

System Approach to Biomass Pyrolysis: Product Characterisation

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Abstract— Engineering a system solution of the biomass pyrolysis process requires thorough investigation of the possible end-use applications of the biomass pyrolysis products (bio-oils and bio-char) in order to determine the most feasible and greenhouse gas abating options for their use. This work investigates the biomass pyrolysis process of three potentially applicable energy crop species and provides characterization of the biooil and biochar products of pyrolysis. The analysis suggests that the biochar contains the OH, aromatic C=C and inorganic Si-O-Si bonds. The biooil samples exhibited much more complex structure and were highly variable in composition suggesting requirement for their further upgrading.

Keywords-biomass, pyrolysis, biofuels, biogas, biooils

I. INTRODUCTION

A renewed interest in biomass as an alternative energy source is apparent in both developing and industrialised countries, primarily because of its renewable character and potential for reducing net atmospheric CO₂ emissions when substituted for fossil fuels. Biomass is the generic term for materials derived from plants or animal manure. According to McKendry [1], biomass materials can be classified in four categories: woody plants, herbaceous plants or grasses, aquatic plants and manures. On average, woody biomass contains about 50 wt% carbon, 43 wt% oxygen, 6 wt% hydrogen and the remaining 1 wt% is nitrogen [2] with the average mean formula expressed as CH_{1.44}O_{0.66} [3].

When biomass is harvested and processed in a sustainable way, biomass to energy conversion has zero net atmospheric CO₂ contribution because the carbon emission from biomass utilisation equals the photosynthetic atmospheric carbon fixed during the lifetime of the plant. The potential climate risk caused by excessive CO₂ emissions from fossil fuel utilisation is cited as the main driver for accelerated developments in renewable based energy generation, with biomass energy generation being one of the most prospective among all renewable energy sources. Biomass use as a fossil fuel replacement has a particular advantage as it can fractionally replace the fossil fuels in existing energy generation technologies without requirement for large and capital intensive engineering adjustments.

The share of energy generation from various biomass sources is estimated as; 64% from wood, 24% from solid wastes, 5% from agricultural wastes and 5% from landfill

gases [4]. The main industries producing biomass wastes are the timber, sugar, cotton, agricultural and food industries. According to the National Renewable Energy Laboratories, the world produces biomass equivalent to 2893 EJ annually. The International Energy Administration estimated that in 1995 the world consumption of biomass was in the order of 343.6 EJ, which is less than 12% of the total production capacity. The developed world still associates biomass with waste and most of the biomass in some countries is destroyed through field burning or disposed in landfills [5]. As an example, in the Sydney region alone 350 Kt/a of wood waste is disposed of to landfill, which is equivalent to one million cubic metres of landfill space [6]. The current disposal practices cause additional environmental concerns as not only do they require energy to maintain the disposal sites but also the biomass undergoes anaerobic decomposition in the landfills producing fugitive CH₄ emissions, which are far more potent than CO₂. Alternatively, field burning produces CO₂ emissions, while the potential energy recovery is wasted. It is therefore more than apparent that biomass disposal requires integration into the current energy technology systems to improve efficiency and sustainability.

A significant advantage of the use of biomass materials is that they are renewable sources and can be purposely grown for energy use. They are generally low in sulphur and nitrogen, hence biomass energy conversion potentially results in lower SO₂ and fuel-NO_x emissions comparing to fossil fuel based energy generation [7]. These materials can be managed more effectively due to the generally lower composition of toxic trace metals when compared to coals [8]. A significant constraint to increased biomass utilisation is its low density which results in higher volume to mass ratios during transportation and storage. Also, most of the biomass materials have high moisture content. Given that the major agricultural and other biomass producing sites are located some distance from the energy utilisation plants, biomass transportation cost can be high because not only are they less dense but will also include transportation of the water. Prior processing and drying may provide a solution, however, biomass should also be handled and stored in a dried environment due to the hygroscopic ability to quickly absorb atmospheric moisture

One of the potential for increasing the net energy capacity of the biomass materials is to thermally upgrade

biomass to higher calorific value fuels. Pyrolysis is one method where biomass materials are heated and decomposed under inert atmospheric conditions converting them to gaseous and liquid products and creating a carbon rich charcoal residue. All of the products of biomass pyrolysis have significant energy value and can be combusted directly to produce energy or they can find other uses. For instance, bio-oils can be further upgraded with catalytic hydrothermal processing [9] to produce bio-diesel, or they can be used as base materials to produce highly marketable chemicals [10]. Bio-char has traditionally been used as metallurgical fuel in ironmaking [11], but recently attracted significant attention as a fertiliser replacement to create highly fertile soils, while at the same time biologically sequestering atmospheric carbon [12].

Pyrolytic processing has been identified in the literature as one of the feasible technologies available to thermally upgrade biomass materials to higher calorific value fuels [13]. Most of the studies to date have been focused on adjusting pyrolysis parameters to achieve maximised bio-oil or bio-char yields. There is significant lack of a systems approach to the biomass upgrading process, an approach which would integrate the pyrolysis conditions, with the upgrading potential of bio-oils to produce bio-diesel and petrochemicals, bio-gas utilisation and bio-char application either as fertilising material or metallurgical fuel, as well as bio-carbon sequestration. A systems approach to the pyrolysis of biomass will not only enhance competitiveness of the higher calorific value renewable fuels and petrochemicals, but will also promote sequestration of atmospheric greenhouse gases.

Fig. 1 details the opportunities for energy and material recovery from biomass where biomass drying and pyrolysis are self driven and maintained through combustion of the produced bio-gas and/or bio-oils. The final pyrolysis products can have various end-of-stream applications, each one offering different advantages and disadvantages. The most feasible stream would be selected by a comprehensive life cycle analysis taking into account the energy balance, material flows and net greenhouse gas savings.

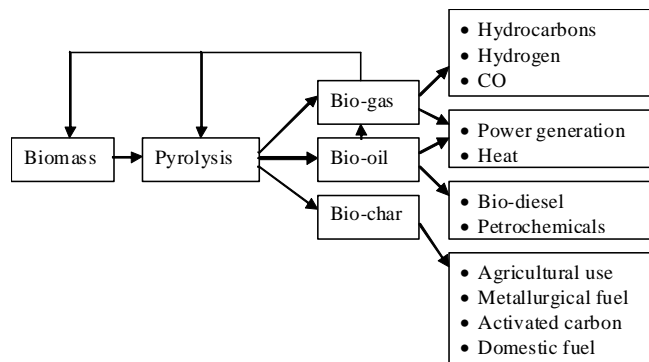


Figure 1. Pyrolysis cycle and options for energy and resource recovery from biomass.

The aim of this paper is to investigate the pyrolysis behaviour of selected biomass species and to characterize the bio-oil and bio-char products of pyrolysis which is essential to model a system approach to biomass pyrolysis.

II. EXPERIMENTAL

A. Samples

Table I shows the properties of the biomass samples used for this study. They are three typical Australian plant species which have potential to be subjected to cultivation as energy crops because of their fast growth rates.

TABLE I. PROXIMATE AND ULTIMATE ANALYSIS OF THE SAMPLES

Sample	Proximate Analysis (air dried)			
	Moisture %	Ash %	Volatile Matter %	Fixed Carbon %
Sugar cane	7.9	6.9	70.6	14.4
Hemp	8.3	4.6	68.7	18.4
Wattle	7.0	2.8	68.2	22.0
Ultimate Analysis (air dried)				
	Carbon %	Hydrogen %	Nitrogen %	Sulphur %
Sugar cane	42.2	5.22	0.56	0.13
Hemp	41.8	5.31	1.31	0.14
Wattle	49.6	5.66	2.82	0.16

B. Experimental techniques

The samples were first subjected to Computer Aided Thermal Analysis to quantify specific and latent heat of the samples during pyrolysis. The technique has been previously detailed by Strezov et al. [14].

A Mettler Toledo thermogravimetric analyzer (TGA) instrument TGA/DSC 1 Stare System, operated with Stare software, was used to determine the weight loss of the samples with temperature. The sample weighing approximately 30 mg was placed in a circular Al crucible with an additional empty crucible employed as a reference. The experiment was carried out using N₂ as a carrier gas, set at a flow rate of 20 ml/min, with a heating rate of 10°C/min. The buoyancy correction for the TGA data was conducted using a blank experiment with no sample placed in either of the crucibles prior to each sample run.

Biooil and biochar samples were then produced in a fixed bed pyrolyser by heating approximately 2 grams of biomass to the temperature of 500°C. The biooils were condensed at room temperature at the outlet of the pyrolyser.

The FT-IR spectra of the biomass, biooil and biochar samples were recorded in Nicolet 6700 FT-IR spectrometer applying Attenuated Total Reflectance (ATR) method with diamond crystal. The total number of scans was 32 with spectral resolution of 4 cm⁻¹.

The bio-oils condensed at room temperature were first dissolved in dichloromethane and then analysed using a Shimadzu GC-MS apparatus (Model QP2010), with a 30

meter long SGE-BP1 column of 0.25µm diameter. Prior to commencement with GCMS experiments the instrument was auto-calibrated using perfluorotributylamine (PFTBA).

III. RESULTS

Fig. 2 shows the specific heat of the samples. The latent heats of pyrolysis were observed through the changes in specific heat with corresponding peaks and troughs. Fig. 2 shows that all of the samples exhibited endothermic heat of reaction starting at 100°C to 180°C associated with decomposition and release of the hydrated compounds. At the temperature range between 200 and 400°C the samples went through a very large endothermic reaction due to the breakdown of the hemicellulose and cellulose and in this temperature region, the major weight loss of the samples is also observed, as determined by the thermogravimetric analysis shown in Fig. 3. At temperatures above 400°C the specific heat showed minor reactions with peaks at 420 and 820°C in case of hemp and 750°C in case of wattle tree. These reactions are followed with only minor loss of weight in the samples (see Fig. 3). According to the thermogravimetric data shown in Fig. 3, at the temperature of industrial pyrolysis, which is typically around 500°C, the samples weigh 28%, 29.5% and 37.2% in case of sugar cane, hemp and wattle tree, respectively. The majority of the weight is lost as non-condensable bio-gas and condensable bio-oil products of pyrolysis.

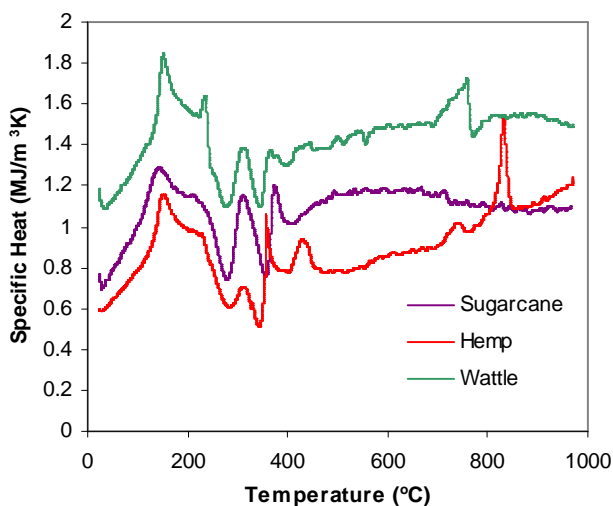


Figure 2. Specific heat of the biomass samples during pyrolysis

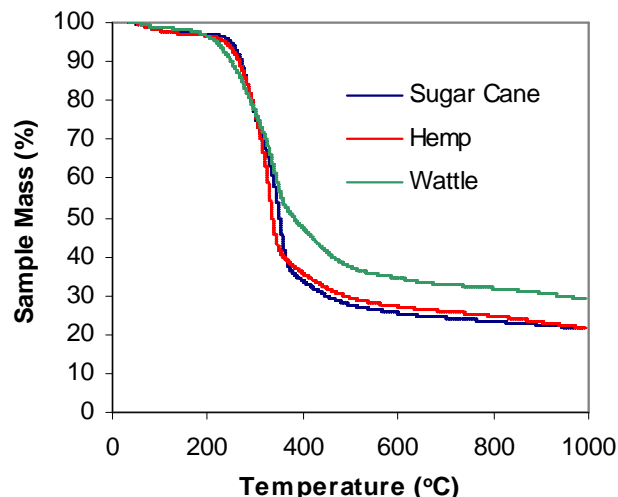


Figure 3. Thermogravimetric analysis of the biomass samples.

Fig. 4 shows FTIR spectra of the unprocessed biomass samples, the biochars produced at 500°C and bio-oils evolved at 500°C and condensed at room temperature. Interpretation of the FTIR spectra was conducted according to the guidelines outlined by Coates [15]. The raw samples all showed a very broad band with a peak at 3340 cm⁻¹ due to OH stretch of the hydroxy group. The same band, although with smaller intensity was also evident in the bio-oil products of all three samples. A very minor presence of the OH groups was also monitored in the bio-chars produced from sugar cane and hemp, but not in the biochar produced from wattle tree. The double peak at 2920 and 2860 cm⁻¹ observed in all biomass samples was associated with the saturated aliphatic group, in particular the methylene C-H stretch. This group was also apparent in the produced biooils, particularly showing strongest appearance in case of the biooil produced from the wattle tree sample. The raw samples also exhibited very strong peak at 1035 cm⁻¹ related to Si-O-Si bond and the intensity of the peak corresponded to the ash content of each sample presented in Table I. Sugar cane, with ash content of 6.9% showed the largest intensity of this peak, followed by hemp at 4.6% and wattle tree at 2.8%. The biochars produced at 500°C also exhibited the same FTIR peak indicating that the silica from the raw biomass samples remains in the solid biochar product. The peak at 1620 cm⁻¹, most apparent in the raw wattle tree sample, was due to the aromatic C=C stretch. The same peak appeared in the biochar and to some extent in the biooil samples. The biooils also showed strong peaks at 1265 cm⁻¹ associated with the phenol C-O stretch and at 734 cm⁻¹ due to the aromatic C-H out of plane bend. The remaining small multiple peaks in the range between 1160 to 1520 cm⁻¹ observed in all raw biomass samples and the produced biooils are likely due to the aromatic ring group frequencies.

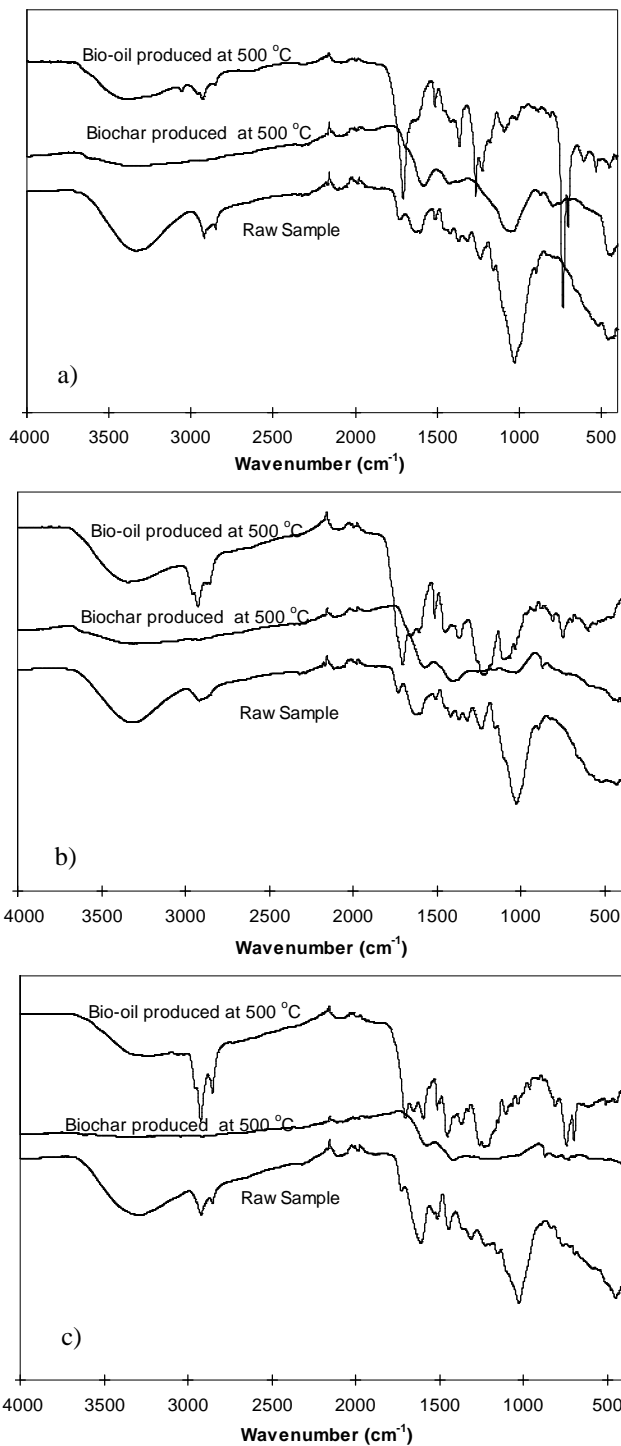


Figure 4. FTIR Analysis of the raw samples, biochars produced at 500°C and bio-oils produced at 500°C for (a) sugar cane; (b) hemp and (c) wattle tree.

The FTIR spectroscopy for analysis of biooil samples is very useful experimental technique that can be used to show how various bonds from the raw samples are redistributed to the biooil products during pyrolysis. However, for the purpose of identification of the various chemical compounds,

this technique needs to be supplemented with Gas Chromatography Mass Spectroscopy (GC-MS). In this work GC-MS technique was further applied to determine the major chemical compounds present in the biooil samples and the results are displayed in Table II.

TABLE II. MAJOR COMPOUNDS OF THE PYROLYSIS OILS PRODUCED AT 500°C

Sugar cane	
Area%	Name
13.97	2-Propanone, 1-hydroxy-
4.61	Phenol
4.56	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
4.37	Furfural
4.3	2-Propanone, 1-(acetyloxy)-
4.27	Pentanal
4.24	Phenol, 4-ethyl-
4.02	Phenol, 2-methoxy-
3.44	2-Propanone, 1-(1-methylethoxy)-
3.07	Phenol, 4-methyl-
Hemp	
Area%	Name
26.91	Acetic acid
14.8	2-Propanone, 1-hydroxy-
4.17	2-Furanmethanol
3.63	Cyclopropyl carbinol
3.29	Phenol, 2,6-dimethoxy-
2.99	2-Furanmethanol, tetrahydro-
2.77	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
2.15	Phenol, 2-methyl-
2.13	Phenol, 2-methoxy-
1.93	Nonacosane
Wattle tree	
Area%	Name
3.88	Phenol
3.38	Acetamide, N-methyl-N-(2-phenylethyl)-
3.12	Acetamide, N-(2-phenylethyl)-
3	Phenol, 4-methyl-
2.91	Phenol, 4-ethyl-
2.85	Dodecanoic acid, 2-hexen-1-yl ester
2.69	Cyclohexene, 1-octyl-
2.26	1,E-11,Z-13-Hexadecatriene
2.21	Phenol, 2-methoxy-
2.13	Acetic acid

Results shown in Table II contain the major 10 compounds detected in the biooil samples after integrating the GC-MS spectra. The results presented here show only the area of the GC-MS spectra integral with the major peak interpretation. The largest compounds detected in the pyrolysis oil sample was 1-hydroxy-2-Propanone (acetol) in case of the sugar cane pyrolysis oil, acetic acid in case of the oil produced from hemp and phenol in case of the wattle tree

pyrolysis oil sample. Various phenol groups were also detected as some of the major compounds in all three samples. The GC-MS result indicated that the bio-oils produced from pyrolysis of the selected biomass samples are highly variable in composition and are unlikely to be suitable for direct use, except for some cases of use of pyrolysis oils as industrial fuels. For the purpose of the use as commercial fuel product, their upgrading would be essential.

IV. CONCLUSIONS

Biomass pyrolysis provides an opportunity for system solution to energy supply and biological sequestration of carbon through agricultural application of the produced biochar. The work presented here outlines some of the product characterization approaches that can be applied to perform energy, mass and life cycle assessment required to model the pyrolysis system. The results indicated that the pyrolysis process has an initial endothermic reaction followed by largely exothermic heat of reaction, which means that the overall heat requirement to complete the pyrolysis process can be partially supported by the internal exothermic reaction. The analysis of the biochar and biooil samples suggest that the biochar contains the OH, aromatic C=C and inorganic Si-O-Si bonds. The biooil samples exhibited much more complex structure and were highly variable in composition suggesting requirement for their further upgrading. Feasibility assessment should also be performed in order to maximize the opportunity of the pyrolysis as a technological solution to biomass processing.

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