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CHARACTERIZATION OF BIO-FUEL AND BIO-FUEL ASH

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Abstract

Three bio-fuels with or without additives and their fly ash samples were characterized using simultaneous Thermogravimetry–Differential Thermal Analysis–Fourier Transform Infrared Spectrometry–Mass Spectrometry (TG–DTA–FTIR–MS), X-ray Diffraction (XRD), X-ray Fluorescence (XRF), and Scanning Electron Microscopy–Energy Dispersive Spectrometry (SEM–EDS). The results show that the additives increase the reactivity of the bio-fuel during combustion. The additives also significantly decrease the amount of unburned carbon in the fly ash. The additives affect the compounds formed in the fly ash sample, and consequently the thermal behaviour of the fly ash. The fly ash samples are thermally stable in air up to 100°C. The fly ash samples contain fine particles with irregular shape, small round particles, and large hollow spherical particles with entrapped gases.

Keywords: bio-fuel, combustion, composition, fly ash, thermal analysis

Introduction

Renewable energy is of growing importance in satisfying environmental concerns about fossil fuel usage. For the past 30 years considerable effort has been directed toward production of liquid fuels from biomass. Since the 1990s, fast pyrolysis technologies have produced high-quality liquid fuels, so-called pyrolysis oil, bio-oil or bio-fuel [1].

The chemical composition of bio-fuel is complex, comprising mainly water, carboxylic acids, carbohydrates and lignin-derived substances [2]. In contrast to petroleum fuels, bio-fuel contains a large amount of oxygen in chemically-bound form, usually 45−50 mass% [3]. The presence of oxygen is the primary reason for differences in the properties and behaviour of hydrocarbon fuels and bio-fuels.

Bio-fuel has the potential to be used as a fuel oil substitute. It is renewable and its use can reduce serious air pollution. It produces nearly half the heat of conventional fuel oil [1]. It has been shown that bio-fuel can be burned efficiently in standard or slightly modified equipment [3]. However, bio-fuels have some undesirable

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properties for fuel applications, such as high water content, high viscosity, poor ignition characteristics and corrosiveness [3].

Orenda Aerospace Corporation (Orenda) is currently evaluating various bio-fuels for use in industrial turbine engines. A study was carried out at the Canadian Explosives Research Laboratory, the Canmet Energy Technology Centre-Ottawa and the Materials Technology Laboratory of Natural Resources Canada (NRCan) to characterize three bio-fuels and their fly ash samples using Thermogravimetry (TG), Differential Thermal Analysis (DTA), Mass Spectrometry (MS), Fourier Transform Infrared (FTIR) Spectrometry, X-ray Diffraction (XRD), X-ray Fluorescence (XRF), and Scanning Electron Microscopy-Energy Dispersive Spectrometry (SEM-EDS).

Experimental

Sample information

Three bio-fuels (Fuels 1, 2 and 3) were obtained from Orenda. The three samples contained organic acids, water, 0.02–0.05 mass% sulfur and traces of sodium, potassium, calcium, magnesium, vanadium, lead and nickel. Fuel 1 had no additives, while Fuels 2 and 3 contained different additives which are proprietary to Orenda.

Two types of fly ash samples were provided by Orenda: filter and cyclone. The filter fly ashes (FFA 1, 2 and 3) and cyclone fly ashes (CFA 1, 2 and 3) were produced from the combustion of the corresponding bio-fuel samples. The CFA were the ash particles carried with the flue gas and precipitated in cyclones placed behind the combustion unit. The FFA were finer ash particles precipitated in a precipitator, which is placed behind the cyclones.

TG–DTA–FTIR–MS

The thermal behaviour of the bio-fuels and their FFAs was determined in air and that for the FFAs was also determined in helium. A TA 5200 Thermal Analysis System with a simultaneous TG-DTA 2960 module was used to measure mass changes (TG), and the temperature difference between the sample and a reference material (DTA). The TG-DTA was connected to a Bomem MB100 Fourier Transform Infrared Spectrometer (FTIR) and a Balzers Thermostar GSD300 Quadrupole Mass Spectrometer (MS) for identification of the evolved gases.

Approximately 40 mg of bio-fuel or 5 mg of FFA were placed in an alumina pan. The sample mass was optimized by filling the sample pan to approximately 3/4 capacity. The DTA reference material was platinum foil of approximately the same mass as the sample. The sample and reference were heated at 20°C min^{-1} from ambient to 1400°C in air or helium flowing at 50 $\text{cm}^3\ \text{min}^{-1}$. TG mass, DTA baseline and temperature calibrations [4] were performed prior to the experiments.

The FTIR interface consisted of a 5 mm i.d. Teflon tube and a 10 cm Pyrex cell with a 50 cm^3 volume and KBr windows. A quartz microfibre filter was placed at the FTIR inlet. The acquisition rate of the FTIR was one scan every minute and the time delay was about 10 s from the TG-DTA furnace outlet to the FTIR cell. After the run, each spectrum was studied, and a characteristic wavenumber was selected for a specific evolved gas in order to generate an evolution profile of total absorbance (A) *vs.* temperature.

For the MS analysis, the heated quartz capillary interface was placed near the sample pan, in the TG-DTA furnace. For the experiments conducted in helium, MS data were acquired using bargraph scans from 5 to 100 amu (atomic mass unit) at a speed of 0.2 s amu^{-1}. For the experiments conducted in air, the operating range was 29 to 100 amu. The electron multiplier detector was set at 960 V for acquisition. The MS was calibrated for mass alignment and amplifier signal. After the run, each mass spectrum was studied and characteristic fragments (mass to charge ratio = m/z) were selected for the ion current intensity *vs.* temperature diagram.

X-ray Fluorescence

FFA 2 and the three CFA were analyzed for elemental content using X-ray Fluorescence (XRF), in accordance with ASTM method E 4326 [5]. A Rigaku RIX3000 spectrometer operating in the wavelength dispersion mode was used. XRF analysis was not performed on FFA 1 and 3 since there were insufficient amounts of samples.

X-ray diffraction

The three FFA and the residues obtained from the TG-DTA experiments were analyzed using X-ray diffraction (XRD). The XRD spectra were collected in regular diffraction mode using CuK$_{\alpha1}$ radiation on a Siemens D500TT diffractometer. For the TG-DTA residues, which were available in limited amount, a zero background quartz plate was used for collecting XRD data overnight. In these cases, minor diffraction peaks due to the quartz plate were removed prior to phase identification. Diffraction peaks on the spectra were detected using the JADE Plus software package. The resulting peak data sets were searched and compounds identified using the phase search/match software of JADE Plus.

Scanning electron microscopy with energy dispersive spectrometry

The morphology and the chemical composition of the three FFA and their residues obtained from the TG-DTA experiments were studied using a Philips XL-30 Scanning Electron Microscope equipped with an URSA Energy Dispersive Spectrometer (SEM-EDS). The samples were placed on double adhesive graphite tape, and were examined without a conductive coating. Secondary Electron images were acquired using an accelerating voltage of 10 kV. The accelerating voltage was 20 kV for acquisition of EDS spectra and Back Scattered Electron images.

Results and discussion

Thermal behaviour of bio-fuel in air

The thermal behaviour of the three bio-fuels in air was studied using TG–DTA–FTIR–MS. Example plots for the TG–DTA–FTIR–MS experiments, using

Fuel 1, are shown in Fig. 1. The mass loss (TG) and the temperature difference (DTA) curves are plotted *vs.* sample temperature in Fig. 1a. The absorbance (A) *vs.* temperature for the evolved gases detected by FTIR is shown in Fig. 1b. The MS data is presented as ion current intensity *vs.* temperature for the selected mass fragments (Fig. 1c). The possible assignments for the selected masses are listed in Table 1.

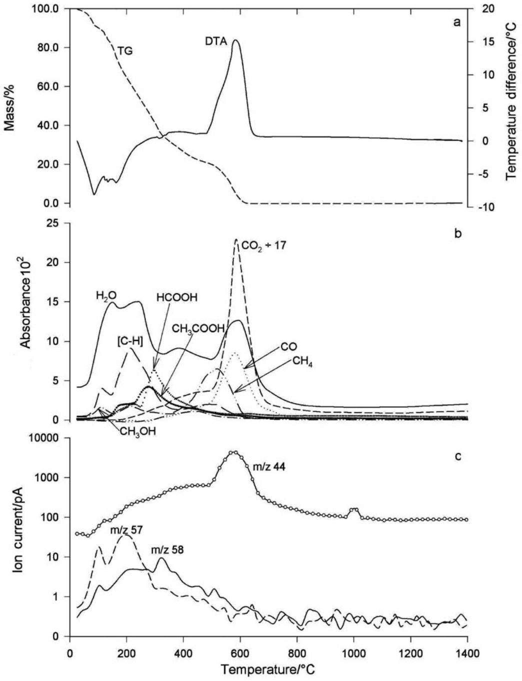

Fig. 1 a – TG-DTA; b – FTIR and c – MS results for Fuel 1 heated in air at 20°C min^{-1}

Table 1 Selected MS masses and possible assignments

Mass/charge ratio (*m*/*z*)	Compound or fragment
18	H_2O
28	CO CO^+ N_2 $C_2H_4^+$
44	CO_2 N_2O $C_xC_y^+$ $C_xH_yO_z^+$
57, 58	$C_xH_y^+$ $C_xH_yO_z^+$
64	SO_2^+

Corresponding to the substantial mass loss of about 78% below 465°C (Fig. 1a), the DTA curve shows several endotherms due to the release of water from two sources, that adsorbed and that in the form of hydrates, and other volatile material. As identified by FTIR, the main compounds obtained from the bio-fuel comprise water

(3854 cm^{-1}), methanol (1034 cm^{-1}), formic acid (1107 cm^{-1}), acetic acid (1176 cm^{-1}) and one or more materials containing a –CH– (2972 cm^{-1}) group (Fig. 1b). The MS results support the findings obtained by FTIR (Fig. 1c).

A substantial exothermic peak accompanied by a mass loss of about 22% was observed at an onset temperature of 465°C. The exotherm may result from the oxidation of bio-fuel. The main gaseous components detected were CO_2 (2361 cm^{-1}), with small amounts of H_2O, CO (2172 cm^{-1}), methane (3016 cm^{-1}) and other compounds containing a C–H group. The FTIR results show that CO_2 and CO started to evolve at approximately 200°C, at which point oxidation of bio-fuel started. After the run, there was no visible residue remaining in the sample pan. A black and brown deposit of ash was found on the in-line FTIR filter.

Similar thermal behaviour was observed for Fuels 2 and 3. The TG–DTA results for the three bio-fuel samples are compared in Table 2 and Fig. 2. Lower onset and peak temperatures, which were obtained from the exotherms for Fuels 2 and 3, suggest that the reactivity of Fuels 2 and 3 is higher than that of Fuel 1. The difference in the reactivity may result from the effect of the additives used in Fuels 2 and 3. The amounts of CO_2

Table 2 TG-DTA results for the bio-fuel samples

Fuel	Δm_1/%[a]	T_{onset}[b]/°C	T_{peak}[b]/°C	Δm/%[b]	Peak area[b]/°C min mg^{-1}
1	79±1	473±12	586±6	21±1	1.5±0.3
2	78±1	456±27	554±18	22±1	2.0±0.3
3	78±1	451±14	551±3	21±1	1.7±0.1

[a] Total mass loss below the onset temperature of the exotherm

[b] Onset temperature, peak temperature, mass loss and peak area of the exotherm

The uncertainties in the values represent one standard deviation of the values obtained from repeated measurements

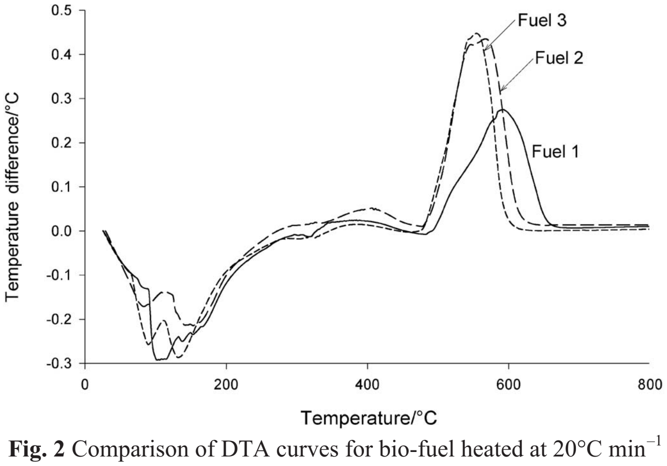

Fig. 2 Comparison of DTA curves for bio-fuel heated at 20°C min^{-1} in air

evolved from the oxidation of Fuels 2 and 3 were ten times higher than that from Fuel 1. The substantial differences in the amount of CO_2 evolved suggest that large amounts of carbon in Fuel 1 was carried in fly ash.

Thermal behaviour of bio-fuel ash

Thermal behaviour in air

The TG–DTA–FTIR results for the FFAs heated in air are summarized in Table 3 and Figs 3–4. In air, an exotherm (Fig. 3) accompanied by a mass loss (Fig. 4) was observed from the three FFA samples at an onset temperature of about 200°C. This exotherm and mass loss may result from the oxidation of carbonaceous residues since H_2O, CO_2 and CO were detected by FTIR and MS.

Table 3 TG–DTA–FTIR results for FFAs heated in air

FFA	Δm_1 /%^{a}	Peak area^a/°C min mg^{-1}	$CO_2{}^b$/A
1	66±1	16.07±0.18	2.29±0.16
2	3±1	0.39±0.02	0.07±0.01
3	7±1^c	0.96±0.05^c	0.23±0.01

[a] Total mass loss or peak area of the exotherm due to the oxidation of carbonaceous residues
[b] Maximum absorbance of CO_2 detected by FTIR
[c] Sum of double steps

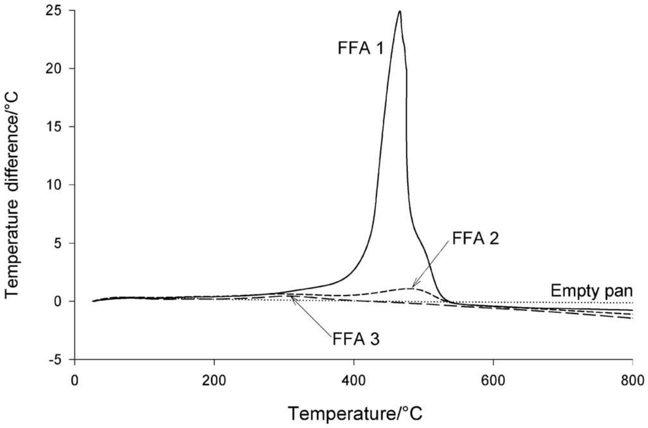

Fig. 3 Comparison of DTA curves for FFAs heated at 20°C min^{-1} in air

The mass loss, the peak area and the amount of CO_2 evolved from the oxidation of possible carbonaceous residues were much higher for FFA 1 than those for FFA 2 and 3. The TG–DTA–FTIR–MS results suggest that FFA 1 contains the largest amount of unburned carbon, while FFA 2 has the least amount among the three samples.

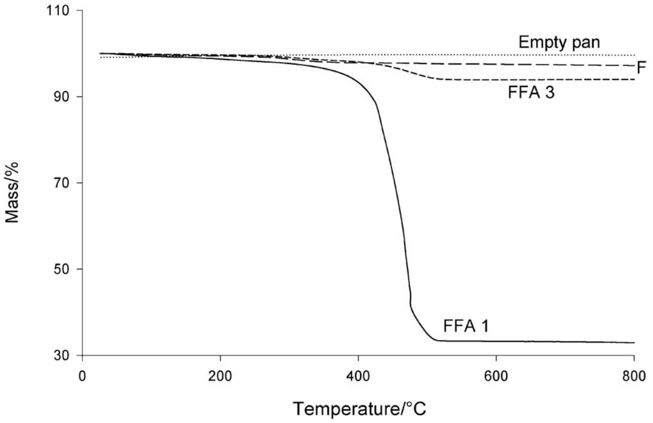

Fig. 4 Comparison of TG curves for FFAs heated at 20°C min^{-1} in air

Thermal behaviour in helium

The DTA curves for the FFAs heated in He are compared in Fig. 5. For all three samples, the DTA curves (Fig. 5) show an endothermic trend between 300 and 1100°C, followed by an exothermic trend from 1100°C and continuing until the end of the run. These broad endothermic and exothermic trends may result from changes in sample heat capacity.

A small endotherm was observed from FFAs 1 and 3 at about 800°C (Fig. 5). This small endotherm may result from a phase transition of a component in the sample.

Evolution of CO_2, CO and traces of H_2O and SO_2 was detected by FTIR and MS. As discussed later in this paper, the SEM micrographs show that the FFA samples contain thin-walled hollow spheres. Kolay and Singh [6] and Vassilev and Vassileva [7] have stated that the cores of these hollow spheres are filled with gas and con-

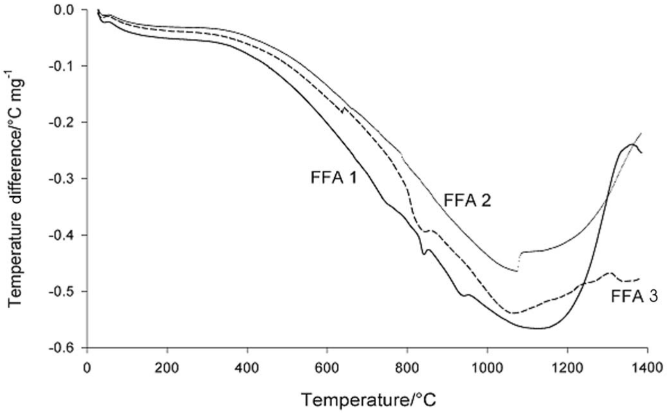

Fig. 5 Comparison of DTA curves for FFAs heated at 20°C min^{-1} in He

densed material formed during burning. Therefore, the gases evolved from the ash during the heating in helium are a result of the expulsion of the entrapped gases. The total mass losses for FFA 1, 2 and 3 are 38±4, 6±1 and 15±1%, respectively. These mass losses mainly result from the evolution of entrapped gases.

Composition of bio-fuel ash

EDS results

The chemical composition of the three FFAs and their residues from the TG-DTA experiments were determined by SEM-EDS. The EDS results are summarized in Table 4.

In general, the EDS analysis shows that the three as-received FFAs contained iron, calcium, oxygen, carbon and sulfur. In addition, silicon, zinc and potassium were found in FFA 1. Although silicon was not detected in FFA 2 and 3, it was found in their residues after heating; therefore, FFA 2 and 3 may also contain silicon. Chromium was also found in FFA 2 and 3, but not in FFA 1. Only FFA 2 contained magnesium. Iron, zinc, silicon and chromium were not present in the original bio-fuel samples, but they may have formed during the transport and storage of the products, as well as through abrasion of equipment (e.g. combustion unit).

The composition of the FFAs changed slightly after heating in the TG-DTA. The sulfur content was significantly decreased or undetected after heating in He and in air. After heating in air, the carbon in the ashes was oxidized and evolved as CO_2 and CO as discussed earlier.

FFA 1-air, 3-He and 3-air contained significant amounts of Al, which was not observed in the other samples. The content of Al may have resulted from contamination, possibly from the alumina pan of the TG-DTA.

Table 4 Summary of EDS results for FFAs

FFA	Treatment	Identified elements
1	as-received	Fe, Ca, O, C, Si, Zn, K, S
1-He	heated in He	Fe, Ca, O, C, Si
1-air	heated in air	Fe, Ca, O, Si, Zn, Al, Cu
2	as-received	Fe, Cr, Ca, Mg, O, S, C
2-He	heated in He	Fe, Cr, Ca, Mg, O, C, Si
2-air	heated in air	Fe, Cr, Ca, Mg, O
3	as-received	Fe, Cr, Ca, O, C, S
3-He	heated in He	Fe, Cr, Ca, O, C, S, Si, A
3-air	heated in air	Fe, Cr, Ca, O, Si, Al

XRF results

Elemental analysis of FFA 2 and the three CFAs was performed using XRF. There were insufficient amounts of FFA 1 and 3 to perform the XRF analysis.

The XRF data listed in Table 5 reveal that FFA 2 contained mostly chromium, iron and magnesium, with lower amounts of silicon, aluminium, calcium, sulfur and zinc. The CFAs contained mostly silicon, aluminium, iron, and to a lesser degree, titanium, calcium, magnesium, potassium, and zinc. CFA 2 also contained a high proportion of chromium. All samples contained lead, which could not be quantified.

As expected, the composition of the FFAs and CFAs varied. However, the XRF results for CFAs can still provide insights into the chemical content of the FFAs and can be used for XRD analysis of FFAs.

Table 5 Summary of XRF results for FFAs and CFAs

Metal oxides/mass%	FFA 2	CFA 1	CFA 2	CFA 3
SiO_2	3.40	40.1	27.9	23.7
Al_2O_3	1.91	19.9	12.9	9.02
Fe_2O_3	16.9	16.3	20.0	25.9
TiO_2	-[a]	1.79	2.59	4.80
P_2O_5	0.104	0.251	0.273	0.337
CaO	1.33	3.94	4.97	5.44
MgO	12.7	1.21	2.44	2.01
SO_3	1.29	< 0.46	< 0.46	1.53
Na_2O	-[a]	0.71	0.69	0.75
K_2O	0.475	1.45	1.49	1.20
BaO	-[a]	0.102	0.091	0.110
SrO	-[a]	0.139	0.096	0.073
V_2O_5	-[a]	0.040	0.041	0.036
NiO	0.030	0.111	0.087	0.094
MnO	-[a]	0.279	0.514	0.947
Cr_2O_3	61.2	0.162	4.93	1.42
CuO	0.078	0.039	0.096	0.122
ZnO	1.05	1.82	4.46	5.62
Sample loss[b]	2.08	9.16	12.7	10.8

[a] Unable to report the concentration of the element with any degree of certainty

[b] Sample loss due to the vaporization of water and volatiles during the fusion with borate flux

XRD results

The chemical content information obtained for the ash samples was used to analyze the XRD data. Compounds identified by XRD are summarized in Table 6.

The XRD findings suggest that the chemistry of the three FFAs was different. FFA 1 contained mostly calcium iron oxide. FFA 2 contained mainly a magnesium-iron-chromium spinel. For FFA 3, a mixed metal oxide with formula in be-

Table 6 Summary of XRD results

FFA	Treatment	Identified compounds
1	as-received	$Ca_xFe_yO_z$, FeO(OH), $Zn_xTi_yO_4$, PbO_2
1-He	heated in He	$Mg(Cr,Fe)_2O_4$, Metal alloy[a], FeS, $Mg_3Ca(CO_3)_4$, ZnO
1-air	heated in air	*
2	as-received	$Mg(Cr,Fe)_2O_4$, MgO, $(Cr,Fe)_2O_3$
2-He	heated in He	$Mg(Cr,Fe)_2O_4$
2-air	heated in air	$Mg(Cr,Fe)_2O_4$
3	as-received	$ZnFe_2O_4$, $(Cr,Fe)_2O_3$, $Ca_xFe_yO_z$
3-He	heated in He	$Mg(Cr,Fe)_2O_4$
3-air	heated in air	$(Cr,Fe)_2O_3$, $Fe(Cr,Al)_2O_4$, mixed metal silicate[b], $MgSO_4$, CrOOH

*The residue attacked the alumina pan and could not be removed for XRD analysis.

[a] Include: Cr and $FeZn_x$

[b] Example: $(Mg,Ca,Fe)_3Al_2Si_3O_{12}$

tween Fe_2O_3 and Cr_2O_3 (i.e., $(Cr,Fe)_2O_3$) and calcium iron oxide were the two main compounds identified.

For FFA 1 and 3, the chemical compositions changed after heating in He and in air. The XRD spectra of the residues 2-He and 2-air were similar to the as-received FFA 2, except they did not contain detectable amounts of MgO and $(Cr, Fe)_2O_3$.

Morphology of bio-fuel ash

The morphology of the three FFA samples and their residues after heating in He and in air was observed using Scanning Electron Microscopy (SEM).

There were three types of particles found in the as-received FFAs: (1) fine particles with irregular shape, (2) small round particles of less than 2 μm, and (3) large hollow spherical particles of 5–10 μm (Fig. 6a).

After heating in He, the residue 1-He had an appearance similar to the original sample (FFA 1), and did not melt. On the other hand, the residue 1-air adhered to the bottom of the TG-DTA crucible and could not be removed. The residue 1-air was composed of crystals in the form of a block (Fig. 6b). FFA 1 recrystallized almost completely after heating in air.

Compared to FFA 2, the residue 2-He had a slightly coarser particle size and was more dense (Fig. 6c). The residue 2-air was composed of fragments of porous sintered material (Fig. 6d). Individual particles within the sintered mass were slightly larger than the fine powders in FFA 2 and the residue 2-He, and were in the form of blocks. The large spherical hollow shells, which were observed in the as-received sample, disappeared after heating in He and in air.

For FFA 3, both the residues 3-He and 3-air were porous solids after TG-DTA processing (Figs 6e and f). The residue 3-He was very hard and could not be crushed. Both FFA 3-He and FFA 3-air recrystallized completely.

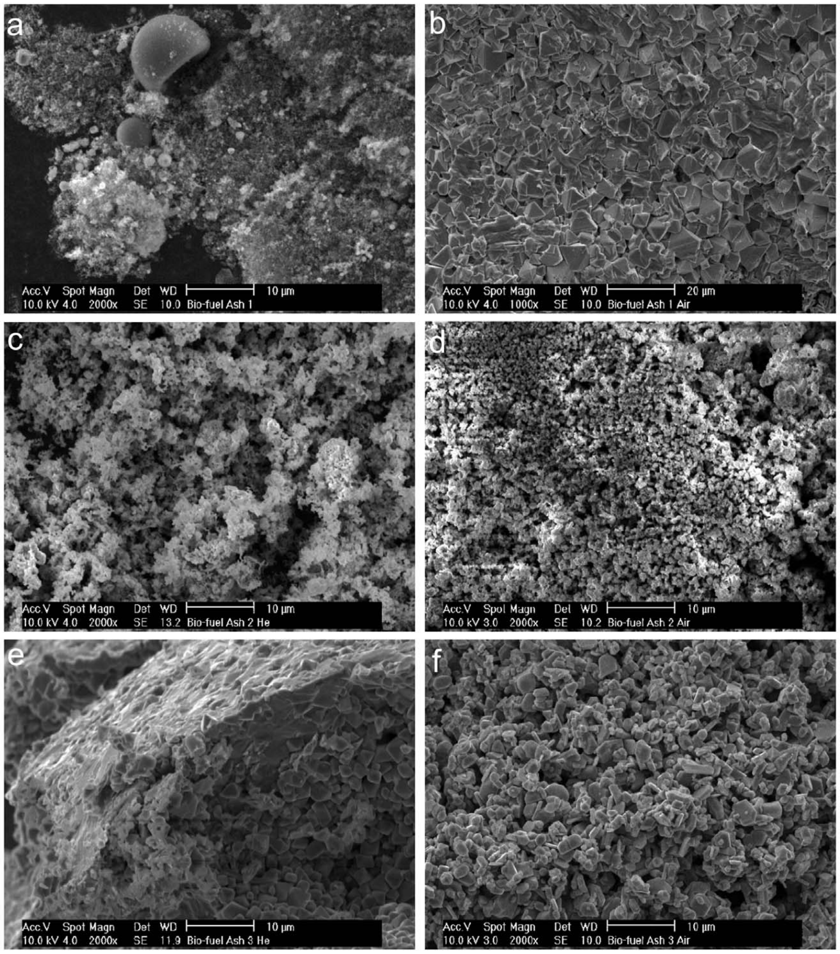

Fig. 6 Micrograph of a – as-received FFA 1; b – FFA 1-air; c – FFA 2-He; d – FFA 2-air; e – FFA 3-He; f – FFA 3-air

Conclusions

From the TG–DTA–FTIR–MS, XRF, XRD and SEM-EDS results obtained for the three bio-fuels and their fly ashes, the following general conclusions can be made:

- The additives increase the reactivity of the bio-fuel during combustion.
- The fly ash contains unburned carbon. The additives significantly decrease the amount of unburned carbon in the fly ash.
- The additives affect the compounds formed in the fly ash samples, and consequently the thermal behaviour of the fly ash.

- The fly ash samples are thermally stable in air up to 100°C.
- The fly ash contains fine particles with irregular shape, small round particles, and large hollow spherical particles with entrapped gases.
- After heating in He and in air, the composition and the morphology of FFA 2 are relatively unaffected compared with those for FFA 1 and 3.

References

1 A.V. Bridgwater, D. Meier and D. Radlein, Org. Geochem., 30 (1999) 1479.
2 K. Sipila, E. Kuoppala, L. Fagernas and A. Oasmaa, Biomass Bioenergy, 14 (1998) 103.
3 A. Oasmaa and S. Czernik, Energy Fuels, 13 (1999) 914.
4 ASTM E967-03, Standard Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers, American Society for Testing and Materials, West Conshohocken, PA, USA.
5 ASTM D4326-03, Standard Test Method for Major and Minor Elements in Coal and Coke Ash by X-Ray Fluorescence, American Society for Testing and Materials, West Conshohocken, PA, USA.
6 P. K. Kolay and D. N. Singh, Cem. Concr. Res., 31 (2001) 539.
7 S. V. Vassilev and C. G. Vassileva, Fuel Process. Technol., 47 (1996) 261.