Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 1271-1278

PREDICTION OF THE BEHAVIOUR OF BIOMASS ASH IN FLUIDIZED BED COMBUSTORS AND GASIFIERS

S. Arvelakis[1], *C. Sotiriou*[2], *A. Moutsatsou*[2] *and E. G. Koukios*[1]

[1]Bioresource Technology Unit
[2]Laboratory of Inorganic and Analytical Chemistry, Department of Chemical Engineering
National Technical University of Athens, Zografou Campus, Athens, GR-15700, Greece

Abstract

Two types of agricultural residues (wheat straw and olive residue) in untreated and pretreated (fractionation, leaching) form were tested as concerns their ash melting behaviour during fluidized bed combustion and gasification by means of thermal analysis techniques. The techniques applied included DSC, simultaneous DSC/TG and TG-MS for the determination of low-temperature ash melts and losses caused by the volatilization of alkali material. In combination with ash elemental analyses on the materials, the applied techniques proved to offer valuable information for prediction of the ash behaviour in fluidized bed reactors.

Keywords: agricultural residues, combustion, gasification, pretreatment, thermal analysis techniques

Introduction

Biomass fuels for the generation of heat and power are of interest because biomass is a renewable form of energy with low ash and sulphur contents, which can contribute significantly to a reduction of the greenhouse effect and to an increase of the energy independence of the user countries. Starting from the first oil crisis in 1973, biomass research has been carried out in many countries around the world and various biochemical and thermochemical technologies have been developed for the utilization of biomass for energy production. Such thermochemical technologies, especially in the form of combustion and gasification, are considered to be promising solutions for energy production from biomass; their most advanced forms are fluidized bed combustion and gasification.

Among the various types of biomass fuels that can be used for energy production, agroresidues resulting as by-products of agricultural or agro-industrial activities, e.g. straws, pits, hulls, pods, cobs, etc., are thought to be the most important, especially in the underdeveloped areas of the planet where the use of these biofuels for energy production could cover a substantial gap in the energy policy of the local communities.

However, the use of these 'low-quality' biomass fuels in sophisticated conversion systems can cause serious problems during operation and even lead to the shut-down of the operating units, thereby increasing the operational costs and impeding the set-

1418-2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

ting up of new biomass units. The majority of these problems are associated with the low melting point ash of these biofuels, which contains large quantities of inorganic elements such as alkali metals (K, Na), alkaline earth metals (Ca, Mg), silicon, chlorine and sulphur, generally regarded as the main troublesome elements. The problems caused by the presence of large quantities of these inorganic elements in the biomass ash include agglomeration of the inert bed material, slagging, deposition, fouling, corrosion and/or erosion of heat exchange surfaces or of the reactor walls [1, 2, 4, 5].

In particular, K and Si in the form of silica or silicate can form mixtures, whereas chlorine acts as a facilitator of the reactions between alkali and Si, to yield alkali metal silicates with melting temperatures below 800°C. Furthermore, chlorine vaporizes rapidly in the combustion/gasification environment, leading to the majority of the potassium present in the ash as potassium chloride entering the gas phase, where it reacts with sulphur to create sulphates that deposit on the reactor walls, initiating further reactions between them and the wall material, leading to corrosion, while they act as collectors of fly ash and aerosol particles, increasing the size of the deposit [2–4].

Thus, prediction of the thermal behaviour of the biomass ash during the conversion to energy in fluidized bed reactors is of crucial importance in order to avoid the use of improper fuels or to allow the necessary precautions to be taken to eliminate the cause of such problems during operation. Thermal analysis techniques, including TG, DSC, TG-MS and combinations of them, offer valuable information as concerns the thermal behaviour of the ash of various biomass fuels. Use of these techniques allows study of the thermal behaviour of the biomass ash, revealing the troublesome elements and clearly defining their problematic behaviour under the specific temperature conditions encountered during the operation of the reactor units. This paper presents recent experimental results from application of the above-mentioned selected techniques to a number of biomass materials.

Materials and methods

Two types of residues, which are abundant in rural Mediterranean regions, were used in this work: wheat straw and olive residue (cakes from olive oil production), each pretreated by two different techniques, fractionation and leaching. The different samples studied here include wheat straw, fraction $L>1$ mm, leached wheat straw, olive residue, olive residue fraction $L>1$ mm, and olive residue leached fraction $L>1$ mm. Data on the analysis and characterization of the wheat straw and olive oil residue materials according to recently revised protocols are given in Tables 1 and 2, while Table 3 reports the ash elemental analysis for each material.

Leaching included treatment of the studied materials with tap water at room temperature in order to investigate the possibility of reducing the ash content and/or altering the ash chemistry of the materials in order to avoid the melting behaviour of the ash of the materials. The experimental methodology for studying the pretreatment techniques, fractionation and leaching, the technique for simulating leaching under laboratory conditions and the results of applying pretreatment techniques to biomass materials have been described elsewhere [6–9].

Table 1 Proximate and elemental analysis of wheat straw samples (% dry basis)

Proximate analysis	Wheat straw	Wheat straw fraction *L*>1 mm	Wheat straw leached
Moisture	6.5	7.5	14.0
Ash	7.5	5.04	5.56
Volatiles	76.0	77.23	82.83
Fixed carbon	16.5	17.73	11.61
	Ultimate analysis		
Nitrogen	0.79	0.63	0.67
Carbon	43.7	47.8	48.67
Hydrogen	5.08	6.023	4.00
Sulphur	0.43	0.25	<0.01
Oxygen	42.4	40.3	41.1
Gross calorific value/kcal kg^{-1}	4520	4699	4207

Table 2 Proximate and elemental analysis of olive residue samples (% dry basis)

Proximate analysis	Olive residue	Olive residue fraction *L*>1 mm	Olive residue, fraction *L*>1 mm, leached
Moisture	5.5	8.76	9.33
Ash	4.6	2.58	1.53
Volatiles	72.0	77.9	80.84
Fixed carbon	23.4	19.5	17.63
	Ultimate analysis		
Nitrogen	1.36	1.00	1.1
Carbon	50.7	51.31	54.1
Hydrogen	5.89	5.82	5.98
Sulphur	0.3	0.28	0.22
Oxygen	37.2	39.00	37.1
Gross calorificvalue/kcal kg^{-1}	5071	4742	5069

The DSC thermal analysis technique was applied to the ash of all materials, the ash of the pretreated olive residue materials (olive fraction *L*>1 mm, leached olive fraction *L*>1 mm) was subjected to simultaneous DSC/TG analysis, and the olive residue material fraction *L*>1 mm was also examined by the TG-MS technique. The DSC thermal analysis was performed with a Stanton Redcroft DSC 1500 instrument, the simultaneous DSC/TG analysis with an STA 409C DSC/TG instrument, and the TG-MS with a universal V1.5B thermogravimeter coupled with an MS575 mass

Table 3 Ash elemental analysis (ash basis %) of wheat straw and olive residue samples

Sample	K_2O	Na_2O	CaO	MgO	SiO_2	Al_2O_3	SO_3	Cl
Wheat straw	14.06	4.3	14.4	4.3	39.2	3.85	5.27	2.73
Wheat straw fraction *L*>1 mm	13.12	3.3	4.43	0.92	38.5	1.73	5.9	2.98
Wheat straw leached	4.23	2.17	11.45	3.15	48	1.74	1.4	<0.005
Olive residue	15.10	8.90	21.30	7.90	32.60	6.03	4.97	1.43
Olive residue fraction *L*>1 mm	41.82	3.94	9.79	3.32	18.86	2.52	0.68	1.42
Olive residue, fraction *L*>1 mm, leached	5.89	1.44	22.89	2.54	22.72	3.70	0.2	<0.005

spectrometer. In all cases, the heating rate was 20°C min^{-1}, with the exception of TG-MS, where it was 50°C min^{-1}; the oxidizing agent used was air and the carrier gas was nitrogen.

Results and discussion

Wheat straw

Figures 1–3 depict the thermal behaviour of the ash of the three different wheat straw samples tested in this work by means of the DSC method.

As is to be seen from Fig. 1, the ash of the wheat straw sample yields three endotherms: two in the temperature range 150–250°C and one in the temperature range 700–900°C. The first two endotherms are attributed to water evaporation during the initial steps, while the third reveals the tendency of the ash to create melting problems in the temperature range 700–900°C, which is the temperature range of operation of fluidized bed reactors. This endotherm in this temperature interval is attributed to the presence of large quantities of alkali metals and alkaline earth materials in the ash of the materials; elemental analysis of the ash indicates that these are present mainly in the form of carbonates and chlorides, e.g. potassium and calcium carbonates and potassium chloride. The carbonates tend to decompose and to produce

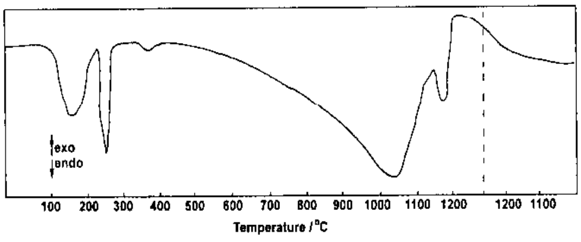

Fig. 1 DSC diagram of wheat straw ash sample

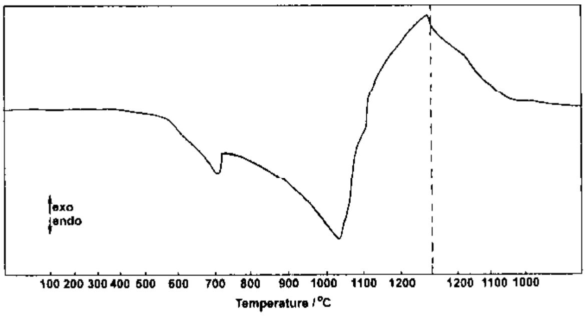

Fig. 2 DSC diagram of wheat straw fraction L>1 mm ash sample

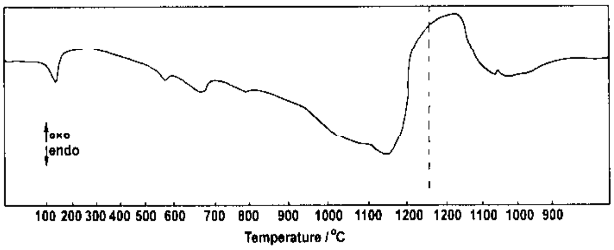

Fig. 3 DSC diagram of leached wheat straw ash sample

alkali metal and alkaline earth metal oxides, which can react with silica to create low-melting silicates, or with sulphur to produce sulphates in the solid and the gas phases, initiating deposition and agglomeration problems. Similarly, the alkali metal chlorides can vaporize in the temperature range 770–900°C and facilitate reactions in the gas phase, leading to the formation of sulphates and consecutively to deposition and corrosion problems.

Figure 2 depicts results from the thermal treatment of the ash of the wheat straw fraction L>1 mm. In this case, the melting endotherm produced starts from the same temperature interval as for the previous straw sample, but the resulting curve demonstrates that the phenomenon is now more acute. In this case too, the DSC analysis findings correlate well with the elemental analysis on the ash of the material in Table 3, where it is seen that the ash contains approximately the same amounts of potassium and silicon, but is now very low in calcium and higher in chlorine and sulphur as compared with the earlier data. The small amount of calcium, which has low vapour pressure and low mobility, is replaced by a large amount of potassium, and also of chlorine and sulphur, which have high mobility, reactivity and a tendency to form sulphates and silicates. Both thermal analysis and elemental analysis of the ash of the tested material reveal that fractionation acts negatively on the ash melting behaviour.

In contrast, the results obtained from the thermal analysis of the ash of the wheat straw leached material show that the melting curve of the ash is shifted to higher temperatures: it seems to start at 900°C and to be concluded at 1250°C. This means a net rise in the melting tendency of the ash of the material of about 100–150°C, which elevates the melting tendency of the straw ash out of the temperature range of operation of fluidized bed reactors. The results are comparable with those from the elemental analysis on the ash of the material depicted in Table 3. The tabulated data clearly demonstrate that the ash of the tested material is substantially depleted in alkali metals, sulphur and chlorine, and contains increased amounts of silicon as compared to the previous two straw materials. As a result, the melting tendency of the ash of the materials seems to decrease significantly in the temperature range 800 900°C.

Olive residue

Figure 4 depicts results obtained from thermal treatment of the ash of the olive residue material by the DSC technique. The Figure reveals a melting endotherm starting at about 800°C and ending at 1100°C. Elemental analysis on the ash of the olive residue material (Table 3) shows that the ash contains large amounts of alkali and alkaline earth metals, as well as significant amounts of sulphur and chlorine, and fully justifies the melting endotherm shown in Fig. 4.

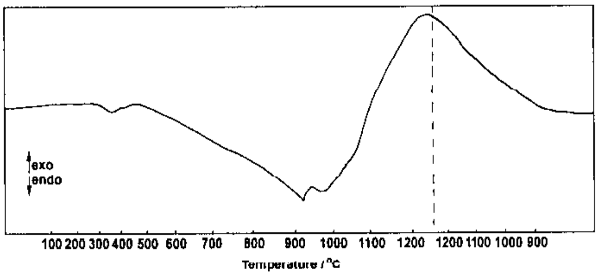

Fig. 4 DSC diagram of olive residue ash sample

Figures 5–7 present the results from thermal treatment of the ash of the olive residue fraction *L*>1 mm by the simultaneous DSC/TG and TG-MS techniques. The DSC/TG diagram demonstrates that the tested ash material is highly reactive since a large endotherm is observed between 750 and 1250°C, accompanied in the same temperature range by a high mass loss according to TG analysis. The elemental analysis of the ash of the sample shows that about half of the ash comprises alkali metals, with significant amounts of chlorine and sulphur. The small early endotherms are attributed to water evaporation from the sample. Moreover, the diagram depicted in Fig. 6 shows that, during the TG thermal treatment of the ash and the analysis of the gases produced in a MS apparatus, the main gas evolved was CO_2, thought to be produced from the decomposition of carbonates, while the gas mixture also included other heavy substances that could not be identified, but which were suspected of being alkali metal chlorides or sulphates. The two analyses give comparable results and, together with the elemental analysis on the ash of the material, afford clear proof that the ash of the material displays a high tendency to melting in the temperature range 750–900°C.

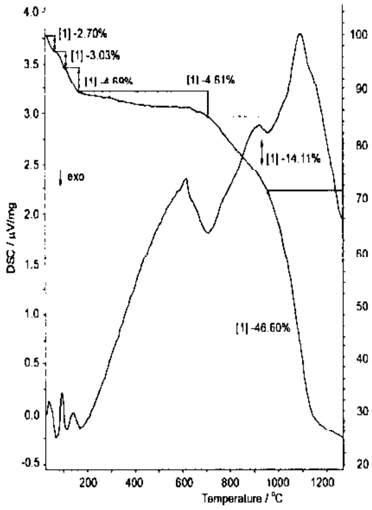

Fig. 5 DSC/TG diagram of olive residue fraction *L*>1 mm ash sample

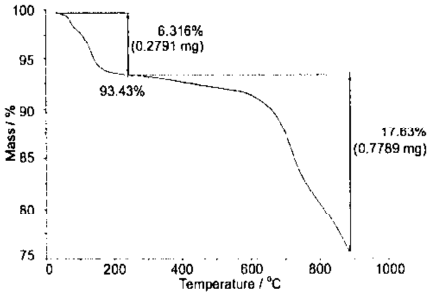

Fig. 6 TG-MS diagram of olive residue fraction *L*>1 mm ash sample

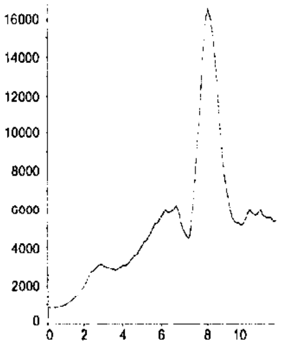

Fig. 7 TG-MS diagram of olive residue fraction *L*>1 mm ash sample

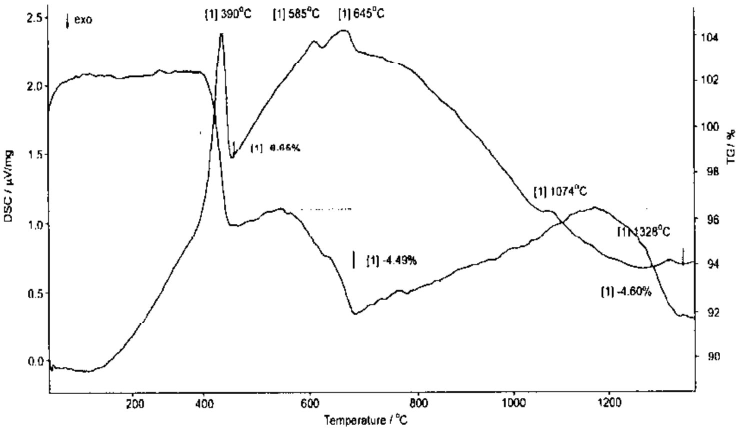

Fig. 8 DSC/TG diagram of leached olive residue fraction $L>1$ mm ash sample

Finally, Fig. 8 illustrates results obtained from DSC/TG of the ash of the material olive residue leached fraction $L>1$ mm. This diagram reveals the lack of any substantial endotherm and mass loss in the temperature range 700–900°C. The only changes observed as concerns both the DSC and the TG analysis appear in the initial stages of treatment and are thought to be due to the evaporation of hydroxides, probably KOH. The total mass loss of the sample is very low, at about 8%, and both DSC and TG diagrams indicate the very stable thermal behaviour of the treated ash. Elemental analysis on the ash of the material (Table 3) again demonstrates, as in the case of the wheat straw leached sample, that the ash appears to be depleted in alkali metals, chlorine and sulphur, and contains mainly silicon.

References

1 L. L. Baxter, Biomass and Bioenergy, 4 (1993) 85.
2 T. R. Miles, P. E. T. R. Miles, Jr., L. L. Baxter, R. W. Bryers, M. M. Jenkins and L. L. Olen, Alkali Deposits Found in Biomass Power Plants. Vol. 1-2. Summary Report for National Renewable Energy Laboratory, NREL Subcontract TZ-2-11226-1, 1995.
3 M. K. Misra, K. W. Ragland and A. J. Baker, Biomass and Bioenergy, 4 (1993) 103.
4 A. Moilanen, M. Nieminen, K. Sipila and E. Kurkela, Ash Behaviour in Thermal Fluidized-Bed Conversion Processes of Woody and Herbaceous Biomass, Proceedings of the 9th European Bioenergy Conference, Copenhagen, 2 (1996) 1227.
5 L. L. Baxter et al., Inorganic Material Deposition in Biomass Boilers, Proc. of the 9th European Bioenergy Conference, Copenhagen, 2 (1996) 1114.
6 M. B. Jenkins, R. R. Bakker and J. B. Wei, Biomass and Bioenergy, 10 (1996) 177.
7 E. G. Koukios and S. Arvelakis, NTUA Group, FIBEGAR Final Report, European Commission, JOULE Programme (JOR3-CT95-0021), 1998.
8 S. Arvelakis, G. Taralas, D. P. Koullas and E. G. Koukios, Upgrading Agricultural Residues as Feedstocks of Electricity Generation by Gasification, Proc. of the 3rd Biomass Conference of the Americas, Montreal, 1997.
9 G. Várhegyi, P. Szabó and M. J. Antal, Jr., Biomass and Bioenergy, 7 (1994) 69.