FAST PYROLYSIS OF ANNUALLY HARVESTED CROPS FOR BIOENERGY APPLICATIONS

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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 selected for their high yield potential are being studied. This paper reports on fast pyrolysis testing on two of these, namely Arundo donax (giant reed) and Cynara cardunculus (cardoon). Tests were performed on a bench-scale fluidised bed rig and product mass balances were determined at a range of pyrolysis temperatures. For cardoon, only the stems with an ash content of circa. 5% were tested. At 500°C bed agglomeration was observed leading to a low organic liquid yield of 31% on a dry ash free basis. Lowering the temperature to 450°C and reducing particle size avoided agglomeration and an organic yield of 45% was obtained (c.f. a typical yield from wood of 60-65%). For giant reed, the whole crop (ash content 4.2%) was pyrolysed successfully at temperatures from 425 to 556°C. The maximum organic liquid yield of 47% d.a.f. was obtained at a temperature of 460°C. Simple cold water washing tests on chipped feedstock reduced ash content to 2.75% and reduced potassium content by over 55%. Pyrolysis of this pretreated feedstock at 457°C increased organic liquid yield to 59% d.a.f.
Keywords: energy crops, fast pyrolysis, biomass pretreatment.

1 INTRODUCTION

Annually harvested perennial grasses offer potentially high biomass yield with minimum fertilization, irrigation and husbandry requirements in southern European climatic conditions [1]. However, herbaceous bio-energy crops tend to have high ash content and, in particular, high levels of chlorine and alkali metals. This can cause problems when the fuel is used in the three traditional thermal conversion methods, combustion, gasification or pyrolysis. In the case of fast pyrolysis, alkali and alkali earth metals catalyse the cleavage of monomeric groups in the structure of lignocellulosic materials, producing highly oxygenated carbonyl and hydroxyl compounds such as hydroxyacetaldehyde, together with increased quantities of carbon monoxide and water vapour [2]. Thus, biomass rich in potassium would be expected to produce lower yields of the energy rich oligomers and anhydrosugars. Practically, this may result in pyrolysis liquids which are high in water content, low in calorific value, and which may be inhomogeneous or phase-separated.

The purpose of the current project is to characterize each of four candidate crops grown in southern Europe, namely Arundo donax (giant reed), Cynara cardunculus (cardoon thistle), Miscanthus giganteus (elephant grass) and Panicum virgatum (switchgrass). The latter two have been subject to pyrolysis experiments in previous studies [3, 4] so initial investigations have focused on giant reed and cardoon.

2 METHODOLOGY

2.1 Feedstocks

The feedstocks used have all been grown under Mediterranean climatic conditions. Arundo was obtained from the Centre for Renewable Energy Sources (CRES) in Greece. Cynara cardunculus was obtained from Universidad Politecnica de Madrid (UPM) in Spain.

In both cases the crop was harvested manually from established crop stands. Arundo was obtained in manually cut lengths of <60mm. and with stem diameters between 8 and 15mm and contained <15% leaf matter. The Cynara was provided in chipped form and contained only stem and branches with no leaf material or seed heads. An ultimate analysis of these feedstocks is shown in Table I.

Table I: Ultimate analysis of feedstock

Biomass	Wt % dry basis				HHV (dry) (MJ/kg)
	Ash	C	H	N	
Arundo (whole)	5.08	45.55	5.70	0.24	18.02
Cynara (stem/branch)	5.28	44.35	5.75	0.52	17.58

Ashing was performed to ASTM-E1755-01 at a temperature of 575°C. CHN analysis was performed by combustion and gas chromatography using an Exeter Analytics CE 440 elemental analyser.

2.2 Feedstock preparation

Feedstock was prepared for washing experiments using a domestic shredder/chipper. Preparation for pyrolysis was by means of a laboratory knife mill fitted with a 500μm screen. The feedstock was then sieved to produce the desired particle size. In most cases the 355 to 500μm size fraction was used. Eliminating fines generally results in a reduction in ash content as small dirt/soil particles are removed. Moisture and ash content of each feedstock was measured before each test.

2.3 Fast Pyrolysis

Pyrolysis experiments were performed in a bench scale fluidised bed rig. A flow diagram is shown in Figure 1. Ground feedstock is introduced into the fluidised bed reactor pneumatically via a central feed tube. Pre-heated nitrogen is used to fluidise the bed. Pyrolysis vapours, gas and eluted char particles pass into a single cyclone, from which separated char particles are collected. The reactor cyclone and char collection vessel are contained in a tubular furnace which regulates the bed temperature within the range 400 to 600°C. Gas and vapours pass via a trace-heated exit tube to a cold-water condenser which initiates condensation of the liquids.

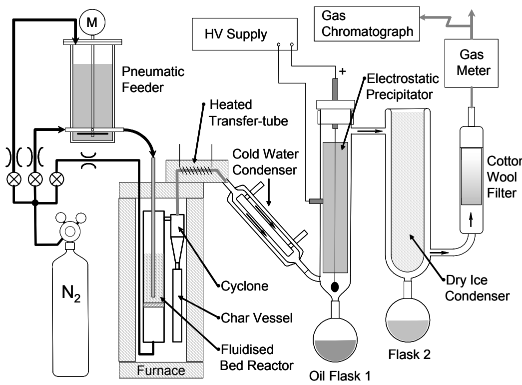

Figure 1: 100 g/hr Bench scale pyrolysis rig

Residual light organics, water vapour and condensed liquids in the form of aerosols then pass into an electrostatic precipitator where the aerosols are removed. The liquid fractions from the water condenser and electrostatic precipitator are mixed in oil flask 1. Residual water and light organic vapours are then removed via a dry-ice/acetone condenser (flask 2) and a final dry cotton wool filter. The dry gas is measured using a volumetric gas meter. Gas samples are taken and analysed on-line using a Varian CP4900 Micro gas chromatograph. Two separation columns and thermal conductivity detectors are used to measure: N_2, H_2, CO, CO_2, CH_4, and alkanes/ alkenes to C_4. The temperature of the fluidised bed is measured at two positions and cyclone and transfer tube temperatures are measured to ensure that liquids remain in the vapour phase before reaching the water condenser.

2.3 Analysis

Mass balances were completed by weighing all apparatus before and after each test to 0.01g resolution using a laboratory balance, The mass of gaseous products was determined by using the average gas composition to calculate an average gas density and then applying this to the measured total volume of gas leaving the rig. The moisture content of the feedstock was measured by drying to constant weight at 105°C. The water content of all liquid fractions collected was measured using Karl Fisher titration using a Metrohm automatic KFD titrator and Hydranal composite 5K reagent and working medium K. The char content of liquids was determined by dilution with methanol and then vacuum filtration using Whatman No1 filter papers. All mass balances are expressed on a dry ash free feedstock basis (d.a.f.). The vapour residence time was estimated from knowledge of system volumes, gas flowrates biomass feedrate and temperatures. This method is sufficiently insensitive to the estimate of specific volume of the pyrolysis vapours since the flow of fluidizing nitrogen is high compared to the rate of evolution of vapours. The product collected in flask 1 is not considered to be representative of liquids produced by a commercial system, since the water condenser has low efficiency, and light organic fractions are carried over to the dry ice condenser (flask 2). The cumulative results for organic liquid and water of reaction are however compatible with those produced by other authors on similar rigs.

2.4 Ash reduction by water washing

Simple water washing has been performed to reduce the inorganic content of Arundo donax. Tests were performed using two batch methods, a packed column (gravity rinse) approach and a stirred vessel. Both methods used cold tap water with low total dissolved solids (TDS) content and an electrical conductivity of < 120 µS/cm. For all tests water was drained through 80µm gauze to ensure retention of biomass fines. Ash content was measured before and after washing. Metals analysis was performed on ash from samples taken before and after washing using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) by a third party laboratory. Washing tests were performed on “shredded” biomass similar to that produced during direct harvesting by means of a forage-harvester with integral chipper. Maximum particle length was c. 50 mm but no particle was greater than 2.5 mm perpendicular to the fibres. The set-up for both types of washing test is shown in Fig. 2.

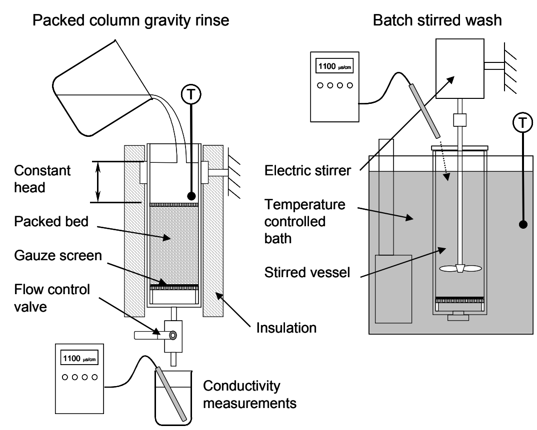

Figure 2: Arrangement for washing tests

Experiments were performed to investigate the influence of washing duration and water quantity. The minimum quantity of water to produce a mobile mixture for stirred washing was 6 to 8 ml/g dry biomass. Tests were performed at values from 15 to 60 ml/g d.b. and for short wash durations between 30 minutes and 2 hrs.

3 RESULTS AND DISCUSSION

3.1 Untreated Arundo donax (giant reed)

Pyrolysis tests were performed over a temperature range of 425 to 556°C, all tests had vapour residence times of less than 1 second. Mass balances data are shown in Table II. Tests 1 and 3 were performed using particles of 355 to 500 microns these caused intermittent feeding problems in the pneumatic feeder so particle size was reduced to 300 to 355 micron with a concomitant slight reduction in ash and increase in moisture content. Average ash content was 4.2 % and average moisture content was 9.35%. Mass balance closures ranged between 88.7 and 95.1 %. In the case of test A1 it is believed that the low closure was due to inaccuracy in volumetric gas measurement due to a faulty meter (value in parentheses in Table II).

Table II: Fast pyrolysis results, untreated Arundo donax

Parameter\Test	A5	A6	A1	A3
Particle size (micron)	300-355	300-355	355-500	355-500
Ash content	4.14	4.14	4.25	4.25
Water content (wt% w.b.)	9.77	9.77	8.94	8.94
Reactor Temperature (°C)	425	460	511	556
Vapour residence time approx. (ms)	775	745	700	665
Mass balance (wt% dry ash free basis)				
Char	19.3	18.6	14.9	13.1
Organic Liquids	**45.8**	**46.8**	**40.9**	**38.9**
Reaction water	14.6	13.6	17.1	16.8
Gas	15.2	16.0	(15.8)	23.4
Closure	94.9	95.1	88.7	92.2
Contents of vessel 1 (wt% Wet basis)				
Water content	39.1	37.4	42.0	41.9

The maximum organic liquid yield of 46.8% d.a.f. was obtained at 460°C. Char and gas yields follow the expected trend i.e. an increase in char yield at low reactor temperature and an increase in gas yield at high temperature. It will be noted that the water content of the oil in collection vessel 1 is very high (a minimum of 37.4%) which for a wood feedstock would normally indicate a phase-separated oil [5]. However in all cases the contents of this vessel were single phase. The low yield is likely to be due to the influence of alkali metal catalysis (as explained above), which will produce more soluble (polar) compounds.

3.2 Washing Tests

Results from preliminary cold water washing tests of Arundo donax are shown in Tables III and IV.

Table III: Arundo donax column **w**ashing results

Parameter \ test	G1	G2	G3	G4
Water quantity (ml/g d.b.)	60	60	31	16
Duration (min)	28	72	72	66
Final ash content (wt % d.b.)	3.54	3.52	3.70	4.07
Ash reduction (% initial ash)	17.7	18.2	14.1	9.0

For the relatively large particles considered, the stirred wash methods yielded significantly greater ash reduction e.g. compare tests G4 (Table III) and S2 (Table IV) of similar duration and water usage. It was notable that for the gravity rinse the duration was less significant than the water quantity used. This is likely to be due to the more uniform bed permeation and more rapid wetting generated by the higher superficial velocity in the column. For the more effective stirred wash there was almost no improvement in ash reduction when the quantity of water was doubled, indicating that even at 15 ml/g the concentration of dissolved ions in the water is sufficiently low that it does not significantly impede diffusion.

Table IV: Arundo donax stirred **w**ashing results

Parameter\ test	S1	S2	S3	S4	M1
Water quantity (ml/g d.b.)	15	15	14.3	30	29.7
Duration (min)	30	60	120	100	120
Final ash content (wt % d.b.)	3.46	3.08	3.03	3.08	2.75
Ash reduction (% initial ash)	20.7	29.5	30.5	31.0	**37.8**

d.b. = dry basis,

The majority of the ash reduction occurs in the first hour of washing. The ash reduction of ca. 30% is far lower than that reported for the washing of straw [6], indicating that the initial rapid reduction probably originates from the fines content of the chipped material where diffusion of soluble ions is rapid, whereas diffusion cannot occur in the largest particles within the duration of the test. Metals content was measured before and after washing for test S3. Results are presented in Table V.

Table V: Metals analysis for test S3

Parameter	Pre-wash	Post-wash	Difference (%)
Total ash (wt % d.b.)	4.36	3.03	1.33 (30.5)
Metals by ICP-AES (mg/kg or wt ppm)			
Potassium	11187	5052	6135 (54.8)
Sodium	61	41	20 (33.0)
Calcium	838	711	127 (15.2)
Magnesium	626	486	140 (22.3)

The reduction in potassium (54.8%) is much greater than the overall ash reduction which may be due to its presence in a highly soluble form such as KCl. Tests of longer duration need to be performed to see whether more gradual diffusion from the larger particles gives a greater ash reduction. The greatest ash reduction obtained in this short series of tests was from Test M1 where a stirred wash of duration 2 hrs was followed by a fast gravity rinse of less than 3 minutes to purge out residual wash water containing dissolved metal ions. Of the total 30 ml/g water usage, half was used for the stirred wash and half for the rinse. This procedure yielded an additional 7.3% of ash reduction. The product from this final washing test was used for the final pyrolysis test described below.

3.3 Fast pyrolysis of washed Arundo donax

Results from a single test on washed Arundo are shown together with those from a typical wood feedstock and Miscanthus of similar ash content in Table VI. All feedstocks were pyrolysed on the same rig. It can be seen that the organic liquid yield for the washed Arundo is low compared to a clean wood feedstock but is very similar to the Miscanthus of similar ash content. It is also evident that the higher ash feedstocks produce more water of reaction than the low ash wood. The reduction in ash from 4.14% (Test A6) to 2.75% (Test A7) together with a 55% reduction in potassium results in an increase in organic liquid yield of 11.9 % d.a.f. It is likely that further improvements in washing would lead to a further increase in organic yields.

Table VI: Pyrolysis results for **w**ashed Arundo donax

Parameter\Feedstock	Washed Arundo (A7)	Poplar [4]	Miscanthus [3]
Particle size (micron)	300-500	<600	<355
Ash content	2.75	0.46	3.16
Water content (wt % w.b.)	4.49	7.25	8.46
Reactor Temperature (°C)	460	477	465
Vapour residence time approx. (ms)	750	550	600
Mass balance (wt% dry ash free basis)			
Char	12.8	8.3	16.8
Organic Liquids	**58.7**	**72.1**	**56.5**
Reaction water	11.1	3.1	7.9
Gas	12.2	12.0	16.2
Closure	94.8	95.5	97.3
Contents of vessel 1 wt% wet basis			
Water content	17.4	15.8	32.2

3.4 Fast Pyrolysis of Cynara cardunculus (Cardoon)

Only two tests have so far been performed on this feedstock: the first test (performed at a nominal 500°C) was abandoned due to bed temperature divergence, indicating de-fluidisation of the bed. When the reactor was opened the bed appeared to be sintered, or capped with a sintered layer but when disturbed the sinter was broken. This may have been due to a low melting point eutectic present in the ash, but no evidence of strongly sintered particles was found. A second test was performed utilizing a reduced particle size and with an increase in fluidisation velocity to ensure a more turbulent bed. The smaller particle size fraction contained a higher quantity of ash. The test was performed at a lower bed temperature in order to reduce the risk of agglomeration due to ash melting. Mass balance results for both tests are shown in Table VII.

Table VII: Fast pyrolysis of Cynara cardunculus

Parameter\Test	C1	C2
Comment	Failed: bed agglomeration	OK
Particle size (micron)	355-500	250-355
Ash content	4.42	5.67
Water content (wt% w.b.)	9.86	10.19
Reactor Temperature (°C)	499	444
Mass balance (wt% d.a.f. basis)		
Char	18.0	15.6
Organic Liquids	**30.6**	**45.1**
Reaction water	20.8	13.8
Gas	21.5	17.3
Closure	90.9	91.8

Since several changes were made at the same time (including a possible difference in ash composition) the cause of the sintering is unknown and this should be the subject of further study since it is unusual to observe this phenomenon at such low temperatures. The results from the successful test show that the organic liquid and char yields are similar to those of untreated Arundo (Table II). However the mass balance closure was poor with an indication that this was caused by an unusually large amount of unidentified light organics escaping in the gas stream. Further testing needs to be performed to understand the bed agglomeration problems and identify maximum yield temperature.

4 CONCLUSIONS AND RECOMMENDATIONS

Results from these experiments indicate that these two perennial crops would not be suitable for the production of liquid fuels from fast pyrolysis without pre-treatment to reduce the content of ash and alkali metals.

For Arundo donax a significant improvement in organic liquid yield (ca. 12%) and reduction in water content of the pyrolysis liquids was obtained by simple cold water washing which resulted in a modest 38% reduction in ash and a reduction in potassium of over 55%. Further optimization of the washing process may yield additional improvements in bio-oil quality.

Further washing work should consider a smaller maximum particle size, the use of hot water and mild acid treatment. When a suitable pre-treatment has been determined then tests at a larger scale using a product collection system more representative of a commercial system should be performed in order to obtain larger oil samples for full compositional and fuel quality assessment.

For Cynara cardunculus problems of bed agglomeration need to be understood before similar tests can be completed.

Washing Arundo donax will add a cost penalty, which should be quantified. A preliminary washing test on Cynara has indicated that the water retention of this feedstock is extremely high due to the highly porous pith contained within the stems. Washing of Cynara may not be economically feasible due to the high cost of drying.

5 REFERENCES

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