Short communication

A comparative assessment of biomass ash preparation methods using X-ray fluorescence and wet chemical analysis

P. Xing [a], P.E. Mason [a], S. Chilton [a], S. Lloyd [a], J.M. Jones [a], A. Williams [a,*], W. Nimmo [b], M. Pourkashanian [b]

[a] School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, UK
[b] Energy Engineering Group, Department of Mechanical Engineering, University of Sheffield, Sheffield S10 2TN, UK

HIGHLIGHTS

- Significant unburned carbon in biomass ash produced at 550 °C is demonstrated by STA.
- Analyses using XRF and wet chemical methods presented for various biomass ashes heated to 850 °C.
- Biomass ash heated to 815 °C gives improved consistency and reliability in XRF ash analysis.

ABSTRACT

X-ray fluorescence (XRF) spectroscopy is a rapid method used to determine the composition of biomass ash, but the accuracy of the method is sensitive to various factors including ash preparation methods. In this study different types of biomass ash were examined by using wet chemical analysis (WCA) and compared with the respective XRF results. The biomass ash was initially prepared in accordance with the European Standard method at 550 °C. At this low combustion temperature the amount of residual unburned carbon is significant. To eliminate this, the ashes were heated at higher temperatures: a batch of twenty biomass ashes were heated at 850 °C and a batch of five heated to 815 °C. At these higher temperatures there may be loss of inorganic components by vaporisation. Variation in these effects may lead to unreliable results. The relationship between XRF and WCA results are given by regression equations. The ashes processed at 815 °C show better agreement between the two analysis methods.
© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

The inorganic content and composition of biomass is important in relation to combustion behaviour in furnaces since it influences corrosion and ash deposition on heat exchange and other surfaces in the combustor. During combustion, the organic matter burns-out leaving metal oxides and other metal adducts. Knowledge of the melting point of these compounds is important in furnace operations [1–4]. Certain metals can also affect the rates of pyrolysis [5] and bio-refinery processes [6]. Inorganic content varies in different types of biomass but may also vary significantly in similar types of biomass from different regions. Some wood-pellet biomass fuels have low silica and low potassium and usually high calcium content whilst agricultural residues such as straw can show high silica, high potassium and low calcium content.

The European Standards for the determination of major elements in solid biofuels [7,8] set out procedures for forming the biomass ash and for determination of the major metals content by acid-digestion and subsequent spectroscopic analysis. Other analytical techniques for ash analysis commonly reported in the published work include X-ray Fluorescence (XRF) spectroscopy, for example [6], since it is a relatively rapid and convenient method. However, XRF spectroscopy is sensitive to interactions between elements in the matrix whereby the respective fluorescent emissions interfere with or obscure each other. This can be corrected for, although the analysis depends on use of known reference samples. Other sources of error in the XRF method include flaws in the sample matrix and inhomogeneity in the ash solid [5]. The way in which the ash sample is prepared from the biomass is therefore crucial for obtaining reliable results. This also applies to other diagnostic methods such as ash melting test methods [9] which rely on representative ashing techniques.

---

* Corresponding author.
  E-mail address: fueaw@leeds.ac.uk (A. Williams).

Table 1
Reference names used for the biomass ash prepared at temperatures of 550/850 °C.

Biomass	Reference name	Biomass	Reference name
Willow pellet	WP	Rape straw	RS
Mixed forestry pellets	MFP	White wood pellet	WWP
Miscanthus A	MA	Pine	PE
SRC willow	SRCW	Olive residue	OR
Wheat straw B	WSB	Miscanthus B	MB
Oatmeal	OAT	Peanut	PEA
Wood	WO	Miscanthus	MIS
Chipped wood	CW	Straw	STR
Torrefied wood	TOR	Wheat straw pellet	WSP
Alstom pine < 90 µm	ALSM	Black pellets	BPZ

This study compares two different ash preparation methods using the results obtained from "wet" chemical analytical techniques with those from XRF analysis.
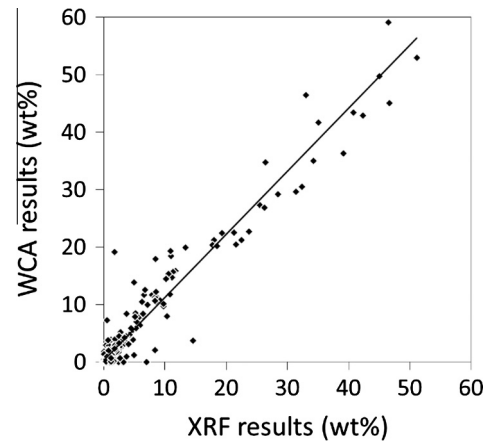

Fig. 1. Correlation of XRF and WCS results for twenty 850 °C biomass ash samples (Case 1).

Table 2
Composition (wt%) of the different types of biomass ash: Case 1 (550/850 °C).

Sample		Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	K$_2$O	CaO	TiO$_2$	MnO	Fe$_2$O$_3$
WSB	XRF	0.270	1.021	0.232	46.639	2.207	11.746	10.149	0.471	0.129	0.239
	WCA	0.470	0.850	0.570	45.100	0.460	15.900	14.500	0.150	0.050	0.040
MB	XRF	0.983	2.506	0.138	46.659	4.953	7.854	8.541	0.464	1.770	0.288
	WCA	0.680	1.890	0.410	63.600	1.180	11.700	11.400	0.150	0.400	0.080
SRCW	XRF	1.112	2.399	0.504	6.492	8.389	11.311	45.013	0.494	0.143	0.490
	WCA	1.210	1.730	1.520	7.900	2.050	15.700	49.800	0.080	0.070	0.150
OR	XRF	2.170	2.413	0.584	5.192	3.523	33.034	8.360	0.477	0.000	0.458
	WCA	0.890	2.190	1.860	8.500	0.940	46.500	11.300	0.070	0.020	0.240
PE	XRF	1.391	4.787	0.413	2.496	9.742	11.131	39.153	0.486	0.120	0.370
	WCA	0.800	3.900	0.700	4.500	10.100	14.700	36.300	0.000	0.100	0.700
MA	XRF	2.189	1.654	0.442	40.794	3.721	10.961	8.311	0.473	0.074	0.397
	WCA	0.810	1.530	1.010	43.400	0.980	18.500	10.700	0.080	0.030	0.160
WWP	XRF	2.485	5.896	3.074	18.029	3.634	10.605	25.535	0.606	3.409	1.905
	WCA	2.060	6.410	2.880	21.200	4.500	15.300	27.300	0.240	3.200	2.130
MFP	XRF	2.310	4.275	4.476	26.446	1.847	6.422	21.244	0.684	2.080	2.786
	WCA	2.780	4.690	5.280	34.800	1.650	8.400	22.500	0.430	1.780	3.560
RS	XRF	1.876	1.958	0.544	9.786	3.419	6.617	51.142	0.479	0.002	0.408
	WCA	2.490	2.300	0.630	9.700	3.620	11.700	53.000	0.050	0.040	0.440
WP	XRF	1.589	1.754	4.216	35.101	2.706	4.449	18.455	0.686	0.133	3.401
	WCA	1.660	2.240	4.740	41.700	2.990	5.900	20.200	0.360	0.150	4.260
PEA	XRF	0.234	2.539	3.743	23.692	2.996	10.874	5.129	0.832	0.210	1.871
	WCA	0.890	3.319	8.368	22.733	0.001	19.317	7.876	0.004	0.266	2.932
OAT	XRF	0.384	2.008	0.198	31.406	6.983	8.433	1.775	0.468	0.147	0.511
	WCA	2.902	2.128	1.689	29.643	0.001	17.969	19.128	0.000	0.067	0.938
MIS	XRF	0.619	1.114	0.439	32.386	2.423	6.265	8.537	0.487	0.112	1.792
	WCA	1.326	2.052	1.293	30.539	0.001	10.454	12.220	0.001	0.154	2.355
WO	XRF	0.864	2.817	3.610	21.567	1.537	4.923	14.568	0.654	1.569	2.633
	WCA	0.803	2.589	0.696	20.421	0.003	13.893	3.721	0.001	0.182	0.669
STR	XRF	0.825	1.229	0.560	22.481	3.208	10.336	13.320	0.493	0.027	0.740
	WCA	2.866	3.897	7.234	21.217	0.000	7.954	19.938	0.002	1.819	3.768
CW	XRF	1.481	2.751	2.782	19.322	2.786	5.678	26.269	0.656	4.062	2.485
	WCA	N/A	2.930	5.190	22.440	2.920	7.680	26.880	N/A	3.090	3.320
WSP	XRF	0.582	1.139	0.360	46.501	1.494	10.258	8.376	0.478	0.071	0.345
	WCA	N/A	1.610	1.330	59.140	1.720	14.440	10.650	N/A	0.440	0.090
TOR	XRF	0.515	5.272	1.823	17.760	1.683	7.129	28.488	0.912	0.077	1.231
	WCA	N/A	5.860	3.940	20.330	1.400	9.920	29.180	N/A	1.400	0.090
ALSM	XRF	0.536	2.843	1.008	10.822	8.503	6.712	34.219	0.534	0.110	1.140
	WCA	N/A	3.563	1.103	11.807	10.516	12.562	34.985	N/A	0.135	0.876
BPZ	XRF	1.139	1.570	0.665	9.214	1.805	5.331	42.308	0.496	0.779	1.213
	WCA	N/A	1.680	2.060	10.750	1.530	7.000	42.950	N/A	1.960	0.650

Table 3
Composition (wt%) of the different types of biomass ash: Case 2 (550/815 °C).

Sample		Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	K$_2$O	CaO	TiO$_2$	MnO	Fe$_2$O$_3$
WWP	WCA	2.406	8.643	4.820	24.655	2.581	10.768	27.488	2.518	2.668	2.501
	XRF	1.661	8.541	3.272	23.140	3.313	11.392	26.327	0.597	2.939	2.426
OR	WCA	1.117	4.642	1.840	9.420	4.210	32.931	13.057	0.489	0.038	0.666
	XRF	0.837	4.666	1.253	9.351	5.277	33.719	13.439	0.489	0.009	0.668
SRCW	WCA	1.535	3.024	1.092	7.208	8.956	9.587	53.362	1.543	0.174	0.537
	XRF	0.901	3.242	0.582	6.602	10.576	10.729	55.103	0.491	0.183	0.520
MB	WCA	0.849	2.940	0.196	53.742	4.918	7.825	9.643	0.626	1.533	0.265
	XRF	0.575	2.740	0.223	52.724	5.195	8.423	9.435	0.458	1.908	0.338
WSB	WCA	0.460	1.610	0.350	52.343	2.273	12.083	10.847	1.406	0.127	0.197
	XRF	0.589	1.159	0.275	52.068	2.309	12.477	11.090	0.472	0.144	0.252

According to Niu [2], different ashing rates and different ashing temperatures lead to different ash compositions, which affect the ash fusion characteristics (AFC). Therefore, it is essential to establish an appropriate standard for ash preparation for determining the biomass AFC. The fusion characteristic of the biomass ash is affected by the high-temperature behaviour of the mixtures, which are often eutectics, and is not a simple function of the major element content in the ash. Changes in the proportions of certain metals can therefore have significant effects on the fusion characteristics. At temperatures above 815 °C, potassium and chlorine begin to be released to the gas phase, reducing the relative content of K$_2$O in the resulting ash.

2. Experimental methods

Twenty solid biomass fuels were selected for this study. These are typical materials used in large scale power plant, many of them being sourced from power plant operators. The selection includes forestry biomass, energy crops, agricultural residues and a torrefied biomass thus providing a range of differing ash compositions. The reference names adopted for these sample fuels are given in Table 1.

The samples of ash for analysis were prepared from portions of the raw materials following the British/European Standards [7,8]. Samples with <2.0 mm particle top size were produced in crucibles in an electric furnace at a temperature of 550 °C for 14 h duration. In order to ensure any unburned carbon was removed, the samples were further heated. Two methods were used: (i) in the first batch (Case 1) the temperature was raised to 850 °C for 2 h; (ii) a second batch of ash from five biomass samples (Case 2) was prepared by

heating to a temperature of 815 °C for 2 h. In each case, the ashes were agitated every 30 min. The resulting ashes were manually ground and sieved to <106 μm.

2.1. Wet chemical analysis

A sample of each ash (in both cases) was prepared as above for wet chemical analysis by acid digestion. Two analyte solutions were produced referred to as "Solution A" and "Solution B". Solution A is from the reaction of ash with sodium hydroxide at 650 °C to produce sodium silicate which was then dissolved in HCl to give silicic acid in solution. The analyte is used only for the determination of silicon content. Solution B was prepared from acid digestion by hydrofluoric, hydrochloric, sulphuric and nitric acid sequentially. The content of ten major inorganic elements from this analyte were quantified using the following analytical methods: (i) Atomic Absorption Spectroscopy for Na, Mg, K, Mn, Fe, spectrophotometry for Si, P, Ti and EDTA titration for Ca.

2.2. XRF analysis

The ash samples were prepared for XRF analysis by forming into fused glass discs. For Case 1, these consisted of 0.5 g of sample (ground to <106 μm), 5.0 g of flux, 0.05 g lithium bromide and a fusion temperature of 1200 °C. For Case 2, flux content reduced to 4.5 g and fusion temperature to 1100 °C. The samples were analysed using an X-Thermo ARL Advant XP sequential X-ray fluorescence spectrometer.

2.3. Simultaneous Thermal Analyser (STA)

Studies were undertaken using a Netzsch 449C Jupiter Simultaneous Thermal Analyser (STA), coupled to a Netzsch QMS 403C Aeolos Quadrupole Mass Spectrometer. This allows the simultaneous application of thermogravimetry (TG) and differential thermal analysis (DTA), which monitors the temperature difference between the sample and an inert reference material. In this study, 10 mg of each ash was heated from room temperature to 1400 °C at 10 °C/min under a gas flow rate of 80 ml/min of 12.5% O$_2$ in He. The gases evolved were transferred to a heated fused silica capillary to a mass spectrometer; the monitored species were H$_2$O, CO, CO$_2$, K and KCl.

3. Results and discussion

The XRF results were compared against the wet chemical analysis results for the respective ash samples for Cases 1 and 2.
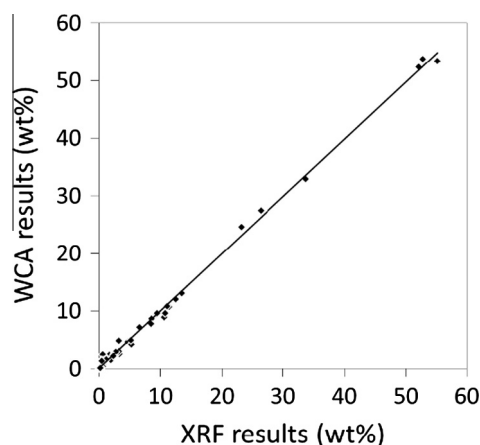

Fig. 2. Correlation of XRF and WCS results for five 815 °C biomass ash samples (Case 2).
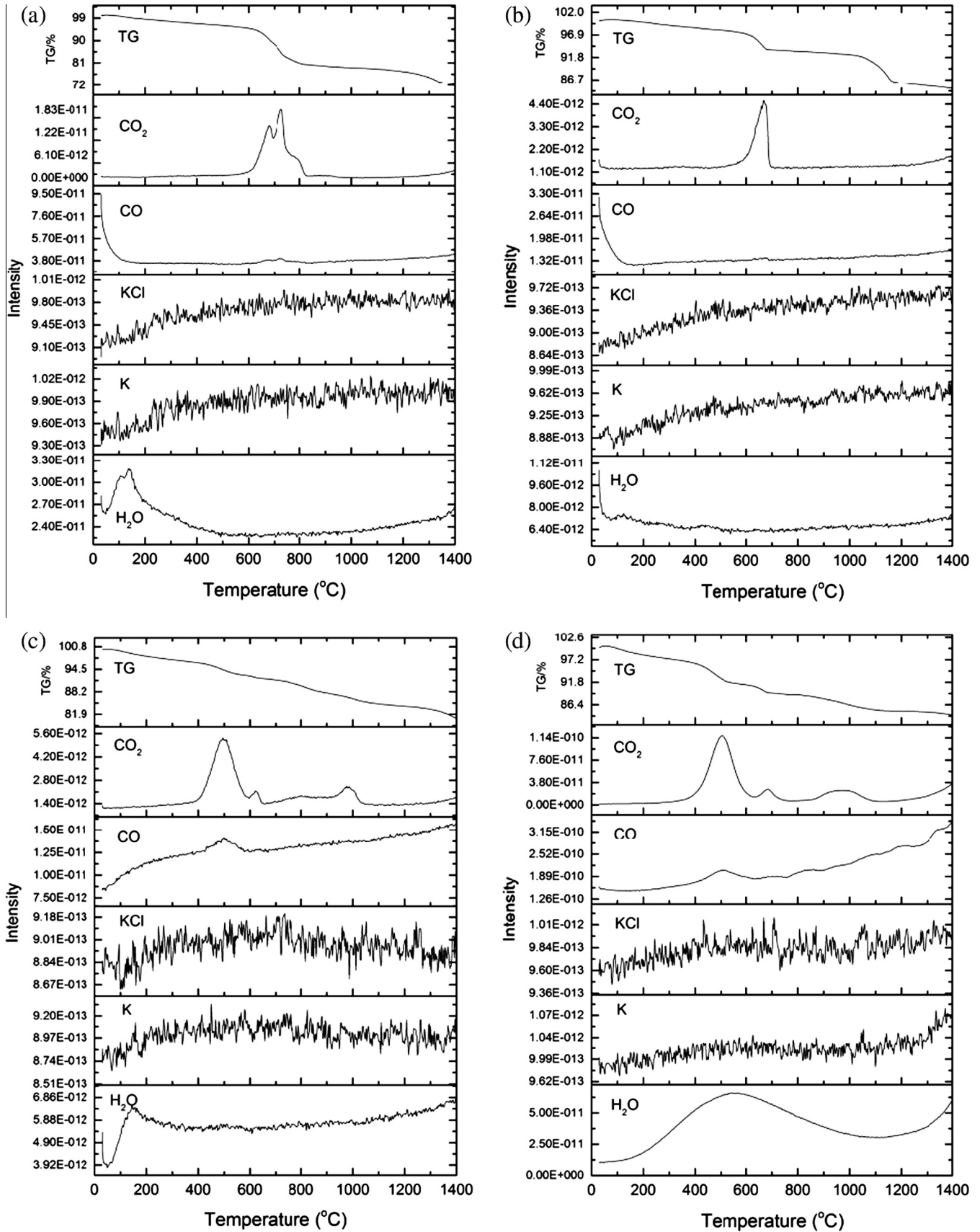
Fig. 3. (a)–(d) STA-MS analyses of four biomass 550 °C ash samples: (a) wood pellet (WWP); (b) SRC willow (SRCW); (c) Miscanthus (MB) and (d) wheat straw (WSB).

3.1. Case 1

The results obtained from the wet chemical and XRF analyses for Case 1 are presented in Table 2. The results are plotted against each other in Fig. 1. for comparison. A linear regression function can be obtained from the data as:

$$y_{(WCA)} = 1.097x_{(XRF)} + 0.296 \qquad (1)$$

With the coefficient of determination, $R^2 = 0.937$.

3.2. Case 2

The results obtained from the wet chemical and XRF analyses for Case 2 are presented in Table 3.

The results are plotted against each other in Fig. 2. for comparison. A linear regression function can be obtained from the data as:

$$y_{(WCA)} = 0.993x_{(XRF)} + 0.131 \qquad (2)$$

With $R^2 = 0.997$.

The coefficient of determination, R^2, for this function is higher than case 1 – a clear improvement in the correlation.

3.3. Simultaneous thermal analysis

STA-MS analysis plots showing the mass loss upon heating four example ash samples alongside the corresponding gas evolution profiles are presented in Fig. 3(a)–(d). The mass loss curves are complex with gradual mass losses up to the final temperature of 1400 °C. There is a notable mass loss from CO and CO_2 in all cases indicating unburned carbon in the ash. Furthermore, much of the mass loss from oxidation of the carbon occurs above 550 °C. Whilst the decomposition of calcium and potassium carbonates could contribute to the signal it has been shown [10] that in the case of the former the main decomposition occurs at 700–830 °C, and in the case of the latter 1200–1400 °C. Thus this demonstrates that the ashing temperature of biomass at 550 °C (in accordance with European Standard method) in not adequate to ensure that there is minimal residual carbon in the ash. The measured K and KCl losses are very low and none of the samples show significant change between 550 °C and 850 °C.

4. Discussion

There have been concerns about the accuracy of the XRF test method where low temperature (550 °C) biomass ashing is used and results for different metal oxides compared to wet chemical analysis show different degrees of reliability. This arises because of unburned carbon that may be present which has been demonstrated in STA-MS analysis of four ash samples. Where higher ashing temperatures are used, there is a risk of some vaporisation of volatile inorganic components. However, the STA-MS analyses show that heating ash up to 850 °C, removal of unburned carbon can be achieved with little loss of other alkali metals.

Two different methods for preparing biomass ash samples for XRF analysis have been evaluated using wet chemical analysis to determine the accuracy of the XRF results. The results of "Case 1" show that there is correlation between the two sets of results but with a notable level of discrepancy indicated by a coefficient of determination less than 0.94. The results for Case 2, (with a reduced set of samples) show a much better agreement in the data implying that the sample preparation method is improved. In the sample preparation for XRF analysis, it is then important that ashing temperature and sample fusion temperature are carefully and consistently chosen.

5. Conclusions

The main conclusions from this investigation are as follows:

(1) Biomass ash prepared at 550 °C ash can give inaccurate results from XRF analysis owing to significant unburned carbon retained in the ash.
(2) Processing the ash at a temperature above 800 °C produces an ash composition more suitable for XRF testing.
(3) Whilst there is correlation between XRF analyses and wet chemical analyses for twenty different biomass ash samples prepared at 850 °C, the method using biomass ash prepared at 815 °C shows better agreement between the two analytical methods.

References

[1] Vassilev SV, Baxter D, Vassileva CG. An overview of the behaviour of biomass during combustion: Part I. Phase-mineral transformations of organic and inorganic matter. Fuel 2013;112:391–449.
[2] Niu YQ, Tan HZ, Wang XB, Liu ZN, Liu HY, Liu Y. Study on fusion characteristics of biomass ash. Bioresour Technol 2010;101:9373–81.
[3] Werkelin J, Skrifvars BJ, Zevenhoven M, Holmbom B, Hupa M. Chemical forms of ash-forming elements in woody biomass fuels. Fuel 2010;89:481–93.
[4] Tonn B, Thumm U, Lewandowski I, Claupein W. Leaching of biomass from semi-natural grasslands – effects on chemical composition and ash high-temperature behaviour. Biomass Bioenergy 2012;36:390–403.
[5] Nowakowski DJ, Jones JM, Brydson RMD, Ross AB. Potassium catalysis in the pyrolysis behaviour of short rotation willow coppice. Fuel 2007;86:2389–402.
[6] Thyrel M, Samuelsson R, Finell M, Lestander TA. Critical ash elements in biorefinery feedstock determined by X-ray spectroscopy. Appl Energy 2013;102:1288–94.
[7] BS EN 15290:2011. Solid biofuels – determination of major elements. British Standards Institute; 2011.
[8] BS EN 14775:2009. Solid biofuels – determination of ash content. British Standards Institute; 2009.
[9] CEN/TS 15370-1:2006. Solid biofuels – method for the determination of ash melting behaviour – Part 1: Characteristic temperatures method. CEN; 2006.
[10] Arvelakis S, Jensen PA, Dam-Johansen K. Simultaneous thermal analysis (STA) on ash from high-alkali biomass. Energy Fuels 2004;18:1066–76.