FUEL QUALITY OF WOOD CHIPS – CHEMICAL ELEMENTS AND FUEL INDEXES

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ABSTRACT: Critical chemical elements such as nitrogen (N), sulphur (S), chloride (Cl), potassium (K) or heavy metals might determine high temperature corrosion, emission behavior and slagging of solid biofuels during combustion. Recently developed biomass fuel indexes may help to pre-evaluate fuel behavior during combustion. In total, 92 samples of wood chips (n = 75), of unchipped material (n = 11) and of twigs and needles (n = 6) were collected and analyzed for elemental composition (As, Ca, Cd, Cl, Cr, Cu, Hg, K, Mg, N, Na, Ni, Pb, S, Si, Zn). Biomass fuel indexes were calculated from the results to pre-evaluate NO_X and particle emissions, high temperature corrosion, K release and slagging behavior. Wood chips from natural wood showed low concentrations of critical chemical elements. With increasing shares of mineral soil, critical elements also increased. Biomass fuel indexes such as the sum of aerosol forming elements (K, Na, Pb, Zn) or the molar Si/(Ca+Mg) ratio for ash-melting behavior indicated that biomass fuels without contamination with mineral soil, road salt or other anthropogenic waste can be considered uncritical for combustion.
Keywords: wood chip quality, chemical elements, fuel indexes

1 INTRODUCTION

Fuel quality of wood chips is critical for failure-free combustion. Especially small scale furnaces < 100 kW require homogeneous and high quality fuels to avoid boiler disturbances such as clogging of screw conveyors or slagging but also to minimize gaseous and particular emissions. Thereby, chemical fuel composition is essential, as critical chemical elements such as nitrogen (N), sulphur (S), chloride (Cl), potassium (K) or heavy metals might determine combustion risks such as high temperature corrosion, emission behavior and slagging in furnaces using solid biofuels.

For small boilers, international standards such as ISO 17225-4 [1] for graded wood chips define fuel specifications that include threshold values for some of these critical elements (N, Cl, S and selected heavy metals) while other elements such as K or Na are usually not limited. In addition, recently developed biomass fuel indexes [2][3] may help to pre-evaluate fuel behavior during combustion [4]. However, for heterogeneous biofuels such as wood chips general assumptions may be limited as these fuels provide a wide range of element concentrations due to a high variety in raw materials or fuel production processes.

2 MATERIALS & METHODS

2.1 Raw materials

In total, 92 samples of wood chips (n = 75), of unchipped material (n = 11) and of twigs and needles (n = 6) were collected. Samples derived from forest residues and "energy round wood" (i. e. small-sized delimbed stem wood) of different tree species, from short rotation coppice (SRC), from cuttings along roadsides and from urban forestry.

2.2 Chemical analyses

Elemental composition (As, Ca, Cd, Cr, Cu, K, Mg, N, Na, Ni, Pb, S, Si, Zn) based on European standards [5][6]. was analyzed for all samples Analysis of N was done according to EN 15104 [5] using an elementary analyzer. For all other elements, samples were analyzed according to EN 15290 [6]. To ensure whole sample digestion including mineral soils and waste, HF digestion was used for both major and minor elements. In addition, Cl was analyzed using X-ray fluorescence analysis (XRF) and Hg was analyzed using a mercury analyzer.

2.3 Fuel indexes

Biomass fuel indexes were calculated from the results according to [2] [3] [4]. These indexes are commonly used to predict a risk of high emission for NO_x, SO_x, HCl and particulate matter and to evaluate any combustion hazards such as high temperature corrosion, K-release and ash fusion related problems (see **Table I**).

Table I: Biomass fuel indexes according [2][3][4]

Index	Prediction
N content	NO_x emissions
$\sum$(K+Na+Pb+Zn)	Particle emission
mol. Si/K	K release
mol. Si/(Ca + Mg)	Slagging
mol. (K + Na)/[x(2S + Cl)]	HCl and SO_x emissions
mol. 2S/Cl	Corrosion

3 RESULTS & DISCUSSION

3.1 Major and minor elements

Wood chips from natural and untreated wood (forest residues, energy round wood) showed low concentrations of critical chemical elements and proved conformity with threshold values of ISO 17225-4 (**Table II, Table III**). Elements necessary for plant metabolism such as Cl, N or S increased in samples with higher shares of green biomass such as "needles/twigs" or forest residues (**Table II**).

Table II: Mean concentration of major elements in wood chip samples

Fuel origin	n	N	S	Cl	K	Na	Ca	Mg	Si
		w-%, dry basis			mg/kg, dry basis				
ISO 17225-4		≤ 1.0	≤ 0.1	≤ 0.05	-	-	-	-	-
Forest residues conifer	11	0.34	0.03	0.02	1,610	103	3,031	457	3,212
Forest residues deciduous	6	0.36	0.04	0.01	1,841	65	5,890	625	1,959
Stem wood conifer	15	0.16	0.01	0.01	854	44	1,499	258	651
Stem wood deciduous	14	0.25	0.02	0.01	1,490	30	2,466	365	253
Needles/Twigs	6	0.99	0.07	0.05	2,787	76	2,137	654	4,440
Short rotation Coppice	7	0.38	0.04	0.01	1,837	38	5,028	384	238
Roadside chipping	7	0.45	0.05	**0.08**	2,211	405	6,196	702	5,554
Urban forestry chipped	15	0.41	0.06	0.05	2,782	344	8,816	1,162	8,972
Urban forestry unchipped	11	0.74	0.11	**0.15**	4,933	749	12,306	1,921	26,295

Table III: Mean concentration of minor elements in wood chip samples (* = contamination of samples with Cr and Ni happened during sample preparation in the lab)

Fuel origin	n	As	Cd	Cr*	Cu	Ni*	Hg	Pb	Zn
		mg/kg, dry basis							
ISO 17225-4		≤ 1	≤ 2.0	≤ 10	≤ 10	≤ 10	≤ 0.1	≤ 10	≤ 100
Forest residues conifer	11	0.10	0.28	**20.74***	3.08	8.98*	0.01	1.16	31.80
Forest residues deciduous	6	0.08	0.05	7.81*	3.00	3.03*	0.01	0.78	14.94
Stem wood conifer	15	0.04	0.14	2.90*	1.93	1.45*	0.01	0.60	17.24
Stem wood deciduous	14	0.02	0.12	1.86*	2.07	0.91*	0.00	0.44	19.41
Needles/Twigs	6	0.12	0.13	**84.04***	4.68	**41.00***	0.02	0.39	34.87
Short rotation Coppice	7	0.03	1.31	1.51*	3.05	1.04*	0.00	0.20	55.06
Roadside chipping	7	0.25	0.14	**15.80***	5.07	6.57*	0.01	0.73	27.64
Urban forestry chipped	15	**1.87**	0.19	**21.17***	6.45	8.39*	0.03	1.88	31.66
Urban forestry unchipped	11	**1.01**	0.15	**82.67***	**15.79**	**30.60***	0.02	4.30	47.31

However, concentrations were still within the limits of specifications according to ISO 17225-4 [1]. With increasing shares of mineral soil (see also poster 2.BV.1.4 [7]) or with shares of anthropogenic impurities such as fertilizers, fungicides or garbage (e. g. in samples from urban forestry), elements such as K, Ca, Mg, Si or heavy metals increased. Thereby, wood chips from urban forestry in some cases could exceed ISO thresholds for critical elements depending on the raw materials and the amount of biofuel processing (Table II, Table III).

Rather high concentrations of Cd were found in SRC-willow (n = 3), possibly due to cultivation of the trees on agricultural fields which had formerly been fertilized with phosphate. High amounts of Na and Cl were found in wood chips from roadside chipping. These values sometimes even exceed Cl threshold values of ISO 17225-4 [1] and may indicate contamination of samples

with road salt. In contrast, high concentrations of Cr and Ni could be allocated to contamination of samples during sample preparation using steel milling tool in the lab and did not relate to the biofuels [7].

3.2 Fuel indexes

Fuel indexes were related to ash content speci-fications of ISO 17225-4 [1], i. e. to ash classes A1.0 (< 1 w-%), A1.5 (< 1.5 w-%), A3.0 (< 3 w-%) and to samples with ash content > 3 w-% (Figure 1 to 4).

Aerosol forming elements, i. e. the sum of K, Na, Pb and Zn, increased with increasing ash content (Figure 1). Thereby, high ash contents indicate high shares of green tree parts such as leaves and needles (for ash content < 3 w-%) but also contamination with mineral soil (e. g. for ash content > 3 w-% in samples from urban forestry, see Poster 2.BV.1.4, [7]). Thereby, K was the major

aerosol forming element in wood chips followed by Na. Moreover, Na strongly increased at ash contents > 3 w-% indicating contamination of samples with road salt (roadside chipping). Thus, lowest particle emissions can be expected during combustion of wood chips with low ash contents, e. g. stem wood or sieved forest residues that can be allocated to ISO 17225-4 specifications A1 and A2 [1]. In contrast, wood chips of ash class A3.0 (i. e. B1 and B2) or with ash contents > 3 w-% could be more critical regarding particle emissions (Figure 1).
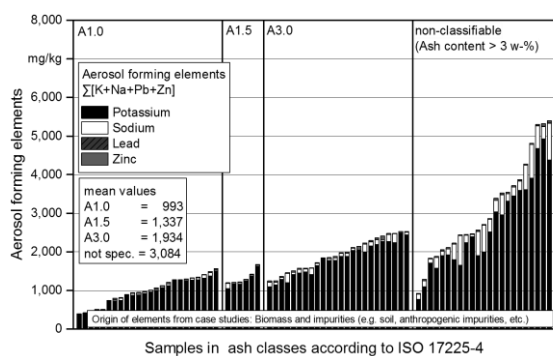
Figure 1: Aerosol forming elements in wood chip samples categorized according to ash content classes of ISO 17225-4

Fine dust emissions not only depend on the amount of aerosol forming elements but also on the release of these elements during combustion. In case of K, this release can be reduced by fixation of K within the ash as potassium silicate [4]. For K fixation, high amounts of Si are necessary. Thus, K release during combustion can be assessed using the molar Si/K-ratio [2][3]. Thereby, Si/K-ratios > 2.5 indicate that high shares of K might be fixed [2]. Samples with ash content above 3 w-% are usually contaminated with mineral soil (see poster 2.BV.1.4) and, thus, have high shares of Si. As a consequence, particulate emissions as predicted by the sum of aerosol forming elements within these samples (see **Figure 1**) might be reduced due to K fixation while overall concentrations of K were still high (see **Figure 2**).
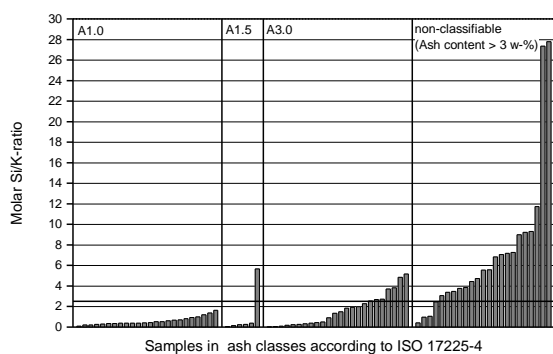

Figure 2: Molar Si/K-ratio in wood chip samples as indicator for K release, categorized according to ash content classes of ISO 17225-4

High amounts of K and Si in a sample might decrease ash melting temperature and facilitate slagging of ashes while Ca and Mg are known to increase ash melting temperatures [2][4]. Thereby, a high molar Si/(Ca+Mg)-ratio > 1 might indicate slagging problems during

combustion while ratios < 1 are deemed uncritical [2][3]. As a consequence, wood chips with specifications A1.0 and A1.5 according to ISO 17225-4 can be considered uncritical regarding ash melting temperatures (excluding one sample of energy round wood of Scots pine that was contaminated with mineral soil) while Si/(Ca+Mg) ratios of samples with ash contents above 3 w-% indicate problems with slagging (see Figure 3). However, direct analyses of ash melting temperatures according to EN 15370 [8] of these samples ($n = 42$) [7] indicate that real ash deformation and ash melting temperatures of wood chips are usually well above 1,100 °C and 1,250 °C, respectively, and therefore can be considered rather uncritical for combustion (Figure 4).
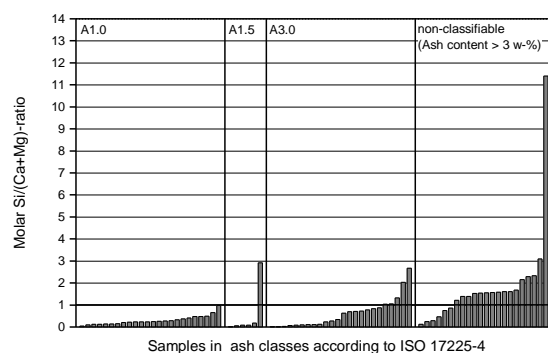

Figure 3: Molar Si/(Ca+Mg)-ratio in wood chip samples as indicator for ash melting behavior, categorized according to ash content classes of ISO 17225-4
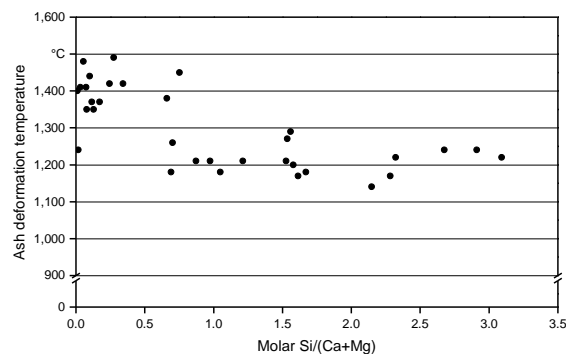

Figure 4: Ash deformation temperature (DT) in relation to the molar Si/(Ca+Mg)-ratio in wood chips

The molar $(K + Na)/[x(2S + Cl)]$-ratio is an indicator for HCl- and SO_x-emissions during combustion [2][3]. Thereby, the factor x is fuel specific. For woody biomass, typical values range from 2.7 to 3.6 (experimental determination in [2][3]). A molar ratio > 1 indicates a surplus of released alkaline metals. Thus, only small HCl or SO_x emissions can be expected for ratios > 1. Moreover, for combustion in fixed bed reactors a ratio > 0.4 is usually deemed sufficient for low HCl and SO_x [4]. Thus, for most of the analyzed wood chip samples only low concentrations of HCl and SO_x emissions can be expected as molar $(K + Na)/[x(2S + Cl)]$-ratios usually were above 0.4 and overall concentrations of Cl and S in samples were rather small (Figure 5, Table I).

The molar 2S/Cl-ratio is an indicator for high temperature corrosion [2][3][4]. S and Cl form alkali sulfates and alkali chlorides during combustion that can

condensate at the surface of heat exchangers. Thereby, fuels with a high 2S/Cl-ratio might form a protective sulfate layer and, thus, might reduce corrosion from HCl. Corrosion should be low for 2S/Cl-ratios > 4 and negligible for ratios > 8 [2][3]. Thus, for wood chips of ash specification A1.0 and A1.5 (ISO 17225-4) some corrosion might occur as individual samples showed ratios < 4 but overall concentrations of Cl were very low in these samples (Figure 6, Table I). For samples with ash content between 1.5 and 3 w-% (A3.0) Cl is higher but corrosion might be reduced due to even higher S concentrations. In contrast, Cl and corrosion might be really hazardous in some samples with ash contents > 3 w-% (e. g. from urban forestry, roadside chipping) as 2S/Cl-ratios were low while overall Cl concentrations were highest compared to samples with lower ash content.
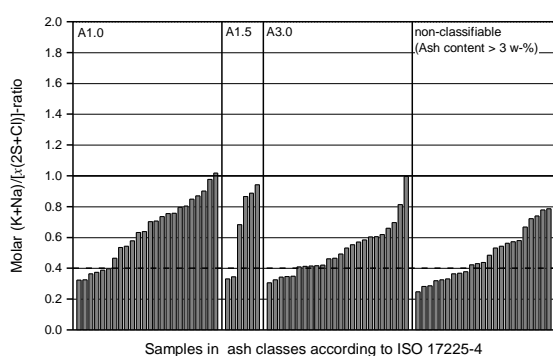

Figure 5: Molar (K+Na)/[x(2S+Cl)]-ratio in wood chip samples as indicator for HCl and SO$_x$ emissions, categorized according to ash content classes of ISO 17225-4
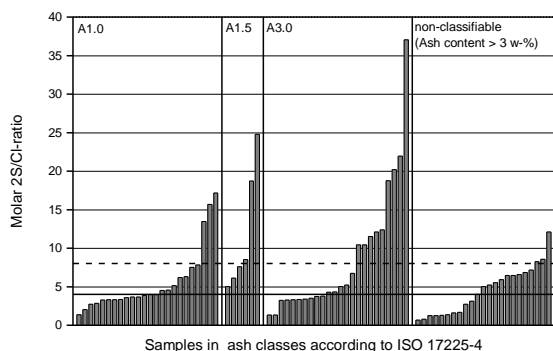

Figure 6: Molar 2S/Cl-ratio in wood chip samples as indicator for high temperature corrosion, categorized according to ash content classes of ISO 17225-4

4 CONCLUSION

In conclusion, element concentration of wood chips can be considered uncritical for combustion as long as natural wood from a provision chain with low soil contamination is used for chipping. However, individual wood chip samples from SRC, roadside chipping and urban forestry exceeded elemental thresholds values of ISO 17225-4 for graded wood chips. Overall, contamination of the biofuels with mineral soil should be avoided. In addition, biomass fuel indexes such as the sum of aerosol forming elements (K, Na, Pb, Zn) or the

molar Si/(Ca+Mg) ratio for ash-melting behavior indicated that biomass fuels without contamination with mineral soil, road salt or other anthropogenic waste can be considered uncritical for combustion.

The results can further increase the awareness of differentiating fuel provision chains according to the desired fuel application and they can contribute to quality assurance by selecting suitable raw materials which shall be carefully processed along the process chain.

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