<td>143,000</td>
<td>155,000</td>
<td>156,000</td>
<td>175,000</td>
<td>176,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si mg/kg d.b.</td>
<td>204,000</td>
<td>200,000</td>
<td>203,000</td>
<td>200,000</td>
<td>188,000</td>
<td>184,000</td>
<td>183,000</td>
<td>179,000</td>
<td>153,000</td>
<td>161,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg mg/kg d.b.</td>
<td>25,500</td>
<td>25,600</td>
<td>40,400</td>
<td>39,700</td>
<td>59,600</td>
<td>58,900</td>
<td>72,600</td>
<td>74,900</td>
<td>95,300</td>
<td>94,700</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K mg/kg d.b.</td>
<td>165,000</td>
<td>167,000</td>
<td>134,000</td>
<td>128,000</td>
<td>88,900</td>
<td>90,200</td>
<td>48,300</td>
<td>48,600</td>
<td>10,200</td>
<td>9020</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na mg/kg d.b.</td>
<td>5180</td>
<td>5350</td>
<td>7160</td>
<td>7160</td>
<td>8870</td>
<td>8780</td>
<td>10,100</td>
<td>10,000</td>
<td>10,400</td>
<td>10,300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P mg/kg d.b.</td>
<td>35,100</td>
<td>34,800</td>
<td>30,500</td>
<td>30,100</td>
<td>23,700</td>
<td>23,500</td>
<td>16,300</td>
<td>16,800</td>
<td>10,200</td>
<td>9940</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al mg/kg d.b.</td>
<td>5240</td>
<td>5380</td>
<td>11,100</td>
<td>11,200</td>
<td>17,400</td>
<td>17,000</td>
<td>24,600</td>
<td>24,000</td>
<td>30,700</td>
<td>30,500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn mg/kg d.b.</td>
<td>108</td>
<td>138</td>
<td>132</td>
<td>128</td>
<td>92,1</td>
<td>101</td>
<td>59,3</td>
<td>60,6</td>
<td>29,5</td>
<td>26,7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb mg/kg d.b.</td>
<td>0.94</td>
<td>1.25</td>
<td>3.5</td>
<td>3.0</td>
<td>3.9</td>
<td>4.2</td>
<td>2.7</td>
<td>3.4</td>
<td>4.6</td>
<td>5.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOC mg/kg d.b.</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIC mg/kg d.b.</td>
<td>1100</td>
<td>1200</td>
<td>1800</td>
<td>1400</td>
<td>1400</td>
<td>1200</td>
<td>1100</td>
<td>1000</td>
<td>500</td>
<td>&lt;500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. Experimentally determined element release from the fuel to the gas phase from lab-scale reactor experiments in comparison with TEC – results for pure Miscanthus and peat as well as the blends. Explanation: TEC – thermodynamic equilibrium calculation, TEC release estimated at 1250°C.
downstream the boiler. According to Ref. [6] a molar 2S/Cl ratio in aerosol emissions of about 0.43 in case of M100 and 2.9 in case of P100 can be estimated from the 2S/Cl ratios in the fuel (1.1 respectively 8.6) (see Section 4.1.4).

Based on the release data and the estimated distribution of S and Cl in the aerosols, an estimation of the aerosol emission potential ranges from 33 to 140 mg/Nm$^3$ at 13 vol.% $O_2$ in the flue gas (Nm$^3$ are m$^3$ at 0 °C and 101325 Pa) for P100 and M100 respectively. Thereby, particle losses caused by condensation of ash-forming vapours on walls and deposit formation in the furnace and the boiler sections, by reactions of ash-forming vapours with coarse fly ash particles or condensation on coarse fly ash particles are not considered.

In Fig. 7, the sum of K, Na, Zn and Pb is plotted against the estimated aerosol emissions. It can clearly be seen (Fig. 7) that with an increasing amount of the sum of K, Na, Zn and Pb the estimated aerosol emissions increase. A very good agreement between the trend of the sum of K, Na, Zn and Pb versus the aerosol emissions investigated in this study and the trend which has been investigated in Ref. [6] is given. It can also be concluded from Ref. [6] that for P100 a comparable behaviour like for softwood regarding the aerosol emissions can be expected. It has to be added that for M100 and the blends the main influencing factor on the estimated aerosol emissions is the amount of K released from the fuel to the gas phase, whereas for P100 the most relevant parameter is the amount of Na released.

Based on the release data and the estimation of aerosol emissions (alkali sulphates and chlorides) also an estimation of the potential of gaseous $SO_2$ and HCl emissions can be made (S and Cl which are not bound by K and Na). This estimation does not consider S and Cl bound by Ca and Mg. In Fig. 8, results of the estimation of gaseous $SO_2$ and HCl are displayed.

It can be seen (Fig. 8) that the $SO_2$ emissions strongly increase with rising amounts of peat. This can be explained with the increasing S content and the decreasing K content in the fuel with increasing peat shares. HCl emissions slightly increase with increasing amount of peat in the blend and remain almost constant for $>50$. This is due to the fact that the Cl concentrations in both fuels are almost the same, but with increasing amount of peat the K content in the blend decreases. Even if at the same time the K release ratio increases, the absolute K release (in mg/kg fuel) decreases. Therefore, less K is available in the gas phase to bind S and Cl which leads to increased $SO_2$ and HCl emissions. Consequently the blending of peat with Miscanthus may lead to strongly increased $SO_2$ emissions which has to be considered regarding the demand for (secondary) measures for $SO_2$ emission control.

### 5. Summary and conclusions

Blending of Miscanthus with peat represents a feasible option to reduce combustion related problems. While the usual approach for the investigation of fuel blends is based on pilot and full-scale combustion tests, in this study novel characterisation tools for a systematic evaluation of the effects of fuel blending on ash-related problems as well as particulate and gaseous emissions for fixed bed/grate combustion systems are presented, which reduce the necessity of expensive and time consuming testing programs.

Miscanthus and peat as well as 3 different blends (75/25, 50/50 and 25/75 wt.% d.b.) were investigated. With increasing shares of peat in the blends the content of K decreased, whereas the contents of N, S, Ca and Mg increased. Regarding the fuel composition, a lower K release, higher ash-melting temperatures and increasing gaseous $SO_2$ and NO$_x$ emissions can be expected with increasing peat shares.

For the evaluation of the ash-melting temperatures fuel indexes (molar $[\text{Si}+\text{P}+\text{K}] / [\text{Ca}+\text{Mg}]$ ratio), TEC and the standard ash-melting test (according to CEN/TS 15370-1) have been used. It has been shown that TEC can predict the trend of the initial
ash-melting temperatures with acceptable accuracy. Evaluations of the ash-melting behaviour proof that M100 shows a low shrinkage starting temperature (SST) (870 °C), whereas for P100 a high SST (1210 °C) has been determined. An increase of the SST for P25 in comparison with M100 and further increasing melting temperatures for higher peat shares are observed.

Furthermore, TEC have been used for a qualitative and for some elements (e.g. S, Cl and Pb) also quantitative prediction of the element release ratios. For a quantitative determination of the release behaviour of volatile and semi-volatile ash-forming elements results from lab-scale reactor experiments were used. For the qualitative prediction of the K release additionally the fuel index (molar \([\text{Si} + \text{P} + \text{K}] / (\text{Ca} + \text{Mg})\) ratio) can be applied. This index predicts increasing K release ratios with an increasing amount of peat in the blend, which is in line with results from TEC. Experimentally the highest K release ratio has also been determined for P100. With decreasing peat shares up to P50 the K released also decreased, for lower peat shares (P25, M100) the K release was rather constant. The release ratios determined from lab-scale reactor experiments have been used for an estimation of the aerosol, HCl and \(\text{SO}_2\) emissions to be expected. The aerosol emissions. These trends and NO emission limits will accompany the decision.

The amount of 25% of peat can be recommended for a preparation of a fuel blend with Micansthus since the ash-melting temperatures are increased to a rather unproblematic level, the aerosol emissions decrease and the increase of gaseous HCl, \(\text{SO}_2\) and \(\text{NO}_x\) emissions is still on a moderate level, whereas for this blend still an increased risk for high-temperature chlorine corrosion exists. Higher peat amounts decrease the corrosion risk and the aerosol emissions further, slightly raise the ash-melting temperatures, but also cause higher gaseous \(\text{SO}_2\) and \(\text{NO}_x\) emissions. These trends have to be considered regarding the final selection of a suitable blend. Economic considerations as well as legal constraints (e.g. emission limits) will accompany the decision.

It has to be noted that the composition of peat strongly depends on its origin and formation. Therefore, the fuel characterisation methods presented in this study should be performed for the specific fuels used in a certain plant/region because the results may strongly differ depending on the chemical composition of the fuels used.

Summing up, a new evaluation method for the characterisation of fuel blends is available considering the influences on ash-melting, fine particulate, HCl, \(\text{SO}_2\) and \(\text{NO}_x\) emissions. With this approach the characterisation of meaningful biomass blends can be performed and thus time-consuming and expensive pilot-and full-scale tests can be minimised.

Acknowledgements

The authors gratefully acknowledge the support of the FFG – Austrian Research Promotion Agency, within the ERANET-Bioenergy project FutureBioTec, future low emission biomass combustion systems. The work was also funded by the companies Andritz AG, Josef Bertsch GmbH & Co. KG, BIOS BIOENERGIESYSTEME GmbH, HET Heiz- und Energie Technik Entwicklung GmbH, KWB Kraft und Wärme aus Biomasse GmbH, MAWERA Holzfeuerungsanlagen GmbH, Standardkessel GmbH and TIWAG Tiroler Wasserkraft AG.

References


