ASH CHARACTERISTICS OF PERENNIAL ENERGY CROPS AND THEIR INFLUENCE ON THERMAL PROCESSING

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ABSTRACT: Perennial grasses offer potential for providing a year round supply of low cost biomass when grown in southern European conditions. Four crops, Giant reed, Cardoon thistle, Miscanthus and Switchgrass have been assessed for ash content, composition and melting behaviour. Ash content for all four crops is high compared to wood and initial data suggests soil contamination is a major contributor. All crops have naturally high levels of potassium and chlorine but it is notable that Cardoon also has high levels of calcium and sodium. Ash melting temperatures are between 1000°C and 1160°C in oxidizing conditions except for Cardoon where some samples have sintered at ca 750°C. Pilot scale combustion tests on Giant reed, Miscanthus and Switchgrass at Graz showed slag accumulation on the grate, high rates of fouling and high emissions. Corrosion problems would also be expected. Preliminary fluidized bed gasification of Switchgrass was successful, however testing on Cardoon was abandoned due to rapid bed agglomeration. Preliminary fast pyrolysis tests on Giant reed and Cardoon gave poor liquid yields and quality, although ash reduction by cold water washing has shown promising results.

Keywords: perennial rhizomatous grasses, ash, biomass conversion

1 INTRODUCTION

Annually harvested perennial energy crops offer a number of potential advantages over wood feedstocks for bio-energy applications in southern European climatic conditions [1]. These include:

- The potential to harvest a number of different crops throughout the year minimizing storage requirements whilst providing a constant supply of fuel to the conversion process.
- Minimal need for intervention during the growing period and with a plantation life of more than 15 years, low amortised planting/sowing costs.
- The possibility of high biomass yields in poor soils with minimum use of fertilisers and irrigation.

These features all act to reduce supply cost and the environmental impact of production.

One key disadvantage of this type of herbaceous crop is the potential for very high ash content. This can lead to problems in combustion, gasification and pyrolysis.

This paper describes initial studies into ash content, composition and characteristics of four bio-energy crops, namely: Arundo donax (Giant reed), Cynara cardunculus (Cardoon thistle), Miscanthus giganteus (Elephant grass) and Panicum virgatum (Switchgrass).

2 METHODOLOGY

2.1 Scope

The ash content of biomass samples taken from both existing stands of the crops and from younger crops has been measured. The crops have all been grown under Mediterranean conditions in test fields in Greece, Spain, Italy and France. In some cases different anatomical parts of the crop have been studied. Values obtained have been compared to the literature and to a typical wood fuel. The chemical composition of ash has been determined. In particular, elements responsible for ash melting, corrosion, pollution and catalytic activity have been measured. Ash fusion tests have been performed to highlight potential problems such as agglomeration of fluid beds and slagging in combustion. In addition, preliminary testing has been performed in laboratory and pilot scale conversion systems. The results of these tests are briefly discussed.

2.2 Analytical methods

Samples of each crop were dried to constant weight at 105°C and then burned in air at either 550°C or 575°C using a muffle furnace as described in SS18771 and ASTM E1755-01 respectively. Ash content is expressed as mass percentage of dry biomass. Ashing temperatures below 600°C were used to avoid volatilization of any low melting point compounds.

Dry ash (produced at 550°C in air) was digested in a mixture of hydrofluoric, nitric and boric acids in a microwave digester at 240°C. Metals analysis was performed using either flame atomic adsorption spectrometry (FAAS) or inductively coupled plasma mass spectrometry (ICP-MS) depending upon detection limits. Chlorine and sulphur content of the raw biomass were determined by oxygen bomb combustion and wet absorption followed by HPLC analysis.

Ash fusibility tests were performed to ASTM D1857-03 (for fusibility of coke and coal ash), whereby triangular pyramidal ash samples or "cones" are heated at a controlled rate in either an oxidising or an inert (N_2) atmosphere. The temperature at each of the fusion stages identified in Figure 1 is recorded. This test is considered to be indicative of ash behaviour in a real system but cannot predict the effects of chemical interactions between the ash and bed materials used in fluidized bed gasification or combustion.

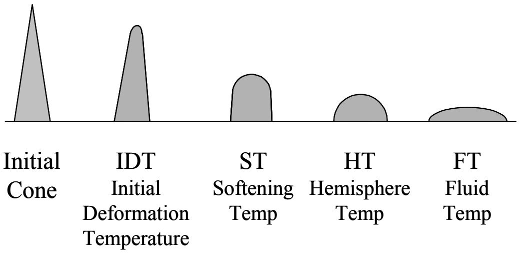

Figure 1: Ash fusion stages (ASTM D1857-03)

3 RESULTS

3.1 Ash content

The ash content of manually harvested biomass samples is shown in Table I. All samples except for Cynara are the whole crop as harvested. The Cynara sample was stems and side branches only. The ash content of the majority of samples was between 5 and 6 % (dry basis) with the exception of Miscanthus at 9.03%.

Table I: Ash content of manually harvested biomass

Crop	Component	No of samples	Ash content wt % d.b.	
			Min.	Max.
Arundo	whole	2	5.08	6.05
Cynara	stem	1	5.28	
Miscanthus	whole	2	1.98	9.03*
Panicum	whole	2	5.15	5.67

* Exceptionally high: see text

Table II: Ash content of mechanically harvested biomass

Crop	Component	No of samples	Ash content wt % d.b.	
			Min.	Max.
Arundo	whole	3	4.18#	8.88
Cynara	stem & leaf	2	9.21	17.39*
Miscanthus	whole	1	2.28#	
Panicum	whole	4	6.95	22.03*

* = Pelletised biomass samples received by TUG

= Single step harvest with Claas Jaguar 690cl.

The ash content of mechanically harvested biomass is shown in Table II. Although the quantity of data is small, the range of ash content for mechanically harvested crops is greater than that for the manually harvested samples and maximum ash content can be much higher. The cause of this additional ash is thought to be soil contamination which may be introduced either by heavy rainfall, by dusty conditions, or during the harvesting process. It is notable that the lowest values were obtained from samples harvested with an adapted forage harvester, where the biomass is collected as it is cut and processed into chips in a single step. Some of the higher ash content samples were cut and allowed to dry on he ground before collection. It is notable that pelletised material had the highest ash content and further investigation is required.

Ash content data from the current project is compared with values obtained from the literature in Figure 2.

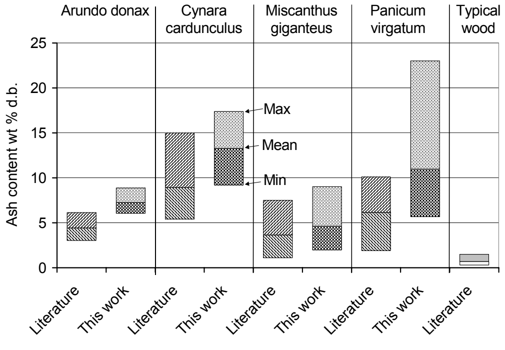

Figure 2: Ash content: comparison with literature

Literature data for Miscanthus and Panicum data is extensive e.g. [2, 3] but is sparse for Arundo and Cynara. It can be seen that the maximum values recorded in this work are, in all cases, greater than those reported in the literature. For Miscanthus and Panicum the majority of the literature data is for North American or northern European conditions, the higher levels of soil contamination seen in this work may be linked either to more arid soil conditions or to less specialised harvesting equipment and working practices.

The high ash content of the manually harvested Miscanthus sample highlighted in Table I was particularly surprising. The composition of the ash was investigated (see 3.2 below) and since silicon, aluminium and calcium content are all very high this may also be due to soil contamination despite manual harvesting (Lime had been added to remediate acid soil).

In the case of Arundo and Cynara it is expected that ash content may vary with the proportion of the parts of the plant collected. In the case of Arundo donax, early harvesting would increase the leaf fraction of the collected material (most leaves have usually dropped before harvest). In the case of Cynara, the seed head (capitula) of the plant may be harvested separately for oil and high cellulose fibres. Ash contents for component parts of Arundo and Cynara are shown in Table III, again the data is from only a small number of samples.

Table III: Ash content of parts of Arundo & Cynara

Crop	Organ	Typical fraction at harvest (% dry mass)	Ash Content (wt% d.b.)
Arundo	stem	95	3.41-5.34
	leaf	5	9.27-9.95
Cynara	stem	27	4.81
	leaf	53	11.2
	capitula	20	15.08

It can be seen that the leaf material has around twice the ash content of the stems therefore early harvesting is likely to increase overall ash content. The seed head of Cynara contributes to the high overall ash content, and harvesting this high value component separately would reduce the ash content of the residual biomass.

3.2 Ash composition

The measured composition of selected samples is shown in Tables IV and V. It is clear that the dominant ash forming elements in these perennial crops are Si, K and Ca. Si is an integral part of the structure of “straw–like” plants whilst K and Ca are important elements involved in the metabolism of these fast growing plants. Cl has no major role in these processes, but is taken up (and accumulated) as the anion associated with dissolved cations like K+. Hence, high concentrations of these elements are found in all samples and are inherent in this type of fuel. High concentrations of Si alone do not present a problem for thermal conversion of biomass. However, in combination with high concentrations of K, Na and Ca, low melting point eutectics may be formed which can cause slagging or bed agglomeration in fluidised bed combustors or gasifiers.

In combustion, high concentrations of Cl increase emissions of HCl, and (in combination with K) can form large amounts of sub-micron KCl particles in the flue gas. These particles are important in the formation of deposits on boiler surfaces and in combination with H_2O or SO_3 cause corrosion.

Table IV: Composition of highest ash content samples

Biomass details				
Crop	Arundo	Cynara	Misc.	Panicum
Component	whole	stem/leaf	whole	Whole
Country	Greece	Spain	Spain	Italy
Harvesting	mech.	mech.	man.	mech.
Ash wt % d.b.	8.88	17.39	9.03	22.03
Ash composition wt ppm (mg/kg dry biomass)				
Cl	3,516	17,780	756	1,396
S	3,025	1,566	542	1,196
K	12,051	21,546	1,731	7,966
Na	633	10,330	45.1	1,381
Ca	2,949	19,025	5,018	18,072
Si	18,753	21,142	27,349	58,888
Mg	1,632	3,936	759	2,714
Al	2,194	4,445	1,011	9,581
P	1,234	1,416	259	1,147
Fe	1,087	2,087	534	5,049
Cu	5.0	7.7	3.9	13.1
Zn	28.0	8.7	44.8	35.6
Ni	6.8	9.0	4.2	14.4
Cr	18.3	6.9	9.3	27.1
Pb	5.0	9.2	9.6	4.6
Cd	2.0	<0,05	0.07	0.06

Table V: Composition of lower ash content samples

Biomass details				
Crop	Arundo	Cynara	Misc.	Panicum
Component	whole	stem/leaf	whole	whole
Country	Spain	Spain	Greece	Spain
Harvesting	man.	mech.	mech.	man.
Ash content wt % d.b.	6.05	9.21	2.28	5.67
Ash composition wt ppm (mg/kg dry biomass)				
Cl	5,410	5,528	880	3,443
S	2,660	944	390	1,219
K	10,545	22,060	1,446	4,016
Na	72.4	6,688	57.8	180
Ca	2,349	12,370	1,776	5,104
Si	9,852	2,718	7,305	12,517
Mg	1,289	2,635	644	2,064
Al	217	376	82.3	244
P	946	1,524	86.6	719
Fe	127	264	73.3	184
Cu	4.5	3.3	1.4	3.8
Zn	24.1	8.4	11.9	27.6
Ni	2.1	0.80	1.0	1.4
Cr	3.7	1.6	1.6	2.7
Pb	2.8	2.3	n.a.	4.7
Cd	0.04	0.05	n.a.	0.03

In pyrolysis, high concentrations of alkali and alkali earth metals lead to catalytic fragmentation of the larger organic molecules resulting in the production of smaller highly oxygenated groups, carbon monoxide and water vapour. This has the effect of reducing the bio-oil yield and increasing its water content which produces an oil of low fuel value and which may be unstable or in multiple and immiscible phases.

It can be seen that the levels of K, Na, Ca and Mg are high for all crops, but for Cynara Na and Ca are significantly greater than for the other crops. High levels of Ca can be explained in part by the physiological demand of this plant but sodium is usually only present in significant quantities (e.g. NaCl) in coastal sites.

The concentration of environmentally relevant heavy metals (Cd, Zn, Cr, Ni, Pb) are generally very low in these crops and should not be a limiting feature in the utilization or disposal of the ash.

The fuel samples with the highest ash content i.e. Panicum and Cynara in Table IV also contain high concentrations of Fe and Al. These elements are not normally taken up by the plant in high concentrations, but are abundant components of soil minerals and are strong indicators of soil contamination.

3.3 Ash fusion tests

Results of ash fusion tests are listed in Table VI.

Table VI: Initial deformation temperatures (IDT)

Crop	IDT (oxidising atmosphere) [°C]	IDT (Inert atmosphere) [°C]
Arundo	1000-1090[a]	930
Panicum	1035 – 1160[a]	1055
Miscanthus	1060	1060
Cardoon	ND	ND.

[a] different samples (location, fertilisation & harvesting method) ND = Not determined

The tests were carried out in air and in nitrogen, encompassing all conditions that could exist in combustion, gasification and pyrolysis. For conversion processes the Initial deformation temperature (IDT) is the most important indicator of problems. The temperature at which the ash starts to soften should be well above the maximum temperature of the process. (An exception is an entrained flow gasifier where ash is removed as a liquid.). Ash from Arundo, Panicum and Miscanthus showed a normal melting behaviour. Melting temperatures were low (for combustion) and indicate possible slagging problems. For gasification at temperatures below 950°C however no problems would be anticipated. The ash from Cardoon stems (with an ash content of ca. 5%) did not melt but sintered at a temperature of ~750°C. This would therefore be considered a high risk for bed agglomeration in fluidized bed gasification.

3.4 Pilot scale conversion tests

Preliminary laboratory and pilot scale conversion tests have been carried out on selected crops. These are reported in separate papers but key results are summarized here for completeness.

Combustion testing has been completed by Graz on Arundo, Cardoon and Switchgrass at laboratory scale and on Switchgrass, Arundo and Miscanthus in a (150 $kW_{thermal}$) KWB rotating grate furnace.

At lab scale, molten ash was observed for pelletised Switchgrass (ash contents 8.2 and 23%) and Cardoon (ash content 17.4%) at peak temperatures of 1130°C and

1240°C respectively. Chopped Arundo (ash content 6.9%) and Cardoon (ash content 9.2%) did not melt due largely to much lower combustion temperatures on the grate caused by lower bulk density and rate of heat release. At the pilot scale Switchgrass (8.3% ash), Arundo (6.13% ash) and Miscanthus (2.28 % ash) gave severe slagging in the primary combustion zone at temperatures of 1000 to 1200°C. High K and Cl gave high concentrations of KCl in the fly ash and high rates of fouling (likelihood of severe corrosion). Increased particulate emissions were measured for all three fuels. The high volume of ash generated together with accumulation of slag on the grate limited operation to ~7 hours before combustion performance deteriorated.

Pilot scale gasification tests have been completed by BTG on Switchgrass and Cynara. A fluidized bed gasifier was selected to permit accurate control of temperature and minimize feedstock preparation requirements (limited size reduction using a hammermill). For Switchgrass the unit was operated without problems for a period of three hours at temperatures of 700 to 750°C i.e. well below the minimum observed IDT of 1030°C. When Cardoon (ash content 13%) was tested at temperatures between 700 and 730°C, the pressure drop of the fluidized bed increased steadily resulting in an automatic shutdown after one hour when the maximum bed pressure drop was exceeded. When the bed was inspected, large agglomerations of bed material and ash were observed. Operation at lower temperatures (<700°C) would result in poor performance with large amounts of tar being formed.

Fast pyrolysis tests have been performed at Aston on Arundo and Cardoon using a small fluidised-bed reactor at temperatures between 425 and 550°C. For Arundo (ash content 4.2%) pyrolysis liquid yields were low due to the catalytic effect of the alkali metals. A maximum organic liquid yield of 47% on a dry ash fee basis (d.a.f.) was measured, this compares to values of 60 to 65% for wood feedstocks. Low oil yield was accompanied by high water content of the bio-oil and high gas and char yields. This bio-oil would be unacceptable as a fuel because of its low calorific value. Limited ash reduction by cold water washing was performed on this feedstock, reducing the ash content to 2.75% d.b. (reducing K by over 55%). This led to an increase in organic liquids to 59% d.a.f. Preliminary tests on Cardoon at 444°C (ash content of 5.7%) gave an organic liquid yield of 45% d.a.f. (i.e. very similar to that of untreated Arundo). Alkali metals reduction (e.g. by washing) will be essential to obtain high bio-oil yields and calorific values.

4 CONCLUSIONS AND RECOMMENDATIONS

The ash content of all four crops is significantly higher than that of wood feedstocks and is likely to cause problems in all three conversion systems considered.

Many of the samples grown in this project have demonstrated ash contents far greater than those previously reported, with evidence of severe soil contamination which is probably due to the use of non specialized harvesting equipment. It is recommended that further work should utilise best agricultural practice (e.g. as described in [4]) to minimise ash content.

Results from laboratory and pilot scale combustion tests clearly reveal that combustion of these perennial crops in existing combustion plants is challenging, due to slag formation, risk of corrosion and high emissions of HCl, SO_2 and particulates. This is particularly problematic in small scale systems which have not been designed to cope with these problems. In larger scale applications similar techniques to those used in straw combustion could be used (e.g. water cooled grate and walls as well as extensive flue gas treatment). For small scale applications, either fuel pre-treatment (e.g. leaching to dissolve K, Na and Cl) and/or the addition of anti-slagging additives (e.g. lime) would be necessary. Another approach would be to blend these fuels with less problematic fuels such as wood.

For trouble free operation of a gasifier the ash melting behaviour is the most important parameter. As long as the initial deformation temperature (IDT) of the ash is well above the operating temperature no specific problems are expected. If low temperatures are required to avoid bed agglomeration then the amount of tar in the product gas might be very high. The high Cl content in the biomass may result in high Cl emissions, and additional gas cleaning may be required.

Ta ensure adequate bio-oil yield from fast pyrolysis (above 60% d.a.f.), and to ensure that oil has adequate heating value and storage stability, it may be necessary to reduce the alkali metal content of even the lowest ash content energy crops. Pyrolysis generally requires combustion of the by-product char in a fluidised bed to produce process heat. Since the char contains the majority of the ash present in the biomass, concentrated by a factor of at least 5 (i.e. ash content of well over 30% is possible) it is likely that ash melting would cause severe bed agglomeration. For this reason alone ash reduction could be considered essential for fast pyrolysis. Simple rinsing of the biomass to remove contamination may be sufficient in some cases but it is likely that more intensive washing processes will be required. The economics of such processes need to be carefully assessed.

5 ACKNOWLEDGEMENT

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