Fast pyrolysis of tropical biomass species and influence of water pretreatment on product distributions

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Executive Summary

A reactor was designed and commissioned to study the fast pyrolysis behavior of tropical biomass species as a function of temperature and volatiles residence time. Four temperatures between 400 and 600 °C were examined as well as four residence times between ~1.2 and 12 seconds. Pyrolysis product distributions of bio-oil, char and permanent gases were determined at each reaction condition. The elemental composition of the bio-oils and chars was also assessed.

The samples pyrolyzed in this study are two hardwoods: leucaena and eucalyptus, and three grasses: banagrass, energy-cane and sugarcane bagasse. Samples of pretreated banagrass and energy-cane were also pyrolyzed. The pretreatment used water washing/leaching to reduce the inorganic content of the banagrass and energy-cane. The untreated banagrass and pretreated banagrass were examined at all 16 reaction conditions (four temperatures at four residence times). The other samples were pyrolyzed at a single reaction condition (450 °C and 1.4 s residence time).

For untreated banagrass, the greatest bio-oil yield was recorded when working at 450 °C with a volatiles residence time of 1.4 s, ~37 wt% relative to the dry ash free feedstock (excluding pyrolysis water). The amounts of char (organic fraction) and permanent gases under these conditions are ~4 wt% and 8 wt% respectively. The bio-oil yield stated above is for 'dry' bio-oil after rotary evaporation to remove solvent, which results in volatiles and pyrolysis water being removed from the bio-oil. The material removed during drying accounts for the remainder of the pyrolysis products. The 'dry' bio-oil produced under these conditions contains ~56 wt% carbon which is ~40 wt% of the carbon present in the feedstock. The oxygen content of the 450 °C, 1.4 s 'dry' bio-oil is ~38 wt%, which accounts for ~33 wt% of the oxygen in the feedstock.

At higher temperature or longer residence time less bio-oil and char is recovered and more gas and light volatiles are produced. Increasing the temperature has a more significant effect on product yields and composition than increasing the volatiles residence time. At 600 °C and a volatiles residence time of 1.2 seconds the bio-oil yield from untreated banagrass is ~21 wt% of the daf feedstock, with a carbon content of 64 wt% of the bio-oil.

Comparing the bio-oil yields from the untreated and pretreated banagrass shows that the yields were greater from the pretreated banagrass by 4 to 11 wt% (absolute) at all reaction conditions. The effect of pretreatment (i.e. reducing the amount of ash, and alkali and alkali earth metals) on pyrolysis products is: 1) to increase the dry bio-oil yield, 2) to decrease the amount of undetected material, 3) to produce a slight increase in CO yield or no change, 4) to slightly decrease CO_2 yield or no change, and 5) to produce a more stable bio-oil (less aging). Char yield and total gas yield were unaffected by feedstock pretreatment.

Considering the results from all seven biomass samples, the best feedstocks for fast pyrolysis are sugarcane bagasse, pretreated energy cane and eucalyptus based on the yields of 'dry bio-oil', CO and CO_2. On the same basis, the least productive feedstock's are untreated banagrass followed by pretreated banagrass and leucaena.

The bio-oil yield from untreated banagrass is significantly lower than from woody biomass or grasses such as switchgrass, miscanthus, energy-cane or sugarcane bagasse, but is similar to barley straw. The reason for the low bio-oil yield from banagrass is thought to be related to its high ash content (8.5 wt% dry basis) and high concentration of alkali and alkali earth metals (totaling ~2.8 wt% relative to the dry feedstock) which are catalytic and increase cracking reactions during pyrolysis. The influence of alkali and alkali earth metals (AAEM) on reducing the bio-oil yield is confirmed by the results from the pretreated samples, where a reduction in AAEM results in greater bio-oil yields from banagrass and energy-cane.

Table of Contents

Introduction

Hawaii is the most fossil fuel dependent state in the United States. The 'Hawaii Clean Energy Initiative' aims to address this with a goal of producing 70 % of the state's energy from clean energy sources by 2030 [1]. Biomass fast pyrolysis is one of the potential pathways under investigation. Fast pyrolysis of woody biomass produces significant amounts of bio-oil, up to ~75 wt% of the dry-ash-free (daf) feedstock [2-7]. However, woody biomass species are typically less productive [8], i.e. lower annual dry matter yield, than herbaceous species. For this reason and in order to utilize biomass produced across the available landscapes, there is interest in the use of grasses and agricultural residues as fast pyrolysis feedstock's [2, 9-12].

Fast pyrolysis of agricultural residues, such as straws, tends to produce less bio-oil than woods or grasses (typically <50 wt% bio-oil from straws) [2, 9]. Sugarcane bagasse tends to produce significantly more bio-oil than straws. Although, the bio-oil yield from sugarcane bagasse can be highly variable depending on the growing conditions and the way cane is harvested, i.e. soil can be incorporated with the cane. Bio-oil yields from sugarcane bagasse typically range from ~50 to 70 wt% [13-17]. Grasses such as switchgrass and miscanthus (energy crops) also produce fairly high bio-oil yields, falling within the lower end of the range seen for woody biomass (~50-60 wt% bio-oil) [9-12].

Pennisetum is a genus of tropical and warm temperate grasses. Banagrass used in the present study is a cross between napier grass *(Pennisetum purpureum*) and pearl millet (*Pennisetum glaucum*) capable of producing 40 to 65 Mg fiber ha^{-1} yr^{-1} with nonirrigated and irrigated conditions representing the lower and higher end of this range, respectively [18-20]. In comparison, typical yields from switchgrass are 5 to 15 Mg fiber ha^{-1} yr^{-1} which can reach up to ~38 Mg fiber ha^{-1} yr^{-1} with longer growing seasons and ample water resources [21]. The higher heating value (HHV) of banagrass ranges from 17 to 18.5 MJ/kg (present study and reference [22]) which makes it an interesting prospect as a nonfood crop suitable for energy applications.

Banagrass has a high ash content (~4-15 wt% dry basis, typically ~9 wt%) and high content of alkali and alkali earth metals (AAEM) compared to most other types of biomass [20, 22, 23]. For

example, woods typically contain low amounts of ash, <2-3 wt% of the dry feedstock [23]. Switchgrass and miscanthus can contain between ~2-6 wt% ash [9, 10, 12], elephant grass ~5-7 wt% ash [24, 25], and napier grass ~3-9 wt% ash [26, 27]. A review of the composition of more than 80 biomass species has been reported [23]. It has recently been demonstrated that modern X-ray fluorescence instruments can provide data that is comparable to inductively coupled plasma methods for the inorganic composition (major and minor elements) of raw biomass, i.e. without the need to ash the sample [28, 29].

Ash chemistry plays an important role during biomass pyrolysis. Inorganic elements, and AAEM in particular, are responsible for catalyzing cracking reactions of biomass pyrolysis vapors which reduce bio-oil yields [2, 6, 9]. Shafidazeh et al. [30] were possibly the first researchers to show that a mild acid washing of wood powders before pyrolysis increased the yield of laevoglucosan. It was suggested that the improved bio-oil yield after acid washing was related to a reduction in potassium and magnesium which reduced cracking reactions.

Oasmaa et al. [2] found that the amount of ash, and in particular, the amount of alkali metals (Na + K) correlated with the amount of bio-oil that was produced via fast pyrolysis. Lower bio-oil yields were recovered for biomass species that contain more ash. Potassium and sodium are thought to be catalytic leading to increased cracking of bio-oil compounds into volatiles, gases and water. Biomass species with high ash contents also tend to produce a less stable bio-oil (more aging) [2, 12].

Mourant et al. [5] looked at the influence of AAEM on the fast pyrolysis of malle wood (*Eucalpytus loxophleba*), ash content < 1 wt%. Malle wood was washed with water or acid to remove AAEM. The results showed that reduction of AAEM did not significantly alter bio-oil or char yields, which is possibly due to the low amount of ash and AAEM originally present in malle wood. Reduction of the AAEM species increased viscosity, and increased yields of sugars and lignin derived oligomers. Washing also decreased the amount of pyrolysis water and light organic compounds in the bio-oil. Acid-washing was found to have a greater affect than water washing, with more Ca removed via acid washing.

Fahmi et al. [11] investigated the role of alkali metals and lignin on the pyrolysis of grasses (*Lolium* and *Festuca* varieties). The grasses where genetically mutated to contained differing amounts of lignin, between 2 and 6 %. Samples were also washed with water to reduce their ash content. The main findings were: 1) K and Na induced a strong catalytic effect on bio-oil cracking activity; 2) as the lignin content increased the metals content decreased; 3) as metals content increases char yields increase; and 4) less metals results in increased laevoglucosan yield and less hydroxyacetaldehyde. These findings support the mechanism suggested by Liden et al.[31], where AAEM promote an ionic route that favors ring-scission and formation of hydroxyacetaldehyde. However, Fahmi's study [11] was carried out using a thermogravimetric analyzer (TGA) and a pyrolysis-GCMS instrument which may give unreliable results compared to fast pyrolysis in a fluidized bed.

A follow up study by Famhi et al. [12] used a fluidized bed reactor to better understand their findings from TGA and PY-GCMS. The main findings were: 1) The role of metals is more dominate than the lignin concentration. 2) The high molecular mass species present in pyrolysis oil are mainly from the lignin. 3) As the amount of metals increases the light fraction increases (greater cracking) and less pyrolysis water is formed; 4) as metals decrease more gas is formed. In general, for biomass with high ash content, the quantity, quality and stability of the bio-oil improves after washing. The affect was less significant for switchgrass which contains low amounts of AAEM. Water washing of switchgrass resulted in a marginally lower viscosity (or no change), whereas for *Festuca arundinace* [12] the viscosity increased matching the behaviour of malle wood [5].

Considering the studies mentioned above, some general trends can be drawn where lowering the concentration of AAEM results in: 1) more bio-oil, 2) less volatiles, 3) less pyrolysis water, 4) less gas, 5) more char, 5) increased bio-oil viscosity, 6) a more stable bio-oil (less aging). However, there is some inconsistency in the findings from different researchers. Oasmaa [2] reported that decreasing AAEM results in less gas, whereas Fahmi [12] reported more gas, and Mourant [5] saw no effect. Oasmaa [2] and Mourant [5] also reported that decreasing amounts of AAEM results in less pyrolysis water but Fahmi [12] found the opposite. Fahmi [11] also reported that decreasing the amount of AAEM produces more char whereas the other groups did

not report that finding. The reason for these discrepancies are unclear but may be related to differences between the biomass varieties being examined, and the difficultly of simultaneously obtaining accurate data (amounts and composition) for all of the products from pyrolysis.

The amount of gas formed during biomass fast pyrolysis is also thought to be related to the hemi-cellulose contents of the feedstock, where higher amounts of hemi-cellulose lead to more acids and gases being formed [2]. More pyrolysis water is typically formed from hardwoods than softwoods under equivalent conditions, which is explained in terms of the hemi-cellulose in hardwoods containing more acetylated groups than softwoods which dehydrate during thermal decomposition producing water and furfural [4].

There are few reports on the pyrolysis of banagrass [20] or of *Pennisetum purpureum* species in general (elephant and napier grasses). Only one fast pyrolysis study was found for elephant grass [24]. However that study focused on charcoal production, bio-oil and permanent gas results were not reported. A couple of slow pyrolysis studies of napier and elephant grasses using fixed bed reactors have also been reported [25-27, 32].

Braga et al. [25] reported on the slow pyrolysis of elephant grass (*Pennisetum purpureum Schum*) after pretreatment via hot water or acid washing. Washing reduced the ash content from 6.9 wt% (wet basis) to 2.5 wt%, although the composition of the ash was not reported. Washing increased the volatiles yield from 77 wt% (wet basis) to 85 wt%. The washing also appeared to reduce the activation energy required to decompose elephant grass. However, the study was carried out using a thermogravimetric analyzer (TGA) and the maximum heating rate was 30 °C/min which makes their findings difficult to interpret. The problems associated with using TGA's for these types of study have been discussed elsewhere [6].

In this study, the fast pyrolysis of untreated and pretreated banagrass was examined in a fluidized bed reactor as a function of temperature (400 to 600 °C) and volatiles residence time (~1.2 to 12 s). The pretreatment used water washing/leaching to reduce the inorganic content of the banagrass. Four other tropical biomass species were also pyrolyzed under one condition (450 °C and 1.4 s residence time) for comparison to the banagrass results. The samples include two

hardwoods: leucaena and eucalyptus, and two grasses: sugarcane bagasse and energy-cane. A sample of pretreated energy-cane was also pyrolyzed. The samples used in this study were grown in the State of Hawaii.

Experimental

This section describes the experimental methods employed.

Sample preparation

Cellulose powder (MP biomedicas, LCC, USA. Part number: 191499, CAS: 9004-34-6) with an mean particle size of ~100 µm, a moisture content of 2.0 wt% and ash content of 0 % was used in the condition it was received.

Approximately 100 kg of ten month old banagrass was harvested from the Waimanalo Experiment Station of the University of Hawaii. The above ground material was processed into nominal 50 mm pieces (stalk and leaves) using a shredder (Vincent Corp., Tampa, FL) and dried to equilibrium moisture content (~10% moisture) using an ambient air drying bed. A representative sub sample of ~200 g was ground to particle sizes that passed through a screen with a 200 µm opening. Examination of the ground sample under a microscope revealed that approximately 60-70 % of the sample was a powder with a particle size in the range of 100 to 200 µm and ~30-40 % was rod-like with a diameter <200 µm and a length of ~400 to 600 µm. The proximate analysis (ASTM D 3172), ultimate analysis (ASTM D 3176) and ash composition (ASTM D3682, 600 °C) of banagrass were determined at an accredited laboratory (Hazen Research Inc., Golden, CO).

Total carbohydrate and lignin content (compositional analysis) of banagrass was measured in triplicate using the National Renewable Energy Laboratory procedure TP-510-42618 and instrumentation described elsewhere [33, 34]. The relative standard deviation of the results from compositional analysis are <2.0 %.

Fluidized bed reactor

A fluidized bed reactor was constructed and used for the first time in the present study. Many aspects of the design were adapted from Stiles [35, 36] including an inert sand fluidized bed, a moveable bed support plate, a mesh screen to retain char and fines in the bed, and a side-arm for volatiles removal from the free-board (Figure 1). Approximately 500 g of fresh sand was used as bed material for each experiment (Acros Organics, USA, acid washed sand, 40-100 mesh, mean particle size 205 μm, code number: 37094-0000, CAS: 14808-60-7). The elemental composition of the sand is SiO_2: 99.8 %, Fe_2O_3: 0.009 %, Al_2O_3: 0.040 %, TiO_2: 0.016 %, K_2O: 0.006 %, CaO: 0.005 %, Cr_2O_3: 0.00005 % (analysis provided by the supplier).

Three mass flow controllers are used to meter nitrogen to 1) fluidize the bed, 2) entrain feedstock from the fuel hopper into the bed and 3) sweep hot volatiles out of the top of the reactor. The latter helps protect the PTFE gaskets, used to seal the top of the reactor, from exceeding material temperature limits. Fluidization velocities of 2.75 to 3.75 times the minimum fluidization velocity were used. The nitrogen flow used to fluidize the bed is 7.5 LPM (STP) in all cases with an additional 1.5 LPM (STP) entering the top of the bed from the feeder drop-tube. Four bed positions were used to produce different volatiles residence times without altering the fluidizing conditions; corresponding residence times (RT) at each bed position (BP) and temperature are given in Table 1 along with the flow rates required to achieve the minimum fluidization velocity.

A three zone split tube furnace is used to electrically heat the reactor (Thermcraft Ltd, USA). Each zone of the furnace can be independently controlled. Two multi-point temperature probes (Omega Engineering Inc., Stamford, CT) were used to measure the axial temperature profile of the bed and free-board. The first multi-point probe contained four thermocouples (TC); T1 is located in the bed ~5 mm above the bed support plate, T2 is ~5 mm below the top of the stationary bed, T3 is ~25 mm above the bed screen and T4 is in the freeboard. A second multi-point probe contained two thermocouples; T5 is located at the exit of the free-board into the side-arm and T6 is positioned in the top of the reactor above the heat shield. The heat shield is a 38

mm thick stainless steel disc suspended from the top end-cap and located 5 mm above the side-arm exit to prevent overheating the PTFE seals in the top of the reactor.

The reactor body is constructed from 316 stainless steel pipe with inner diameter of 82.8 mm, outer diameter of 88.9 mm, and length of 1.57 m. The central 1.22 m of the reactor body is heated by the furnace and 18.5 cm protrude from either end. A stainless steel water cooled sample drop-tube with an additional, outer, vacuum jacket was used to transfer the feedstock from a glass hopper into the bed. The heating rate of the feedstock as it enters the bed is estimated to be ~400 °C/s.

The position of the bed support plate / gas distributor can be adjusted to alter the volatiles residence times without changing fluidizing conditions in the bed. Four inch stainless steel sanitary fittings are used to seal the top and bottom of the reactor with Swagelok tube fittings welded into the end-caps to support the drop tube, temperature probes, and the gas distributor, see Figure 1. PTFE seals were used on these connections to allow positioning within the reactor to be altered. Water cooling is applied to the top and bottom 15 cm of the reactor via external copper coils to protect the PTFE gaskets and ferrules in the end-caps from excessive heat.

As in the Stiles design the fluidizing gas enters through the 'support tube' for the bed support assembly. The 'support tube' is blocked after it enters the reactor body, with holes drilled in the tube so the gas is forced out into the reactor body and is heated through contact with the reactor walls before passing through a gas distributor packed with ceramic chips. The bed support plate assembly acts as a gas distributor and gas pre-heater. A 25 mm wide strip of woven ceramic cord is wrapped around a recessed groove in the top section of the gas distributor body to seal the space between the assembly and the reactor wall. The bed support plate is made by stretching a piece of wire mesh screen over the top of the distributor body which creates a seal against the inner wall of the reactor body when it is inserted into the reactor. The wire mesh cloth / screen used in the reactor is made of 304 stainless steel, 230 x 230 mesh, 0.0014" wire (McMaster-Carr, USA, part number: 85385T879).

A wire-mesh screen attached to the drop tube, denoted as the 'bed screen,' is located ~5 cm above the stationary bed to prevent losses of char from the bed (see Figure 1). An additional wire mesh screen was placed in the flange gasket that connects the exit side-arm to the first bio-oil trap. The side-arm is heat traced from the exit of the furnace to the flange to maintain a gas temperature of 340-360 °C. The flange connecting the side arm and the traps is cooled with dry-ice to quench the exiting vapors and collect them in two, liquid-nitrogen cooled, stainless steel traps in series. A slip-stream of the permanent gases exiting the second bio-oil trap passes through a train of on-line gas analyzers. The standard operating procedure (SOP) for setting-up the pyrolysis reactor is provided in Supporting Information section S1 and the SOP for disassembling the reactor in section S2.

Residence times are based on the dimensions of the freeboard and do not include the time taken for the vapors to pass through the side-arm to the bio-oil traps. Including the side-arm volume increases the RT by ~0.5 seconds.

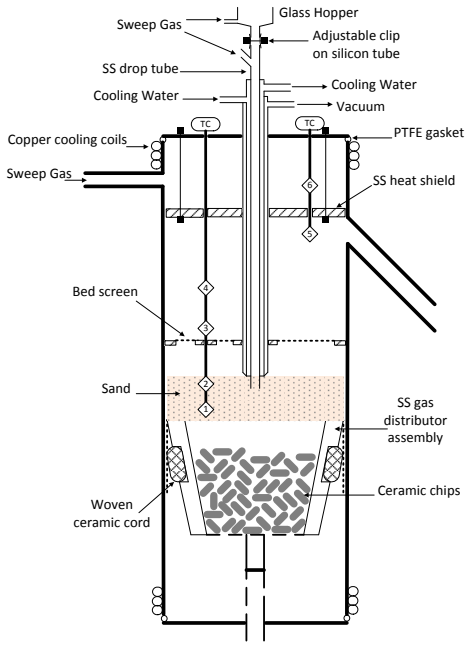

Figure 1. Schematic diagram of the variable-freeboard pyrolysis reactor. Numbers 1 through 6 show the locations of the thermocouples in the multi-point temperature probes (SS - stainless steel).

Table 1. Volatiles residence times (seconds) at the working velocity and flow rates (LPM, STP) to achieve minimum fluidization velocity, for the four different bed positions and four temperatures used in this study. The times are derived from the volume of the freeboard alone, excluding the side-arm where the volatiles pass to the bio-oil traps.

Temperature	Flow rate	Bed Position			
°C	SLPM	BP-1	BP-2	BP-3	BP-4
		Seconds			
400	~2.7	12.2	8.3	4.6	1.5
450	~2.5	11.3	7.7	4.2	1.4
500	~2.3	10.6	7.2	4.0	1.3
600	~2.0	9.4	6.4	3.5	1.2

Experimental procedure

The reactor was heated to the desired temperature and held at these conditions for at least 45 minutes to ensure uniform heating throughout the reactor before introducing the feedstock. The feedstock was fed into the bed from a gravity-flow hopper connected to the top of the drop-tube. Approximately 7.5 g of feedstock was used for each experiment and took 1.5 to 2.5 minutes to feed into the reactor. Fuel pyrolysis was considered complete when the elevated CO concentration in the exit gas from the process returned to <0.1 vol.% as observed with online gas analyzers. At 600 °C, pyrolysis was completed within ~4-5 minutes of starting to feed the fuel; at 400 °C it took ~8-10 minutes. The majority of the gas (>90 %) was released in a 3-4 minute time interval independent of temperature. In all cases, heating and all gas flows were stopped 15 minutes after fuel feeding was initiated. Immediately after stopping the experiment, the oil traps were removed from the reactor at the side-arm flange and the bio-oil recovered.

The first oil trap contained an inline soxhlet thimble (Whatman, UK, part number: 2800-373). Both traps were packed with stainless steel wire balls (Scotch-Brite® Stainless Steel Scrubber 84-1-4) to aid heat transfer and to provide additional cold surfaces for condensation. In addition,

four small pieces of wire mesh were placed in the tubing connecting the outlet of trap-1 to the inlet of trap-2 to further aid bio-oil condensation.

Bio-oil was recovered from the traps by washing with a mixture of 80 vol. % acetone and 20 vol. % methanol (HPLC grade, Fisher Chemicals). Liquids from the soxhlet extraction of the thimble from the first oil trap and the rinse from the first oil trap were combined. The rinse from the second oil trap was analyzed separately. The amount of bio-oil recovered from the second trap was always less than 5 wt% of the total bio-oil (typically <2 wt% of the total bio-oil) indicating that all the bio-oil was being captured. Bio-oil solutions were filtered after recovery (Whatman, UK, part number: 1004090).

Samples of the bio-oil solutions (trap-1 and trap-2) were analyzed separately by GCMS. The two bio-oil solutions were stored overnight at -20 °C. A rotary evaporator operating at 55 °C with a nitrogen purge and a maximum vacuum of ~25" Hg was used to remove the solvent. Three sub-samples from each bio-oil solution were dried and the mean of these determinations is defined here as the 'dry' bio-oil yield. Repeatability of the dry bio-oil yield was assessed by repeating the experiment three times, producing bio-oil solutions from the two oil traps from each experiment, and then sub-sampling and analyzing each oil trap solution three times. In total, three experiments produced a total of eighteen dry bio-oil samples. From this, a standard deviation of ≤2 wt% (absolute) of the daf feedstock was determined. The bias in the dry bio-oil yield is discussed in the results section. A sample of the dry bio-oil was dissolved in fresh solvent and analyzed by GCMS. Comparing this dry bio-oil analysis with the analysis of bio-oil solutions before they were dried provides an estimate of the ‘volatile bio-oil’ fraction removed with the solvent during rotary evaporation. The repeatability and bias of the 'volatile bio-oil' yield is discussed in the GCMS experimental section. Rotary evaporation resulted in water being lost from the bio-oil samples, therefore determination of pyrolysis water was not attempted.

After the reactor cooled down, the drop tube assembly was removed and any char caught in the bed screen collected. The top of the reactor was then capped off and the side-arm gasket, with wire mesh screen, was installed at the exit flange. The bed was fluidized with ambient temperature air at 45 LPM for 5 minutes to elutriate the char from the bed. The char was

recovered from the side-arm gasket screen and weighed. The amount of char remaining in the bed was estimated by combusting the bed material in a muffle furnace at 600 °C and recording the difference in weight. Typically, less than 10 wt% of the char remained in the bed after air recovery. When the bed was in its highest position (BP-4) the air flow rate was reduced to 15 LPM to prevent sand from being ejected with the char which typically resulted in more char (up to ~30 %) remaining in the bed. The reported char yields included char recovered by the soxhlet thimble and by filtering the bio-oil solutions. The repeatability of the char yield determinations was ~±1.5 wt% (absolute). The bias in the char yield is estimated to be ≤±2.0 wt% (absolute). Char samples were ashed in a muffle furnace at 600 °C, accordingly, char yields were corrected to a dry ash free (daf) basis. Char yields are reported for the organic fraction ($Char_{Org}$) excluding ash, i.e. on a daf basis relative to the daf feedstock. Char yields are also reported inclusive of ash ($Char_{Org+Inorg}$) on a dry basis relative to the dry feedstock.

Uncertainty, Repeatability and Bias

The terminology used to discuss uncertainty associated with the pyrolysis experiments are defined as follows. The repeatability (or precision) of the results is assessed in terms of the standard deviation which is derived from repeated measurement of the same sample under the same conditions. The bias refers to an estimate of the accuracy of the results based on an assessment of potential sources of losses throughout the various procedures, as well as referring to systematic uncertainties in the data which are estimated through comparison with literature values, where possible.

GCMS

A Bruker SCION GCMS with a BPx-1701 column (Restek corp., USA. 60 m x 0.25 mm, x 0.10 µm) was used to analyze the bio-oils. The analysis used an injector temperature of 280 °C. The column temperature was held at 40 °C for 4 minutes, ramped to 280 °C at 3 °C/min and then

held at 280 for 20 minutes. The conditions are based on those reported by Mohan et al. [37]. A certified standard (Restek corp., USA) was used to produce a calibration curve for 17 individual compounds: cyclohexane (CAS 110-82-7), furfural (CAS 98-01-1), 3-methyl-2-cyclopenten-1-one (CAS 2758-18-1), phenol (CAS 108-95-2), 4-methylphenol (p-cresol, CAS 106-44-5), 2-methylphenol (o-cresol, CAS 95-48-7), 3-methylphenol (m-cresol, CAS 108-39-4), 2-methoxyphenol (guaiacol, CAS 90-05-1), 2,4-dimethylphenol (CAS 105-67-9), 4-ethyl phenol (CAS 123-07-9), 2-methoxy-4-methyl phenol (creosol, CAS 93-51-6), indole (CAS 120-72-9), 2-methoxy-4-(prop-1-en-1-yl)phenol (isoeugenol, CAS 97-54-1), 2,6-dimethoxy phenol (CAS 91-10-1), 2,2-dimethoxy propane (CAS 77-76-9), benzene (CAS 71-43-2) and naphthalene (CAS 91-20-3). A six point calibration covered the concentration range of ~5 to ~150 µg/mL. Dodecane (CAS 112-40-3) was used as an internal standard.

Each bio-oil solution was analyzed in triplicate so that the relative standard deviation (RSD) could be determined, with regular blank runs (solvent only) performed to avoid carryover of species from one sample to the next. The RSD derived from the calibration and sample data was ≤5 %. The lower limit of quantification (LLQ) for each compound in the calibration is presented in Supporting Information, Tables S3.1-S3.9. The LLQ is defined as the point where the calibration became unreliable, i.e. where the RSD exceeded 20 %.

Note: The compounds removed from the bio-oil samples during rotary evaporation are referred to as 'volatile bio-oil' in the tables. In almost all cases the 'volatile bio-oil' yields are below the LLQ for the calibrated compounds (17 compounds). The reason for these low concentrations is mainly due to the amount of solvent required to recover the bio-oil from the traps (~1 L). If each calibrated compound was present in the sample at the LLQ it would introduce a total bias of ~2.0 wt% to the volatile bio-oil yield relative to the feedstock (daf). However, this '~2 wt%' bias is probably a gross underestimate due to the low concentration of the solutions (~3 mg/mL) which is further exacerbated as less than half the peaks observed in the bio-oil GC chromatograms are calibrated. The concentration of the bio-oil solutions would have to be increased by an order of magnitude to obtain more reliable GCMS data.

Elemental Analysis of the bio-oils and char (for C, H and N)

The carbon, hydrogen and nitrogen contents of the 'dry bio-oil' and char samples were determined by combustion analysis (Exeter Analytical Model CE 440 elemental analyzer). Using 3 to 6 mg subsamples, a minimum of five (typically eight) analyses were performed on each dry bio-oil and char sample. The standard deviations associated with these analyses are reported in the results section. The bias of the instrument, based on analysis of known samples, is on the order of 1.0 % relative [38].

Permanent Gas analysis (CO, CO_2, CH_4 and H_2)

Permanent gases were analyzed using two online gas analyzers, 1) a Uras 10E three channel non-dispersive infrared analyzer for CO, CO_2 and CH_4, and 2) a Caldos 5G continuous flow thermal conductivity detector for H_2. The analyzers were supplied by Applied Automation/Hartmann & Braun, Bartlesville, USA. The detectors were calibrated using certified zero and span gases.

Values reported for permanent gases can only be considered as 'indicative' due to cross interference between gas species and the transient nature of the gases emitted from the batch pyrolyzed sample. In a previous gasification study using the same analyzers the results were found to be very close to those obtained from GC analysis [39]. The greatest deviation was for CO_2, where in the worst case, the online analyzer was determined to be 10 % (relative) lower than the GC measurement. Therefore the bias in the permanent gas yield determinations is estimated to be ± 10 % (relative); although the bias may be higher due to the lower amount of producer gas generated in the present study compared to gasification, e.g. nitrogen accounted for >95 vol. % of the gas passing through the analyzers. The repeatability of the permanent gas yields are presented in the results section. The term 'permanent gases' refers solely to CO, CO_2, CH_4 and H_2 and not to other gases formed during pyrolysis.

Results - feedstock properties:

The fuel properties (proximate, ultimate and compositional analysis, and heating values) of the biomass feedstocks used in this study are presented in Table 2. The label 'S3' refers to pretreated samples which have undergone water washing. Figure 2 presents the results from compositional analysis in a ternary plot. The elemental analysis of the ashes from the various feedstock's are displayed in a ternary plot as wt% of the ash in Figure 3 and in Table 3 as wt% of the dry feedstock. The data plotted in Figure 3 is tabulated in Supporting Information, Table S4.1.

Table 2. Fuel properties of leucaena, eucalyptus, sugarcane bagasse, energy cane, pretreated energy cane (S3), banagrass and pretreated banagrass (S3).

	Leucaena	Eucalyptus	S-Bagasse	E-Cane	E-Cane S3	Banagrass	Banagrass S3
Moisture[#] wt%	6.2	6.1	5.5	6.7	5.6	3.0	0.5[α]
Proximate analysis (wt% dry basis)[β]							
Ash	1.5	0.7	7.6	6.6	3.2	8.5	5.1
Volatiles	83.2	86.3	82.4	78.7	86.4	83.3	84.6
Fixed C	15.3	13.0	10.0	14.7	10.4	8.3	10.4
SUM	100.0	100.0	100.0	100.0	100.0	100.1	100.0
Heating values (MJ/kg dry basis)							
HHV	18.9	18.4	18.0	17.1	18.6	16.8	18.5
LHV	17.6	17.1	16.8	15.9	17.4	15.7	17.2
Ultimate analysis (wt% dry-ash-free basis)[β]							
Carbon	49.8	50.3	51.7	50.4	53.0	51.1	52.3
Hydrogen	6.1	6.0	6.0	5.9	5.9	5.7	6.0
Nitrogen	0.3	0.1	0.5	0.4	0.3	0.5	0.2
Sulfur	0.02	0.05	0.04	0.32	0.05	0.11	0.03
Oxygen*	43.7	43.5	41.9	42.6	40.7	41.2	41.4
Chlorine	0.09	0.06	0.02	0.3	0.01	1.3	0.03
SUM	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Compositional analysis (wt% dry-ash-free basis)[ε]							
Lignin	28.0	26.7	25.5	22.7	26.9	23.5	22.5
Cellulose	41.5	43.7	39.2	37.0	36.3	35.5	36.9
Hemi-cellulose	12.8	9.9	20.2	14.7	17.3	17.5	18.1
SUM	82.2	80.3	84.9	74.4	80.5	76.5	77.5

Moisture content of the biomass samples after grinding to <200 μm particle size
*Oxygen by difference
[α] Banagrass S3, this sample was oven dried to aid grinding.
[β] Standard deviation is estimated to be < 0.5 wt% of the absolute values
[ε] Relative standard deviation is < 10 %.

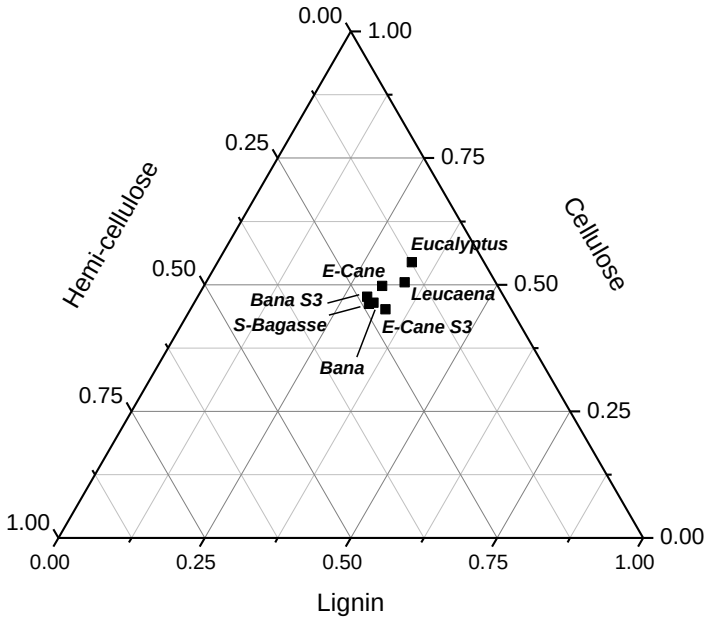

Figure 2. Ternary plot of the compositional analysis of biomass samples examined in this study - using the approach proposed by Vassilev et al. [23]. The data from Table 2 was normalized to 100% before plotting the points.

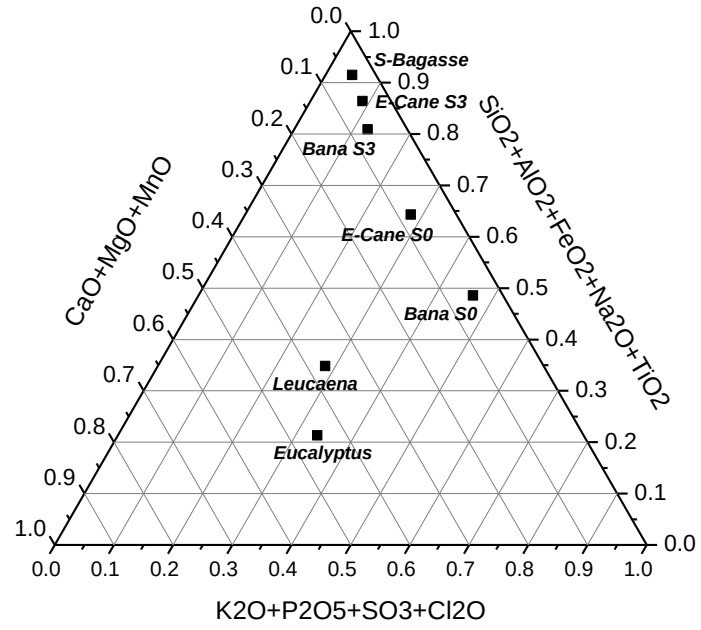

Figure 3. Ternary plot of the ash forming elements in the biomass samples - using the approach proposed by Vassilev et al. [23]. The data from Table S4.1 was normalized to 100% before plotting the points (wt% of the ash), and no data was available for MnO.

Table 3. Elemental analysis of the ash from leucaena, eucalyptus, sugarcane bagasse, energy cane, energy cane S3, banagrass and banagrass S3, the ash was calcined at 600 °C prior to analysis. Presented as wt% of the dry feedstock.

Sample	Element	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3	Cl	CO_2
Leucaena	wt%	0.3	0.1	0.002	0.11	0.4	0.1	0.03	0.3	0.1	0.01	0.10	0.1
Eucalyptus	wt%	0.02	0.02	0.001	0.04	0.2	0.04	0.04	0.1	0.1	0.01	0.01	0.1
S-bagasse	wt%	3.0	1.6	0.30	1.5	0.2	0.1	0.1	0.2	0.1	0.1	0.001	0.02
E-Cane	wt%	4.1	0.1	0.001	0.03	0.4	0.1	0.1	0.9	0.2	0.5	0.20	0.02
E-Cane S3	wt%	2.1	0.04	0.003	0.06	0.1	0.03	0.02	0.1	0.05	0.05	0.001	0.01
Banagrass	wt%	4.0	0.1	0.001	0.04	0.2	0.2	0.04	2.3	0.5	0.1	1.00	0.1
Banagrass S3	wt%	3.1	0.1	0.001	0.09	0.2	0.1	0.03	0.3	0.1	0.04	0.02	0.1

The values for untreated banagrass in Table 2 are in close agreement with those previously reported for banagrass [20, 23]. The composition of the ash (Table 3) is also fairly typical for 'herbaceous and agricultural grasses (HAG)' [23], although the ash content of banagrass is greater than most other types of biomass or HAG energy crops such as switchgrass. In particular, K_2O (~27 wt%) and Cl (~12 wt%) are present in very high concentrations in the ash and there are significant amounts of MgO and CaO (~2.5 wt% each). SiO_2 accounts for about 50 wt% of the ash.

Furthermore, the results in Table 2 show that the woods have greater HHV than the grasses. Pretreatment of banagrass and energy cane increased their heating values to similar levels as the woods. The main effect of pretreatment was to decrease the amount of ash and, and as a result increase the percentage of volatiles. For energy cane, pretreatment reduced the amount of fixed carbon, whereas for banagrass fixed carbon increased. Pretreatment also reduced the amounts of chlorine, sulfur and possibly nitrogen, and concomitantly increase the percentage of carbon.

The compositional analysis (Table 2, Figure 2) shows that pretreatment results in a slight increase (or no change) in the amount of lignin, cellulose and hemi-cellulose which is more significant for energy cane than banagrass. This is thought to be due to the pretreatment removing some of the extractives from the samples. All the samples fall into the CLH type

classification; i.e. based on the order of decreasing content of the components [23]. A review of > 80 biomass varieties has shown that straws, grasses and sugarcane bagasse tend to be CHL type; although elephant grass is HLC type. Woods are typically CLH type [23]. In comparison to literature [23], our samples contain relatively low amounts of hemi-cellulose which matches previous analyses of these samples [8]. The hardwoods have the highest cellulose content with energy cane and banagrass having the lowest. The hardwoods and pretreated energy cane have the highest lignin contents. For hemi-cellulose, sugarcane bagasse, pretreated energy cane and untreated or pretreated banagrass have the highest contents. Overall, the differences between the samples are relatively small as can be seen in Figure 2.

The ternary plot of ash forming elements (Figure 3) shows that eucalyptus and leucaena are located in a region typical for woody biomass species. Refer to reference [23] for the locations and classification of > 80 biomass varieties based on plots of their ash composition. The untreated banagrass and energy-cane are in the region typical for 'herbaceous and agricultural grasses' [23]. Whereas, after pretreatment the banagrass and energy-cane (S3) ashes are more similar in composition with rice husks and coals - mostly due to the high proportion of silica. The ash from sugar-cane bagasse also falls in the coal region close to bituminous coals which is the result of high concentrations of iron and alumina due to soil incorporation with the sugarcane during harvest. Biomass that is located in the coal region of the ternary plot typically have high melting points and are unlikely to cause deposition problems during combustion - although they are abrasive. For banagrass, its high potassium content is likely to cause deposition problems during combustion even after pretreatment. Further details of the conclusions that can be drawn from the ternary plot can be found elsewhere [23].

Table 3 shows that Si is the dominant inorganic element in the grasses accounting for ~4 wt% of banagrass and energy cane (dry basis) and 3 wt% for sugarcane bagasse which is similar to the amount in the pretreated banagrass and energy cane. Potassium is the next most dominant element with 2.3 wt% in banagrass and 0.9 wt% for energy cane, which are reduced to 0.3 and 0.1 wt% respectively, after pretreatment which is similar to the amount of K in sugarcane bagasse. Sugarcane bagasse contains 1.6 wt% Al, whereas all the other samples contain ≤ 0.1

wt% Al. Pretreatment of banagrass and energy cane reduces the amount of Si, K, P, Na, Ca, Mg, Cl and S.

Results - cellulose data, reactor performance and uncertainty:

Tests were first performed with cellulose to evaluate the repeatability performance of the reactor system in terms of product distribution, with bias being assessed through comparison to literature values. Only four process conditions were examined with cellulose, two bed positions (BP-1 gives the maximum residence time and BP-4 the minimum RT) and two temperatures (400 and 600 °C). Table 1 presents the set of 16 residence times spanning an order of magnitude range from 1.2 s to 12.2 s (i.e. four temperatures and four bed positions) that were used to pyrolyze banagrass.

The bio-oil, char, and gas yields from cellulose pyrolyzed at the longest residence time (BP-1) are presented in Table 4 and for the shortest residence time (BP-4) in Table 5. A summary of the char yields from cellulose pyrolysis are given in Table 6. Repeat experiments were made with cellulose and banagrass to determine standard deviations as shown in Tables 4 and 7, respectively. For all the other conditions only one experiment was performed due to time considerations. The repeatability of the data, as shown in Tables 4 and 7, is considered representative of the general reactor performance.

Table 4. Bio-Oil, char and gas yields (daf) from cellulose pyrolysis, at the longest residence times (BP-1)

Temperature	Dry Bio-oil	Volatile Bio-oil[#]	Char*	^CO CO_2 CH_4 H_2	Undetected**
°C	wt%	wt%	wt%	wt%	wt%
400	60.5	n.d.	3.2	n.d.	n.a.
400	63.1	n.d.	3.7	n.d.	n.a.
400	62.3	n.d.	4.4	n.d.	n.a.
400	64.3	n.d.	2.8	5.9	27.0
600	16.2	n.d.	0.6	50.6	32.5
600	16.9	n.d.	0.2	44.5	38.4
600	12.7	n.d.	1.3	42.8	43.1
400 mean	62.5	n.a	3.5	n.a.	n.a.
400 S.D.	1.4	n.a	0.6	n.a.	n.a.
600 mean	15.3	n.a	0.7	46.0	38.0
600 S.D.	1.8	n.a	0.4	3.3	4.3

[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during rotary evaporation and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be ≤±2 wt% (absolute).
** 'Undetected' is derived as: 100% - (dry bio-oil + volatile bio-oil + char + CO, CO_2, CH_4 and H_2 yields).
n.d. not determined, due to instrument unavailability.
n.a. not applicable.
S.D. is the standard deviation.

Table 5. Bio-oil, char and gas yields (daf) from cellulose pyrolysis, at the shortest residence times (BP-4)

Temperature	Dry Bio-oil	Volatile Bio-oil[#]	Char*	^CO CO_2 CH_4 H_2	Undetected**
°C	wt%	wt%	wt%	wt%	wt%
400	69.5	0.1	2.6	2.4	25.4
600	55.3	<LLQ	1.8	11.8	31.1

<LLQ, less than the lower limit of quantification.
[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during rotary evaporation and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be ≤±2 wt% (absolute).
** 'Undetected' is derived as: 100% - (dry bio-oil + volatile bio-oil + char + CO, CO_2, CH_4 and H_2 yields).

Table 6. Summary of char yields (daf) from cellulose pyrolysis

Temperature	Mean Char	Standard Deviation	Number of tests
°C	wt%	wt%	n
400	*3.3*	*0.6*	5
600	*1.0*	*0.6*	4
The bias in the char yield is estimated to be ≤± 2 wt% (absolute).			

The results presented in Table 4 characterize the pyrolysis bio-oil, char, and gas yields obtained from the reactor system at two temperatures using cellulose as feedstock at the maximum residence time, BP-1. At 400 °C, the dry bio-oil and char yields were 62.5 ±1.4 wt% and 3.5 ±0.6 wt%, respectively, of the daf feedstock. Note that the uncertainty is the standard deviation of repeated experimental results and is reported on wt% absolute basis. At 600 °C, the dry bio-oil and char yields were 15.3 ±1.8 wt% and 0.7 ±0.4 wt%, respectively, of the daf feedstock. Measurements at 600 °C provided an estimate of gas yields of 46 ±3.3 wt%. The "Undetected" amount in Tables 4, 5 and 7 includes gases other than CO, CO_2, CH_4 and H_2 and volatile material that could not be quantified by GCMS due to interference by the solvent (acetone/methanol), including pyrolysis water. This is in addition to compounds that were detected by GCMS but were not calibrated (at least half the peaks in the chromatograms were not calibrated) and poor quantification of calibrated compounds due to the low concentration of the bio-oil solutions as described in the GCMS experimental section.

Reactor performance and uncertainty: The standard deviations in Table 4 are presented as percentages of the measurements in Figure 2. The uncertainty follows a decreasing trend as the product yield increases. Table 6 displays the repeatability of product yields from banagrass pyrolysis. Despite the less homogeneous molecular structure of the banagrass compared to cellulose, the standard deviations for repetitive bio-oil and char results are <0.5 wt% (absolute) and for permanent gas results are <1.5 wt% (absolute). The data indicate excellent performance of the reactor system and experimental protocols.

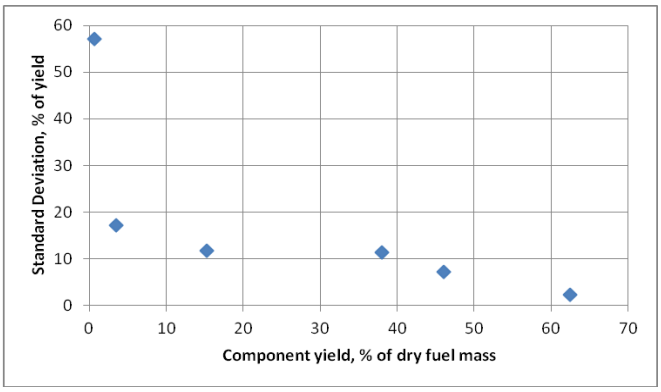

Figure 2. Component yields and their associated standard deviations.

To further assess the reactor performance and to check for systematic bias in the results, the bio-oil yields from cellulose pyrolysis are compared to those reported by Stiles et al. [35]. As shown in Table 5, the shortest residence times (BP-4) is 1.5 s at 400 °C and 1.2 s at 600 °C, the bio-oil yields are 69.5 wt% and 55.3 wt% of the daf feedstock, respectively. The corresponding bio-oil yields reported by Stiles for a residence time of 1.21 s are ~80 wt% and ~60 wt% at 400 and 600 °C, respectively; the values were estimated from a graphical representation of their results (Figure 3, Stiles et al. [35]). The 80 wt% oil yield from cellulose pyrolysis at 400 °C has also been confirmed by Fraga who used a wire-mesh reactor which greatly reduces extra-particle reactions (i.e. vapor RT <0.1 s) [6, 15]. The yields from the present study are ~10 wt% (absolute) lower than reported by Stiles at 400 °C and ~5 wt% at 600 °C. The possible reasons for the differences in bio-oil yield between the two studies are discussed below.

The char yields from cellulose pyrolysis at 400 and 600 °C are 3.3 and 1.0 wt% daf (S.D. 0.6 wt%), respectively (Table 6). The corresponding char yields reported by Stiles at 400 and 600 °C were 3 wt% (daf) and "a value too small to be determined", respectively, and both values were less than the uncertainty (±5% of daf feedstock, absolute) associated with the measurement [35]. Despite this, the char yields from Stiles show close agreement with the Table 6 values. Differences in char yields between the two studies are therefore not the cause of differences in the cellulose pyrolysis oil yields. Incomplete bio-oil recovery, cracking of the bio-oil vapors into lighter products, experimental error, or slight differences in experimental conditions are possible reasons.

The lower cellulose bio-oil yields (Table 5) compared to those reported by Stiles [35] are unlikely to be related to slight differences in residence times between the two studies; i.e. in the present study the residence time at 400 °C is ~1.5 seconds and ~1.2 seconds at 600 °C, while in the Stiles study the residence time at 400 and 600 °C is 1.21 seconds. This is because Stiles data shows that at 400 °C the bio-oil yield from cellulose was ~80 wt% over a range of residence time from 0.25 s to 2.44 s. Therefore, a more probable cause for the different bio-oil yields is a difference in the temperature regime across the bed and free-board between the two studies. In Stiles's work, a single temperature measurement was made in the bed to control the single heating-zone furnace. In the present study two temperature measurements are made across the bed as well as four positions along the freeboard. The three furnace heating zones were set to produce as uniform a temperature profile as possible across the bed and freeboard. Therefore, in the present study the temperature in the freeboard is likely to be higher than in Stiles's work. For example, the bio-oil yield from cellulose at 450 °C reported by Stiles is ~74 wt% at 1.21 s residence time, which is similar to the bio-oil yield at 400 °C in the present study (~70 wt%).

The temperature distribution across the bed and freeboard for each reaction condition is given in Supporting Information, Tables S5.1 to S5.4. Here it is shown that at shorter residence times the temperature distribution is less uniform due to the position of the bed relative to the three zones of the furnace. For example, when the bed support plate is in its highest position (BP-4) both the bed and freeboard are mainly being heated by the top zone of the furnace. This means it is not possible to maintain the same temperature in the freeboard as in the bed.

The other main source of bias identified for the bio-oil yield was related to deposition of bio-oil in the side-arm where pyrolysis vapors exit the freeboard enroute to the oil traps. Heavy-oil deposits were observed in the section of the side-arm that transitions from being heated to being cooled. This occurs in the ~5 cm of tubing immediately after the heated flange connection and immediately preceding the dry ice-cooled section leading to the first trap. Despite the cooling, it appears that bio-oil that deposits in this section quickly ages (recombination/polymerization reactions) into a heavy oil/tar due to the tubing still being hot. It is probable that the heavier bio-oil compounds preferentially deposit in this region due to their higher condensation

temperatures. Although it is not possible to quantify the deposited bio-oil fraction, it appears to be minor compared to the total experimental mass balance, given the geometry of the arm and possible maximum amount of condensation in this area

The potential sources of bio-oil losses due to deposition, as discussed above, would not be unique to the present study; i.e. the same types of losses would be anticipated in Stiles's results due to the similarities of the reactor designs. It is probable, therefore, that the differences in the bio-oil yields reported here and in the Stiles study are a reflection of differences in experimental conditions and / or experimental error.

In summary of the cellulose results, the reactor system shows good repeatability with a standard deviation of ≤2.0 wt% for dry bio-oil and char yields, and ≤3.5 wt% for the gas yields. There may be a systemic bias in the data, however, that underestimates cellulose bio-oil yield by a maximum of ~10 wt% (absolute) at 400 °C and ~5 wt% at 600 °C. This level of bias is considered acceptable in light of the points described above and is probably a reflection of small differences in experimental conditions (temperature and residence time) and/or due to experimental errors.

Results - Untreated banagrass pyrolysis, bio-oil, char and gas yields:

The bio-oil, char and gas yield data obtained from the pyrolysis of banagrass as a function of temperature at the longest residence time (see Table 7) demonstrate the experimental repeatability. Figures 3 and 4 show the dry bio-oil and permanent gas yields, respectively, as a function of temperature and vapor residence time. Char and ash yields are summarized in Table 8. The complete set of data tables can be found in the Supporting Information, Tables S6.1 to S6.3.

Table 7. Bio-oil, char and gas yields (wt% daf) from banagrass pyrolysis at longest residence times (BP-1)

Temperature	Dry Bio-oil	Volatile Bio-oil[#]	$Char_{org}$*	^CO CO_2 CH_4 H_2	Undetected**
°C	wt%	wt%	wt%	wt%	wt%
400	29.1	<LLQ	8.0	8.1	54.8
450	27.7	<LLQ	4.5	12.0	55.8
450	27.0	<LLQ	3.9	12.5	56.6
450	28.1	<LLQ	4.1	11.4	56.4
500	25.3	<LLQ	3.2	15.0	56.5
600	9.7	<LLQ	1.4	36.7	52.1
600	10.0	<LLQ	1.7	34.6	53.7
600	9.3	<LLQ	n.a.	33.6	n.a.
450 mean	27.6	<LLQ	4.2	12.0	56.3
450 S.D.	0.4	n.a.	0.3	0.4	0.4
600 mean	9.7	<LLQ	1.5	35.0	52.9
600 S.D.	0.3	n.a.	0.1	1.3	0.8

<LLQ, less than the lower limit of quantification.
[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during rotary evaporation and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be ≤±2 wt% (absolute), values are for the daf char
** 'Undetected' is derived as: 100% - (dry bio-oil + volatile bio-oil + char + CO, CO_2, CH_4 and H_2 yields).

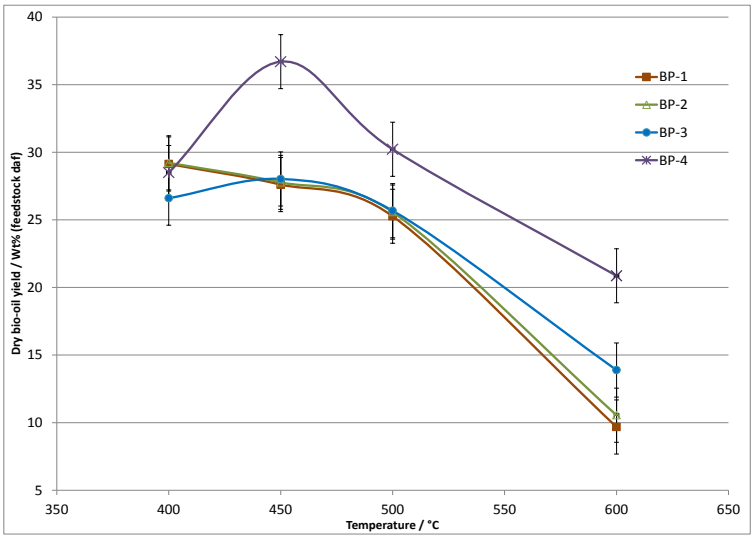

Figure 3. Dry bio-oil yields relative to daf feedstock as a function of temperature and vapor residence time, S.D. ≤2.0 wt% absolute.

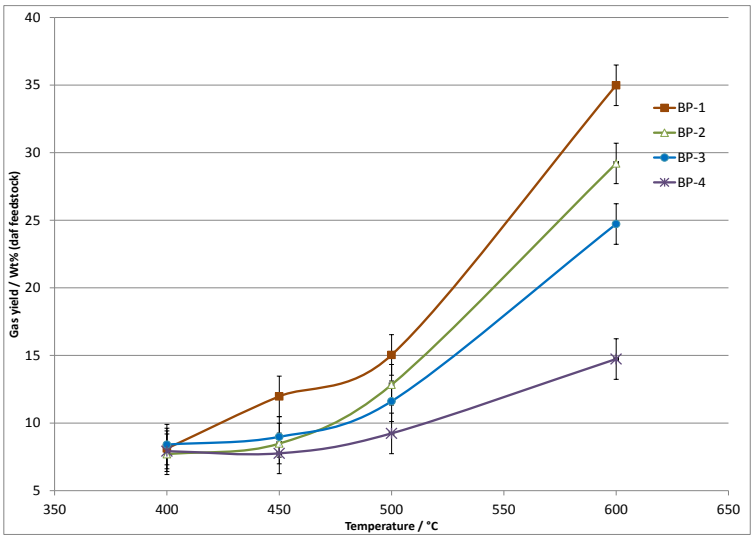

Figure 4. Permanent gas yields relative to daf feedstock as a function of temperature and vapor residence time, S.D ≤1.5 wt% absolute.

Table 8. Summary of char and ash yields from banagrass pyrolysis

Temperature	Mean $Char_{Org}$	Char S.D.	Number of tests	$Char_{Org+Inorg}$	Ash*
°C	wt% daf basis		n	wt% dry basis	
400	8.4	0.4	3	14.8	5.7
450	3.9	0.4	6	8.1	3.9
500	3.1	0.3	4	6.9	3.6
600	1.7	0.5	5	5.0	3.1

Bias is estimated at ≤±2 % (absolute).
* Ash refers to the ash contained within the char, given as wt% of the feedstock on a dry basis, the S.D. of the ash yield is 1.5 wt% (absolute).
$Char_{Org}$ refers to the organic fraction of the char relative to the daf feedstock.
$Char_{Org+Inorg}$ refers to the sum of the organic and inorganic fractions of the char relative to the dry feedstock.

The data presented in Table 7 show that at the longest residence time (BP-1, ~10-12 seconds), the maximum bio-oil yield was recovered when operating at temperatures of 400 and 450 °C (28 to 29 wt% bio-oil, daf). Increasing the temperature to 500 °C produced a slightly lower bio-oil yield, ~25 wt% bio-oil yield. At 600 °C the bio-oil yield is significantly lower, ~10 wt% bio-oil. The permanent gas data (CO, CO_2, CH_4 and H_2) shows a clear trend of increasing yield with

increasing temperature. Approximately 8 wt% of the daf banagrass is converted to CO, CO_2, CH_4 and H_2 at 400 °C, increasing to ~12 wt% at 450 °C, ~15 wt% at 500 °C, and ~35 wt% at 600 °C. A more detailed account of the gas analysis is given later. The daf $Char_{org}$ yields also show a clear trend with lower yields at higher temperature, decreasing from ~8.0 wt% char at 400 °C to ~1.7 wt% at 600 °C.

The data shows that on going from 400 °C to 450 °C at the longest residence time there is an increase in permanent gases by ~4.0 wt% while the amount of bio-oil is roughly constant (~28-29 wt%), and the char yield decreases by ~4.5 wt%. This implies that the additional volatile material released from the biomass at 450 °C than at 400 °C is not recovered as bio-oil, instead it increases the permanent gas yield.

The trends in the bio-oil, char and gas yields in response to temperature changes at BP-2 (~6-8 s) and BP-3 (~3.5-4.5 s), respectively, are virtually identical to those outlined above for BP-1. The actual dry bio-oil and gas yields at each temperature are also similar across BP-1, BP-2 and BP-3 (i.e. they are within experimental error), see Figures 3 and 4. The similarity in bio-oil and gas yields at a particular temperature across BP-1, BP-2 and BP-3 shows that increasing the vapor residence time from ~4 to ~11 seconds results in no additional cracking of the bio-oil compounds into permanent gases.

As shown in Figure 3, when operating at 400 °C, the bio-oil yield at the shortest residence time (BP-4, 1.5 s) is within experimental error of the values obtained at longer residence times (BP-3 to BP-1, 4.6 to12.2 s). This implies that there is no significant increase of bio-oil vapor cracking at residence time longer than ~1.5 s when operating at 400 °C. However, at 450 °C there is a significant increase in the bio-oil yield at the shortest residence times, with ~37 wt% at BP-4 (1.4 s) compared to ~28 wt% bio-oil at longer times (BP-3, BP-2 and BP-1, 4.2 to 11.3 s). A small increase in the bio-oil yield is also observed at 500 °C due to a shorter residence time with a bio-oil yield of ~30 wt% at BP-4 (1.3 s) compared to ~25 wt% at BP-3, BP-2 and BP-1 (4.0 to 10.6 s). At 600 °C the effect of increased residence time is more significant with bio-oil yield of ~21 wt% at BP-4 (1.2 s), decreasing to ~14 wt% at BP-3 (3.5 s) and ~10 wt% at BP-2 and BP-1 (6.4 and 9.4 s).

The permanent gas data correlates well with the trends observed for the bio-oil yields, with more gas formed at higher temperature and longer residence times. At 600 °C and BP-1 the highest gas yield is observed, ~35 wt%, dropping slightly at BP-2 and BP-3 with the lowest gas yield at 600 °C recorded at the shortest residence time (BP-4, ~15 wt%). When operating at 500 °C the gas yield at BP-1 is ~15 wt% which decreases to ~12-13 wt% at shorter residence times (BP-2 and BP-3) and to ~9 wt% at the shortest residence time (BP-4). The gas yields at 450 °C are similar to those at 500 °C ranging from ~12 wt% at the longest residence time (BP-1) to ~8 wt% at the shortest residence time (BP-4). The gas yields at 400 °C appear to be independent of residence time with all four residence times giving a value of ~8 wt%. The gas results support the conclusion that at 400 °C all the cracking of bio-oil vapors to permanent gases has occurred within the first 1.5 s and extending the residence time up to 12 s results in no increase in the permanent gas yield.

The char yields are not influenced by changes in the residence time of the vapors and are solely a function of the bed temperature and solids residence time in the bed, which is 15 minutes in all cases. The results show that the $char_{org}$ yield (daf) decreased with increasing temperature, from ~8.4 wt% at 400 °C to ~1.7 wt% at 600 °C relative to the daf feedstock (Table 8).

The ash recovered from the char after pyrolysis of banagrass is ~3-4 wt% relative to the dry feedstock independent of temperature (Table 8). The ash content of the feedstock is 8.2 wt% (dry basis, Table 2). Therefore it appears that more than half the ash originally present in the banagrass is unrecovered, partitioning either to the bed or into the bio-oil. It is unlikely that ash species would be lost due to volatilization at the temperatures used in these experiments [40].

The trends in product distributions due to pyrolysis temperature described above are in agreement with the general observations reported in the literature [6, 16, 41]. The results also show that a significant proportion of the products (~55-60 wt%) were not quantified as they were not detected by GCMS or by the permanent gas analyzers as described earlier (labeled 'undetected' in Table 7 and Supporting Information Tables S6.1 to S6.3). The amount of undetected material appears to be largely independent of temperature and residence time. The

amount of undetected material for cellulose was ~40 wt%. The lower amount of undetected material for cellulose than banagrass indicates that the bio-oil vapors from banagrass have undergone more extensive cracking than the cellulose vapors. This is also confirmed by the GCMS results. It is likely that this additional cracking occurs as the vapors exit the particles (intra-particle) and may relate to the high ash content of the banagrass. Additional discussion of these points is presented below.

In summary of the banagrass pyrolysis product yields, the highest bio-oil yield (~37 wt%) was recovered when operating at the shortest residence time (BP-4, ~1.4 s) and a temperature of 450 °C. These conditions also produced the least permanent gases (CO, CO_2, CH_4 and H_2 totaled ~8 wt% of daf fuel). Extending the volatiles residence time in the freeboard from BP-4 to BP-3 (from ~1.4 s to 4.2 s) resulted in a significantly lower bio-oil yield (~28 wt%) but only a negligibly higher gas yield (~9 wt%), at 450 °C. This implies that the additional cracking of the bio-oil vapors that occurs at longer residence time when operating at 450 °C does not create more permanent gases but instead forms compounds that fall in the window between methanol and CO_2 that could not be analyzed ('undetected' in Table 7).

The results obtained from the shortest residence time show that bio-oil yield increases from ~28 wt% at 400 °C to ~37 wt% at 450 °C while the gas yield is ~8.0 wt% in both cases, and the corresponding char yields decrease from 8.4 wt% at 400 °C to ~4.0 wt% at 450 °C. These results indicate that some of the bio-oil may have been lost when operating at 400 °C as the 10 wt% increase in bio-oil yield by increasing the temperature from 400 to 450 °C is not matched by a 10 wt% drop in the char yield as would be expected. This discrepancy is thought to reflect experimental error and indicates that more bio-oil may have been lost to deposition in the top of the reactor when working at 400 °C than at 450 °C. From comparison to other types of biomass in literature [15, 35], it is probable that the 400 °C bio-oil yield should be somewhat closer to the 450 °C results. This 'missing' bio-oil (~5 wt%) at 400 °C may partly explain the 10 wt% lower bio-oil yield from cellulose in this studied compared to that reported by Stiles [35] or Fraga [6, 15].

A breakdown of the GCMS results for the bio-oil samples is provided in Supporting Information, Tables S3.1 to S3.4 along with a brief discussion of the findings. It was found that no single compound is present in any of the bio-oil samples in a significant concentration, instead there are >40 peaks all at low concentration (<0.5 wt% relative to the amount of daf feedstock). The GCMS results provide limited information, partly due to the bio-oil solutions being too dilute, therefore they will not be discussed further.

Results - Pretreated banagrass pyrolysis, bio-oil, char and gas yields:

The bio-oil and permanent gas yields obtained from the pyrolysis of banagrass before and after pretreatment are presented in Figures 5 and 6, respectively. A summary of the char yields from the pretreated banagrass are given in Table 9. Full data tables for the pretreated banagrass bio-oil, char and gas yields are provided in Supporting Information, Table S6.4 to S6.7.

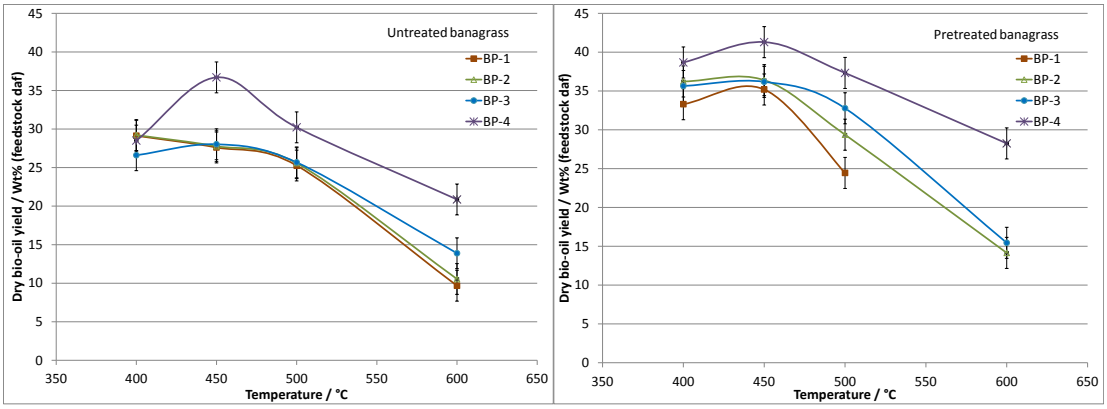

Figure 5. Pyrolysis bio-oil yields (dry bio-oil, daf feedstock) from banagrass as a function of temperature and residence time (bed position, BP). Left side shows untreated banagrass and right side pretreated banagrass.

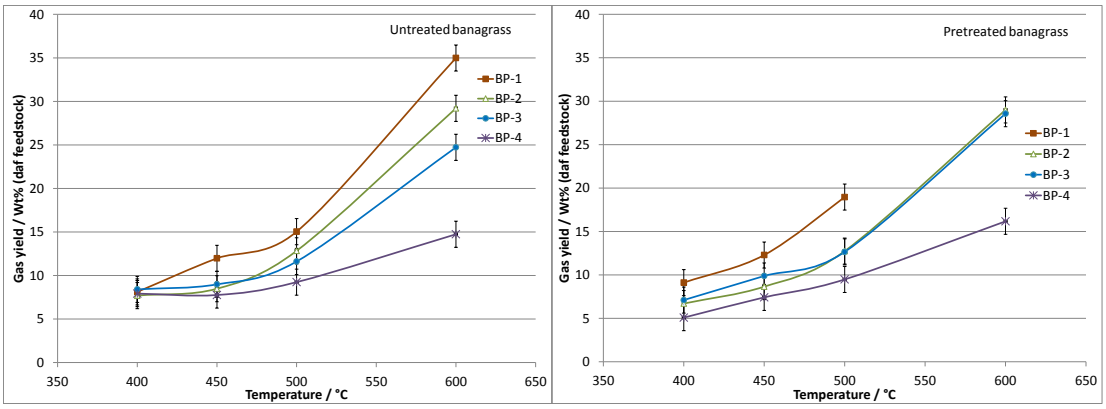

Figure 6. Permanent gas yields (daf feedstock) from banagrass as a function of temperature and residence time (bed position, BP). Left side shows untreated banagrass and right side pretreated banagrass.

Table 9. Summary of char and ash yields from pyrolysis of pretreated banagrass

Temp	$Char_{Org}$	Char S.D.	Number of tests	$Char_{Org+Inorg}$	Ash*
C	wt% daf basis		N	wt% dry basis	
400	6.4	1.3	4	9.3	2.6
450	4.8	0.9	4	7.2	2.3
500	4.4	0.5	3	7.5	2.8
600	1.5	0.5	3	4.4	2.8

Bias is estimated at ≤±2 % (absolute).
$Char_{Org}$ refers to the organic fraction of the char relative to the daf feedstock.
$Char_{Org+Inorg}$ refers to the sum of the organic and inorganic fractions of the char relative to the dry feedstock.
* Ash refers to the ash contained within the char, given as wt% of the feedstock on a dry basis, the S.D. of the ash yield is 1.5 wt% (absolute).

The bio-oil yields follow a clear trend with the highest yields obtained at 400 to 450 °C and lower yields at higher temperature, for the same vapor residence time. The permanent gas results show opposing trends to the bio-oil results with higher gas yields at higher temperatures. The amount of $char_{org}$ (organic fraction, excluding ash) decreases with increasing temperature, from 6.4 wt% (daf) at 400 °C to 1.5 wt% at 600 °C.

The amount of bio-oil that is lost during rotary evaporation to remove the solvent is termed 'volatile bio-oil' in Tables S6.4 to S6.7 (Supporting Information). In all cases, the volatile bio-oil

accounted for < 1 wt% of the products. However, the volatile bio-oil is thought to be greatly underestimated due to the extremely low concentration of bio-oil in the washing solvent (~3 mg/mL) combined with the fact that less than half the peaks that are observed are calibrated. The high variability in GCMS response factors for bio-oil compounds [42] means it is not possible to obtain a useful estimate of the concentrations of un-calibrated compounds through a comparison to the internal standard.

The results displayed in Tables S6.4 to S6.7 also show that between 48 and 56 wt% of the starting material is not accounted for in the quantified products (labeled as 'undetected' in the tables). The undetected material is comprised of compounds that could not be quantified as they fall in a window between the species detected by the online gas analyzers (CO, CH_4, H_2 and CO_2) and those quantified by the GCMS method; i.e. the undetected material includes other gases and compounds more volatile than or obscured by the GC solvent (acetone/methanol), including water and un-calibrated compounds in the GC range.

Effect of residence time: There are clear trends in the data which show higher bio-oil yields and lower gas yields are obtained as the vapor residence time decreases. Considering the results obtained at 400 °C, the maximum bio-oil yield is ~39 wt% at the shortest residence time (RT-4, 1.5 s) with 5 wt% gas. At the second shortest (RT-3, 4.6 s) and second longest (RT-2, 8.3 s) residence times the bio-oil yields at 400 °C are ~36 wt% and gas yields ~7 wt%. At the longest residence time (RT-1 12.2 s) the bio-oil yield is ~33 wt% and gas yield ~9 wt%.

Effect of temperature: The highest overall bio-oil yield was recorded when operating at 450 °C and the shortest residence time (RT-4, 1.4 s), ~41 wt% bio-oil with ~7.5 wt% gas. The $char_{org}$ yield at 450 °C is ~4.5 wt% and at 400 °C, ~6.5 wt%. The results indicate that a few extra percent of volatile material can be released from the char particles by increasing the bed temperature from 400 to 450 °C with only marginally more cracking of the bio-oil vapors into permanent gases. Increasing the bed temperature to 500 °C results in no further decrease in the char yield but induces more cracking of the bio-oil vapors producing more permanent gases. Increasing the bed temperature to 600 °C produces even less char (~1.5 wt% $char_{org}$), however there is much greater cracking of the bio-oil vapors which produces a significantly higher gas

yield. The permanent gas data is discussed later in the manuscript. A summary of the GCMS results from the pretreated banagrass pyrolysis oils is provided in Supporting Information Section S3-1 to S3.8.

Results - Comparison of banagrass product yields before and after pretreatment:

Comparison of product yields before and after banagrass pretreatment shows that in all cases the bio-oil yields (daf basis, Figure 7) are higher when using the pretreated banagrass. Depending on the temperature and residence time, the bio-oil yields are between ~4 and 11 wt% (absolute) higher for the pretreated banagrass, which is considered experimentally significant.

Pretreatment of banagrass has a less significant effect on the permanent gas yields from pyrolysis (Figure 6). In almost all cases the total amounts of permanent gases from banagrass before and after pretreatment are within experimental uncertainty of one another, for equivalent reaction conditions. For the shortest residence time experiments (BP-4) there was slightly more gas produced from the pretreated banagrass. For the char yields, any differences in the values before and after pretreatment are within experimental uncertainty and are *not* considered experimentally significant.

The values of 'undetected' material, as referred to in Tables S6.1 to S6.7, are always lower for the pretreated banagrass than the untreated banagrass by between ~5 to 10 wt%, which is considered to be experimentally significant and is in agreement with measured increases in the bio-oil yield.

Taken together the data strongly indicates that water pretreatment of banagrass results in higher bio-oil yields, under all the conditions examined. There was also less undetected material and approximately the same amount of char and permanent gases (or slightly more gas). This observation implies that the primary bio-oil vapors released from untreated banagrass undergo significantly more cracking as they escape the particles (intra-particle) than for the pretreated banagrass. However, this increase in bio-oil vapor cracking for untreated banagrass does not

significantly increase the permanent gas yield (in some cases it slightly decreases the gas yield), instead it increases the amount of undetected material. This may well be related to changes in the amount of pyrolysis water and volatiles, although this could not be examined during the present study.

Furthermore, the data from the untreated and pretreated banagrass suggests that the bio-oil vapors that escape the particles contain different compounds. Evidence for this comes from the fact that the bio-oil from the untreated banagrass is less stable toward increased residence time or increased temperature than the equivalent bio-oils from the pretreated banagrass. For the untreated banagrass there is sharp decline in the bio-oil yield on going from the shortest residence time (RT-4) to the second shortest residence time (RT-3) at 450 °C or greater; whereas the decline in bio-oil yield is less dramatic for the pre-treated banagrass. At 400 °C, the bio-oil yields are between 26 and 29 wt% for the untreated banagrass over all four residence times studies; whereas for the pretreated banagrass the bio-oil yield decreases with increasing residence time (~39 wt% at BP-4, ~36 wt% at BP-3 and BP2, and ~33 wt% at BP-1).

Results - CHN of the dried bio-oils and char from untreated banagrass:

C, H and N contents of the bio-oils recovered at different temperatures and vapor residence times were directly measured to provide an indication of fuel quality. O was determined by difference. Figure 7 displays the elemental analysis results for the dry bio-oils in terms of weight percent of C, H, N and O in the bio-oil.

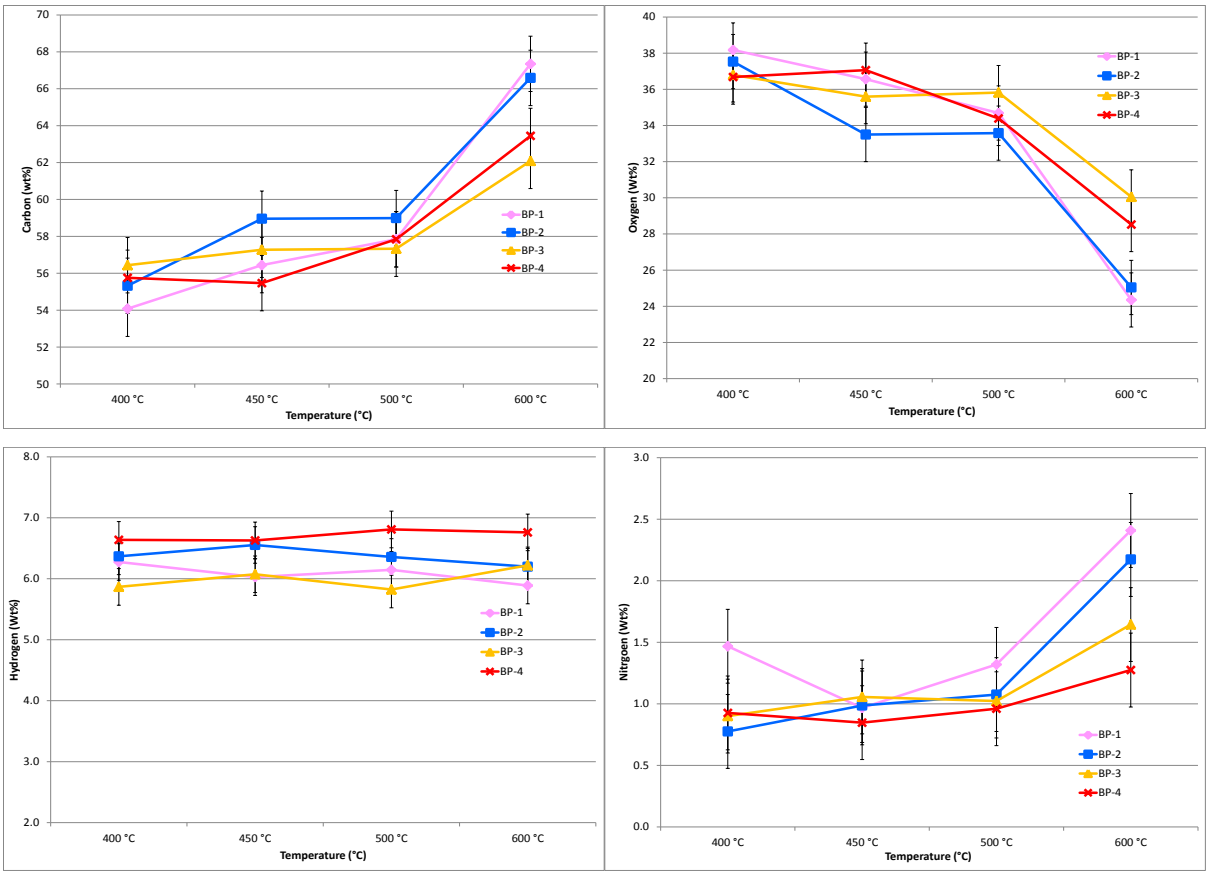

Figure 7. Elemental analysis (C, H, N, and O by difference) results for the dry bio-oil samples from banagrass pyrolysis as a function of temperature and vapor residence time (bed position, BP). Results are presented as wt% of the **bio-oil**. The standard deviation of the C and O results is ≤1.5 wt% (absolute) and for H and N ≤0.3 wt% (absolute).

In general, the effect of increasing residence time on the C, H, N and O contents of the bio-oil is minor compared to the influence of temperature. At 400 °C the amount of carbon in the bio-oil is ~54 wt% at the longest residence time (BP-1), ~55 wt% at the 2nd longest RT (BP-2), and ~56 wt% at the shorter residence times (BP-3 and BP-4). The standard deviations of the C and O results are ≤1.5 wt% which indicates the carbon values at 400 °C are within experimental error of each other. The amount of oxygen in the bio-oils also appears to be largely independent of residence time at 400 °C with ~38 wt% at the longest residence time and ~36.5 wt% at the shortest residence time; i.e. these values are within experimental error of one another, but some

dependence on residence time is observed at 600 °C, implying that greater deoxygenation occurs at higher temperatures and residence times .

Carbon in the bio-oils produced at 450 °C ranges from 55.5 to 59.0 wt% and is comparable to the data at 400 °C. Similarity to 400 °C data is also displayed by O, N, and H results. No clear trend due to differing residence times is displayed for any of the elements in bio-oils formed at 450 °C. Differences can be attributed to experimental error.

At 500 °C there is a minor increase in the amount of carbon in the bio-oil produced at the shortest residence time (BP-4) compared to 400 or 450 °C (~58 wt% at 500 °C, and ~55.5 to 56 wt% at 400 and 450 °C). Increasing the residence time at 500 °C appears to have little effect on the carbon contents of the bio-oils with all the results falling between 57.5 to 59.0 wt%.

At 600 °C there is a clear increase in the carbon contents of the bio-oils compared to those produced at lower temperatures. The bio-oils recovered at the shorter residence times contain 62.0 to 63.5 wt% carbon, while at longer residence times this increases to between 66.5 to 67.5 wt% carbon. In all cases, the differences are larger than the experimental error.

Due largely to its measurement by difference, the oxygen contents of the bio-oils show opposing trends to the carbon results described above. The effect of residence time on the oxygen contents of the bio-oils is less significant than temperature and bio-oils contain markedly less oxygen at higher temperature.

The hydrogen contents of the bio-oils are independent of temperature or residence time. There is marginal evidence to suggest that the bio-oils produced at the shortest residence time contain slightly more hydrogen than at the longer residence times, at all temperatures.

For nitrogen the values are fairly similar across 400 to 500 °C and at all residence times, expect for one point (400 °C, BP-1) which appears high compared to the rest of the data. This is possibly an anomalous result. At 600 °C the amount of nitrogen increases compared to the lower temperature bio-oils and differences due to residence time are greater.

In summary of the elemental analysis of the dried bio-oils, the influence of residence time on the amounts of carbon and oxygen in the bio-oils appears to be minor at temperatures below 600 °C. Increasing the temperature has a greater effect, the carbon contents of the bio-oils increases from ~55-56 wt% at 400 °C to ~65 wt% at 600 °C. For oxygen, the amount decreases from ~37-38 wt% at 400 °C to ~25-30 wt% at 600 °C. However, working at a higher temperature results in a significantly lower bio-oil yield (Figure 3). To account for the differing bio-oil yields at each condition, the C, H, N and O results are also presented in terms of wt% of the element relative to the total amount of the element in the feedstock (daf), Figure 8.

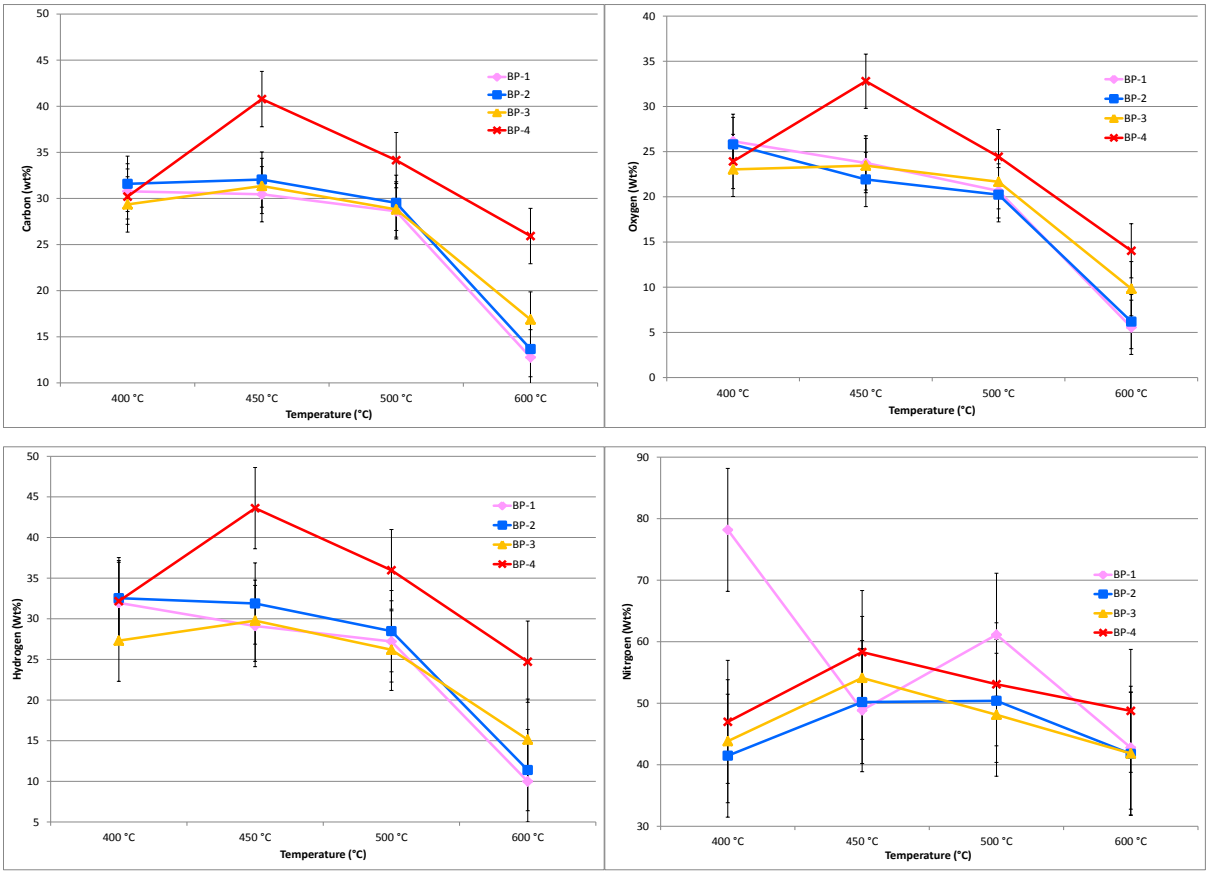

Figure 8. Elemental conversion efficiency (C, H, N and O by difference) results for the dry bio-oil samples from banagrass pyrolysis as a function of temperature and vapor residence time (bed position, BP). Results are presented as wt% of the element in the **Feedstock** (daf). The standard deviation for the C and O results is ≤3.0 wt%, for H ≤5.0 wt% and for N ≤10.0 wt% (absolute).

Figure 8 shows that the amount of carbon in the bio-oil relative to the amount of carbon in the daf banagrass is approximately constant over all four residence times when operating at 400 °C (between 29 and 32 wt% C). At 450 °C the amount of carbon in the bio-oils is approximately the same as at 400 °C for the longer residence time bio-oils (BP-1 to BP-3), only the shortest residence time (BP-4) resulted in more carbon in the bio-oil, ~41 wt% C.

At 500 °C the amount of carbon in the bio-oil at the longer residence times (BP-1 to BP-3) are within experimental error of the values at 400 and 450 °C, i.e. ~29 wt% C. For the shortest residence time (BP-4) at 500 °C the amount of carbon in the bio-oil is ~34 wt%. At 600 °C the amount of C in the bio-oils is ~13 to 17 wt% for BP-1 to BP-3 and ~26 wt% C at BP-4, which is a significant decrease when compared to the 500 °C results.

The oxygen contents of the bio-oils, when presented relative to the amount of oxygen in the daf feedstock, show the exact same trends as described above for carbon. At 400 °C the amount of oxygen is between 23 and 26 wt% over all four residence times. At 450 °C the amount of oxygen in the bio-oils is ~22-24 wt% for BP-1 to BP-3 and ~33 wt% for BP-4. At 500 °C there is ~20 to 22 wt% oxygen in the bio-oils recovered at BP-1 to BP-3, and ~24 wt% O at BP-4. At 600 °C the amount of oxygen in the BP-1 to BP-3 bio-oils is ~6 to 10 wt%, and ~14 wt% at BP-4.

The hydrogen results also show the same trends as for carbon and oxygen. At 400 °C the amount of hydrogen in the bio-oils appears independent of residence time, ~27 to 32 wt% H. At 450 °C there is ~29-32 wt% H in the BP-1 to BP-3 bio-oils and ~44 wt% for BP-4. At 500 °C the amount of H appears to decrease slightly for BP-1 to BP-3 bio-oils compared to the 400 and 450 °C results with ~26-29 wt% H, for BP-4 there is ~36 wt% H. At 600 °C there is a significant decrease in the amount of hydrogen in the bio-oils than at lower temperatures with ~10-15 wt% H for BP-1 to BP-3 and ~25 wt% H for BP-4.

The results for nitrogen are less clear due to the lower absolute amounts of nitrogen present in the feedstock which inevitably results in more significant errors. Overall, the trends in the

nitrogen results are the same as for carbon, oxygen and hydrogen with the notable exception of the longest residence time (BP-1) data set which appears to contain some anomalous results. The amount of nitrogen in the bio-oils relative to the nitrogen in the feedstock is ~40-60 wt% (typically ~50 wt%) over all the conditions studied. Considering the repeatability of the data (S.D is 10 wt% absolute), all the values can be considered to be within experimental error.

Elemental analysis was also performed on the char samples. Table 10 present the C, H, N and O results as weight percent of the char (daf). Table 11 present the same data in terms of weight percent of the element in the feedstock (daf).

Table 10. Elemental analysis results for the chars (daf), given as wt% of the **char** (daf)

Temperature	C	H	N	O
°C	wt%	wt%	wt%	wt%
400	61.0	2.8	1.0	35.2
450	65.2	2.6	1.1	31.1
500	65.4	2.3	0.9	31.4
600	75.4	2.4	1.1	21.0
RSD is estimated to be <20 %.				

Table 11. Elemental analysis results for the chars (daf), given as wt% of the element in the **feedstock** (daf)

Temperature	C	H	N	O
°C	wt%	wt%	wt%	wt%
400	10.0	4.1	14.7	7.0
450	5.0	1.8	7.9	2.9
500	4.0	1.2	5.1	2.3
600	2.5	0.7	3.4	0.8
RSD is estimated to be <20 %.				

The carbon contents of the chars, relative to the mass of $char_{org}$ (daf) ranges from ~60-65 wt% in the temperature range from 400 to 500 °C to ~75 wt% at 600 °C (Table 10). The oxygen contents of the chars are between 30 and 35 wt% at 400 to 500 °C, decreasing to ~20 wt% at 600 °C. The

hydrogen contents of the chars are between 2 and 3 wt% over all four temperatures and nitrogen is ~1 wt% in all cases. The repeatability of the char elemental analyses is fairly poor due to the small sample size and difficulty of recovering clean char samples, the standard deviation is up to 20 % (relative).

Presenting the elemental analysis results for the chars relative to the amount of the element in feedstock (daf) reveals clear trends (Table 11). The amount of carbon in the char decreases with increasing temperature, from ~10 wt% at 400 °C to ~2.5 wt% at 600 °C. For oxygen the maximum is ~7 wt% at 400 °C decreasing to ~1 wt% at 600 °C. Hydrogen decreases from ~4 wt% at 400 °C to ~1 wt% at 600 °C, and nitrogen decreases from ~15 wt% at 400 °C to ~3 wt% at 600 °C.

The results from elemental analysis of the chars are in general agreement with the trends reported in literature.[24] The chars contain low amounts of carbon and hydrogen relative to the amounts present in the feedstock (≤10 wt% for carbon and ≤5 wt% for hydrogen).

Results - CHN of the dried bio-oils and char from pretreated banagrass:

The quality of the bio-oils recovered at different temperatures and vapor residence times from pretreated banagrass was assessed by comparing their C, H and N contents from elemental analysis (O determined by difference). Figure 9 displays the elemental analysis results of the dry bio-oils from pretreated banagrass in terms of weight percent of C, H, N and O in the bio-oil. Figure 10 shows the same data presented relative to the element in the feedstock (daf).

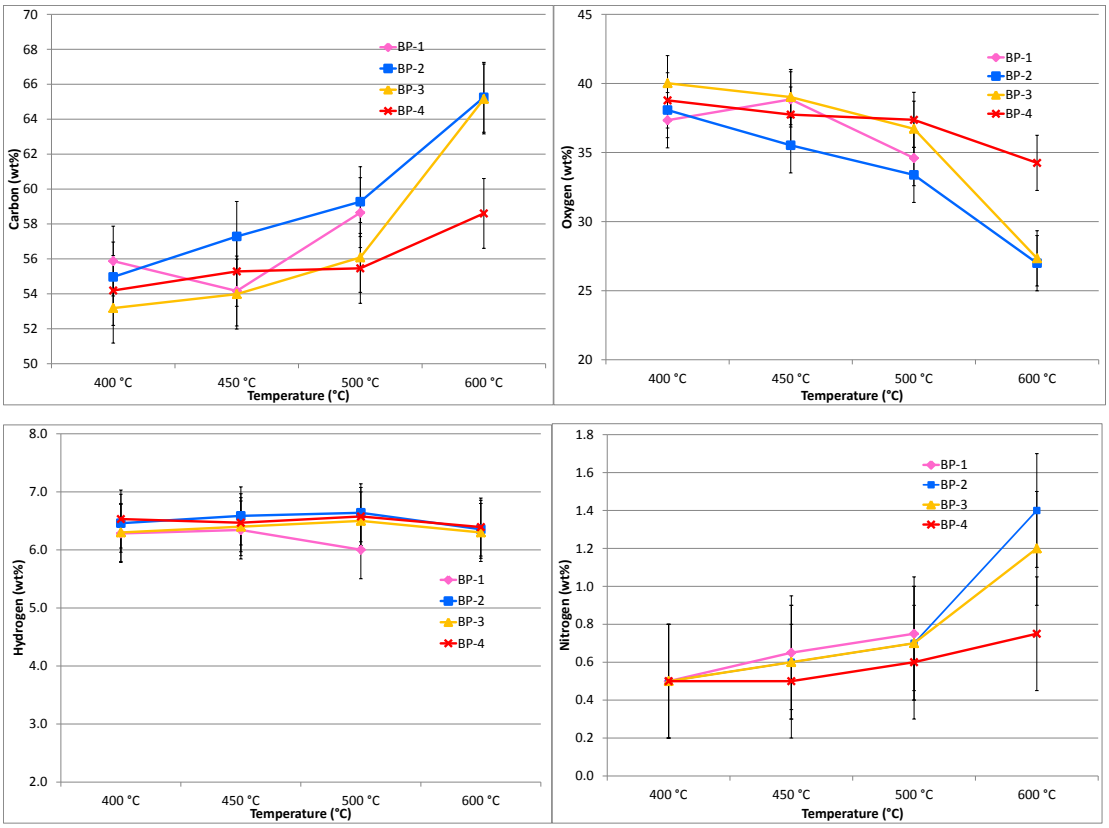

Figure 9. Elemental analysis (C, H, N and O by difference) results for the dried bio-oils from pyrolysis of pretreated banagrass as a function of temperature and vapor residence time. Results are presented as wt% of the **bio-oil**. The standard deviation of the C and O results is < 2.0 wt% (absolute) and for H < 0.5 wt% and N < 0.3 wt% (absolute).

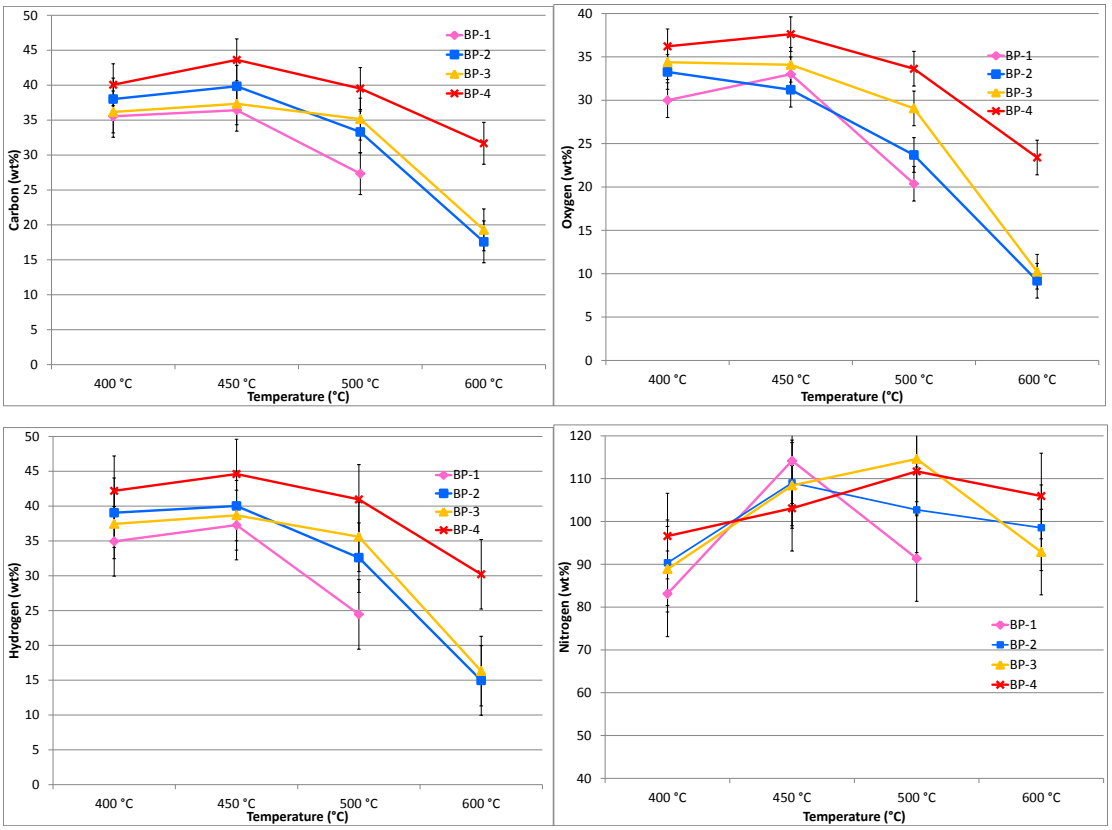

Figure 10. Elemental analysis (C, H, N and O by difference) results for the dried bio-oils from pyrolysis of pretreated banagrass as a function of temperature and vapor residence time. Results are presented as wt% of the **element** in the **Feedstock** (daf). The standard deviation for the C and O results is ≤ ±3.0 wt%, for H ≤ ±5.0 wt% and for N ~±10 wt% (absolute).

The elemental analysis of the bio-oils shows the proportion of carbon increases with increasing temperature and to a lesser extent with increasing residence time (Figure 9). At 400 °C there is ~53-56 wt% carbon in the bio-oil independent of residence time (i.e. differences are within experimental uncertainty). At 450 °C there is 54-57 wt% carbon in the bio-oils with no clear trend due to increasing residence time. At 500 °C differences start to emerge, with ~55-56 wt% carbon in the bio-oils recovered at shorter residence times (BP-3 and BP-4) and ~59 wt% at longer residence times (BP-1 and BP-2). At 600 °C there is a marked increase in the amount of carbon, with ~59 wt% at the shortest residence time (BP-4), increasing to ~65 wt% at longer

residence times (BP-3 and BP-2). No data is available for the longest residence time (BP-1) at 600 °C as that condition was *not* examined.

The oxygen results show directly opposing trends to the carbon results which is a reflection of the values being determined by difference (Figure 9). At 400 to 450 °C at the shortest residence time (BP-4) there is 36-38 wt% oxygen which decreases to ~ 30 wt% at the longest residence time (BP-1). In general, there is less oxygen in the bio-oils formed at higher temperature or longer residence time, the lowest value being ~10 wt% oxygen at 600 °C. For hydrogen, there is no trend due to increasing temperature or residence time with all the values falling between 6 and 7 wt%. At 500 °C there appears to be slightly less hydrogen in the bio-oil from the longest residence time (BP-1) compared to the shorter RT bio-oils. For nitrogen there is a slight trend of increasing N with increasing temperature which is more significant at longer residence times; in general there is ~0.5-0.7 wt% N across all RT's from 400 to 500 °C. At 600 °C, N content increases from ~0.7 wt% at the shortest residence time (BP-4) to ~1.2 wt% at second shortest RT (BP-3) and finally to ~1.4 wt% at second longest RT (BP-2).

Plotting the elemental analysis results from the bio-oil relative to the amount of the element in the feedstock (daf) shows clearer trends (Figure 10). The carbon, oxygen and hydrogen results all show the same general trends. The greatest carbon content is in the bio-oil recovered at the shortest residence time (BP-4) at 450 °C, ~45 wt% C, decreasing to ~37 wt% at the longest residence time (BP-1). At 600 °C there is significantly less carbon partitioned to the bio-oils with ~32 wt% carbon at the shortest residence time (BP-4) decreasing to ~17 wt% carbon at longer residence times (BP-3 and BP-2).

The amount of oxygen in the bio-oils relative to the oxygen in the feedstock is ~34-38 wt% across the temperature range of 400 to 500 °C at the shortest residence time (BP-4), with less oxygen in the bio-oils exposed to longer RT's or higher temperature (Figure 10). For hydrogen, it is ~40-45 wt% at the shortest RT at 400 to 500 °C, dropping to 40-35 wt% at longer RT's. At 600 °C, the H content is <30 wt% at the shortest residence time, falling to ~15 wt% at longer RT's. The nitrogen partitioned to the bio-oil is less clear due to the low absolute amount of nitrogen in the banagrass, which results in larger uncertainty. The amount of N present in the oils is typically

80-115 wt% with no clear trend due to RT, although there appears to be more N present at higher temperatures.

Comparing the bio-oil CHNO results from pretreated banagrass (Figures 9 and 10) with equivalent data sets from the untreated banagrass (Figures 7 and 8) shows that the amounts of carbon and hydrogen in the oils are about the same, considering experimental uncertainty. The oxygen content of the bio-oils from pretreated banagrass is marginally higher or unchanged. The amount of nitrogen is slightly lower or unchanged than from untreated banagrass. Therefore, these results, when taken with yields of bio-oils relative to the feedstock, indicate that there is greater partitioning of C, H, O, and N to bio-oil after pretreatment. For example, at 450 °C and the shortest residence time (BP-4) the amount of carbon in the bio-oil relative to the carbon in the pretreated banagrass is ~44 wt% and for untreated banagrass ~41 wt%. Oxygen content in the bio-oil from pretreated banagrass is ~38 wt% and from untreated banagrass ~33 wt%. This is a reflection of the greater bio-oil yields from the pretreated banagrass.

Elemental analysis was also performed on the char samples. Table 12 presents the C, H, N and O results as weight percent of the $char_{org}$ (daf). Table 13 present the same data in terms of weight percent of the element in the feedstock (daf).

Table 12. Elemental analysis results for the chars (daf) from pretreated banagrass, given as wt% of the char (daf)

Temperature	C	H	N	O
C	wt%	wt%	wt%	Wt%
400	64.2	2.3	0.9	32.6
450	62.3	2.0	1.0	34.8
500	63.0	2.3	1.2	33.4
600	74.8	3.0	1.3	20.9
RSD is estimated to be <15 %				

Table 13. Elemental analysis results for the chars (daf) from pretreated banagrass, given as wt% of the element in the feedstock (daf)

Temperature	C	H	N	O
C	wt%	wt%	wt%	Wt%
400	7.8	2.4	30.3	5.0
450	5.7	1.6	23.3	4.0
500	5.3	1.7	26.0	3.6
600	2.1	0.8	10.1	0.8
RSD is estimated to be <20 %				

The results in Table 12 show that there is ~63-65 wt% carbon in the $char_{org}$ (daf) at 400 to 500 °C, and ~75 wt% carbon at 600 °C. Hydrogen accounts for ~2 wt% at 400 to 500 °C and ~3 wt% at 600 °C. Nitrogen is ~1.0 wt% across all temperatures. There is ~33-35 wt% oxygen in the 400 to 500 °C chars and ~20 wt% O at 600 °C.

Considering the same data in terms of partitioning of elements in the $char_{org}$ (daf) relative to the element in the feedstock (daf) shows clear decreasing trends. The amount of carbon retained by the chars decreases with increasing temperature from ~8 wt% at 400 °C to ~2 wt% at 600 °C. Hydrogen retention ranges from ~2.5 wt% at 400 °C to ~ 1.0 wt% at 600 °C. Nitrogen retention is ~30 wt% at 400 °C falling to ~10 wt% at 600 °C. Oxygen retention is ~5 wt% at 400 °C and ~1 wt% at 600 °C. For all elements, the retention is roughly the same for the 450 and 500 °C chars (i.e. values are within experimental uncertainty).

Comparing the elemental analysis of the chars from the pretreated banagrass (Tables 12 and 13) with those from the untreated banagrass (Tables 10 and 11) reveals that there is no significant differences in the weight percentage composition of carbon, hydrogen, nitrogen and oxygen. However, there are small differences when the result are considered in terms of partitioning of elements to the char. The 400 °C chars from untreated banagrass retained slightly more carbon, hydrogen and oxygen than the chars from pretreated banagrass, whereas nitrogen retention was slightly less for the untreated chars. At higher temperatures the retention of carbon, hydrogen and

oxygen is roughly the same for the chars from untreated and pretreated banagrass; whereas, there appears to be more retention for nitrogen in the char from the pretreated samples.

Results - Permanent gas data, untreated banagrass:

A breakdown of the permanent gas data in terms of weight percent of CO, CO_2, CH_4 and H_2 relative to the amount of feedstock (daf) as a function of temperature and vapor residence time is presented in Figure 11 (data tables are provided in Supporting Information, Tables S7.1 to S7.4). The total amount of gas produced at each condition is reported in Supporting Information, Tables S6.1 to S6.4, as liters of gas per gram of feedstock (daf). The permanent gas data was derived from online gas analyzers which are not guaranteed to give quantitative results, as explained in the experimental section. The results therefore should only be considered as indicative. Nonetheless, the repeatability of the results was found to be good (see Figure 11). Note, it is assumed that all the oxygen in the gases is from the organic part of the sample.

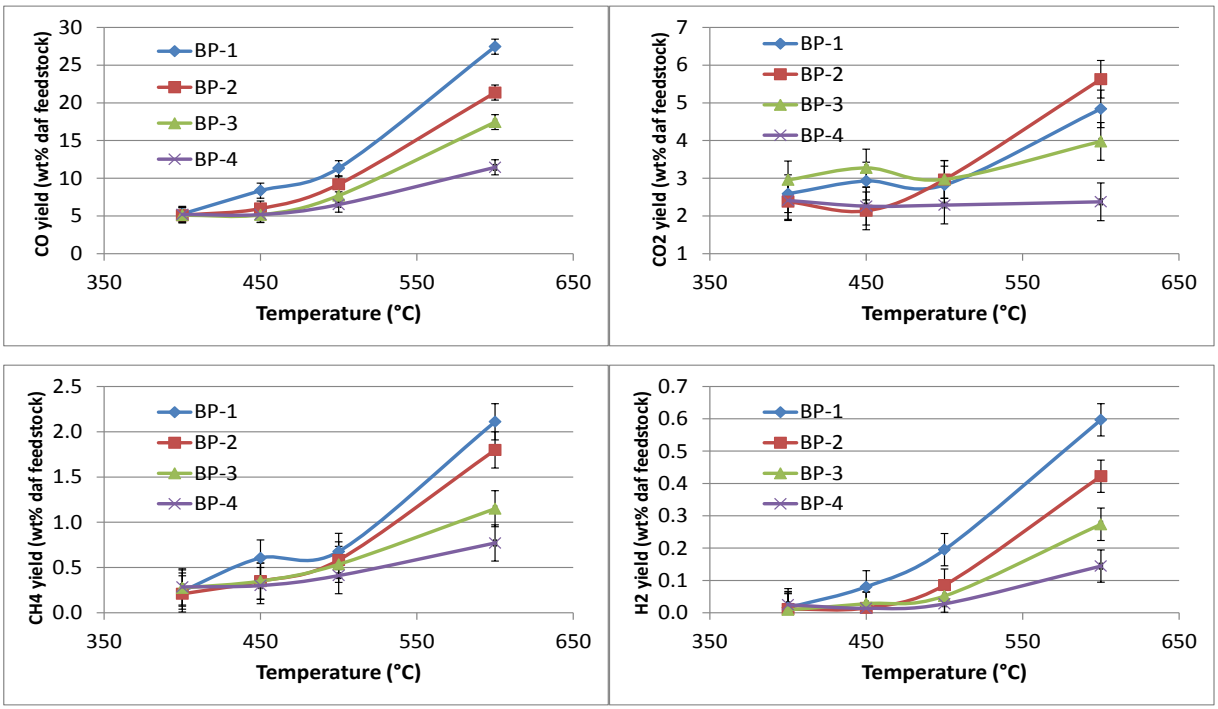

Figure 11. Permanent gas data (CO, CO_2, CH_4 and H_2) from the pyrolysis of banagrass as a function of temperature and vapor residence time, presented as wt% of the daf feedstock (BP, bed position). The standard deviation for the CO values is ≤1.0 wt% (absolute), for CO_2 ≤0.5 wt%, for CH_4 ≤0.2 wt% and for H_2 ≤0.05 wt%.

The permanent gases produced from the pyrolysis of banagrass are in all cases dominated by CO, followed by CO_2, then CH_4 and H_2. There is a clear increasing trend in the absolute amount of gas produced with increasing temperature. The low CO_2 yield (~2-5 wt% relative to the daf feedstock) is promising in terms of energy recovery in a potentially integrated process.

At 400 °C, hydrogen accounts for less than 0.05 wt% of the daf feedstock across all the residence times examined. Differences start to emerge at 450 °C. At shorter residences times (BP-4 to BP-2) the amount of H_2 remains <0.05 wt% with a significant increase to ~0.08 wt% H_2 at the longest residence time (BP-1). At 500 °C the weight percentage of H_2 steadily increases with residence time from ~0.03 wt% at the shortest residence time to ~0.2 wt% at the longest. At 600

°C the amount of hydrogen also increased with residence time with ~0.14 wt% at the shortest residence time incrementally increasing to ~0.6 wt% at the longest residence time.

The amount of CO is unaffected by residence time at 400 °C, accounting for ~5 wt% of the daf feedstock. At 450 °C there is ~5-6 wt% CO at shorter residence times (BP-4 to BP-2) and ~8 wt% at the longest RT (BP-1). At 500 °C the amount of CO incrementally increased from ~6.5 wt% at the shortest residence time to ~11 wt% at the longest. At 600 °C more CO is formed, with ~11 wt% at the shortest residence time increasing to ~27 wt% at the longest RT.

Methane shows trends similar to CO, although the absolute amounts are much lower. Over the temperature range of 400 to 500 °C and across all residence times the amount of CH_4 was ≤1 wt%. At 600 °C the amount of CH4 increased from ~0.8 wt% at the shortest residence time to ~2 wt% at the longest.

For CO_2, the amount is also fairly constant over the temperature range of 400 to 500 °C across all residence times, accounting for ~2-3 wt% of the daf feedstock. At 600 °C the amount of CO_2 increases from 2.4 wt% at the shortest residence time to 5-6 wt% at longer residence times.

Results - Permanent gas data, pretreated banagrass:

The permanent gas data from the pyrolysis tests are reported in terms of wt% of CO, CO_2, CH_4 and H_2 relative to the dry ash free feedstock in Figure 12; the same data are tabulated in Supporting Information, Tables S7.5 to S7.8. The permanent gas data were obtained from online gas analyzers with associated measures of uncertainty as explained in the experimental section. The results should be considered as indicative. Nonetheless, the repeatability of the results was good, see Figure 12.

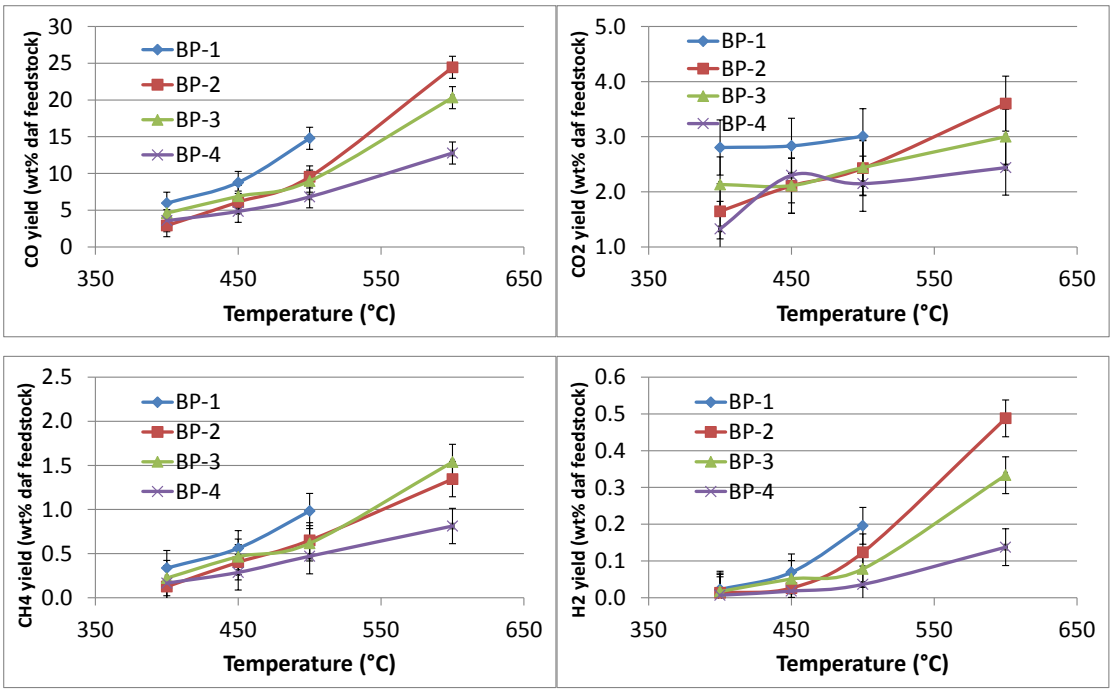

Figure 12. Permanent gas data (CO, CO_2, CH_4 and H_2) from the pyrolysis of banagrass S3 as a function of temperature and vapor residence time, presented as wt% of the daf feedstock (BP, bed position). The standard deviation for the CO values is $\leq \pm 1.5$ wt% (absolute), for $CO_2 \leq \pm 0.5$ wt%, for $CH_4 \leq \pm 0.2$ wt% and for $H_2 \leq \pm 0.05$ wt%.

Figure 12 shows that the amounts of CO, CO_2, CH_4 and H_2 generated during pyrolysis gradually increases with increasing temperature from 400 to 500 °C with more significant increases across the 500 to 600 °C range. There is also a trend of increasing amounts of gases as volatiles residence time increases, with small increases associated with increasing the residence time from BP-4 to BP-3 to BP-2 and then a more significant increasing residence time from BP-2 to the longest BP-1 tests.

CO increased from ~4 wt% at 400 °C at the shortest residence time (BP-4) to ~6 wt% at the longest RT (BP-1). At 450 °C the amount of CO increased from ~5 wt% at shortest RT (BP-4) to ~9 wt% at the longest RT. At 500 °C the amount of CO increases from ~7 wt% at the shortest RT to ~15 wt% at the longest RT. At 600 °C the amount of CO increases from ~13 wt% at the

shortest RT to ~25 wt% at the second longest RT (note: no data are available for the longest RT at 600 °C).

With the exception of the lowest pyrolysis temperature (400 °C), methane produced in the pyrolysis process generally increases as a function of temperature and residence time. Less than 0.5 wt% methane was produced at 400 °C across all residence times. At 450 °C the amount of CH_4 increases from ~0.3 wt% at the shortest RT to ~0.6 wt% at the longest RT. At 500 °C there is ~0.5 wt% CH_4 at the shortest RT, increasing to ~1.0 wt% at the longest RT. At 600 °C the amount of CH_4 increase from ~0.8 wt% at the shortest RT to ~1.5 wt% at the second longest RT.

Very little H_2 (< 0.1 wt%) is generated at temperatures below 500 °C across all residence times. At 500 °C, H_2 increases from ~0.05 wt% at the shortest RT to ~0.20 wt% at the longest RT. More H_2 is formed at 600 °C, with ~0.15 wt% at the shortest RT and ~0.50 wt% at the second longest RT.

The production of CO_2 in the pyrolysis process was found to fall within a range of 1.5 to 3.5 wt% of fuel mass over the range of temperatures and residence times, with a general increasing trend with increasing reaction temperature and residence time.

Comparing the permanent gas data from the untreated (Figure 11) and pretreated banagrass (Figure 12) shows that for CO there is no significant difference in the results over the temperature range 400 to 500 °C and across all residence times. Differences start to emerge for the longest RT data sets at 500 °C with ~12 wt% CO from the untreated banagrass and ~15 wt% for the pretreated banagrass which is considered to be experimentally significant. At 600 °C the amount of CO is slightly greater from the pretreated banagrass than the untreated banagrass, by ~2-4 wt% at each residence time. For CH_4, the results are roughly the same from the untreated and pretreated banagrass, i.e. within experimental uncertainty; likewise for the H_2 results. For CO_2, in general, all the values are within experimental uncertainty with the exception of the 600 °C results, where there is slightly more CO_2 generated from the untreated banagrass than the pretreated banagrass (by ~1-2 wt%) at all residence times.

In summary, there is slightly more CO and less CO_2 generated during the pyrolysis of pretreated banagrass than the untreated banagrass at temperatures ≥ 500 °C, and no significant differences at temperatures < 500 °C.

Results - Comparison of cellulose and untreated banagrass product yields with literature:

To gain a better understanding of the banagrass pyrolysis results our findings are compared with similar studies of other solid fuels. The reactor used in this study is based on a design by Stiles et al. [35] who examined two coals, one biomass (silver birch - a hardwood) and municipal solid waste (MSW). Therefore, it is relevant to compare our findings with those reported by Stiles (see Tables 14 and 15). Bio-oil and char yields from other biomass species converted in fluidized beds under similar conditions are also included in Tables 14 and 15, respectively. Ash, AAEM, lignin and volatiles contents (wt% dry basis) are also listed in Table 14. In the present study the dry bio-oil yields exclude pyrolysis water as it was removed along with the solvent during rotary evaporation (true also for Stiles's results). The other literature sources either report a bio-oil yield inclusive of pyrolysis water (whole bio-oil) or the organic fraction of the bio-oil and pyrolysis water separately. The 'dry bio-oil' yields in Table 14 are loosely comparable to the 'organic bio-oil' yields.

Table 14. Bio-oil yields from the fast pyrolysis of various biomass species presented as wt% relative to the feedstock (daf), feedstock particle size <1000 μm.

	Banagrass	Silver Birch	Willow SRC	Pine saw dust*	Switchgrass	Miscanthus	Wheat straw	Barley straw	Rapeseed Straw*	Rice straw	Sugarcane Bagasse	Sugarcane Bagasse
Temperature	Dry Bio-oil	Dry Bio-oil	Organic Bio-oil	Organic Bio-oil	Organic Bio-oil	Organic Bio-oil	Organic Bio-oil	Organic Bio-oil	Organic Bio-oil	Whole bio-oil	Whole bio-oil	Whole bio-oil
°C	wt% daf											
~400	28	56	-	-	-	-	-	-	-	44	53	48
~450	37	56	-	-	-	-	-	-	-	-	-	-
~500	30	52	43-47 (10-16)	62 (11)	49-53 (11-13)	43 (6)	23 (14)	38 (17)	48 (13)	28	50	54
RT (s)	1.3-1.5	1.2	<1.5	0.5-2.0	<1.5	<1.5	<1.5	0.6-0.7	0.5-2.0	1.2	2.0	<0.1
Ash (d.b. wt%)	8.2	0.3	3.0	0.1	2.6-5.7	4.5	4.9	5.8	6.1	9.2	6.2	1.6
AAEM (d.b. wt%)	~2.8	-	~1.9	<0.05	~0.7	~1.5	~1.2	~2.4	~2.8	~2.0	-	-
K (d.b. wt%)	2.30	-	0.59	~0.03	0.09	1.20	0.57	~2.0	~1.3	1.61	-	-
Na (d.b. wt%)	0.04	-	0.01		0.02	0.00	0.01			0.03	-	-
Mg (d.b. wt%)	0.21	-	0.16	~0.01	0.06	0.15	0.07	~0.4	~1.5	0.09	-	-
Ca (d.b. wt%)	0.22	-	1.15		0.50	0.18	0.51			0.23	-	-
Volatiles (d.b. wt%)	83	-	81	84	83	76	80	74	78	-	73	-
Lignin (d.b. wt%)	24.4	18.4	19.0-20.0	~29	6.1-12.0	12.5-14.9	7.5-23.4	-	-	19.3	-	-
Reference	Present	[35]	[9]	[2]	[9] [10]	[9]	[9]	[2]	[2]	[42]	[16]	[15]

Values in parentheses show the pyrolysis water yield. *Particle size 3-5 mm.

Table 15. $Char_{org}$ yields (estimated to a daf basis) from the fast pyrolysis of various biomass species presented as wt% relative to the feedstock (daf), feedstock particle size <1000 µm.

Temp	Banagrass	Silver Birch	Willow SRC	Pine saw dust*	Switchgrass	Miscanthus	Wheat straw	Rice straw	Sugarcane Bagasse	Sugarcane Bagasse
°C	wt% daf									
~400	8	17	-	-	-	-	-	18	26	11
~450	4	10	-	-	-	-	-	-	-	-
~500	3	6	17-18	12	10-14	26	23	11	20	6
Reference	Present	[35]	[9]	[2]	[9] [10]	[9]	[9]	[42]	[16]	[15]
*Particle size 3-5 mm.										

Table 14 shows that woody biomass typically produces the greatest bio-oil yield. The yields from sugarcane bagasse and switchgrass fall within the lower end of the range of wood values, with miscanthus giving a significantly lower yield. The lowest yields are from the straws except rapeseed straw which is similar to bagasse. Banagrass gives a similar bio-oil yield as barley straw, which is significantly greater than the yields from wheat straw and rice straw.

If the ash, AAEM, lignin and volatiles contents are also considered (Table 14) more detailed conclusions can be drawn. Banagrass and rapeseed straw have similar volatiles (~80 wt%) and AAEM (~2.8 wt%) contents but banagrass produces much less bio-oil. The reason for this appears to be related to the differing amounts of Na + K verses Ca + Mg for banagrass and rapeseed straw. Rapeseed contains ~1.5 wt% of Ca + Mg and ~1.3 wt% of K + Na, whereas banagrass contains 2.3 wt% K and low amounts of Ca + Mg (~0.4 wt%). This indicates that K has a greater effect on reducing the bio-oil yield than Ca and Mg. Barley straw produces a similar amount of bio-oil as banagrass and it contains similar AAEM contents where K and Na are the dominant species (~2.0 wt%) and Ca + Mg account for ~0.4 wt%. These observations appear to support the assertion that K and Na play a more significant role in suppressing the bio-oil yield than Ca and Mg. The role of lignin is less clear, partly due to a lack of accurate data (Table 14). Nonetheless, it appears that samples with low amounts of AAEM and high amounts of lignin produce the greatest bio-oil yields (i.e. woods).

It is unclear why wheat straw produces so little bio-oil and so much char and gas, according to Greenhalf et al. [9] the reason is the high concentration of K. The ash content of wheat straw is fairly high (~5 wt%), but the AAEM content is medium (~1.2 wt%) when compared to the other samples in Table 14. The amounts of K + Na in wheat straw is ~0.6 wt% which is similar to willow and less than miscanthus (1.2 wt% K + Na) or banagrass (K is 2.3 wt%). It is unlikely therefore that K on its own is responsible for low bio-oil yield from wheat straw. It is possible that the low bio-oil yield from wheat straw is related to its lignin content. However, the lignin content of wheat straws appears to be highly variable with literature values ranging from 7.5 to 23.4 wt% (Table 14).

Table 15 shows that the char yield from banagrass is significantly lower than any of the other materials and that the results from Stiles and Fraga are similar. This may be related, in part, to the small particle size used in this study (<200 µm) and by Stiles and Fraga (100-150 µm) compared to the other results shown in Table 15 (typical partial size 500-1000 µm). Nonetheless it is clear that banagrass does not produce significant amounts of char under fast pyrolysis conditions. A similar low char yield (~14 wt% dry basis) was reported for elephant grass from a 200 kg/h fast pyrolysis pilot plant (feedstock particle size 3 mm, ~5 wt% ash) [24].

Stiles et al. [35] reported bio-oil yields of ~56 wt% for silver birch at 450 °C and residence time of 1.21 s, with ~59 wt% bio-oil at 0.25 s RT and extrapolated back to estimate the bio-oil yield at zero residence time (~60 wt%). The corresponding results for cellulose (450 °C) was ~74 wt% at 1.21 s residence time and ~77 wt% for zero residence time. In both examples, the extent of bio-oil vapor cracking in the first 1.2 s is 3-4 wt% (absolute). Fraga et al. [15] reported bio-oil and char yields for silver birch from a wire-mesh reactor where the volatile residence time was effectively zero seconds (<0.1s). Fraga's silver birch results are similar to that of Stiles, where the bio-oil yield (daf basis) at zero RT is ~56 wt% at 400 °C and ~58 wt% at 500 °C; char yields were ~11 wt% at 400 °C and ~4 wt% at 500 °C. Admittedly this is not an ideal comparison due to the differences in stability of the bio-oil vapors from cellulose, silver birch and banagrass; however, if we assume the same extent of bio-oil vapor cracking for banagrass as for silver birch and cellulose we can estimate a banagrass 'dry bio-oil' yield of ~42 wt% at 450 °C with zero residence time.

Pyrolysis water typically accounts for 10-20 wt% of products from biomass on a daf basis, as shown in Table 14. Biomass species with high ash contents and/or high concentrations of AAEM typically produce less pyrolysis water and more light/volatile compounds than species with low amounts of AAEM according to Fahmi et al. [12], although this is not apparent from the data in Table 14. Based on Fahmi's results [12] and the data in Table 14, we can estimate the amount of pyrolysis water from banagrass to be ~15 wt% relative to the daf feedstock. The amount of useful volatile material from banagrass pyrolysis can be estimated by subtracting the amounts of CO_2 and pyrolysis water from the total volatiles yield. Total volatiles from banagrass at 450 °C and 1.4 s RT account for ~95 wt% of the daf feedstock, CO_2 accounts for ~2.5 wt% and

pyrolysis water is estimated to be ~15 wt%. By difference, ~77 wt% of the daf banagrass is converted into useful products, i.e. flammable/reactive gases, volatiles and bio-oil.

Comparing the present data with Stiles's data [35] indicates that the conversion of daf feedstock to oil at the ideal conditions follows a trend of decreasing yield; cellulose > woody biomass > grasses > straws (and banagrass) > MSW > coals. The temperature which produces the greatest oil yield from the aforementioned substrates is ~400 °C for cellulose, 400-450 °C straws, ~450 °C for banagrass, 450-500 °C for woods and other grasses, ~500 °C for MWS and >550 °C for coals.

The high bio-oil yield from fast pyrolysis of cellulose is well documented, ~80 wt% or greater at residence time of ~≤1 s when secondary reactions are minimized (at 400 °C) [6, 35, 43]. Under these conditions, levoglucosan accounts for as much as ~75 wt% of the bio-oil. Lignocellulosic biomass produces lower yields of levoglucosan, and bio-oil in general, than would be anticipated from the cellulose content of the biomass, as has been discussed elsewhere [6, 43]. Briefly, the low yield of levoglucosan from biomass pyrolysis is related to its reactivity at temperatures above ~350 °C. Levoglucosan decomposes quickly as it interacts with the pyrolyzing solid mass of the biomass particle. More specifically, there is evidence that during biomass pyrolysis the cellulose and hemicellulose components start to decompose/react at lower temperatures than the lignin. This leads to reactions between the primary bio-oil vapors as they come into contact with remnants of solid lignin and ash species as they escape the particle. These reactions result in a low yield of levoglucosan, typically less than ~3 wt% of the bio-oil.

The amount of levoglucosan was not quantified in the present study, however it was detected during the GCMS analysis of the bio-oils. For the cellulose bio-oils, levoglucosan is the major component of the bio-oils at all temperatures and residence times, with higher yields at lower temperatures and shorter residence times, which is consistent with findings from other reactor configurations [6, 43]. For the banagrass bio-oils, levoglucosan was present at a very low concentration having a similar peak area as isoeugenol (the compound typically present in the highest concentration in the bio-oils), indicating that the concentration of levoglucosan is less than ~1 wt% relative to the amount of feedstock (daf).

In the present study, the bio-oil yield from cellulose pyrolysis at 400 °C and the shortest residence time (BP-4, 1.5 s) is ~69.5 wt%, falling to 62.5 wt% at the longest residence time (BP-1, 12.2 s). The corresponding bio-oil yields from banagrass are ~28-29 wt% at 400 °C, across all four residence times. This shows that the bio-oil yield from cellulose is reduced as the vapor residence time increases, whereas the bio-oil yield for banagrass was much lower and remained unchanged when increasing the residence time. This is further evidence that during banagrass pyrolysis almost all of the levoglucosan has decomposed within 1.5 seconds (at 400 °C). Furthermore, the amount of bio-oil vapors entering the freeboard (zero residence time) from banagrass is unlikely to be much greater than the yield after 1.5 s residence time, based on Stiles's [35] and Fraga's [6, 15] findings as discussed earlier. Therefore, the lower bio-oil yield from banagrass compared to silver birch and most of the other biomass materials listed in Table 14 appears to be caused by intra-particle cracking of primary bio-oil vapors as they exit the particles.

As mentioned earlier, the high ash content of banagrass (8.2 wt% ash, db, Table 2) and the high concentrations of AAEM species (K, Mg and Ca, Tables 3 and 14), in particular K, appears to be responsible for the relatively low bio-oil and char yields from banagrass. A number of researchers have shown a link between concentrations of AAEM in biomass and bio-oil and char yields and properties [2, 5, 9, 12, 30, 31, 42].

Results - Pyrolysis products from the other tropical biomasses:

Results are presented below from the fast pyrolysis of eucalyptus, leucaena, sugarcane bagasse, energy cane and pretreated energy cane (S3) at a single reaction condition (450 °C and 1.4 s residence time) for comparison to the banagrass results. Table 16 presents pyrolysis product yields in terms of bio-oil, char and permanent gases. Table 17 gives a summary of the char and ash yields. Table 18 provides a breakdown on the permanent gases in terms of wt% of CO, CO_2, CH_4 and H_2 relative to the amount of feedstock (daf).

Table 16. Bio-oil, char and gas yields (wt% feedstock daf) from pyrolysis of eucalyptus, leucaena, sugarcane bagasse, energy cane, pretreated energy cane (S3), banagrass and pretreated banagrass (S3) at the shortest residence time (BP-4)

Sample	Temperature	Dry bio-oil[¥]	Volatile bio-oil[#]	$Char_{org}$*	^CO CO_2 CH_4 H_2	Undetected**
	°C	wt%	wt%	wt%	wt%	wt%
Eucalyptus	450	48.1	0.1	4.2	6.8	40.8
Leucaena	450	40.8	0.3	2.6	6.5	49.9
S-Bagasse	450	55.1	<LLQ	2.2	5.6	37.1
E-Cane	450	46.8	0.2	3.7	6.3	42.9
E-Cane S3	450	55.3	<LLQ	3.5	6.1	35.1
Banagrass	450	36.7	0.2	3.0	7.8	52.5
Banagrass S3	450	41.3	<LLQ	3.5	7.4	47.8

[¥] S.D. of the 'dry bio-oil' yield is < ±2.0 wt% (absolute).
[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during drying and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
<LLQ, less than the lower limit of quantification, which equates to a yield of less than 2.0 wt% of the 'daf' feedstock.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be < ±2 % (absolute) and S.D. < ±1.5 wt%, see Table 17 for the amount of ash contained within the char.
** 'Undetected' is derived as: 100% - (Dry bio-oil + Volatile bio-oil + Char + CO, CO_2, CH_4 and H_2 yields).

Table 17. Summary of char and ash yields (wt% feedstock) from fast pyrolysis of eucalyptus, leucaena, sugarcane bagasse, energy cane, pretreated energy cane (S3), banagrass and pretreated banagrass (S3)

Sample	Temperature	$Char_{Org}$	$Char_{Org+Inorg}$	Ash*	Feedstock Ash
	°C	wt% daf	wt% db		wt% db
Eucalyptus	450	4.2	5.1	0.9	0.7
Leucaena	450	2.6	3.1	0.5	1.5
S-Bagasse	450	2.2	6.3	3.9	7.6
E-Cane	450	3.7	7.1	3.2	6.6
E-Cane S3	450	3.5	4.8	1.2	3.2
Banagrass[#]	450	3.9	8.1	3.9	8.5
Banagrass S3[#]	450	4.6	7.1	2.3	5.1

Bias in the char yield is estimated at ≤ ±2 % (absolute) and S.D. < ±1.5 wt%.
* Ash refers to the ash contained within the char, given as wt% of the feedstock on a dry basis, the S.D. of the ash yield is < ±1.5 wt% (absolute).
$Char_{Org}$ refers to the organic fraction of the char relative to the daf feedstock.
$Char_{Org+Inorg}$ refers to the sum of the organic and inorganic fractions of the char relative to the dry feedstock.
[#] The results for banagrass are the average of 4 tests, whereas the other samples are based on a single result.

Table 18. Permanent gas data (wt% feedstock daf) from the pyrolysis of eucalyptus, leucaena, sugarcane bagasse, energy cane, pretreated energy cane (S3), banagrass and pretreated banagrass (S3) at the shortest residence time (BP-4) and 450 °C.

Sample	Temperature	CO	CO_2	CH_4	H_2	Total Producer Gas
	C	wt%	wt%	Wt%	wt%	L/g daf
Eucalyptus	450	5.0	1.3	0.4	0.02	0.06
Leucaena	450	4.1	2.1	0.3	0.01	0.05
S-Bagasse	450	3.8	1.5	0.3	0.01	0.05
E-Cane	450	4.0	2.0	0.3	0.01	0.05
E-Cane S3	450	4.1	1.7	0.3	0.01	0.05
Banagrass	450	5.2	2.3	0.3	0.01	0.06
Banagrass S3	450	4.8	2.3	0.3	0.02	0.06
S.D. for the CO values is $\leq \pm 1.5$ wt% (absolute), for $CO_2 \leq \pm 0.5$ wt%, for $CH_4 \leq \pm 0.2$ wt% and for $H_2 \leq \pm 0.05$ wt%.						

The results in Table 16 are presented in order of decreasing yield in Table 19. The greatest dry bio-oil yields are from pretreated energy cane (S3) and sugarcane bagasse (~55 wt%) followed by eucalyptus and energy cane (~48 wt%). The greatest char yields are from eucalyptus, energy cane and pretreated energy cane. The results for eucalyptus in Tables 16 and 18 do not match literature, i.e. eucalyptus typically produces a high bio-oil yield (organic fraction ~50-60 wt% daf) and relatively low amounts of char [2-5]. The slightly low bio-oil and high char yields for eucalyptus may be due to the reaction temperature used herein (450 °C) compared to literature sources (~500 °C). A detailed account of the char yields is given in Table 17.

Table 19. Products from fast pyrolysis of the various feedstock's, shown in order of decreasing yield, based on the data in Tables 16 and 18.

Product	Order of decreasing yield by feedstock
Bio-oil yield	E-cane S3 = S-bag > Eucalyptus ≥ E-cane >> Leucaena = Bana S3 >> Bana
Char yield*	Eucalyptus ≥ E-Cane = E-Cane S3 = BanaS3 > Bana > Leucaena > S-bag
Gas yield	Bana ≥ Bana S3 > Eucalyptus ≥ Leucaena ≥ E-Cane ≥ E-Cane S3 ≥ S-bag
CO yield	Bana ≥ Eucalyptus ≥ Bana S3 > Leucaena = E-Cane S3 ≥ E-Cane ≥ S-bag
CO2 yield	Bana = Bana S3 ≥ Leucaena ≥ E-Cane > E-Cane S3 > S-bag > Eucalyptus
Undetected	Bana > Leucaena > Bana S3 > E-Cane > Eucalyptus > S-Bag > E-Cane S3
* The trend for $char_{org}$ yield is based on the results in Table 16 which are from a single experiment with the bed in its highest position. Char recovery is more difficult when working with the bed in its highest position and always results in an underestimation when compared to char yields from lower bed positions. The banagrass char yields shown in Table 17 are the average of tests at each bed position (4 tests) which results in higher values than in Table 16. Considering the S.D. all the samples generate the same amount of char expect for sugarcane bagasse and leucaena which produce less.	

Table 17 shows that all the samples generate ~4 wt% $char_{org}$ except for leucaena and sugarcane bagasse which produced ~2.0 to 2.5 wt% $char_{org}$. The standard deviation of the char values is < ±1.5 wt% (absolute). The ash results show that most, if not all, the ash from eucalyptus and leucaena is retained in the char (within experimental uncertainty), while for the other fuels about half the ash is retained within the char.

The greatest permanent gas yield is from untreated banagrass followed by pretreated banagrass and the hardwoods. Pretreated energy cane and sugarcane bagasse produced the least gas (Tables 16 and 18). Note however, that almost all differences between the gas yield values are within experimental uncertainty. The amounts of CO and CO_2 produced rather than the total amount of product gas (Tables 16 and 18) are better indicators of performance. Banagrass produces the most CO followed by eucalyptus and pretreated banagrass, with energy cane and sugarcane bagasse yielding the least. CO_2 production is the highest for pretreated and untreated banagrass

followed by leucaena. Sugarcane bagasse and eucalyptus were observed to generate the least CO_2.

The amounts of 'undetected' material (Tables 16 and 19) in the pyrolysis products of the seven biomass materials were greatest for untreated banagrass and leucaena, and lowest for eucalyptus, sugarcane bagasse and pretreated energy cane. The undetected material provides an indicator of the combined amount of pyrolysis water and volatiles in the bio-oil, products that were not quantified in the analysis.

In summary, the data in Tables 16 to 19 shows that based on the yields of 'dry bio-oil', CO and CO_2, sugarcane bagasse, pretreated energy cane and eucalyptus were the best feedstocks for fast pyrolysis. On the same basis, the worst feedstocks were untreated banagrass followed by pretreated banagrass and leucaena. This ranking system placed untreated energy cane in the middle of the grouping.

Tables 20 and 21 display the elemental analysis results for the dry bio-oils and chars, respectively, from fast pyrolysis of eucalyptus, leucaena, sugarcane bagasse, energy cane, pretreated energy cane (S3), banagrass and pretreated banagrass (S3) at the shortest residence time (BP-4, 1.4 s) and 450 °C.

Table 20. Elemental analysis results for the dry bio-oil from eucalyptus, leucaena, sugarcane bagasse, energy cane, energy cane S3, banagrass and banagrass S3 at the shortest residence time (BP-4) and 450 °C. Presented as wt% of the element in the feedstock (daf).

Sample	C	H	N	O
	wt%	wt%	wt%	wt%
Eucalyptus	51.0	52.1	117.0	44.1
Leucaena	46.3	45.1	109.1	33.6
S-Bagasse	56.4	61.3	52.6	52.6
E-Cane	50.1	52.3	50.5	42.5
E-Cane S3	55.4	59.7	86.8	54.3
Banagrass	40.8	43.6	58.3	32.8
Banagrass S3	43.6	44.6	103.1	37.6
The standard deviation for the C and O results is ≤ ±3.0 wt%, for H ≤ ±5.0 wt% and for N ~±20 wt% (absolute).				

Table 21. Elemental analysis results for the $char_{org}$ (daf) from eucalyptus, leucaena, sugarcane bagasse, energy cane, energy cane S3, banagrass and banagrass S3 at the shortest residence time (BP-4) and 450 °C. Presented as wt% of the element in the feedstock (daf).

Sample	C	H	N	O
	wt%	wt%	wt%	wt%
Eucalyptus	6.2	1.8	16.6	2.1
Leucaena	3.5	1.1	10.2	1.7
S-Bagasse	3.1	1.4	6.1	1.2
E-Cane	5.5	1.7	15.8	1.8
E-Cane S3	4.2	1.2	11.0	2.9
Banagrass	5.0	1.8	7.9	2.9
Banagrass S3	5.7	1.6	23.3	4.0
RSD is estimated to be <20 %				

The results in Table 20 show the partitioning of carbon, hydrogen, nitrogen and oxygen in the bio-oils relative to the element in the feedstock (daf) and overall trends are similar to the trend observed in dry bio-oil yields. Sugarcane bagasse, pretreated energy cane and eucalyptus have the highest C partitioning (~51-56 wt%), whereas banagrass and pretreated banagrass (~40-44

wt%) defined the lower end of the range. Oxygen partitioning followed a similar trend to that of carbon, with bio-oil from sugarcane bagasse and pretreated energy cane containing ~50-55 wt% of the feedstock oxygen, with the lowest amounts, 33 wt%, determined for banagrass and leucaena bio-oils. Hydrogen partitioning to bio-oil was greatest for sugarcane bagasse and pretreated energy cane (~60 wt%) and lowest for banagrass and pretreated banagrass (~44 wt%). Data for nitrogen are less conclusive due to the small amounts of nitrogen present in the feedstocks which resulted in larger measurement uncertainties. Despite this limitation, there appears to be a greater partitioning of nitrogen to the bio-oils from eucalyptus, leucaena, pretreated banagrass and pretreated energy cane than for the other feedstocks.

Comparison of the feedstocks that had untreated and pretreated samples shows that in all cases there is greater partitioning of all elements to the bio-oil from the pretreated samples. The effect appears to be more significant for nitrogen than other elements but this may be a reflection of the greater uncertainty in the nitrogen results.

The partitioning of elements to the char product is fairly low in all cases, with values for C < 7 wt%, H < 2 wt%, N < 20 wt% and O < 4 wt% (Table 21). The chars from eucalyptus, pretreated banagrass and untreated energy cane appear to retain slightly more carbon (~6 wt%) than the other feedstocks, with the lowest retention of carbon (~3.0-3.5 wt%) in the chars from sugarcane bagasse and leucaena. The char from pretreated banagrass appears to retain the most oxygen (~4 wt%) followed by banagrass and pretreated energy cane (~3 wt%).

Comparison to Literature

As noted in the introduction, various correlations between feedstock properties and fast pyrolysis product yields have been reported [2, 4, 5, 9, 12]. Correlations between bio-oil yields and feedstock properties include: the amounts of ash, Na + K, AAEM, volatile matter, and hemi-cellulose, and the O/C wt./wt. ratio of the feedstock. Based on the data in the previous sections, Table 22 summarizes the predicted trends for bio-oil yields based on the literature correlations, along with the trend determined from measured bio-oil yields.

Table 22. Predicted bio-oil yields from fast pyrolysis based on correlations to feedstock properties as reported in literature [2, 4, 5, 9, 12].

Basis	Predicted trend
Ash	Eucalyptus > Leucaena > E-Cane S3 > Bana S3 > E-Cane > S-bag >> Bana
Na + K	Eucalyptus > S-bag = E-Cane S3 > Leucaena > Bana S3 >> E-Cane >> Bana
AAEM	E-Cane S3 > Eucalyptus > S-bag > Bana S3 > Leucaena >> E-Cane >> Bana
Volatiles	E-Cane S3 = Eucalyptus > Bana S3 > Bana = Leucaena > S-Bag > E-Cane
O/C (wt/wt)	Woods: Leucaena = Eucalyptus Grasses: E-Cane > Bana > S-Bag > Bana S3 > E-cane S3
Cellulose	Eucalyptus ≥ Leucaena ≥ S-Bagasse > E-cane = Bana S3 ≥ E-Cane S3 ≥ Bana
Lignin	Leucaena ≥ E-Cane S3 ≥ Eucalyptus > S-Bag > Bana ≥ E-cane ≥ Bana S3
Hemi-cellulose	S-Bag > Bana S3 ≥ Bana ≥ E-Cane S3 > E-cane > Leucaena > Eucalyptus
Actual Yields	*E-cane S3 = S-bag > Eucalyptus ≥ E-cane >> Leucaena = Bana S3 >> Bana*

The actual trend in bio-oil yields is in closest agreement with the yields predicted by volatile matter content of the feedstock with the exception of sugarcane bagasse which is predicted to produce less bio-oil than was observed experimentally. The trend based on amounts of Na + K was also similar to the measured trend, although the energy cane experimental yield of bio-oil was greater than predicted. Using AAEM as a predictor of bio-oil yield did not completely agree with measured values; energy cane was predicted to produce less bio-oil than leucaena. The total amount of ash and O/C ratio in the feedstock both proved to be poor indicators of bio-oil yield. Differences in the O/C ratios between feedstock's was relatively small even when both woods and grasses were included (woods ~0.85-0.90 and grasses ~0.80-0.85, Table 2). This finding differs from the results reported by Oasmaa et al. [2] where straws displayed O/C ratios of ~0.95-1.05 and woods ~0.80-0.85. Finally, the percentages of cellulose, lignin and hemi-cellulose do not appear to be useful predictors of bio-oil yields from the feedstocks.

The above predictions show that trying to draw simple correlations between the feedstock properties and pyrolysis bio-oil yields can be confusing or contradictory. It appears from the results and trends shown in Tables 16, 19 and 22, and the literature, that the weight percentages of volatile matter and AAEM are currently the most useful indicators of bio-oil yield [2, 5, 9, 12]. The actual bio-oil yield is however dependent on the combined effects of several of the above mentioned variables and it is not entirely clear which, if any, of these properties are dominate.

Based on the data, the effects of pretreatment (i.e. reducing the amount of ash and AAEM) of banagrass and energy cane on pyrolysis products include: 1) an increase in the amount of dry bio-oil, 2) a decrease in the amount of undetected material, 3) little or no change in char yield, 4) no effect on the total gas yield, 5) a slight increase, if any, in CO yield, and 6) a slight decrease or no change in CO_2 yield. These findings are in general agreement with those reported in literature [2, 5, 9, 11, 12]. There are, however, some discrepancies. Oasmaa [2] found that decreasing amounts of AAEM resulted in less permanent gases being formed, whereas Fahmi [12] reported the opposite, and Mourant [5] saw no effect which matches the findings reported here. Note: Oasmaa compared different types of biomass, whereas Fahmi and Mourant compared samples before and after pretreatment. Fahmi [11] also found that the char yields increased with increasing AAEM content which differs from results reported here.

There is indirect evidence from the current study that bio-oils from pretreated banagrass are more stable (less aging reactions) than the bio-oils from untreated banagrass produced at identical reaction conditions. The evidence comes from GCMS analysis of the bio-oils (see Supporting Information, Section S3). For the untreated banagrass, very high concentrations of 2, 2-dimethoxypropane were present in the bio-oils (5 to 80 wt% relative to the feedstock daf, at 400 to 600 °C respectively) and the amount increased significantly with increasing storage time. For the pretreated banagrass, the bio-oils contain less 2, 2-dimethoxypropane (~2 to 15 wt% at 400 to 600 °C respectively) and the amount increased less rapidly during storage. Our data suggests that 2, 2-dimethoxypropane is a product of reactions between the bio-oil and the solvent (mixture of acetone and methanol) used to recover the bio-oil from the traps, which matches the findings of other researchers [44]. This evidence for a more stable bio-oil from pretreated banagrass matches

literature findings where biomass species with higher ash contents produce a less stable bio-oil [2, 12].

Conclusions

In this study the fast pyrolysis behavior of untreated and pretreated banagrass was examined in terms of the influence of temperature and vapor residence time on product distributions and elemental composition of the products. Two hard woods and two other grasses were also pyrolyzed at a single reaction condition for comparison to the banagrass results.

For untreated banagrass, the maximum yield of 'dry bio-oil' (~37 wt%) was obtained when working at 450 °C and the shortest residence time (RT 1.4 s). The corresponding $char_{org}$ and gas yields are ~4 wt% and ~8 wt% respectively. The carbon contents of the 450 °C bio-oil (RT 1.4 s) is ~56 wt%, oxygen accounts for ~37.5 wt%, hydrogen ~6.5 wt% and nitrogen ~1 wt%. The absolute amount of carbon in the 450 °C bio-oil (RT 1.4 s) is ~40 wt%, relative to the element in the feedstock (daf basis), oxygen ~33 wt%, hydrogen ~44 wt% and nitrogen ~58 wt%. On the same basis, the amount of carbon in the 450 °C char is ~5 wt%, oxygen ~3 wt%, hydrogen ~2 wt% and nitrogen ~8 wt%. The composition of the gas in terms of wt% relative to the daf feedstock is ~5 wt% CO, ~2.5 wt% CO_2, <0.5 wt% for CH_4 and <0.1 wt% for H_2. The amount of gas produced at 450 °C and 1.4s residence time is ~0.1 liters per gram of banagrass (daf basis), or ~8 wt% relative to the daf feedstock. Under these conditions (450 °C and 1.4 s residence time) the maximum retention of carbon in the bio-oil is achieved and the least amount of carbon is lost as CO_2.

Working at a residence time of less than 1.0 second should increase the bio-oil yield by a few percent, as discussed earlier, and result in slightly greater retention of carbon in the bio-oil.

If the goal of fast pyrolysis of untreated banagrass is to produce a bio-oil with the lowest oxygen and highest carbon content, the conditions to use are 600 °C with a residence time longer than 1.5 seconds. However, under these conditions the bio-oil yield is significantly less than at lower

temperatures and shorter residence times, ~14 wt% bio-oil at 600 °C, RT 3.5 s which contains ~62 wt% carbon and ~30 wt% oxygen. These conditions also produce the greatest yields of CO, CH_4 and H_2, but also result in a significant loss of carbon as CO_2 (~4 wt% relative to the daf feedstock).

For pretreated banagrass, the greatest yield of bio-oil was obtained when working with the shortest residence time (1.4 s) at 450 °C, ~41 wt% dry bio-oil with ~7.5 wt% gas and ~4.5 wt% $char_{org}$ relative to the feedstock (daf). The dry bio-oil produced under these conditions contains ~55 wt% C relative to the bio-oil, ~6.5 wt% H, ~0.5 wt% N and ~38 wt% O. Element partitioning to the bio-oil relative to their occurrence in the feedstock (daf) was determined to be ~45 wt% for C, ~45 wt% for H, ~100 wt% for N and ~16 wt% for O. The permanent gases were dominated by CO (~5 wt% relative to feedstock daf) and CO_2 (~2.3 wt%).

Comparing the dry bio-oil yields from the untreated and pretreated banagrass showed that the yields were greater from the pretreated sample by 4 to 11 wt% (absolute) across all test conditions. The same was found for pretreated energy cane. There appears to be no significant difference in the char yields due to pretreatment, or the total gas yields. There is, however, possibly slightly more CO and less CO_2 generated during the pyrolysis of pretreated banagrass than the untreated banagrass at pyrolysis temperatures ≥ 500 °C, or no significant difference at temperatures < 500 °C. For energy cane the same trend was observed, although the differences in CO and CO_2 yields before and after pretreatment were smaller than the experimental uncertainty.

The results show that the primary bio-oil vapors from untreated banagrass pyrolysis are highly reactive, the data indicates that almost all of the cracking of bio-oil vapors occurs as the vapors exit the particles (intra-particle). This is thought to be due to the high ash content of untreated banagrass (8.5 wt%, dry basis) and in particular due to the high concentration of alkali and alkali earth metals (totaling ~2.8 wt%, dry basis). Potassium accounts for ~2.3 wt% of the daf feedstock.

Test results from eucalyptus, leucaena, sugarcane bagasse, energy cane and pretreated energy cane, indicated that the greatest dry bio-oil yields were from sugarcane bagasse and pretreated

energy cane (~55 wt% relative to feedstock daf) followed by eucalyptus and untreated energy cane (~47-48 wt%). The total amounts of permanent gases were similar from all the feedstocks; banagrass and pretreated banagrass produce the most (~7.5-8.0 wt% relative to feedstock daf) followed by eucalyptus and leucaena (~6.5-7.0 wt%). Yields of CO are also similar from all feedstocks, with the highest yields observed from banagrass, pretreated banagrass and eucalyptus (~5 wt% relative to feedstock daf) while all the other feedstock's produce ~4 wt%. Banagrass and pretreated banagrass yielded ~2.3 wt% CO_2 with ~1.5 wt% produced from the other feedstock's. $Char_{org}$ yields (daf) were the lowest for sugarcane bagasse and leucaena (~2.5 wt% relative to feedstock daf) whereas the remaining feedstocks produced ~4 wt% $char_{org}$.

Of the materials tested, the best feedstocks for fast pyrolysis were sugarcane bagasse, pretreated energy cane and eucalyptus based on the yields of 'dry bio-oil', CO and CO_2. On the same basis, the least productive feedstock's are untreated banagrass followed by pretreated banagrass and leucaena.

Based on these results, the effect of pretreating banagrass and energy cane (i.e. reducing the amount of ash and AAEM) on pyrolysis products is: 1) to increase the dry bio-oil yield, 2) to decrease the amount of undetected material, 3) to produce a slight increase in CO yield or no change, 4) to slightly decrease CO_2 yield or no change, and 5) to produce a more stable bio-oil (less aging). Char yield and total gas yield were unaffected by feedstock pretreatment. These findings are in general agreement with those reported in the literature [2, 5, 9, 11, 12].

Supporting Information:

S1. Standard operating procedure for setting-up the pyrolysis reactor
S2. Procedure for post experiment and disassembling the pyrolysis reactor
S3. GCMS results
S4. Elemental analysis of the biomass ashes - Tabulated
S5. Temperature distributions across the bed and freeboard
S6. Pyrolysis product yields (bio-oil, char and gas) - Data tables
S7. Breakdown of the permanent gas yields - Data tables

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Final Report - Supporting Information

S1. Standard operating procedure for setting-up the pyrolysis reactor

S2. Procedure for post experiment and disassembling the pyrolysis reactor

S3. GCMS results

S4. Elemental analysis of the biomass ashes - Tabulated

S5. Temperature distributions across the bed and freeboard

S6.. Pyrolysis product yields (bio-oil, char and gas) - Data tables

S7. Breakdown of the permanent gas yields - Data tables

S1. Standard operating procedure for setting-up the pyrolysis reactor

1. Dry clean the side-arm with a scouring pad
2. Set the position of the gas distributor and *[measure distance to top flange]*
3. Install reactor body to the furnace
4. Add the bed material (~500 g) and *[measure dist. to top flange and side-arm]*
5. Check feeder-tube, clean and set Bed-screen position *[measure dist. Screen to tip]*
6. Install feeder-tube into the reactor body
7. Make all connections for water, gas and thermocouples to reactor and feeder-tube
8. Install side-arm gasket and screen
9. Assemble oil-traps
10. Install trap-1, then trap-2, cap exit from trap-2 and check if the system is leak tight
11. Connect outlet of trap-2 to gas analyzer train
12. Check leak tight (before installing hopper)
13. Clean hopper *[and weigh empty],* Install Hopper and purge for >30 mins
14. Turn on cooling water and evacuate the vacuum jacket on the feeder-tube
15. Start heating the reactor
16. Start the process gas (N2), Feeder = 1.25 LPM, Top = 0.25 LPM, Bottom = 3.0 LPM
17. Prepare fuel *[weigh]* and add to Hopper, purge for >30 mins
18. Once reactor at 3/4 of reaction temp. start heating the side-arm
19. At this time ADD Liquid N_2 and Dry-Ice to the oil-traps
20. Once at reaction temp, Hold for 45 min BEFORE start feeding fuel

21. At this time also check U_{mf} and then set flow to working velocity (U_o = 7.25 LPM)
22. Feed fuel and CHECK pressure's OK *[note the time taken to feed fuel]*
23. Stop heating 15 min. after fuel fed, or 5 min. after CO returned to 0.0%, whichever is greater

S2. Procedure for post experiment and disassembling the pyrolysis reactor

1. Stop gas flows and heating as soon as experiment is finished - to reduce oil loses
2. Remove side-arm as soon as possible (within 30 minutes)
    2a. Need to catch char that falls from side-arm screen *[weigh char]*
    2b. Wash traps to recover the oil, or put traps in freezer until ready to wash

Once the reactor has cooled to below 50 °C (approx. 8 hrs)

3. Remove hopper and *[weigh]*
4. Remove feeder-tube and catch any sand/char from SIDE-ARM and BED-Screen
5. Cap the top of reactor and attach side-arm then blow out the Char from the bed at 45 LPM for at least 5 minutes [weigh char]
6. Visually examine the bed after air blowing to assess the amount of char still in the bed, record this estimated value and add to the error in the char yield (typically less than 10% of the char remains in the bed after air blowing)
7. Remove the bed using a vacuum cleaner
8. Check bed by Loss on ignition test for any remaining char (not performed after every experiment, only now and then to aid the estimate of char remaining in the bed after air blowing)
9. Dry clean the reactor side-arm with a scouring pad

S3. GCMS results

Untreated banagrass: Tables S3.1 to S3.4 display a summary of the quantitative results for the untreated banagrass pyrolysis oils as a function of vapor residence time (bed positions BP-1 to BP-4) and temperature (400 to 600 °C). The values represent the amount of each compound relative to the amount of feedstock (daf basis) in weight percent. The lower limit of quantification (LLQ) is also given in the tables, which is derived from the calibration data as described in the experimental section of the manuscript. A value of zero means the compound was not detected. It is important to note that the GCMS results presented below are for the absolute yield of each compound present in the oil, which is not the same as the 'volatile oil yield' referred to in the report (Tables 4 and 7) which is a measure of the amount of material removed from the bio-oil samples during rotary evaporation.

Pretreated banagrass: Tables S3.5 to S3.8 displays a summary of the quantitative results for the Banagrass pyrolysis oils as a function of vapor residence time (BP-1 to BP-4) and temperature (400, 450, 500 and 600 °C). Table S3.9 presents the equivalent data for leucaena, eucalyptus, sugarcane bagasse, energy cane and pretreated energy cane at the shortest residence time (BP-4) at one temperature (450 °C). The values represent the amount of each compound relative to the amount of feedstock (daf) in weight percent. The lower limit of quantification (LLQ) is also given in the tables, which is derived from the calibration data as described in the experimental section of the manuscript. A value of zero means the compound was not detected. Note: the GCMS results presented below are for the absolute yield of each compound present in the bio-oil, which is *not* the same as the 'volatile oil yield' referred to in the manuscript, which is a measure of the amount of material removed from the bio-oils during drying.

In summary of the GCMS results, no single compound in the GC range was found to be present in any of the oil samples in a significant concentration. Instead the chromatograms showed at least ~40 peaks are detected but all at low concentrations. All the bio-oil samples showed a large

peak due to 2, 2- dimethoxypropane, which ranged in concentration from ~2 wt% relative to the amount feedstock (daf) at 400 °C, which increased significantly with increasing vapor residence time or increasing temperature, reaching a maximum of ~15 wt% relative to the amount of feedstock (daf) at 600 °C. These results are *not* included in the tables below as it is apparent that 2, 2- dimethoxypropane is a product from reactions between the oil compounds and the solvent (mixture of acetone and methanol). It is possible that some of the 2, 2 dimethoxypropane present in the oils is produced during pyrolysis as other researcher have reported this finding.[1] However, in the present study it was clear that the concentration of 2, 2 dimethoxypropane greatly increased in the samples over time, this could be clearly seen from the three analyses that are performed on each sample, with the first analysis always containing a lower concentration than subsequent analyses.

A brief aging study was performed and the concentration of 2, 2 dimethoxypropane in the oil solutions keep increasing over a period of at least 10 days, with the biggest increases observed within the first few hours of recovering the bio-oils with smaller increases over extended lengths of time. Comparing the GCMS results for the untreated [Ref] and pretreated banagrass shows that the amount of 2, 2 dimethoxypropane is significantly lower in the bio-oils from the pretreated banagrass (2 to 15 wt%) than untreated banagrass (5 to 80 wt%). This is an indication that the bio-oil from pretreated banagrass is more stable (less aging reactions) than the bio-oil from untreated banagrass.

Table S3.1. Quantitative GCMS results for the Banagrass pyrolysis oils recovered at the longest residence time (BP-1) over four temperatures. Results are presented as wt% relative to feedstock (daf).

Target Compound	*LLQ*	Temperature / °C			
		400	450	500	600
	ug/mL	wt%	wt%	wt%	wt%
Cyclohexane	*5*	<LLQ	0	0	0
Furfural	*15*	<LLQ	0	<LLQ	0
3-methyl-2-cyclopenten-1-one	*15*	0	0	0	0
Phenol	*5*	0	<LLQ	0	<LLQ
2-methoxy-phenol	*10*	<LLQ	0	<LLQ	<LLQ
o-Cresol	*10*	<LLQ	<LLQ	<LLQ	<LLQ
p-Cresol	*10*	0	<LLQ	<LLQ	<LLQ
m-Cresol	*5*	<LLQ	<LLQ	<LLQ	<LLQ
Creosol	*5*	<LLQ	<LLQ	<LLQ	<LLQ
2,4-Dimethyl-phenol	*5*	0	<LLQ	<LLQ	<LLQ
4-ethyl-phenol	*10*	<LLQ	<LLQ	<LLQ	<LLQ
2,6-dimethoxy-phenol	*5*	<LLQ	<LLQ	<LLQ	<LLQ
Indole	*5*	<LLQ	<LLQ	<LLQ	<LLQ
Isoeugenol	*10*	<LLQ	<LLQ	<LLQ	<LLQ
Benzene	*10*	0	0	<LLQ	<LLQ
Naphthalene	*10*	<LLQ	<LLQ	<LLQ	<LLQ

<LLQ, less than the lower limit of quantification.
0 means the compound was not detected.

Table S3.2. Quantitative GCMS results for the Banagrass pyrolysis oils recovered at the second longest residence time (BP-2) over four temperatures. Results are presented as wt% relative to feedstock (daf).

Target Compounds	LLQ	Temperature / °C			
		400	450	500	600
	ug/mL	wt%	wt%	wt%	wt%
Cyclohexane	5	0	0	0	0
Furfural	15	<LLQ	<LLQ	<LLQ	0
3-methyl-2-cyclopenten-1-one	15	<LLQ	<LLQ	<LLQ	<LLQ
Phenol	5	0	0.14	0.07	0
2-methoxy-phenol	10	0.16	0.20	0.15	0.17
o-Cresol	10	<LLQ	<LLQ	<LLQ	<LLQ
p-Cresol	10	0.15	<LLQ	0.17	<LLQ
m-Cresol	5	0.09	0.07	0.09	<LLQ
Creosol	5	0.18	0.19	0.16	0.11
2,4-Dimethyl-phenol	5	<LLQ	0.11	<LLQ	0.09
4-ethyl-phenol,	10	0.20	0.19	0.20	0.20
2,6-dimethoxy-phenol,	5	0.24	0.22	0.21	0.27
Indole	5	<LLQ	<LLQ	<LLQ	<LLQ
Isoeugenol	10	0.37	0.38	0.32	0.42
Benzene	10	0	0	0	0
Naphthalene	10	<LLQ	<LLQ	<LLQ	<LLQ

<LLQ, less than the lower limit of quantification.
0 means the compound was not detected.

Table S3.3. Quantitative GCMS results for the Banagrass pyrolysis oils recovered at the second shortest residence time (BP-3) over four temperatures. Results are presented as wt% relative to feedstock (daf).

Target Compounds	LLQ	Temperature / °C			
		400	450	500	600
	ug/mL	wt%	wt%	wt%	wt%
Cyclohexane	5	0	0	0	0
Furfural	15	<LLQ	<LLQ	<LLQ	<LLQ
3-methyl-2-cyclopenten-1-one	15	<LLQ	<LLQ	<LLQ	0
Phenol	5	0.16	0.08	0.16	0.17
2-methoxy-phenol	10	0.17	0.20	0.17	<LLQ
o-Cresol	10	<LLQ	<LLQ	<LLQ	<LLQ
p-Cresol	10	<LLQ	<LLQ	0.15	<LLQ
m-Cresol	5	0.07	0.07	0.08	0.07
Creosol	5	0.19	0.19	0.08	0.14
2,4-Dimethyl-phenol	5	0	0.16	<LLQ	0.14
4-ethyl-phenol,	10	0.21	0.19	0.16	0.19
2,6-dimethoxy-phenol,	5	0.23	0.23	0.19	0.20
Indole	5	<LLQ	<LLQ	<LLQ	0
Isoeugenol	10	0.39	0.39	0.26	0.38
Benzene	10	0	0	<LLQ	<LLQ
Naphthalene	10	0	0	<LLQ	<LLQ

<LLQ, less than the lower limit of quantification.
0 means the compound was not detected.

Table S3.4. Quantitative GCMS results for the Banagrass pyrolysis oils recovered at the second shortest residence time (BP-4) over four temperatures. Results are presented as wt% relative to feedstock (daf).

Target Compounds	LLQ	Temperature / °C			
		400	450	500	600
	ug/mL	wt%	wt%	wt%	wt%
Cyclohexane	5	0	0	0	0
Furfural	15	<LLQ	<LLQ	<LLQ	0
3-methyl-2-cyclopenten-1-one	15	0	0	<LLQ	<LLQ
Phenol	5	0.20	0.18	0.07	<LLQ
2-methoxy-phenol	10	<LLQ	<LLQ	<LLQ	<LLQ
o-Cresol	10	<LLQ	<LLQ	<LLQ	<LLQ
p-Cresol	10	<LLQ	<LLQ	<LLQ	<LLQ
m-Cresol	5	<LLQ	0.08	0.08	<LLQ
Creosol	5	<LLQ	<LLQ	<LLQ	0
2,4-Dimethyl-phenol	5	0.10	<LLQ	<LLQ	<LLQ
4-ethyl-phenol,	10	0.15	0.19	0.21	<LLQ
2,6-dimethoxy-phenol,	5	<LLQ	0.15	<LLQ	<LLQ
Indole	5	<LLQ	<LLQ	<LLQ	<LLQ
Isoeugenol	10	<LLQ	<LLQ	<LLQ	<LLQ
Benzene	10	0	0	<LLQ	0
Naphthalene	10	<LLQ	<LLQ	<LLQ	<LLQ

<LLQ, less than the lower limit of quantification.
0 means the compound was not detected.

Table S3.5. Quantitative GCMS results for the pretreated banagrass bio-oils recovered at the longest residence time (BP-1) over four temperatures. Results are presented as wt% relative to the amount of feedstock (daf).

Target Compounds	*LLQ*	Temperature / °C		
		500	450	400
	ug/mL	wt%	wt%	wt%
Cyclohexane	*5*	0	0	0
Furfural	*15*	<LLQ	<LLQ	<LLQ
3-methyl-2-cyclopenten-1-one	*15*	0	<LLQ	0
Phenol	*5*	0	<LLQ	<LLQ
2-methoxy-phenol	*10*	<LLQ	<LLQ	<LLQ
o-Cresol	*10*	<LLQ	<LLQ	<LLQ
p-Cresol	*10*	<LLQ	<LLQ	<LLQ
m-Cresol	*5*	<LLQ	<LLQ	<LLQ
Creosol	*5*	<LLQ	<LLQ	<LLQ
2,4-Dimethyl-phenol	*5*	<LLQ	<LLQ	0
4-ethyl-phenol,	*10*	<LLQ	<LLQ	<LLQ
2,6-dimethoxy-phenol,	*5*	<LLQ	0.07	0.08
Indole	*5*	<LLQ	<LLQ	<LLQ
Isoeugenol	*10*	<LLQ	<LLQ	<LLQ
Benzene	*10*	0	<LLQ	0
Naphthalene	*10*	<LLQ	<LLQ	<LLQ

Repeatability is +/- 0.1 wt% of the absolute values.

Table S3.6. Quantitative GCMS results for the pretreated banagrass bio-oils recovered at the second longest residence time (BP-2) over four temperatures. Results are presented as wt% relative to the amount of feedstock (daf).

Target Compounds	LLQ	Temperature / °C			
		600	500	450	400
	ug/mL	wt%	wt%	wt%	wt%
Cyclohexane	5	0	0	0	0
Furfural	15	<LLQ	<LLQ	<LLQ	<LLQ
3-methyl-2-cyclopenten-1-one	15	<LLQ	<LLQ	<LLQ	<LLQ
Phenol	5	0.15	0.24	0.11	0
2-methoxy-phenol	10	<LLQ	0.16	0.18	0.19
o-Cresol	10	<LLQ	<LLQ	<LLQ	<LLQ
p-Cresol	10	<LLQ	<LLQ	<LLQ	<LLQ
m-Cresol	5	0.07	<LLQ	0.07	0.08
Creosol	5	0.09	0.12	0.18	0.18
2,4-Dimethyl-phenol	5	<LLQ	0.11	0.17	0.15
4-ethyl-phenol,	10	0.16	0.19	0.17	0.18
2,6-dimethoxy-phenol,	5	0.18	0.18	0.23	0.22
Indole	5	<LLQ	<LLQ	0.11	<LLQ
Isoeugenol	10	0.36	0.31	0.35	0.37
Benzene	10	<LLQ	<LLQ	0	<LLQ
Naphthalene	10	<LLQ	<LLQ	<LLQ	<LLQ

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Table S3.7. Quantitative GCMS results for the pretreated banagrass bio-oils recovered at the second shortest residence time (BP-3) over four temperatures. Results are presented as wt% relative to the amount of feedstock (daf).

Target Compounds	LLQ	Temperature / °C			
		600	500	450	400
	ug/mL	wt%	wt%	wt%	wt%
Cyclohexane	5	0	0	0	0
Furfural	15	0	<LLQ	<LLQ	<LLQ
3-methyl-2-cyclopenten-1-one	15	<LLQ	<LLQ	0	<LLQ
Phenol	5	0	<LLQ	0.10	0.19
2-methoxy-phenol	10	<LLQ	<LLQ	0.17	0.16
o-Cresol	10	<LLQ	<LLQ	<LLQ	<LLQ
p-Cresol	10	<LLQ	0.15	0.14	0.15
m-Cresol	5	0.08	<LLQ	0.07	0.09
Creosol	5	<LLQ	0.08	0.16	0.19
2,4-Dimethyl-phenol	5	0.07	<LLQ	0.10	<LLQ
4-ethyl-phenol,	10	0.19	0.17	0.18	0.19
2,6-dimethoxy-phenol,	5	<LLQ	0.17	0.23	0.25
Indole	5	<LLQ	0	0.08	<LLQ
Isoeugenol	10	0.14	0.19	0.35	0.38
Benzene	10	<LLQ	<LLQ	0	0
Naphthalene	10	<LLQ	<LLQ	<LLQ	<LLQ

Table S3.8. Quantitative GCMS results for the pretreated banagrass bio-oils recovered at the shortest residence time (BP-4) over four temperatures. Results are presented as wt% relative to the amount of feedstock (daf).

Target Compounds	LLQ	Temperature / °C			
		600	500	450	400
	ug/mL	wt%	wt%	wt%	wt%
Cyclohexane	5	0	0	0	0
Furfural	15	<LLQ	<LLQ	<LLQ	0
3-methyl-2-cyclopenten-1-one	15	<LLQ	<LLQ	<LLQ	0
Phenol	5	0.20	0	0.10	<LLQ
2-methoxy-phenol	10	<LLQ	0.18	<LLQ	<LLQ
o-Cresol	10	<LLQ	<LLQ	<LLQ	<LLQ
p-Cresol	10	<LLQ	<LLQ	<LLQ	<LLQ
m-Cresol	5	0.09	0.11	0.12	<LLQ
Creosol	5	0	0.12	<LLQ	<LLQ
2,4-Dimethyl-phenol	5	0.09	0.15	<LLQ	<LLQ
4-ethyl-phenol,	10	0.20	0.23	0.28	0.24
2,6-dimethoxy-phenol,	5	<LLQ	0.22	<LLQ	0.14
Indole	5	0	<LLQ	<LLQ	0
Isoeugenol	10	<LLQ	0.35	<LLQ	<LLQ
Benzene	10	0	0	0	0
Naphthalene	10	<LLQ	0	<LLQ	0

Table S3.9. Quantitative GCMS results for leucaena, eucalyptus, sugarcane bagasse, energy cane and pretreated energy cane (S3) bio-oils recovered at the shortest residence time (BP-4) at 450 °C. Results are presented as wt% relative to the amount of feedstock (daf).

Target Compounds	LLQ	Leucaena	Eucalyptus	S-Bagasse	E-cane	E-Cane S3
	ug/mL	wt%	wt%	wt%	wt%	wt%
Cyclohexane	5	0	0	0	0	0
Furfural	15	0	<LLQ	0	<LLQ	0
3-methyl-2-cyclopenten-1-one	15	<LLQ	0	0	0	<LLQ
Phenol	5	0	0	0.08	0.09	0
2-methoxy-phenol	10	<LLQ	<LLQ	0.15	<LLQ	0.11
o-Cresol	10	<LLQ	<LLQ	<LLQ	<LLQ	<LLQ
p-Cresol	10	<LLQ	0	<LLQ	0	0
m-Cresol	5	0	0	<LLQ	0	0
Creosol	5	0.15	0.15	0.13	<LLQ	0.14
2,4-Dimethyl-phenol	5	0.12	0.13	<LLQ	0.09	<LLQ
4-ethyl-phenol,	10	0.18	<LLQ	0.20	0.17	0.15
2,6-dimethoxy-phenol,	5	0.21	0.19	0.20	0.21	0.20
Indole	5	<LLQ	<LLQ	<LLQ	<LLQ	0.07
Isoeugenol	10	0.30	0.29	0.31	0.31	0.28
Benzene	10	0	<LLQ	<LLQ	<LLQ	<LLQ
Naphthalene	10	<LLQ	<LLQ	<LLQ	<LLQ	<LLQ

S4. Elemental analysis of the biomass ashes - Tabulated

Table S4.1. Elemental analysis of the ash from leucaena, eucalyptus, sugarcane bagasse, energy cane and pretreated energy cane (S3), banagrass and pretreated banagrass (S3), the ash was calcined at 600 °C prior to analysis. Presented as wt% of the ash.

Sample	Element	SiO2	Al2O3	TiO2	Fe2O3	CaO	MgO	Na2O	K2O	P2O5	SO3	Cl	CO2	*Sum*
Leucaena	wt%	16.7	5.7	0.1	7.4	24.2	9.3	1.7	17.3	4.0	0.8	3.6	6.6	*90.7*
Eucalyptus	wt%	2.8	2.9	0.1	5.6	31.3	5.7	6.1	12.4	11.4	1.7	2.1	15.2	*82.2*
S-Bagasse	wt%	39.4	21.6	3.5	19.5	2.4	1.3	0.7	2.1	1.4	0.7	<0.01	0.3	*92.7*
E-Cane	wt%	62.2	0.8	0.02	0.5	6.2	1.6	1.7	14.4	3.6	7.8	2.7	0.4	*101.4*
E-Cane S3	wt%	67.8	1.2	0.1	1.9	3.0	1.0	0.7	4.3	1.5	1.6	0.0	0.4	*83.1*
Banagrass	wt%	47.1	0.8	<0.01	0.5	2.6	2.5	0.5	27.0	6.1	1.5	12.1	0.8	*100.7*
Banagrass S3	wt%	61.6	1.4	<0.01	1.7	4.1	1.3	0.6	6.5	2.5	0.7	0.3	1.0	*80.7*
Repeatability is estimated to be less than +/- 0.5 % of the absolute value, It is not clear why some of the ashes only sum to ~80 wt%, possible due to an underestimation of silica.														

S5. Temperature distributions across the bed and freeboard

Table S5.1 to S5.4 present the temperature distributions across the bed (T1 and T2) and the freeboard (T3 to T5) when operating the pyrolysis reactor with different bed positions. The positions of the thermocouples are described in the experimental section of the manuscript. The temperatures displayed in Tables S5.1 to S5.4 are the values noted 5 minutes before feeding the fuel, the temperatures remained within +/- 10 °C of the stated values during the course of an experiment. A three zone furnace is used to heat the reactor with the temperature of each zone set to obtain a uniform as possible temperature across the bed and freeboard. When the reactor is set up for the shortest vapor residence time experiments (bed position BP-4) the bed is located between the top two zones of the furnace which makes it difficult to keep the freeboard at a similar temperature as the bed. To avoid having a dramatically lower temperature in the freeboard than in the bed it was necessary to work with a slightly higher bed temperature than when the bed was in lower positions.

Table S5.1. Temperature distribution across the bed and freeboard for the four different bed positions when operating at 400 °C.

Thermocouple position	Bed position			
	BP-1	BP-2	BP-3	BP-4
	°C	°C	°C	°C
T1	397	409	408	418
T2	401	405	402	406
T3	406	379	410	378
T4	404	422	382	n/a
T5	404	401	389	354
n/a, not applicable as when the bed is in its highest position (BP-4) thermocouple T4 is no longer in the freeboard of the reactor				

Table S5.2. Temperature distribution across the bed and freeboard for the four different bed positions when operating at 450 °C.

Thermocouple position	Bed position			
	BP-1	BP-2	BP-3	BP-4
	°C	°C	°C	°C
T1	451	460	455	471
T2	449	449	453	444
T3	453	408	472	420
T4	449	473	434	n/a
T5	450	450	440	400

Table S5.3. Temperature distribution across the bed and freeboard for the four different bed positions when operating at 500 °C.

Thermocouple position	Bed position			
	BP-1	BP-2	BP-3	BP-4
	°C	°C	°C	°C
T1	500	503	510	520
T2	497	498	506	501
T3	503	459	512	466
T4	498	521	458	n/a
T5	498	500	475	436

Table S5.4. Temperature distribution across the bed and freeboard for the four different bed positions when operating at 600 °C.

Thermocouple position	Bed position			
	BP-1	BP-2	BP-3	BP-4
	°C	°C	°C	°C
T1	n/a	598	604	614
T2	n/a	597	600	611
T3	n/a	554	609	562
T4	n/a	618	560	n/a
T5	n/a	598	567	531

S6. Pyrolysis product yields (bio-oil, char and gas) - Data tables

Table S6.1. Oil, char and gas yields (wt% daf) from untreated banagrass pyrolysis at 2nd longest residence time (BP-2)

Temperature	Bed Position	Dry Bio-Oil	Volatile Bio-Oil[#]	$Char_{Org}$*	^CO CO_2 CH_4 H_2	Undetected**
°C		wt%	wt%	wt%	wt%	wt%
400	BP-2	29.2	<LLQ	8.3	7.7	54.8
450	BP-2	27.8	<LLQ	3.9	8.5	59.9
500	BP-2	25.6	<LLQ	2.6	12.8	59.0
600	BP-2	10.5	<LLQ	2.5	29.2	57.8

<LLQ, less than the lower limit of quantification.
[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during rotary evaporation and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be ≤±2 wt% (absolute), values are for the daf char
** 'Undetected' is derived as: 100% - (dry bio-oil + volatile bio-oil + char + CO, CO_2, CH_4 and H_2 yields).

Table S6.2. Oil, char and gas yields (wt% daf) from untreated banagrass pyrolysis at 2nd shortest residence time (BP-3)

Temperature	Bed Position	Dry Bio-Oil	Volatile Bio-Oil[#]	$Char_{Org}$*	^CO CO_2 CH_4 H_2	Undetected**
°C		wt%	wt%	wt%	wt%	wt%
400	BP-3	26.6	0.2	8.9	8.4	56.0
450	BP-3	28.0	0.2	3.9	9.0	58.9
500	BP-3	25.7	0.2	3.5	11.6	59.0
600	BP-3	13.9	0.2	1.0	24.7	60.3

<LLQ, less than the lower limit of quantification.
[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during rotary evaporation and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be ≤±2 wt% (absolute), values are for the daf char
** 'Undetected' is derived as: 100% - (dry bio-oil + volatile bio-oil + char + CO, CO_2, CH_4 and H_2 yields).

Table S6.3. Oil, char and gas yields (wt% daf) from untreated banagrass pyrolysis at shortest residence time (BP-4)

Temperature	Bed Position	Dry Bio-Oil	Volatile Bio-Oil[#]	$Char_{Org}$*	^CO CO_2 CH_4 H_2	Undetected**
°C		wt%	wt%	wt%	wt%	wt%
400	BP-4	28.5	0.2	n/a	7.9	n/a
450	BP-4	36.7	0.2	3.0	7.8	52.5
500	BP-4	30.2	<LLQ	3.0	9.2	57.6
600	BP-4	20.9	<LLQ	2.1	14.7	62.3

<LLQ, less than the lower limit of quantification.
[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during rotary evaporation and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be ≤±2 wt% (absolute), values are for the daf char
** 'Undetected' is derived as: 100% - (dry bio-oil + volatile bio-oil + char + CO, CO_2, CH_4 and H_2 yields).

Table S6.4. Bio-oil, char and gas yields (wt% feedstock daf) from pyrolysis of pretreated banagrass at the longest residence time (BP-1)

Temperature	BP	Dry bio-oil[¥]	Volatile bio-oil[#]	$Char_{org}$*	^CO CO_2 CH_4 H_2	Undetected**
C	Second	wt%	wt%	wt%	wt%	wt%
400	BP-1	33.3	<LLQ	7.2	9.1	50.4
450	BP-1	35.2	<LLQ	4.6	12.3	47.9
500	BP-1	24.4	<LLQ	4.9	19.0	51.7

[¥] S.D. of the 'dry bio-oil' yield is < ±2.0 wt% (absolute).
[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during drying and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
<LLQ, less than the lower limit of quantification, which equates to a yield of less than 2.0 wt% of the 'daf' feedstock.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be < ±2 % (absolute) and S.D. < ±1.5 wt%.
** 'Undetected' is derived as: 100% - (Dry bio-oil + Volatile bio-oil + Char + CO, CO_2, CH_4 and H_2 yields).

Table S6.5. Bio-oil, char and gas yields (wt% feedstock daf) from pyrolysis of pretreated banagrass at the 2nd longest residence time (BP-2)

Temperature	BP	Dry bio-oil[¥]	Volatile bio-oil[#]	$Char_{org}$*	^CO CO_2 CH_4 H_2	Undetected**
C	Second	wt%	wt%	wt%	wt%	wt%
400	BP-2	36.2	<LLQ	7.5	6.7	49.6
450	BP-2	36.4	<LLQ	5.6	8.6	49.4
500	BP-2	29.4	0.1	3.8	12.7	53.9
600	BP-2	14.1	<LLQ	0.8	29.0	56.0

[¥] S.D. of the 'dry bio-oil' yield is < ±2.0 wt% (absolute).
[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during drying and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
<LLQ, less than the lower limit of quantification, which equates to a yield of less than 2.0 wt% of the 'daf' feedstock.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be < ±2 % (absolute) and S.D. < ±1.5 wt%.
** 'Undetected' is derived as: 100% - (Dry bio-oil + Volatile bio-oil + Char + CO, CO_2, CH_4 and H_2 yields).

Table S6.6. Bio-oil, char and gas yields (wt% feedstock daf) from pyrolysis of pretreated banagrass at the 2nd shortest residence time (BP-3)

Temperature	BP	Dry bio-oil[¥]	Volatile bio-oil[#]	$Char_{org}$*	^CO CO_2 CH_4 H_2	Undetected**
C	Second	wt%	wt%	wt%	wt%	wt%
400	BP-3	35.6	0.1	6.6	7.1	50.5
450	BP-3	36.2	<LLQ	5.5	9.9	48.5
500	BP-3	32.8	<LLQ	4.6	12.6	50.0
600	BP-3	15.5	<LLQ	1.8	28.6	54.2

[¥] S.D. of the 'dry bio-oil' yield is < ±2.0 wt% (absolute).
[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during drying and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
<LLQ, less than the lower limit of quantification, which equates to a yield of less than 2.0 wt% of the 'daf' feedstock.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be < ±2 % (absolute) and S.D. < ±1.5 wt%.
** 'Undetected' is derived as: 100% - (Dry bio-oil + Volatile bio-oil + Char + CO, CO_2, CH_4 and H_2 yields).

Table S6.7. Bio-oil, char and gas yields (wt% feedstock daf) from pyrolysis of pretreated banagrass at the shortest residence time (BP-4)

Temperature	BP	Dry bio-oil[¥]	Volatile bio-oil[#]	$Char_{org}$*	^CO CO_2 CH_4 H_2	Undetected**
C	Second	wt%	wt%	wt%	wt%	wt%
400	BP-4	38.7	0.4	4.1	5.1	51.7
450	BP-4	41.3	<LLQ	3.5	7.4	47.8
500	BP-4	37.3	0.8	-	9.5	-
600	BP-4	28.3	0.2	1.9	16.2	53.5

[¥] S.D. of the 'dry bio-oil' yield is < ±2.0 wt% (absolute).
[#] Volatile bio-oil refers to the amount of bio-oil removed from the sample during drying and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried.
<LLQ, less than the lower limit of quantification, which equates to a yield of less than 2.0 wt% of the 'daf' feedstock.
^ Indicative values derived from on-line gas analysis.
* The bias in the char yield is estimated to be < ±2 % (absolute) and S.D. < ±1.5 wt%.
** 'Undetected' is derived as: 100% - (Dry bio-oil + Volatile bio-oil + Char + CO, CO_2, CH_4 and H_2 yields).

S7. Breakdown of the permanent gas yields - Data tables

Table S7.1. Permanent gas data from the pyrolysis of untreated banagrass at the longest residence time (BP-1), presented as wt% relative to the daf feedstock.

Temp	CO	CO2	CH4	H2	Total Producer Gas
°C	wt%	wt%	wt%	wt%	L/g daf
400	5.3	2.6	0.2	0.02	0.07
450	8.4	2.9	0.6	0.08	0.11
500	11.3	2.8	0.7	0.20	0.15
600	27.4	4.8	2.1	0.60	0.38
The relative standard deviation in the 'total producer gas' values is less than ± 4 %. The standard deviation for the CO values is ≤±1.0 wt% (absolute), for CO_2 ≤±0.5 wt%, for CH_4 ≤±0.2 wt% and for H_2 ≤±0.05 wt%.					

Table S7.2. Permanent gas data from the pyrolysis of untreated banagrass at the second longest residence time (BP-2), presented as wt% relative to the daf feedstock.

Temp	CO	CO2	CH4	H2	Total Producer Gas
°C	wt%	wt%	wt%	wt%	L/g daf
400	5.1	2.4	0.2	0.01	0.06
450	6.0	2.1	0.3	0.01	0.07
500	9.2	3.0	0.6	0.09	0.12
600	21.4	5.6	1.8	0.42	0.30
The relative standard deviation in the 'total producer gas' values is less than ± 4 %. The standard deviation for the CO values is ≤±1.0 wt% (absolute), for CO_2 ≤±0.5 wt%, for CH_4 ≤±0.2 wt% and for H_2 ≤±0.05 wt%.					

Table S7.3. Permanent gas data from the pyrolysis of untreated banagrass at the second shortest residence time (BP-3), presented as wt% relative to the daf feedstock.

Temp	CO	CO2	CH4	H2	Total Producer Gas
°C	wt%	wt%	wt%	wt%	L/g daf
400	5.1	3.0	0.3	0.01	0.07
450	5.1	3.3	0.3	0.03	0.07
500	7.7	3.0	0.5	0.05	0.10
600	17.4	4.0	1.1	0.27	0.23
The relative standard deviation in the 'total producer gas' values is less than ± 4 %. The standard deviation for the CO values is ≤±1.0 wt% (absolute), for CO_2 ≤±0.5					

wt%, for CH_4 ≤±0.2 wt% and for H_2 ≤±0.05 wt%.

Table S7.4. Permanent gas data from the pyrolysis of untreated banagrass at the shortest residence time (BP-4), presented as wt% relative to the daf feedstock.

Temp	CO	CO2	CH4	H2	Total Producer Gas
°C	wt%	wt%	wt%	wt%	L/g daf
400	5.2	2.4	0.3	0.02	0.07
450	5.2	2.3	0.3	0.01	0.06
500	6.5	2.3	0.4	0.03	0.08
600	11.4	2.4	0.8	0.14	0.14
The relative standard deviation in the 'total producer gas' values is less than ± 4 %. The standard deviation for the CO values is ≤±1.0 wt% (absolute), for CO_2 ≤±0.5 wt%, for CH_4 ≤±0.2 wt% and for H_2 ≤±0.05 wt%.					

Table S7.5. Permanent gas data from the pyrolysis of pretreated banagrass at the longest residence time (BP-1). Data presented as wt% relative to the daf feedstock.

Temp	CO	CO2	CH4	H2	Total Producer Gas
C	wt%	wt%	wt%	wt%	L/g daf
400	6.0	2.8	0.3	0.02	0.08
450	8.8	2.8	0.6	0.07	0.11
500	14.8	3.0	1.0	0.20	0.19

Table S7.6. Permanent gas data from the pyrolysis of pretreated banagrass at the second longest residence time (BP-2). Data presented as wt% relative to the daf feedstock.

Temp	CO	CO2	CH4	H2	Total Producer Gas
C	wt%	wt%	wt%	wt%	L/g daf
400	2.9	1.6	0.1	0.01	0.04
450	6.1	2.1	0.4	0.03	0.08
500	9.5	2.4	0.7	0.12	0.12
600	24.4	3.6	1.3	0.49	0.31

Table S7.7. Permanent gas data from the pyrolysis of pretreated banagrass at the second shortest residence time (BP-3). Data presented as wt% relative to the daf feedstock.

Temp	CO	CO2	CH4	H2	Total Producer Gas
C	wt%	wt%	wt%	wt%	L/g daf
400	4.6	2.1	0.2	0.02	0.06
450	6.9	2.1	0.5	0.05	0.09
500	9.0	2.4	0.6	0.08	0.11
600	20.3	3.0	1.5	0.33	0.27

Table S7.8. Permanent gas data from the pyrolysis of pretreated banagrass at the shortest residence time (BP-4). Data presented as wt% relative to the daf feedstock.

Temp	CO	CO2	CH4	H2	Total Producer Gas
C	wt%	wt%	wt%	wt%	L/g daf
400	3.6	1.3	0.2	0.01	0.04
450	4.8	2.3	0.3	0.02	0.06
500	6.8	2.1	0.5	0.04	0.08
600	12.8	2.4	0.8	0.14	0.16

1. Steele PH, Pittman CU, Jr., Ingram LL, Jr., Gajjela S, Zhang Z, Bhattacharya P, inventors; Mississippi State University, assignee. Method to upgrade bio-oils to fuel and bio-crude. patent US 8,603,199 B2. 2013.