Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 1019–1030

STUDYING THE ASH BEHAVIOUR OF AGRICULTURAL RESIDUES USING THERMAL ANALYSIS

S. Arvelakis[1*], *H. Gehrmann*[2], *M. Beckmann*[3] *and E. G. Koukios*[1]

[1]Bioresource Technology Unit, Laboratory of Organic and Environmental Technologies
Department of Chemical Engineering, National Technical University of Athens, Zografou
Campus, Athens, Greece, 15700
[2]Clausthaler Umwelttechnik Institut GmbH, Clausthal-Zellerfeld, Germany
[3]Bauhaus Universitat Department of Process Engineering and Environment Weimar Coudray
Straße 13C D-99423 Weimar, Germany

Abstract

In this paper, the ash behaviour of some typical Mediterranean agricultural residues, such as peach stones, cotton gin wastes and grape residues is studied via simultaneous, (DTA/TG), thermal analysis methods. Furthermore, the effect of various pre-treatment techniques, such as fractionation and leaching, on the ash behaviour of the specific residues is also studied.

Fractionation improves some of the main biomass properties such as calorific value, volatiles and ash content but deteriorates significantly the ash chemical composition of the remaining ash fraction.

Leaching improves both the main properties of the treated biomass samples and the chemical composition of the remaining ash fraction, while the combination of the two pre-treatment methods results in a merge of their main advantages leading to an even larger improvement of the ash thermal behaviour.

Keywords: agricultural residues, ash, DTA, fractionation, leaching, TG

Introduction

The use of agricultural residues and wastes as primary and/or supplementary fuels for energy production via combustion and gasification processes appears to be an attractive option. These fuels are largely CO_2-neutral because of their short regeneration time and due to the fact that they contribute to CO_2-increase only through the fossil fuels consumed during their cultivation and transport to the energy production plants. However, the presence of large amounts of alkali and alkali earth metals, (Na, K, Ca), chlorine and sulfur in their ash increase its reactivity and enhances the formation of ash-related problems, e.g. agglomeration, deposition, corrosion, etc., during their thermochemical treatment. All these phenomena affect the efficiency and/or availability of the power plant and conse-

---

[*] Author for correspondence: E-mail: sa@kt.dtu.dk

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

quently the power costs. It becomes obvious that the accurate prediction of the ash behaviour of these bio-fuels can contribute significantly to their safe and economical exploitation for heat and energy production [1–5, 24].

The ash behaviour of an ash sample is usually studied using a variety of methods such as the conventional coal ash fusion tests, or using methods based on electrical resistivity or conductance measurements of the ash during heat up.

However, all these methods have been proved not to be very suitable for biomass fuels showing significant difficulties in application and low reproducibility and reliability concerning the produced results [6–11].

On the other hand, thermal analysis methods, (DSC/DTA/TG/DMA/TMA), have been proved to be a very useful tool regarding the analysis and the characterization of the thermal properties of various fuels such as biomass, coals and wastes [12–22, 26].

In this paper the ash behaviour of three different Mediterranean agricultural residues, peach stones, cotton gin wastes and grape residues produced as by-products from different agro-industrial processes, such as juice and wine production and the production of cotton for the garment industries in Greece, has been studied using simultaneous thermal analysis, (DTA/TG), in combination with SEM-EDX analytical technique.

All three residues constitute a very significant portion of the agricultural biomass available in the Mediterranean region and comprise a set of unique characteristics such as large availability, lack of transportation expenses and high energy value, which make them ideal candidates as feeding streams for small decentralized power plants especially in the scale of 0.5–5MWe.

The performed study includes also the influence of two different pre-treatment techniques, fractionation and leaching, on the ash behaviour of the specific agricultural residues using the thermal and SEM analysis methods.

Experimental

Two different pre-treatment techniques fractionation and leaching were applied to the various agricultural residues in order to study their effect on the ash behaviour of each residue. Fractionation includes the splitting of the original material in two fractions one with particle size above 1 mm, which was selected for the study, and one with particle size below 1 mm. The splitting was performed using a screen with 1 mm openings and a laboratory mechanical shaker. On the other hand, leaching includes the treatment of the original material with tap water in order to achieve partial removal of the inorganic constituents included in the biomass such as potassium, sodium, chlorine and sulfur partly or mainly as water-soluble salts, and thought to be responsible for the formation of ash problems during the thermal treatment of biomass [4, 5, 23, 24].

In our case, the leaching of the samples was performed using tap water at room temperature. The samples were put into a 200 mesh plastic grid and were submerged into the tap water for 24 h. The water mass ratios used were 45, 200 and 120g/g for peach stones, cotton gin residues and grape residues respectively. Additional information regarding the leaching process can be found elsewhere [23–25].

In total, nine different biomass samples were studied regarding their ash thermal behaviour using simultaneous thermal analysis methods (DTA/TG) followed by SEM-EDX elemental analysis. The ash samples studied were prepared according to the ASTM D-1102-84 standard method, using a laboratory muffle furnace. The peach stones samples are encoded as P, PF and PFL, the cotton gin residues samples as C, CF and CFL, while the grape residue samples as G, GF and GFL for use in the next pages of the paper. The codes P, C and G are used for the original untreated samples, while the codes PF, CF and GF for the fractionated samples and the codes PFL, CFL and GFL for the fractionated and leached samples respectively.

The thermal analysis measurements were carried out in a Netzsch STA 429C (simultaneous thermal analyzer-STA), which was used in the differential thermal analysis/thermogravimetric analysis (DTA/TG) mode. The experiments were performed using air atmosphere and open top alumina crucibles. The heating rate applied during the experiments was 10°C min^{-1} and the final temperature 1050°C, while the amount of the ash placed in the sample crucible was varying from 15–30 mg depending on the density of the sample. After the end of each test the alumina crucible was visually inspected in order to determine the final condition of the ash sample and possible reactions with the alumina crucible. The heated ash sample was kept for SEM-EDX analysis and characterization using a JEOL 6300 electron microscope.

Results and discussion

Table 1 presents the main characteristics and Table 2 the ash elemental analysis of the specific biomass samples. The values appeared in the Tables are the means of two repetitive measurements differing by less than 1% in each case. As it is seen from Table 1 all the biomass samples show high values of volatiles, heat content and nitrogen, while the amounts of chlorine and sulfur appear to be low to average. The ash fraction

Table 1 Characterization of various biomass samples (% dry basis)

Proximate analysis	P	PF	PFL	C	CF	CFL	G	GF	GFL
Moisture	8.53	7.62	7.7	6.06	6.53	6.7	7.37	8.74	7.55
Ash	0.65	0.38	0.35	10.68	6.44	4.82	7.5	5.79	2.94
Volatiles	81.3	80.54	80.8	73.05	76.98	80.2	70.7	70.32	74.9
Fixed carbon	18.1	19.08	18.85	16.27	16.58	14.98	21.8	23.89	22.16
Ultimate analysis									
Nitrogen	0.79	0.89	0.93	1.73	1.21	1.32	2.00	1.99	1.94
Carbon	51.95	52.66	53.13	44.1	46.55	46.97	49.8	52.6	56.3
Hydrogen	5.76	6.1	6.77	4.96	6.8	7.02	5.2	5.59	6.07
Sulfur	<0.01	<0.01	<0.01	0.44	0.26	<0.01	0.30	0.28	0.26
Chlorine	0.14	0.1	<0.01	0.28	0.32	0.06	0.24	0.12	0.07
Oxygen	40.7	39.87	38.81	37.81	38.71	39.81	34.96	33.73	32.4
GCV (MJ/kg)	21.55	22.02	21.02	20.08	22.56	22.75	21.02	21.22	21.67

Table 2 Ash elemental analysis of various biomass samples (% dry basis)

Samples	K_2O	Na_2O	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	SO_3	Cl
P	38.45	0.07	7.14	2.73	5.97	0.47	0.52	0.15	5.24	0.06
PF	45.78	0.07	6.13	1.4	5.03	0.03	0.63	0.08	5.09	0.03
Difference%	19.07	0	–14.11	–48.8	–15.92	–93.1	19.83	–51.6	–2.88	–50.8
PFL	21.24	0.02	19.32	2.53	10.47	0.02	0.086	0.04	3.16	0.02
Difference%	–44.74	–76	170.58	–7.25	75.15	–95.9	–83.6	–72.0	–39.7	–60.6
C	23.17	1.88	20.92	1.89	21.71	5.09	1.75	0.16	6.9	2.88
CF	24.53	1.23	21.05	1.88	19.74	4.01	1.59	0.08	7.2	2.95
Difference%	5.86	–34.5	0.62	–0.64	–9.07	–21.2	–9.14	–51.6	4.35	2.43
CFL	5.7	0.04	30.10	1.55	37.5	0.55	1.98	0.26	4.80	0.58
Difference%	–75.39	–97.8	43.86	–18.1	72.73	–89.2	13.46	59.25	–30.3	–80
G	43.05	0.29	24.02	2.43	15.52	2.32	0.31	0.1	3.77	0.47
GF	45.86	0.24	25.82	2.14	14.42	0.02	0.36	0.05	4.33	0.45
Difference%	6.53	–16.3	7.47	–11.9	–7.08	–99.2	14.19	–48.3	14.75	–5.32
GFL	4.78	0.05	38.82	1.49	35.10	0.02	0.29	0.05	3.49	0.31
Difference%	–88.88	–81.4	61.62	–38.7	126.2	–99.2	–8.55	–50	–7.45	–33

in the case of the peach stones samples appears to be very low (<1%w/w), while in the case of the other two sets of samples varies from average to high (7–10%w/w).

Both fractionation and leaching, pre-treatment methods appear to have a positive effect to the main properties of the original biomass samples. Fractionation decreases in all cases the amount of ash contained in the original biomass samples by more than 20%, while it also causes a low increase of calorific value and volatile content in most of the cases. On the other hand, leaching appears to have a small effect on the ash content in the case of the PFL sample, while it decreases the ash content of the CFL and GFL samples significantly. Furthermore, leaching appears to decrease the amounts of chlorine and sulfur in all cases, while calorific value and volatiles appear to remain at the same level or to be slightly improved compared to the original samples in all cases.

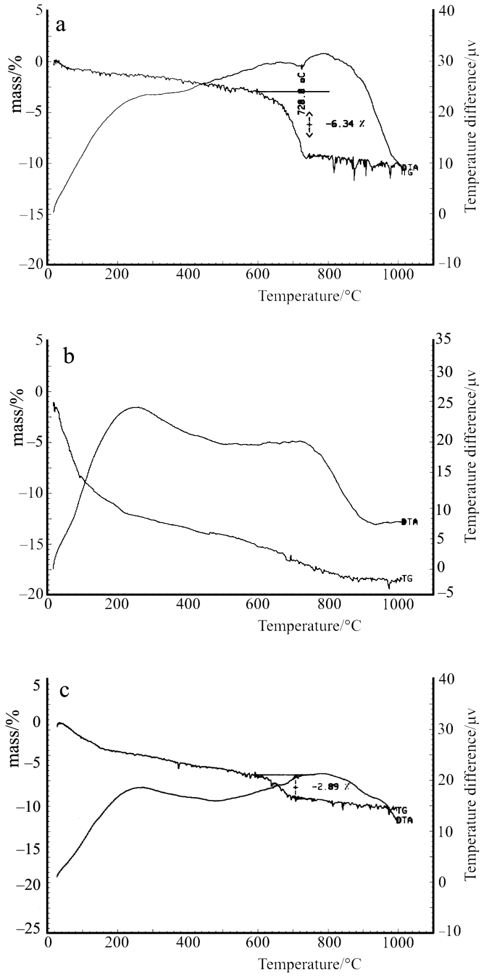
The results in Table 2 show that the ash of all the original biomass samples, (P, C and G), appears to be highly reactive containing large amounts of alkali metals and sulfur, with C and G samples to contain also large amounts of chlorine, calcium and silicon, while the amount of these elements varies from small in the case of silicon and calcium to traces in the case of chlorine for the P sample. Moreover, elements such as magnesium, iron, aluminum and titanium are also present in all the cases in amounts below 2%w/w. Fractionation appears to deteriorate the ash chemical composition and subsequently to increase the ash reactivity in all cases leading to a small to medium increase of the amounts of alkali metals, chlorine and sulfur contained in the ash of the different biomass samples. The only exception to the rule appeared in the case of the PF sample, where the chlorine content appears to decrease by 50% compared to the case of the P sample. However, this is believed to have no effect on the ash reactivity of the peach stones samples due to the very low content of chlorine.

On the contrary, leaching shows to affect positively the ash chemistry of the different biomass samples in all cases. Alkali metals and chlorine appear to decrease from 30–99% depending on the material, while also the amount of sulfur in the ash appeared to decrease up to 40% in the case of the peach stones PFL sample, which may lead to improved ash thermal behaviour during thermal conversion of biomass.

Peach stones

Figures 1a–c present the results from the thermal treatment of the three different peach stones samples P, PF and PFL using simultaneous thermal analysis.

As it is seen from Fig. 1 the DTA curve of the ash P sample shows a small endothermic peak in the area of 650–729°C accompanied by a mass loss of 6.3%w/w probably due to the decomposition of calcium carbonates. The DTA curve starts to bend down rapidly after 800°C showing the initiation of a melting effect among the ash constituents. The effect seems to continue until the temperature of 1050°C where the test terminates. The results from the ash thermal analysis of the fractionated PF sample appeared to follow the same pattern as in the case of the P sample according to Fig. 1b. The DTA curve shows a large endothermic peak at the beginning of the heating process due to increased moisture content that is accompanied by a simultaneous



Figs 1a–c Simultaneous thermal analysis of various peach stones ash samples: a – P sample, b – PF sample, c – PFL sample

mass loss of almost 12%w/w. A further mass loss of almost 3%w/w described from the TG curve in the temperature range of 300–750°C is not accompanied by the presence of a peak in the DTA curve probably due to the large temperature area under which this change occurs. However, the DTA curve starts to bend sharply showing signs of melting after the temperature of 750°C. The specific change in the DTA curve is accompanied by a mass loss of almost 3%w/w probably due to the partial melting and evaporation of alkali compounds (carbonates, chlorides, sulfates) present in the ash material, while the phenomenon seems to terminate at 1050°C.

On the contrary, the thermal behaviour of the leached PFL sample appears to be improved according to the results depicted in Fig. 1c. The ash of the PFL sample appears to show melting tendency after the temperature of 850°C that is higher com-

Table 3 SEM-EDX elemental analysis of various thermally treated (STA) ash samples

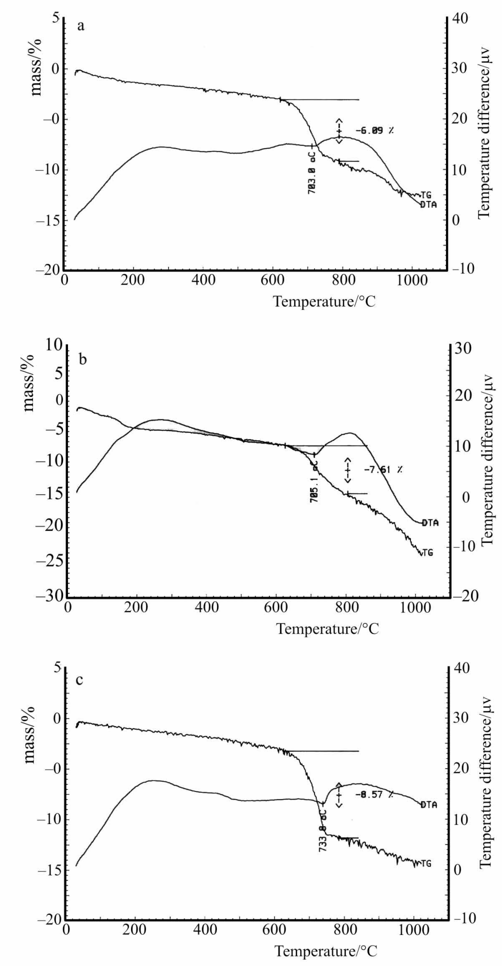
Samples	K_2O	Na_2O	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	SO_3	Cl
P	43.65	0.00	17.62	6.75	3.28	0.23	7.41	18.59	4.46	0.00
PF	61.30	0.00	9.65	6.71	0.38	0.26	0.32	18.44	1.95	0.00
PFL	21.2	0.35	41.4	13.00	0.53	0.08	0.00	21.38	2.06	0.00
C	14.93	1.47	28.42	10.55	21.00	5.46	3.29	9.42	5.18	0.00
CF	49.23	2.1	17.24	5.46	7.11	1.51	1.09	11.99	4.26	0.00
CFL	3.91	1.01	42.61	9.34	19.19	7.53	3.37	7.42	4.98	0.14
G	71.03	0.00	4.5	0.00	17.9	3.02	1.76	0.00	1.57	0.00
GF	78.33	0.00	8.55	1.49	0.86	0.00	0.00	6.71	3.84	0.17
GFL	3.56	0.00	74.67	3.14	2.13	0.00	1.54	9.15	1.54	0.00

pared to the cases of the P and PF samples, while also the DTA curve shows to bend down in a slower and less sharp mode.

The visual inspection of the three thermally treated ashes after the end of the STA tests verified the results appeared in Figs 1a–c showing that the ash material has turned from a loose material to a partially sintered deposit. The SEM-EDX analysis of the different ash samples presented in Table 3 showed that potassium in combination with phosphorus and also calcium are the main elements forming the produced ash deposits in all cases. However, the PFL sample appeared to contain significantly lower amounts of potassium and to have a less compact structure compared to the P and PF samples. This indicates a significant improvement of the ash thermal behaviour, complying also with the results from the STA test. Potassium content in the case of the PF sample appeared to be almost 50% higher compared to the case of the P sample indicating a deterioration of the ash behaviour caused by fractionation

Cotton gin residues

The results from the thermal analysis of the cotton gin residues ash samples are presented in Figs 2a–c. The ash of both the C and CF samples appears to show melting behaviour around of 800°C. In both cases the DTA curves show the presence of small endothermic peaks appeared at almost the same temperature of 600–700°C accompanied by a mass loss of 6% and 7.6%w/w respectively as it is seen from the TG curves.This is probably due to the partial calcination of the large amounts of calcium carbonates these samples contain according to Table 2. The observed melting tendency in the DTA curve is sharper in the case of the CF sample, while it follows a slower pattern in the case of the C sample. The melting process appears to start at the temperature of 800°C in the case of the CF sample and at 850°C for the C sample, indicating an increased ash reactivity in the case of the CF sample. The melting curves in both cases are accompanied by a mass loss of 4 and 10%w/w respectively, due to the partial evaporation of mainly alkali chlorides as it is also indicated by the large



Figs 2a–c Simultaneous thermal analysis of various cotton gin residues ash samples: a – C sample, b – CF sample, c – CFL sample

amounts of potassium and chlorine contained in the specific ash samples according to Table 2. Inspection of both ash samples after the end of the heating process showed that the ash material has been agglomerated. The SEM-EDX analysis revealed that the main elements participating in the structure of the C and CF thermally treated ash samples are potassium, calcium, silicon, phosphorus and sulfur, which form a low melting point silicate mixture.

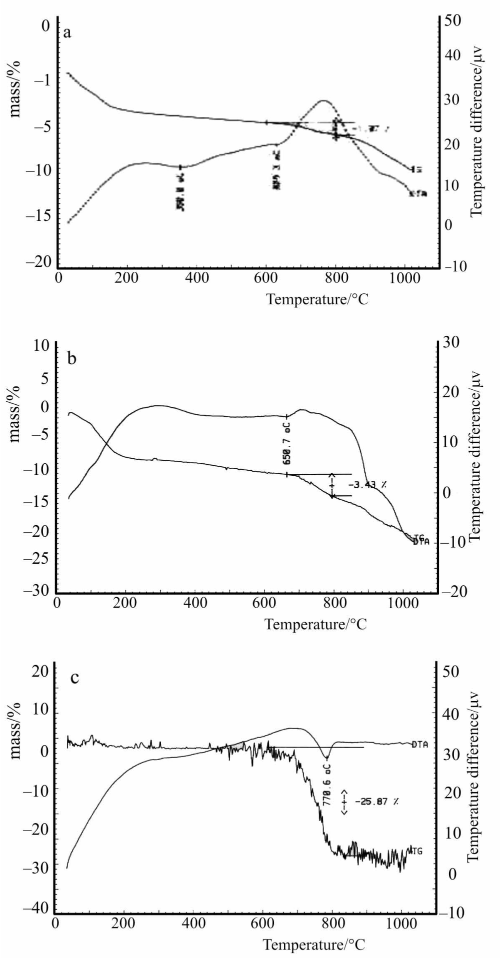
The results presented in Fig. 2c and in Table 3 regarding the ash thermal behaviour of the leached CFL sample reveal a totally different behaviour. The DTA curve presents a small endothermic peak at the temperature range 600–733°C together with a mass loss of 8.6%w/w mainly due to the dissociation of calcium carbonates, while it does not show any signs of melting processes until the end of the heating process. A small endothermic peak appeared after the 750°C accompanied by a mass loss of almost 3%w/w is attributed to the partial evaporation of mainly potassium chlorides and also to the dissociation of potassium carbonates due to the small amounts of potassium and chlorine still present in the specific ash sample according to Table 2. The inspection of the material after the end of the STA test showed that the ash preserves its original, grainy, loose structure. The results from the SEM-EDX analysis presented in Table 3 showed that very low amounts of alkali metals were detected on the surface of the ash particles. Calcium, silicon and phosphorus appeared to be now the dominating elements in the ash structure.

Grape residues

The results from the thermal analysis of the G, GF and GFL ash samples are presented in Figs 3a–c. As it is seen from the STA analysis of the G sample depicted in Fig. 3a, the DTA curve presents one small endothermic peaks at the 100–300°C segment accompanied by a mass loss of 5%w/w due to moisture evaporation. A small peak is observed around 630°C accompanied by a very small mass loss in the range of 1.3%w/w probably due to the decomposition of calcium carbonate.The DTA curve starts to show signs of a melting process at the level of 780°C where it starts to bend down. The process was seen to continue until the end of the heating treatment and is accompanied by a simultaneous mass loss of approximately 4.0%w/w that is attributed to the evaporation of probably melted alkali chlorides due to the high amounts of alkali and chlorine observed in the specific ash sample. The inspection of the ash material after the end of the STA test revealed that the ash has been turned to a green colored hard agglomerate. The SEM-EDX analysis showed that potassium and silicon appear to be the main forming elements as it is presented in Table 3 verifying the formation of a low melting point silicate during the thermal treatment of the G ash.

Furthermore, the results from the STA treatment of the GF ash sample show a deterioration of its thermal behaviour compared to the original G ash sample. The ash melting process starts now at the temperature level of 720°C accompanied with a small mass loss and it continues until the end of the STA test at 1050°C without showing signs of conclusion. A higher mass loss of almost 7%w/w is observed now in the temperature range 800–1050°C probably due to the higher release of potassium chloride during the thermal process. The inspection of the ash material after the end of the process shows that again the original loose ash material has been transformed to a green colored hard agglomerate. The SEM-EDX analysis showed that the chemical composition of the agglomerate is similar to that observed in the case of the G ash sample. The content of potassium and calcium in the ash material showed a small increase compared to the G ash sample.

The results from the STA measurement of the leached GFL ash sample showed a completely different melting behaviour compared to the G and GF ash samples. According to Fig. 3c the DTA curve shows the formation of a large endothermic peak between 600 and 800°C accompanied by a large mass loss reaching the 25%w/w as it is seen from the TG curve. This peak is attributed to the dissociation of carbonates and complies with the ash elemental analysis of the GFL sample presented in Table 2



Figs 3a–c Simultaneous thermal analysis of various grape residues ash samples: a – G sample, b – GF sample, c – GFL sample

where it is seen that calcium accounts for almost 40%w/w of the ash material. After the end of the endothermic process the DTA curve does not show signs of other endothermic or exothermic processes until the termination of the measurement at 1050°C. The inspection of the ash material after the cooling down of the STA furnace revealed that the ash material does not show any signs of reaction and has the original, loose, grainy structure.

The SEM analysis of the heated GFL ash sample shows that the main elements participating now to the formation of the ash structure are calcium up to 70%w/w and phosphorus, while the amount of potassium appears to be at the same levels (3.5%) with the amount in the initial GFL ash sample as it is seen from Table 2.

These results show a clear and significant improvement of the ash thermal behaviour in the case of the leached GFL biomass sample compared to both the original G and the fractionated GF samples.

Conclusions

STA proved to be a valuable technique for the determination of the ash thermal behaviour of the various agricultural residues studied. The produced results appeared to be in good agreement with the elemental analysis of the ash samples before and after the heating treatment.

The observed mass loss remained low in most cases probably due to the low amounts of chlorine present in the ash, to the complex melting interactions among the different ash constituents leading to the formation of silicates and/or due to the mineralogical form of the majority of the ash forming constituents.

All the agricultural residues studied showed to have a very reactive ash composition that is expected to cause severe ash-related problems during combustion or gasification.

Fractionation pre-treatment appeared to improve some of the main properties of the different biomass samples such as calorific value, volatiles and ash content. On the other hand, fractionation increased the amounts of alkali metals, chlorine and sulfur present in the ash of the biomass samples. This resulted in a greater reactivity of the ash material and in the deterioration of the ash thermal behaviour. As a result the use of this pre-treatment method is considered to be unsuitable for the improvement of the biomass ash behaviour.

Leaching, showed to improve both, the main properties of the treated biomass samples, and the chemical composition of the remaining ash fraction. The amounts of alkali metals, chlorine and partly sulfur, were reduced significantly resulting in a substantial improvement of the ash thermal behaviour. Furthermore, the combination of the two pre-treatment methods, fractionation and leaching, was seen to result in a merge of their main advantages leading to an even larger improvement of the ash thermal behaviour

References

1 S. A. Benson, M. L. Jones and J. N. Harb, in L.D. Smoot (Ed.), Fundamentals of Coal Combustion for Clean and Efficient Use, Elsevier, New York 1993, p. 299.
2 R. W. Bryers, Prog. Energy Com. Sci., 22 (1996) 29.
3 F. J. Frandsen, L. A. Hansen, H. S. Sørensen and K. Hjuler, Characterisation of ashes from biofuels, Final Report from EFP-95 Project, Journal No. 1323/95-0007, The Danish Energy Research Programme, 1998, ISBN 87-7782-000-2.
4 D. C. Dayton, B. M. Jenkins, S. Q. Turn, R. R. Bakker, R. B. Williams, D. Belle-Oudry and L. M. Hill, Energy and Fuels, 13 (1999) 860.
5 B. Coda, M. Aho, R. Berger and K. R. G. Hein, Energy and Fuels, 15 (2001) 680.
6 ISO 540, International Standard Organisation, 1981.

7 DIN 51730, German Standard, 1984.
8 ASTM D1857-87, American Society for Testing and Materials, 1987.
9 AS1038.15, Australian Standards Association, 1987.
10 I. W. Cumming, A. Sanyal and R. W. Bryers (Ed.), US Engineering Foundation Conference on Fouling and Slagging Resulting from Impurities in Combustion Gases, Engineering Foundation, New York, 1981, p. 135.
11 E. J. Raask, J. Thermal Anal., 16 (1979) 91.
12 Y. He, Fuel Processing Technology, 60 (1999) 69.
13 M. Otero, C. Diez, L. F. Calvo, A. I. Garcia and A. Moran, Biomass and Bioenergy, 22 (2002) 319.
14 M. Stenseng, A. Zolin, R. Cenni, F. Frandsen, A. Jensen and K. Dam-Johansen, J. Therm. Anal. Cal., 64 (2001) 1325.
15 K. E. Benfell, B. B. Beamish and K. A. Rodgers, Thermochim. Acta, 286 (1996) 67.
16 I. Pitkänen, J. Huttunen, H. Halttunen and R. Vesterinen, J. Therm. Anal. Cal., 56 (1999) 1253.
17 M. C. Mayoral, M. T. Izquierdo, J. M. Andres and B. Rubio, Thermochim. Acta, 370 (2001) 91.
18 Y. Chen, S. Mori and W-P. Pan, Thermochim. Acta, 275 (1996) 149.
19 L. A. Hansen, F. J. Frandsen, K. Dam-Johansen and S. Sørensen, Thermochim. Acta, 326 (1999) 105.
20 J. V. Kumar and B. C. Pratt, Thermochim. Acta, 279 (1996) 111.
21 S. St. J. Warne, Thermochim. Acta, 272 (1996) 1.
22 S. Arvelakis, C. Sotiriou, A. Moutsatsou and E. G. Koukios, J. Therm. Anal. Cal., 56 (1999) 1271.
23 B. M. Jenkins, R. R. Bakker and J. B. Wei, Biomass and Bioenergy, 10 (1996) 177.
24 R. R. Bakker, B. M. Jenkins and R. B. Williams, Energy and Fuels, 16 (2002) 356.
25 S. Arvelakis and E. G. Koukios, Biomass&Bioenergy, 22 (2002) 331.
26 T. Lupascu, I. Dranca, V. T. Popa and M. Vass, J. Therm. Anal. Cal., 63 (2001) 855.