# energy&fuels

# Advanced Biomass Fuel Characterization Based on Tests with a Specially Designed Lab-Scale Reactor

Thomas Brunner,<sup>\*,†,‡,§</sup> Friedrich Biedermann,<sup>†,‡</sup> Werner Kanzian,<sup>†,§</sup> Nikola Evic,<sup>†,§</sup> and Ingwald Obernberger<sup>†,‡,§</sup>

<sup>†</sup>BIOENERGY 2020+ GmbH, Inffeldgasse 21b, 8010 Graz, Austria

<sup>‡</sup>BIOS BIOENERGIESYSTEME GmbH, Inffeldgasse 21b, 8010 Graz, Austria

<sup>§</sup>Institute for Process and Particle Engineering, Graz University of Technology, Inffeldgasse 13, 8010 Graz, Austria

ABSTRACT: To examine relevant combustion characteristics of biomass fuels in grate combustion systems, a specially designed lab-scale reactor was developed. On the basis of tests performed with this reactor, information regarding the biomass decomposition behavior, the release of NO<sub>x</sub> precursor species, the release of ash-forming elements, and first indications concerning ash melting can be evaluated. Within the scope of several projects, the lab-scale reactor system as well as the subsequent evaluation routines have been optimized and tests with a considerable number of different biomass fuels have been performed. These tests comprised a wide variation of different fuels, including conventional wood fuels (beech, spruce, and softwood pellets), bark, wood from short rotation coppice (SRC) (poplar and willow), waste wood, torrefied softwood, agricultural biomass (straw, Miscanthus, maize cobs, and grass pellets), and peat and sewage sludge. The results from the lab-scale reactor tests show that the thermal decomposition behavior and the combustion behavior of different biomass fuels vary considerably. With regard to NO<sub>2</sub> precursors (NH<sub>3</sub>, HCN, NO, N<sub>2</sub>O, and NO<sub>2</sub>), NH<sub>3</sub> and, for chemically untreated wood fuels, also HCN represent the dominant nitrogen species. The conversion rate from N in the fuel to N in  $NO_x$  precursors varies between 20 and 95% depending upon the fuel and generally decreases with an increasing N content of the fuel. These results gained from the lab-scale reactor tests can be used to derive NO<sub>x</sub> precursor release models for subsequent computational fluid dynamics (CFD)  $NO_x$  post-processing. The release of ash-forming vapors also considerably depends upon the fuel used. In general, more than 91% of Cl, more than 71% of S, 1-51% of K, and 1-50% of Na are released to the gas phase. From these data, the potential for aerosol emissions can be estimated, which varies between 18 mg/Nm<sup>3</sup> (softwood pellets) and 320 mg/  $Nm^3$  (straw) (dry flue gas at 13%  $O_2$ ). Moreover, these results also provide first indications regarding the deposit formation risks associated with a certain biomass fuel. In addition, a good correlation between visually determined ash sintering tendencies and the sintering temperatures of the different fuels (according to ÖNORM CEN/TS 15370-1) could be observed.

# 1. INTRODUCTION AND OBJECTIVES

The use of conventional wood fuels, new agricultural biomass fuels, biomass residues from different processes, and pretreated fuels is of increasing interest in all European Union (EU) countries because of the growing relevance of energy use from biomass. Moreover, fuel flexibility is of rising importance for utilities as well as biomass furnace and boiler manufacturers. Therefore, an improved characterization of fuels and fuel mixtures is gaining increasing relevance.

In this respect, it is essential to gain knowledge about the combustion and volatiles release behavior of different fuels and fuel mixtures. This is of special relevance for "new" and "difficult-to-use" fuels (e.g., short rotation crops, energy grasses, and residues from agricultural industries), which usually show considerably higher ash contents and lower first ash melting points in comparison to conventional wood fuels (wood pellets, woodchips, and bark), leading to increased problems concerning slagging, ash deposit formation, and fine particulate emissions. Moreover, these fuels may also contain other precursors of pollutants, such as nitrogen, as part of the organic structure that may be oxidized into nitrogen compounds released from the fuel and carried to the exhaust gas may form a basis for reduction

procedures to convert the nitrogen compounds into elemental nitrogen instead of nitrogen oxides.

To realize an advanced fuel evaluation tool, which tackles the problems mentioned above, a special lab-scale reactor has been designed and constructed at the Institute for Process and Particle Engineering, Graz University of Technology. The aim was to design a batch reactor, with which the combustion on a grate can be simulated and which can be applied to cover all fuel characterization aspects mentioned above. Therefore, test runs with this reactor should provide information regarding the biomass decomposition behavior, the release of NO<sub>x</sub> precursor species, the release of ash-forming elements, and first indications concerning ash melting.

In this paper, first the idea behind this lab-scale reactor is explained and then the reactor itself is introduced. Furthermore, results from recently performed test runs with 10 different biomass fuels are presented and compared to each other as

 Received:
 March 29, 2013

 Revised:
 July 22, 2013

 Published:
 July 23, 2013

Special Issue: Impacts of Fuel Quality on Power Production and the Environment



Figure 1. Scheme of the lab-scale reactor, including measurement setup. B1, B2, and B3 indicated the three different height levels of the temperature measurements in the fuel bed. Dimensions are in millimeters.

examples for the application of the reactor as an efficient novel fuel characterization method.

#### 2. METHODS

**2.1. Description of the Lab-Scale Reactor.** The basic idea was to develop, design, and construct a lab-scale batch reactor, which is capable for the simulation of the fuel decomposition behavior in real-scale fixed-bed thermal biomass conversion systems. Therefore, the following constraints were given: (i) reasonable sample intake to consider secondary reactions in the fuel bed appropriately, (ii) high heating rates of the fuel comparable to real-scale grate furnaces, (iii) inert reactor material to avoid reactions of the gases with the reactor, (iv) high flexibility regarding analytical equipment connected with the reactor, and (v) online recording of relevant operation data and emissions as well as the mass loss.

Finally, the following concept was realized (Figure 1): The core of the reactor is a cylindrical retort (height, 35 cm; inner diameter, 12 cm), which is heated electrically and controlled by two separated proportionalintegral-derivative (PID) controllers (see Figure 1). The fuel is put in a cylindrical sample holder of 100 mm height and 95 mm inner diameter. This size provides the possibility to use a fuel mass between around 100 g (for low-density fuels, such as chopped or chipped fuels) and more than 400 g (for pelletized fuels), which is a reasonable quantity for the simulation of a packed bed. Moreover, the sample holder is equipped with five thermocouples (NiCr-Ni) to monitor the fuel bed temperatures during the test runs (see Figure 1). The material of the reactor wall and the sample holder is silicon carbide. This material had already proven its applicability for such types of reactors in former experimental setups and was selected because it is inert under reducing and oxidizing conditions and, therefore, 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) and is used to determine the weight loss of the sample over the test run period.

The sample holder with the biomass is introduced into the preheated reactor, and therefore, a rapid heating, which is well comparable to the heating in real-scale thermal conversion processes, can be achieved. Flue gas samples are extracted from the gas volume above the fuel bed, partly treated, respectively conditioned (dilution and temperature stabilization), and introduced into the following gas analysers: (i) Fourier transform infrared spectroscopy (FTIR) (Ansyco), CO<sub>2</sub>, H<sub>2</sub>O, CO, CH<sub>4</sub>, NO, NH<sub>3</sub>, HCN, NO<sub>2</sub>, N<sub>2</sub>O, and basic hydrocarbons; (ii) Emerson NGA 2000; paramagnetism, O<sub>2</sub>; nondispersive infrared analysis (NDIR), CO<sub>2</sub> and CO; heat conductivity, H<sub>2</sub>; (iii) flame ionization detector (FID) (Bernath Atomic 3005), OGC (C<sub>x</sub>H<sub>y</sub>); (iv) chemiluminescence detector (CLD) (ECO Physics CLD 700 EL ht), NO, NO<sub>x</sub>; and (v) wide band  $\lambda$ sensor, O<sub>2</sub>.

Moreover, the flow and temperatures of the reaction medium (e.g., air,  $N_2$ , or different mixtures of  $O_2$  and  $N_2$ ) and several flue gas and reactor temperatures are recorded with NiCr–Ni thermocouples.

The testing protocol was defined as follows: (i) Before the test run, the fuel is pre-dried to 10 wt % wet basis (wb) moisture content and a sub-sample of the fuel is forwarded to wet chemical analyses. (ii) First, the fuel is filled into the sample holder and lightly compressed to gain a packed bed with a realistic density. (iii) Then, the reactor is preheated, applying 750 and 450 °C as pre-settings for the upper and lower heating element. These settings are kept constant during the whole test run. (iv) Then, the sample holder with the fuel is introduced into the reactor, and the reaction gas flow through the grate and the fuel bed is activated. All experiments documented in this paper have been performed with dry air (21 vol %  $O_2$  and 79 vol %  $N_2$ ) as the reaction agent and a gas flow of  $30 L_N$ /min. The reaction gas flow rate is kept constant during the whole test run. (v) All parameters mentioned above are continuously recorded in a 2 s interval over the whole test run, which usually lasts between 30 and 60 min depending upon the fuel mass applied. (vi) At the end of the test run, first the residues (ashes) are visually evaluated regarding ash sintering and slag formation and then removed and forwarded to chemical analyses.

The lab-scale reactor has been designed to represent the burning conditions of a biomass fuel layer on a grate as good as possible (Figure 2). It reproduces the behavior of a fuel segment moving along the grate and, thereby, passing first through the drying zone, then through the devolatilization and charcoal gasification zone, and finally, through the char burnout zone. Because the air flow through the fuel bed remains the same during the whole experiment, the excess air ratios vary depending



**Figure 2.** Projection of the lab-scale reactor fuel bed to the fuel layer in a grate furnace. *h*, fuel bed height; *t*, time.

upon the stage of combustion from high  $\lambda$  values (during drying) over understoichiometric conditions (usually a  $\lambda$  between 0.6 and 0.9) during the devolatilization phase back to high  $\lambda$  values during charcoal burnout, which is well-comparable to the different stoichiometries prevailing in the different zones of a real-scale moving grate. 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.<sup>1,2</sup> Consequently, with the setup and testing protocol presented, comprehensive information on the thermal decomposition process of biomass on a grate can be gained, which can also be transposed to real-scale systems. This includes the mass losses during drying, pyrolysis, and charcoal combustion, the compositions of the gases produced, and comprehensive information about the formation of NO<sub>x</sub> precursors. Moreover, the data gained from the fuel and the residual ash analysis as well as the weight measurements can be used to calculate the release of inorganic elements to the gas phase by calculating mass and element balances.

**2.2. Wet Chemical Fuel Analyses.** Chemical analyses of the fuels used as well as the residues play an important role in the evaluation of the lab-scale reactor tests. Therefore, the application of analysis methods, which provide the highest level of accuracy possible, is of relevance.<sup>3</sup> In the following, the methods applied for the fuel and ash analyses are briefly introduced.

The moisture content of fuel samples is determined according to ÖNORM EN 14774 (determination of the weight loss during drying at 105 °C until a constant weight is reached). For further analyses, sample preparation according to ÖNORM EN 14780 is carried out. The samples are homogenized and reduced by forming a cone, which is divided into four portions, of which one portion is milled in a cutting mill to a particle size of <4 mm. Then again, sample division takes place, and the final analysis sample is ground in an ultracentrifugal mill equipped with a titanium rotor and screen to <0.2 mm.

The ash content is determined according to ÖNORM EN 14775 by determination of the loss of ignition at 550 °C. Additionally, the total inorganic carbon (TIC) content of the ashed fuel is determined and used to calculate a carbonate-free (only oxide-based) ash content. This is important for the later calculation of ash balances over the test runs. Moreover, the ash-melting behavior is determined according to prCEN/TS 15370-1.

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

For the determination of the contents of major and minor ashforming elements (excluding Cl), a multi-step pressurized digestion with  $HNO_3$  (65%)/HF (40%)/H<sub>3</sub>BO<sub>3</sub> followed by measurement by inductively coupled plasma-optical emission spectroscopy (ICP-OES) or inductively coupled plasma-mass emission spectroscopy (ICP-MS) (depending upon detection limits) is applied.

The samples of the residues (ashes) are analyzed regarding total organic carbon (TOC) and TIC. For TIC analyses, an aliquot is

treated with acid and the generated  $CO_2$  is measured by infrared (IR). TOC is determined by the amount of total carbon (determined by an element analyzer) minus the TIC. For the determination of major and minor elements, expect Cl, multi-step pressurized digestion with HNO<sub>3</sub> (65%)/HF (40%)/H<sub>3</sub>BO<sub>3</sub> followed by measurement by ICP–OES is applied. The Cl content of ashes is measured by ion chromatography after elution for 24 h with deionized water.

**2.3. Evaluation of Lab-Scale Reactor Test Runs.** In this section, the evaluation strategy of lab-scale rector test runs is briefly presented to provide a better basis for the understanding of section 3, where results from test runs with different biomass fuels are discussed.

At first, a validity check regarding all data gained from the test runs has to be performed. Therefore, from the reaction gas flows measured, the weight loss recorded by the balance, and the results of the flue gas analyses, cumulative balances for the main elements C, H, and O are calculated. Moreover, using the results of the fuel analyses regarding the oxide-based ash content and the ash analyses regarding the TOC and TIC contents, an ash mass balance is calculated. Considering the inhomogeneous composition of biomass fuels and the possible measurement and analysis error ranges, a full closure of the mass and element balances is not realistic. However, experience has shown that recovery rates in the range between 80 and 120% are reasonable, and therefore, only test runs with recovery rates within these margins are further evaluated. The recovery rate is thereby calculated by dividing the mass of an element in the flue gas and the ashes with the mass of the respective element in the initial test run fuel.

In a next step, characteristic data describing the thermal fuel decomposition are evaluated. These data include the start and duration of the volatilization and charcoal gasification phase and the main charcoal combustion phase and the maximum fuel bed temperatures measured and the decomposition rates determined during these phases. Then, the flue gas species and the trend of the excess air ratio over the whole test run duration are investigated. Special emphasis is thereby put on the trends regarding the release of NO<sub>x</sub> precursors.

Finally, the data gained from the chemical analyses of the ashes are evaluated. In a first step, element balances for the major ash-forming refractory species (Ca, Si, Mg, Al, and Fe) based on the initial fuel sample mass (determined prior to the test run), the mass of the residual ash (determined after the end of the test run), and the results of the fuel and ash analyses are calculated as a plausibility check for the ash sampling and the analyses. It is important that these balances show a good closure with recovery rates between 80 and 120%. However, this balance closure is often not accurate enough to calculate release rates for, e.g., K, which can reach values <10 wt %. Provided a good quality of the chemical analyses, the major source for deviations is the entrainment of ash particles from the fuel bed with the flue gases, and therefore, additionally, a correction according to guiding elements is performed. Guiding elements are elements, such as Ca and Mg (for wood fuels) or Si (for herbaceous fuels), which are known to have a very low volatility and additionally show high concentrations in the ashes. Using these elements as tracers, the mass balances can be corrected for ash losses. From the corrected element balances, the release rates for, e.g., K, Na, S, Cl, Z, and Pb are subsequently calculated.

On the basis of the release rates of the main aerosol-forming elements, K, Na, Zn, and P, the potential for aerosol formation can be estimated. Thereby, these elements are then considered as  $K_2SO_4$ , KCl,  $Na_2SO_4$ , NaCl, ZnO, and  $P_4O_{10}$ .<sup>4</sup> In addition, the formation of carbonates ( $K_2CO_3$  and  $Na_2CO_3$ ) is probable if there is not enough S and Cl available to completely bind K and Na as chlorides and sulfates. Usually there is a surplus of S and Cl compared to K and Na, indicating a certain potential for gaseous emissions. If it is considered that the whole sulfur reacts with K and Na available, the maximum potential for aerosol emissions can be calculated, while if it is assumed that all Cl is bound to Na and K, the minimum aerosol emission potential results. The reason for this difference is the higher molar weight of sulfates compared to chlorides. This estimation of the aerosol emissions does of course not take into account particle losses caused by condensation of ashforming vapors on walls and deposit formation in the furnace and the

	softwood pellets	spruce woodchips	torrefied softwood	beech woodchips	SRC poplar	spruce bark	waste wood pellets	straw pellets	Miscanthus pellets	sewage sludge
ac 550 °C (wt % db)	0.43	0.34	0.5	0.6	1.8	4.8	2.7	5.2	2.0	41.4
ac corr (wt % db)	0.33	0.24	0.39	0.45	1.4	3.4	2.4	4.8	1.9	41.1
C (wt % db)	49.5	48.9	57.0	48.5	48.5	49.8	48.4	46.6	48.2	29.6
H (wt % db)	6.1	6.2	5.7	6.1	6.1	5.7	6.0	5.9	6.0	4.4
O (wt % db)	44.0	44.6	36.9	44.9	43.7	40.8	41.9	42.2	43.6	20.5
N (wt % db)	0.05	0.04	0.07	0.08	0.36	0.34	1.4	0.5	0.28	4.3
S (mg/kg db)	49.6	42.9	36.9	92.0	346.0	288.0	512	1035	299.5	11850
Cl (mg/kg db)	16.0	26.9	12.5	36.9	37.8	101.4	881	1580	1715	830
Ca (mg/kg db)	950	1040	1195	1340	4330	13450	4980	3895	1275	35300
Si (mg/kg db)	300.0	69.0	82.5	53.0	381.0	1810	3410	12450	4365	43650
Mg (mg/kg db)	122.0	106.0	249.5	284.0	488.0	822	676	788	530	5750
K (mg/kg db)	507	358.0	584	1280	3100	1825	834	8790	4655	3650
Na (mg/kg db)	15.0	7.3	6.5	5.0	58.3	78.9	498.0	128.0	26.0	1880
P (mg/kg db)	38.0	31.3	58.8	53.2	817	338.0	85.6	836	174.5	36150
Zn (mg/kg db)	12.4	7.6	30.8	3.1	27.2	85.0	166.0	5.8	10.2	970
Pb (mg/kg db)	0.14	0.17	0.7	0.14	0.48	0.8	60.6	0.17	0.50	28.6
SST (°C)	1390	1320	1310	1380	1390	1310	1230	850	820	1080

"wb, wet basis; db, dry basis; ac 550 °C, ash content determined at 550 °C; ac corr, ash content without carbonates (on the basis of oxides); and SST, shrinkage starting temperature.



Figure 3. Measured trends regarding the mass loss, the fuel bed and flue gas temperatures, and the main gas species and the  $NO_x$  precursor concentrations for test runs with beech woodchips. For positions of the fuel bed temperature measurements, see Figure 1.

boiler sections of real-scale plants. Moreover, particle losses caused by the reaction of ash-forming vapors with coarse fly ash particles or condensation on coarse fly ash particles and gaseous emissions of S (i.e.,  $SO_x$ ) and Cl (i.e., HCl) are not considered. Following, it is an approximation but suitable to evaluate the aerosol emission potential.

#### 3. RESULTS

Up to now, more than 30 different biomass fuels have been tested with the lab-scale reactor. This paper focuses on results of tests with 10 fuels recently performed within the ERANET Project "SciToBiCom—scientific Tools for Fuel Characterization for

#### **Energy & Fuels**

Clean and Efficient Biomass Combustion", which cover a broad range of different biomass fuel types: (i) conventional chemically untreated wood fuels, such as softwood pellets, softwood chips (spruce), hardwood chips (beech), and bark (spruce), (ii) torrefied softwood, (iii) short rotation coppice (SRC), such as poplar, (iv) quality assorted waste wood (Q1–Q4 according to Austrian regulations and A1 and A2 according to German regulations), (v) herbaceous fuels, such as straw (pelletized) and *Miscanthus* (pelletized), and (vi) sewage sludge.

**3.1. Fuel Composition.** In Table 1, the chemical compositions and the results of ash-melting tests regarding the 10 fuels tested are presented.

It can be seen that the fuel selection covers a wide range of N, ash, K, S, and Cl contents; thus, results regarding the possible variations concerning the release of  $NO_x$  precursors, the release of ash-forming elements and the potential for aerosol formation, and the ash-melting behavior can be expected in advance.

**3.2. Case Study Beech.** First, a test run with beech woodchips is discussed in detail to present and explain the whole evaluation procedure, and subsequently, for all 10 fuels, relevant results are summarized.

The chemical composition of the beech wood applied can be taken from Table 1. Three test runs have been performed to investigate the reproducibility of the results. Because all three tests showed about the same results, here only test run 3 is discussed. Fuel masses of 147.4 g (wb) and 136.4 g (db) were used.

In Figure 3, the trends regarding the mass loss, the fuel bed and flue gas temperatures, and the concentrations of the main gas species and the  $NO_x$  precursors over the test run are displayed.

As seen, the test run duration was about 1020 s. At the beginning, mainly drying takes place, indicated by a moderate mass loss, low fuel bed temperatures, and the release of H<sub>2</sub>O. After about 140 s, fuel decomposition starts, indicated by decreasing O2 concentrations and increasing CO2 concentrations in the flue gas. The main decomposition phase starts with a rapid decrease of the O<sub>2</sub> concentration to zero level after 360 s. The release of volatiles and parallel charcoal gasification take place until around 600 s of the test run duration. A rapid mass loss, an increase of the bed temperatures to 400-550 °C, and combustion air ratios below 1 (in this case, on average 0.89 for the whole release of volatile and charcoal gasification phase) are typical indicators for this phase. Mainly CO<sub>2</sub>, CO, H<sub>2</sub>O, CH<sub>4</sub>, and H<sub>2</sub> as well as minor amounts of other hydrocarbons are released to the gas phase. After 560 s,  $H_2$  and  $CH_4$  drop to zero, which is taken as an indicator for the end of the release of volatiles and the start of the charcoal combustion phase. This phase is characterized by smaller amounts of CO and increasing CO<sub>2</sub> concentrations in the flue gas as well as slowly increasing O<sub>2</sub> concentrations (increasing excess air ratio with a mean value of 1.71 over the whole phase). During this phase, typically the highest fuel bed temperatures, in this case 1127 °C, are measured.

The NO<sub>x</sub> precursor species are mainly released during the release of volatiles and charcoal gasification. Thereby, the dominating species is HCN, followed by  $NH_3$  and NO. During charcoal combustion, a second release peak, clearly dominated by NO, is observed.

After the end of the test run, the amount of residues (ashes) amounted to 0.8 g. No sintered ash pieces or slag could be identified (see Figure 4), which is not surprising because the maximum fuel bed temperature achieved (1127  $^{\circ}$ C) is significantly below the shrinkage starting temperature of the beech investigated (1380  $^{\circ}$ C; see Table 1).





**Figure 4.** Photos of the (above) fuel before and (below) ashes after the test run.

Element balances performed on the fuel analysis data and the process data recorded showed good closures for C (103.5%), H (98.3%), O (106.5%), and the total ash (94.3%). This good balance closure is a relevant aspect regarding the representative-ness of the test run.

In Figure 5, the evaluation of the test run data regarding  $NO_x$  precursors is presented. It can be seen that 86.6 wt % of



**Figure 5.** Release of  $NO_x$  precursors from the fuel. TFN = total fixed nitrogen (sum of N in NO, NH<sub>3</sub>, HCN, NO<sub>2</sub>, and N<sub>2</sub>O).

N contained in the fuel is converted into N in the  $NO_x$  precursor compounds determined. HCN is, with 44.4% of the total released  $NO_x$  precursors, the most relevant species, followed by NO (18.4 wt %) and  $NH_3$  (18.2 wt %).  $NO_2$  (0.5 wt %) and  $N_2O$  (5.2 wt %) provide only minor contributions.

On the basis of the results of the fuel and ash analyses, element balances for ash-forming elements have been performed. They shown an acceptable closure for non-volatile elements, such as Ca (118%) and Mg (107%), which is an important prerequisite for the plausibility of the release rates calculated for ash-forming elements from these data. In Figure 6, these release rates are



**Figure 6.** Release of ash-forming elements from the fuel to the gas phase. The release is in weight percent. db = dry basis.

presented. The easily volatile elements Cl and S show, as expected, the highest release rates (99.1 and 88.1 wt %, respectively). Also, the easily volatile heavy metals show significant release rates of 97.7 wt % for Pb and 88.3 wt % for Zn. Moreover, 32.5 wt % of K and 19.5 wt % of Na contained in the fuel have been released to the gas phase.

Assuming that K and Na mainly form sulfates and chlorides, while Zn and Pb are most likely bound as oxides, the potential for fine particle (aerosol) formation can be estimated on the basis of these release rates. For the test run presented, the maximum potential for aerosol emissions amounts to  $68.2 \text{ mg/Nm}^3$  (related to dry flue gas and 13 vol % O<sub>2</sub>).

**3.3. Comparison of Results for Different Fuels.** In the following, the most relevant results from the test runs with the 10 SciToBiCom fuels are presented and compared to each other. Table 2 provides an overview of some characteristic test run data.

As show in Table 2, the sample mass applied varied depending upon the fuel bulk density between 80 g (SRC poplar) and 445 g (sewage sludge). The duration of the two main reaction phases, the release of volatiles and char coal gasification, and the charcoal combustion generally increase with an increasing fuel sample mass. A clear difference between the air ratios resulting for these two phases can be identified, whereas for most of the fuels during the release of volatiles and char coal gasification, a  $\lambda$  below 1 was

achieved, and during charcoal combustion, always hyperstoichiometric conditions prevailed.

The maximum fuel bed temperatures during volatilization and charcoal gasification vary between 791  $^{\circ}$ C (sewage sludge) and 1290  $^{\circ}$ C (softwood pellets). During charcoal combustion, they reached the highest values between 1033 (SRC poplar) and 1301 (softwood pellets). These temperature levels are comparable to those achieved during real-scale combustion processes, which is important for the applicability of the lab-scale reactor data.

With regard to the conversion of the fuel N into N bound in  $NO_x$  precursors, a decreasing ratio with an increasing fuel N content is observed. While for the N-poor fuels, such as softwood pellets, spruce woodchips, and torrefied wood, almost 100% of the fuel N is converted; this number decreases to 33.7 wt % for the N-rich fuel sewage sludge.

In Figure 7, the share of different  $NO_x$  precursors on TFN is summarized.



**Figure 7.** Share of  $NO_x$  precursors related to TFN. TFN, total fixed nitrogen (sum of N in NO, NH<sub>3</sub>, HCN, NO<sub>2</sub>, and N<sub>2</sub>O); P, pellets; and WC, woodchips.

An interesting information that can be gained from this diagram is that, for chemically untreated wood fuels, HCN is the most relevant NO<sub>x</sub> precursor, while for waste wood, sewage sludge, *Miscanthus*, and straw, NH<sub>3</sub> strongly dominates and HCN only plays a minor role. The detailed reason for this different release behavior of N species is not yet clear and must be further investigated with respect to fuel chemistry. It may have an influence on the subsequent NO<sub>x</sub> formation pathways. In detail, the share of NH<sub>3</sub> related to total fixed nitrogen (TFN) is (i) high (70.2–87.7 wt %) for waste wood pellets, straw pellets, *Miscanthus* pellets, and sewage sludge, (ii) medium (37.7–51.9 wt %) for torrefied softwood, SRC poplar, and spruce bark, and (iii) low

Tabl	le 2.	Characteristic	Data G	ained fro	om the	Test Runs	with tl	he 10	SciToB	iCom 1	Fuels"
------	-------	----------------	--------	-----------	--------	-----------	---------	-------	--------	--------	--------

	softwood pellets	spruce woodchips	torrefied softwood	beech woodchips	SRC poplar	spruce bark	waste wood pellets	straw pellets	Miscanthus pellets	sewage sludge
sample mass (g wb)	410	118	91	147	80	100	420	435	377	445
sample mass (g db)	381	104	89	136	74	87	374	379	331	405
maximum fuel bed temperature (°C)	1301	1118	1262	1127	1033	1140	1310	1244	1229	1177
duration of the release of volatiles and charcoal gasification (s)	1100	356	232	434	362	490	1468	1260	982	1880
average $\lambda$ during the release of volatiles and charcoal gasification	0.7	0.9	0.5	0.9	1.1	1.3	0.6	0.7	0.7	1.0
duration of charcoal combustion (s)	694	316	260	446	270	476	542	744	766	556
average $\lambda$ during charcoal combustion	1.5	1.8	1.3	1.7	2.3	1.9	2.0	1.5	1.4	1.5

<sup>*a*</sup>wb, wet basis; and db, dry basis.



Figure 8. Release of inorganic elements from the fuel to the gas phase. Release rate =  $1 - (\text{element mass in the ash/element mass in the fuel}) \times 100$ . P, pellets; and WC, woodchips.

(24.2–30.7 wt %) for softwood pellets, spruce woodchips, and beech woodchips.

In contrast, the share of HCN related to TFN is (i) high (47.6–51.1 wt %) for softwood pellets, spruce woodchips, and beech woodchips, (ii) medium (24.1–39.6 wt %) for torrefied softwood, SRC poplar, and spruce bark, and (iii) low (1.8–10.7 wt %) for waste wood pellets, straw pellets, *Miscanthus* pellets, and sewage sludge.

During charcoal combustion, NO formation clearly dominates. The share of NO related to TFN is (i) medium (16.1– 22.7 wt %) for wood fuels and (ii) low (3.5–6.9 wt %) for waste wood pellets, straw pellets, *Miscanthus* pellets, sewage sludge, and torrefied softwood.

These data can be very useful input data for the simulation of  $NO_x$  formation in combustion processes because they represent the flue gas leaving the fuel bed and before any further  $NO_x$  formation or reduction processes.

With regard to ash-related problems, the slagging tendencies and the release behavior are of relevance. On the basis of an optical evaluation, the particle size of the ash increased (in increasing order) from spruce woodchips over SRC poplar, torrefied softwood, beech woodchips, spruce bark, softwood pellets, *Miscanthus* pellets, waste wood pellets, and straw pellets to sewage sludge. The amount of sintered particles was (i) very high for sewage sludge, (ii) high for waste wood pellets and straw pellets, (iii) medium for *Miscanthus* pellets, and (iv) low for softwood pellets, spruce woodchips, SRC poplar, torrefied softwood, beech woodchips, and bark.

For waste wood and straw pellets, also slagging on the thermocouples in the fuel bed occurred. These results are in a good agreement with expectations based on the comparison of the shrinkage starting temperature (according to CEN/TS 15370-1) of ashes and the maximum bed temperatures that where achieved. For softwood pellets, spruce woodchips, SRC poplar, torrefied softwood, beech woodchips, and bark, the maximum bed temperature was below the shrinkage starting temperature, while for sewage sludge, waste wood pellets, straw pellets, and *Miscanthus*, it was above this level.

In Figure 8, the data concerning the release of aerosol-forming elements from the fuel is summarized, and Figure 9 shows the maximum potential for aerosol emissions that can be calculated from these data. For all fuels, high Cl (>91 wt %) and S (>71 wt %) release rates occur. Also, Pb shows for all fuels, with the exception of straw, and sewage sludge release rates of more than 93 wt %. The Zn release is, with the exception of sewage



Figure 9. Estimated aerosol emissions as well as compositions of the aerosol emissions. P, pellets; and WC, woodchips.

sludge, poplar, and straw, always higher than 70 wt %, reaching values of more than 94 wt % for softwood pellets, torrefied softwood, and waste wood. With regard to K and Na, significant differences regarding the release are observed when comparing the different fuels. The rates vary from 1 wt % for sewage sludge to around 51 wt % for torrefied softwood.

The release (in mg/kg of dry fuel) of ash-forming vapors is dominated by K species, except for sewage sludge (dominated by P). Overall, softwood pellets and spruce show the lowest aerosol emission potential. The potential increases over bark, torrefied softwood, beech, waste wood, *Miscanthus*, SRC, and sewage sludge to straw.

## 4. SUMMARY AND CONCLUSION

A total of 10 different biomass fuels have been investigated with a lab-scale reactor, which has been specially developed as a fuel characterization tool for biomass fuels to be applied in fixed-bed combustion units. The results of the test provide relevant information about the thermal decomposition behavior of the fuels in a fixed-bed as well as concerning the main flue gas species released from the fuel during volatilization and charcoal combustion. These data can further be used for the development, validation, and calibration of models for fixed-bed combustion, which can then form the basis for more detailed CFD simulation models. Moreover, the information gained about the release of NO<sub>x</sub> precursors from the fuel can be used as input data for NO<sub>x</sub> formation simulations in the gas phase. Also, the data gained

#### **Energy & Fuels**

regarding ash-related problems, such as the release data for easily volatile elements, such as S and Cl, semi-volatile elements, such as K and Na, and easily volatile heavy metals, such as Zn and Pb, are important for the characterization of a fuel with respect to aerosol emissions and deposit formation tendencies. They can also be used as input data for CFD-based aerosol and deposit formation modeling.<sup>5,6</sup>

In conclusion, the test runs performed with the new lab-scale reactor proved to be a valuable instrument to gain advanced fuel characterization data.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*Telephone: +43/316/48130013. Fax: +43/316/4813004. E-mail: thomas.brunner@bioenergy2020.eu.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the FFG, Austrian Research Promotion Agency, within the ERANET-Bioenergy Project SciToBiCom (Scientific Tools for Fuel Characterization for Clean and Efficient Biomass Combustion; Project 825790) and the Austrian COMET Programme, which is funded by the Republic of Austria and the federal provinces of Styria, Lower Austria, and Burgenland.

#### REFERENCES

(1) Weissinger, A. Experimentelle untersuchungen und theoretische simulationen zur  $NO_x$ -reduktion durch primärmaßnahmen bei rostfeuerungen. Ph.D. Thesis, Graz University of Technology, Graz, Austria, 2002.

(2) Weissinger, A.; Obernberger, I.; Scharler, R.  $NO_x$  reduction in biomass grate furnaces by primary measures—Evaluation by means of lab-scale experiments and chemical kinetic simulation compared with experimental results and CFD calculations of pilot-scale plants. *Proceedings of the 6th European Conference on Industrial Furnaces and Boilers (INFUB-6), Estoril, Portugal, April 2–5, 2002; CENERTEC: Rio Tinto, Portugal, 2002; ISBN: 972-8034-05-9.* 

(3) Bärnthaler, G.; Zischka, M.; Haroldson, C.; Obernberger, I. Determination of major and minor ash-forming elements in solid biomass fuels. *Biomass Bioenergy* **2006**, *30*, 983–997.

(4) Brunner, T. Aerosols and coarse fly ashes in fixed-bed biomass combustion. *Thermal Biomass Utilization*; BIOS BIOENERGIESYS-TEME GmbH: Graz, Austria, 2006; Vol. 7, ISBN: 3-9501980-4-0.

(5) Schulze, K.; Scharler, R.; Obernberger, I. Development of biomass fired boilers with an advanced CFD model for ash deposit and aerosol formation. *Proceedings of the 9th European Conference on Industrial Furnaces and Boilers (INFUB-9), Estoril, Portugal, April 26–29, 2011;* CENERTEC: Rio Tinto, Portugal, 2011; ISBN: 978-972-99309-6-6.

(6) Mehrabian, R.; Stangl, S.; Scharler, R.; Obernberger, I.; Weissinger, A. CFD simulation of biomass grate furnaces with a comprehensive 3D packed bed model. *Proceedings of the 25th German Flame Day Conference, Karlsruhe, Germany*; VDI Verlag GmbH: Düsseldorf, Germany, 2011; pp 189–204, ISBN: 978-3-18-092119-8.