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Investigating the potential for a self-sustaining slow pyrolysis system under varying operating conditions



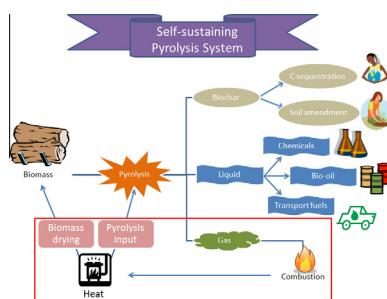
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HIGHLIGHTS

- H₂, CH₄, C₂H₆ and CO increased with temperature resulted in a higher gas HHV.
- The lower energy limit was surpassed by all pyrolysis at ≥ 450 °C.
- The upper energy limit was only reached during pyrolysis at 650 °C.
- Solid and liquid by-products utilised for high value products rather than as a fuel.

GRAPHICAL ABSTRACT



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ABSTRACT

This work aimed to investigate the impact of highest treatment temperature (HTT), heating rate, carrier gas flow rate and feedstock on the composition and energy content of pyrolysis gas to assess whether a self-sustained system could be achieved through the combustion of the gas fraction alone, leaving other co-products available for alternative high-value uses. Calculations based on gas composition showed that the pyrolysis process could be sustained by the energy contained within the pyrolysis gases alone. The lower energy limit (6% biomass higher heating value (HHV)) was surpassed by pyrolysis at ≥ 450 °C while only a HTT of 650 °C consistently met the upper energy limit (15% biomass HHV). These findings fill an important gap in literature related to the energy balance of the pyrolysis systems for biochar production, and show that, at least from an energy balance perspective; self-sustained slow pyrolysis for co-production of biochar and liquid products is feasible.

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1. Introduction

Out of the three pyrolysis co-products, biochar (HHV ~ 18 MJ kg⁻¹) and bio-oil (HHV ~ 17 MJ kg⁻¹) can be regarded as medium to high-energy-density materials, while pyrolysis gas (HHV ~ 6 MJ kg⁻¹) (Bridgwater, 2006; Laird et al., 2009) is a low-energy-density product. Besides their use as solid and liquid biofuels, biochar and bio-oil have a host of alternative high value applications which could considerably improve the economic viability of the

pyrolysis system. Extraction of high-value chemicals from pyrolysis liquids (bio-oil) and/or their upgrading to liquid biofuels is a promising route to efficient decarbonisation of transport and chemical industry (Bridgwater, 2012; Czernik and Bridgwater, 2004). Such chemical products can provide comparable revenue to fuel and energy products even with such relatively small amounts (around 5%) used for this purpose, making for an attractive alternative use for bio-oil (Bridgwater, 2012; Czernik and Bridgwater, 2004). In addition to bio-oils added benefits, biochar can also offer numerous environmental and agricultural benefits such as improved soil fertility and long-term storage of carbon (C) in the environment (Lehmann, 2007; Lehmann et al., 2009; Woolf et al., 2010). This is achieved through the highly recalcitrant nature of biochar as well

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as its ability to influence nutrient retention, water holding capacity, soil pH, cation exchange capacity and reducing or suppressing the emission of greenhouse gas such as CO₂, N₂O and CH₄ (Chan and Xu, 2009; Lehmann, 2007; Manyà, 2012). Woolf et al. (2010) described how the C mitigation impact of biochar is about 25% larger, on average, than the impact obtained if the same biomass was fully combusted for energy. Therefore, the incorporation of biochar into soils to provide soil amendment benefits, reduced environmental pollution as well as long term C sequestration may in many cases be the preferred alternative to combustion (Lehmann, 2007; Lehmann et al., 2009; Manyà, 2012; Sohi, 2012).

Due to its typically low heating value, pyrolysis gas is potentially better suited for heating of the unit or feedstock drying than for power generation (Becidan et al., 2007; Chen et al., 2012). The mixture of non-condensable gases produced during pyrolysis consists of a number of combustible gases, e.g., CO, CH₄, H₂ and C₂-hydrocarbons but also a high concentration of incombustible CO₂. These gases are produced during pyrolysis due to thermally favoured reactions such as depolymerisation, decarboxylation, demethanation, etc. (Duman et al., 2011; Fu et al., 2011; González et al., 2003), and the processes are relatively well understood. However, there are only a few studies focused on the composition and application of gases released during slow pyrolysis (Chen et al., 2012; Duman et al., 2011; Fu et al., 2011; Williams and Besler, 1996). Several studies have attempted to assess the energy required for pyrolysis as a fraction of the feedstock calorific value (Bridgwater, 2006; Daugaard and Brown, 2003; Gronnow et al., 2013; Yang et al., 2013), however these studies have not considered how varying production conditions during slow pyrolysis may influence the final energy distribution among pyrolysis co-products. Therefore, there is a gap in understanding of the energy balance of biochar production, which has been reflected in LCA studies to date.

To address this gap, the work reported here focused on investigating the influence that feedstock, HTT, heating rate and carrier gas flow rate have on the composition and related energy content of pyrolysis gases. The energy content of the pyrolysis gas was then used to assess the extent to which pyrolysis gases alone could sustain a pyrolysis process. To our knowledge no literature currently exists which has attempted to investigate the impact of this combination of production conditions on the yield and composition of slow pyrolysis gas in one study. Therefore an alternative source of fuel to run the pyrolysis system could free up the solid and liquid co-products of pyrolysis to be used for higher-value applications, e.g. transportation fuels, bio-chemicals and biochar for environmental and soil applications, to maximise the energy and agricultural benefits of the entire system.

2. Methods

2.1. Feedstock

Pyrolysis experiments were performed using five types of biomass: mixed pine chips (PC), raw wheat straw (WS), wheat straw pellets (WSP), mixed 50/50 wheat:oilseed rape straw pellets (SP) and mixed 5/95 pine:spruce softwood pellets (WP). Full details of SP and WP material can be found in Crombie and Mašek (in press). All feedstock was used as received with no pre-treatment, i.e. with initial moisture content (measured gravimetrically loss on drying at 105 °C for 24 h) of 4.5% for PC, 4.5% for WS and 13.3% for WSP. PC (ranging 15 × 5 × 4 mm to 100 × 40 × 15 mm in dimensions) was obtained from Stonelaws Farm in East Lothian, Scotland while both WS (10 × 3 × 1 mm to 90 × 5 × 4 mm) and WSP (Ø 6 mm) were purchased from StrawPellet Ltd., Rookery Farm, Lincolnshire, England. The natural heterogeneity within the bulk supply of the

PC and WS feedstock was minimised as far as possible by thoroughly mixing a volume sufficient for all experiments. The biomass composition of cellulose, hemicellulose and lignin was determined using a thermogravimetric analyser (Netzsch STA 409) connected to a FTIR spectrometer (EQUINOX-55, Bruker) at the University of York. A sample of each feedstock (typically 50 mg) was heated to 800 °C at a rate of 10 °C min⁻¹ under N₂ gas at 100 ml min⁻¹ and the resulting data curves were processed to individual Gaussian peaks using OriginLab software and the FTIR spectra of volatile products. Composition data for all feedstock was shown in Table 1.

2.2. Pyrolysis system

A detailed description of the equipment type and set up can be found in Crombie et al. (2013). A fixed bed batch pyrolysis unit (Fig. 1) consisting of a vertical quartz tube (50 mm diameter) heated by a 12 kW infra-red gold image furnace (P610C; ULVAC-RIKO, Yokohama, Japan) was used for production of all biochar samples. Nitrogen (N₂) carrier gas, preheated at the base of the reactor, was used to sweep volatiles and pyrolysis gas into a staged condensation system developed for the collection and separation of condensable and non-condensable volatiles. The condenser system consisted of three stages to separate and collect heavy tar components, water, water soluble organic compounds and light aromatics. The first section was heated (160 ± 10 °C) to allow for the removal of entrained particulates on a filter while collecting high-boiling tars in a separate trap. The second stage consisted of a receiver for the collection of volatile material condensing at room temperature. The final section of the condensation system was comprised of a series of cold traps, cooled to less than -40 °C, to remove any remaining condensable volatiles. The remaining non-condensable gases were swept from the system by the carrier gas, collected in a 200 L multi-layered gas bag (Jensen Inert Products, Coral Springs, Florida) and analysed for overall composition using a mass spectrometer (HPR-20 QIC, Hiden Analytical, Warrington, UK). Following the composition analysis the gaseous product was vented through a volumetric gas meter (TG5; Ritter, Bochum, Germany) and total volume recorded.

2.3. Pyrolysis conditions

A standard volume of feedstock (200 mm bed depth) was used for each pyrolysis experiment, resulting in a different mass of material used for each biomass: 40 g for PC, 15 g for WS and 120 g for WSP. The mass of WSP material was reduced to 60 g for runs using 100 °C min⁻¹ heating rate as the rapid release of gas exceeded the handling capacity of the condensation system. The PC, WS and WSP feedstock were selected for investigating the effect of HTT and heating rate on the gas composition obtained from pyrolysis. Four HTTs (350, 450, 550 and 650 °C) were selected for the pyrolysis experiments to cover a typical range of temperatures used in slow pyrolysis and carbonisation. The effect of heating rate was investigated by using the heating rates of 100 °C min⁻¹ (a typical heating rate for industrial size slow pyrolysis) and 5 °C min⁻¹ (chosen to provide adequate heat transfer while being considerably lower than 100 °C min⁻¹). All runs were carried out applying one standard carrier gas flow rate (0.33 ± 0.02 L min⁻¹) of N₂ and holding time at HTT (20 min). WP and SP pyrolysis, described in Crombie and Mašek (in press), was carried out to investigate the influence of HTT, residence time and carrier gas flow rate on the properties of biochar. Therefore throughout these studies the HTTs of 350 and 650 °C was chosen to provide data at both ends of the typical slow pyrolysis temperature scale. The hold times at HTT (residence time) of 10, 20 and 40 min were selected to cover an acceptable range for industrial sized continuous pyrolysis units as substantially holding times would not be economically feasible. The carrier gas flow rates of 0, 0.33 ± 0.02 and

Table 1
Composition of feedstock used throughout pyrolysis experiments on a dry weight basis (db).

Sample	Proximate analysis [wt.% (db)]			Ultimate analysis [wt.% (db)]							Biomass components [wt.% (db)]		
	Fixed C %	Volatile matter %	Ash %	C %	H %	N %	O %	O:C	H:C	HHV [MJ kg ⁻¹]	Cellulose	Hemicellulose	Lignin
Pine wood chips	22.3	75.7	2.0	50.7	4.8	0.0	42.4	0.6	1.1	16.7	52.0	21.0	12.6
Wheat straw	15.0	78.5	6.5	43.1	5.8	0.0	44.6	0.8	1.6	18.0	22.0	42.0	30.0
Wheat straw pellets	18.0	81.8	0.2	48.0	6.2	1.8	43.8	0.7	1.5	19.0	23.0	44.0	26.0
Straw pellet feed	15.3	77.2	7.4	42.0	5.5	0.1	44.9	0.8	1.6	15.8	23.0	49.0	22.0
Wood pellet feed	17.2	77.2	5.7	53.7	6.7	0.0	33.9	0.5	1.5	17.6	58.8	9.4	21.9

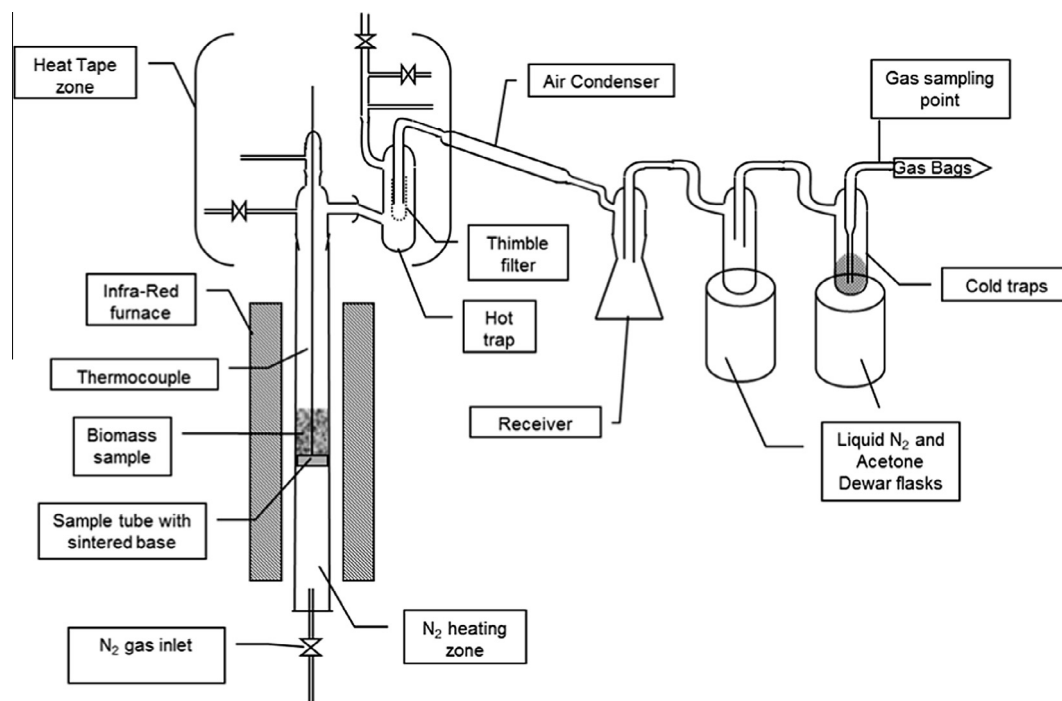


Fig. 1. Schematic of UKBRC small-scale batch pyrolysis unit and condensation system.

$0.66 \pm 0.02 \text{ L min}^{-1}$ were applied during pyrolysis experiments to maintain a safe handling capacity for the condensation system while also covering an acceptable range for flow rate. When investigating the impact of 0 L min^{-1} , the system was purged with N_2 , sealed and the progression of volatiles through the system was controlled by the evolution of gas species during biomass decomposition. Due to the high volatile matter content of WP and SP biomass the lower heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ was used for WP and SP pyrolysis to maintain a safe handling capacity of the condensation system. After pyrolysis, the different products were collected, measured and stored as described in Crombie et al. (2013).

2.4. Product analysis

2.4.1. Biochar analysis

As the pyrolysis gas composition (and therefore heating value) was the main focus of this work the detailed analysis of the respective biochar fractions can be found in Crombie and Mašek (in press) (SP and WP biochar) and Crombie et al. (2014) (PC, WS and WSP biochar). Due to a lack of comparable material no pyrolysis run could be performed for WSP biomass at $350 \text{ }^\circ\text{C}$ and $100 \text{ }^\circ\text{C min}^{-1}$.

2.4.2. Gas analysis

Gas samples were collected during each pyrolysis run using 200 L multilayer gas bags and analysed for the concentration of N_2 , H_2 , CO , CO_2 , CH_4 , O_2 , Ar and C_2 hydrocarbons on a volume basis,

using a mass spectrometer (HPR-20 QIC, Hiden Analytical, Warrington, UK). As both CO and N_2 give parent peaks at mass 28 it was difficult to differentiate between them particularly as other species being analysed also have peaks present at mass 28. To solve this problem pure N_2 was sampled and the ratio of N_2 at mass 14 and 29 was determined which then allowed for the calculation of N_2 at mass 29 by measuring N_2 at mass 14 during the experiments. Once the amount of N_2 at mass 29 was determined it was subtracted from the remaining measurements at mass 29 leaving only CO at mass 29. The mass spectrometer could not distinguish between C_2 hydrocarbons so for the sake of mass and HHV calculations the C_2 hydrocarbon fraction was assumed to be and therefore further referred to as ethane (C_2H_6). The final composition of the pyrolysis gas, expressed in Figs. 2 and 3, was corrected for the dilution effect of the carrier gas (N_2) but the heating values of pyrolysis gas were still calculated with N_2 concentration taken into account. This was to allow for a direct indication of the energy contained in the gas stream of the pyrolysis system without any upgrading processes. The results of gas HHV/lower heating value (LHV) and cold gas efficiency were calculated by the following equations and shown in Table 3:

$$m_{\text{gas}} [\text{kg}] = m_{\text{H}_2} + m_{\text{CO}} + m_{\text{CH}_4} + m_{\text{C}_2\text{H}_6} + m_{\text{CO}_2}$$

$$\text{HHV}_{\text{gas}} [\text{MJ/kg}] = ((m_{\text{H}_2} \times \text{HHV}_{\text{H}_2}) + (m_{\text{CO}} \times \text{HHV}_{\text{CO}}) + (m_{\text{CH}_4} \times \text{HHV}_{\text{CH}_4}) + (m_{\text{C}_2\text{H}_6} \times \text{HHV}_{\text{C}_2\text{H}_6}) / m_{\text{gas}}$$

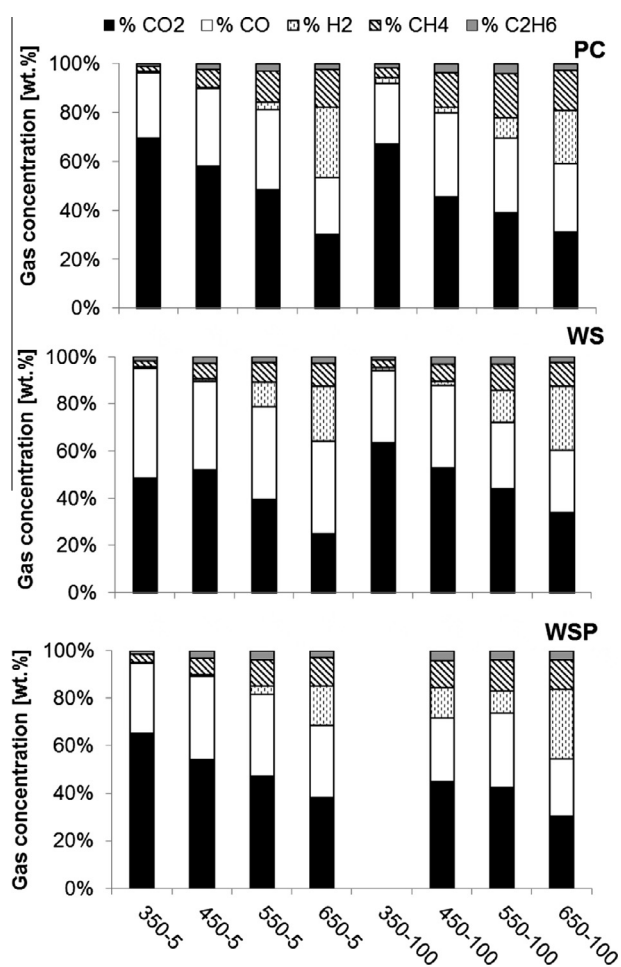


Fig. 2. Influence of HTT and heating rate on the gas composition obtained from PC, WS and WSP pyrolysis. Composition corrected for dilution effect of carrier gas.

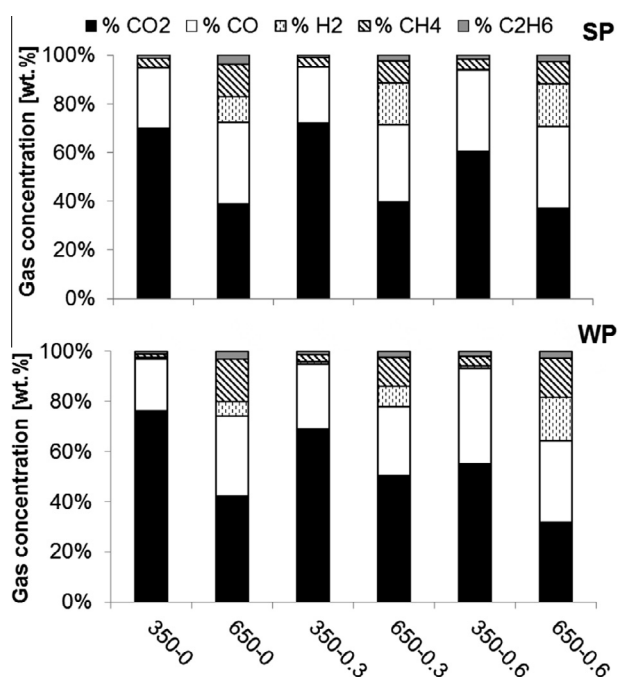


Fig. 3. Investigating the effect of flow rate and HTT on the gas composition of CO, H₂, CH₄, C₂H₆ (Crombie and Mašek, in press) and CO₂, measured from SP and WP experiments. Composition corrected for dilution effect of carrier gas.

The LHV of the product gas was then determined through subtracting the latent heat of water. To compare the efficiency of converting biomass using different technologies and under different conditions, the Cold Gas Efficiency (CGE) is often used. The CGE can be determined as:

$$\text{CGE} [\%] = ((\text{LHV}_{\text{gas}} \times m_{\text{gas}}) / (\text{LHV}_{\text{feed}} \times m_{\text{feed}})) \times 100$$

2.5. Statistical analysis

Analysis of variance (ANOVA) was applied through a general linear model using Minitab 16 statistical software and significance of results were calculated at a significance level of $P < 0.05$ for all materials and production conditions. Correlations were performed using Spearman rank method and R values were categorised by considering correlation coefficients < 0.35 to represent low or weak correlations, 0.36 – 0.67 to be moderate correlations, 0.68 – 0.90 strong or high correlations and > 0.9 to be a very high correlation (Taylor, 1990).

3. Results and discussion

3.1. Product distribution

Production yields for char, liquid and gas co-products for SP, WP, PC, WS and WSP are shown in Table 2 (for more details see Crombie and Mašek (in press) and Crombie et al. (2014)).

In brief, for all feedstock, increasing the HTT caused the biochar yield to decrease and subsequently increase the liquid and gas yields. HTT was identified as the dominant variable in determining the distribution of the char, liquid and gas co-products ($P < 0.0001$) where as feedstock only influenced the liquid and gas yields thus accounting for further variation between the different biomass types. As HTT increased for each heating rate, there was a decrease in the yield of char and a corresponding increase in the gas and liquid yields. Overall, heating rate, in the range from 5 to 100 °C/min, showed no statistically significant influence ($P > 0.05$) on the final char, liquid or gas yield due to different trends seen for different feedstock. When focusing on each individual feedstock varying the heating rate did result in significant differences in the yield of char (PC and WS), liquid (WS and WSP) and gas (PC, WS and WSP). No influence of heating rate was still seen for PC liquid and WSP char yields due to a convergence towards similar values compared to 5 °C min⁻¹ for these products at elevated HTT.

In addition to HTT, SP and WP experiments were also designed to investigate the influence of carrier gas flow rate on the product distribution. Increasing the carrier gas flow rate decreased the vapour residence time within the fixed bed reactor, thus decreasing the contact time of primary vapours and hot char surfaces diminishing secondary char formation (Antal and Grønli, 2003; Crombie and Mašek, in press; Demiral and Ayan, 2011; Duman et al., 2011; Huang et al., 2013). As the carrier gas flow rate was increased there was a significant decrease in char yield ($P < 0.05$). Increased the carrier gas flow rate also resulted in higher gas and liquid yields for runs at 350 °C however no effect was observed for liquid yields at 650 °C ($P = 0.41$) (Crombie and Mašek, in press).

3.2. Influence of pyrolysis conditions on gas composition

3.2.1. Highest treatment temperature

The composition and yields of pyrolysis co-products are a result of the thermal decomposition of biomass constituents, such as cellulose, hemicellulose and lignin. The composition of these components and the temperature regions over which they decompose ultimately determine the gas composition obtained during

Table 2
Distribution of solid, liquid and gas products from the pyrolysis of PC, WS, WSP, SP and WP material under varying conditions on a dry weight basis (db) (Crombie and Mašek, in press; Crombie et al., 2014).

Sample	Product distribution [wt.% (db)]						
	Temperature [°C]	Heating rate [°C/min]	Flow rate [L/min]	Biochar %	Liquid %	Gas %	Total %
Pine	350	5	0.33	49.2	30.7	19.1	99.0
	450	5	0.33	36.8	41.3	24.1	102.2
	550	5	0.33	32	42.9	25.5	100.4
	650	5	0.33	28.1	50.2	23.2	101.5
	350	100	0.33	41.4	42.9	13.3	97.6
	450	100	0.33	29.1	45.9	19.5	94.5
	550	100	0.33	25.4	45.7	21	92.1
	650	100	0.33	23	48.8	22.2	94.0
Wheat straw	350	5	0.33	39	34.7	21	94.7
	450	5	0.33	31.2	40.9	27.5	99.6
	550	5	0.33	29	40.0	32.2	101.2
	650	5	0.33	27.3	40.6	37.7	105.6
	350	100	0.33	41.2	37.7	17.9	96.8
	450	100	0.33	34.7	41.6	23.4	99.7
	550	100	0.33	29.8	45.1	25.2	100.1
	650	100	0.33	29.4	43.8	27.9	101.1
Wheat straw pellets	350	5	0.33	43.7	38.2	20.9	102.8
	450	5	0.33	35	41.1	23.5	99.6
	550	5	0.33	31.7	42.9	22.6	97.2
	650	5	0.33	29.7	43.2	27.3	100.2
	350	100	0.33	N/A	N/A	N/A	0.0
	450	100	0.33	30.5	38.1	27	95.6
	550	100	0.33	30.6	39.4	28.1	98.1
	650	100	0.33	27.8	38.1	32.1	98.0
Straw pellets	350	5	0	42.4	34.2	18.1	94.7
	650	5	0.33	31.1	40.1	23.9	95.1
	350	5	0.66	44.1	35.2	24.2	103.5
	650	5	0	29.3	41.0	31.8	102.1
	350	5	0.33	39.4	36.0	26.1	101.5
	650	5	0.66	29.5	38.9	34.5	102.9
Wood pellets	350	5	0	53.7	32.7	13.8	100.2
	650	5	0.33	28.8	45.2	20.8	94.8
	350	5	0.66	43.2	37.4	19.1	99.7
	650	5	0	28.6	46.3	25.7	100.6
	350	5	0.33	41.6	40.4	16.1	98.1
	650	5	0.66	27.3	48.3	25.3	100.9

pyrolysis (Di Blasi et al., 1999; Mohan et al., 2006; Williams and Besler, 1996). Hemicellulose has been shown to decompose between 200 and 375 °C leading mainly to the release of CO and CO₂ while cellulose decomposes at slightly higher temperatures between 250 and 380 °C leading to additional release of CO, CO₂ and small amounts of CH₄. Lastly lignin gradually decomposes over a wide temperature range (180–550 °C) predominately leading to the release of H₂, CH₄ and C₂ hydrocarbons (Becidan et al., 2007; Chen et al., 2012; Duman et al., 2011; González et al., 2003; Mohan et al., 2006). While the decomposition of these biomass constituents is largely responsible for the variation in gas composition up to approximately 500 °C above this HTT the secondary cracking of vapours becomes the dominant mechanism influencing the gas composition (Becidan et al., 2007; Chen et al., 2012; González et al., 2003; Yang et al., 2006).

The gas composition data for all five feedstock was used to investigate the influence of HTT on gas composition, as shown in Fig. 2 (PC, WS and WSP) and Fig. 3 (SP and WP). The larger concentration of CO and CO₂ at low HTT is mainly due to the breaking of carboxyl, carbonyl and ether groups as a result of hemicellulose and cellulose decomposition (Becidan et al., 2007; Chen et al., 2012; Duman et al., 2011; Yang et al., 2006). Therefore at 350 °C CO and CO₂ represented over 94% of the total gas produced. Figs. 2 and 3 show that with increasing HTT the concentration of H₂, CH₄ and C₂H₆ increased considerably while the concentration of CO₂ decreased. The reduced volume of CO₂ at elevated temperatures

is due to the increased production of other gas species at higher HTT as well as the decreased formation of CO₂ above 450 °C. The reactions which lead to the formation of CO₂ are more favourable at lower temperature pyrolysis as they are a result of cellulose and hemicellulose decomposition (Di Blasi et al., 1999; Fu et al., 2011). The concentration of CO was found to peak between 350–450 °C for WS and 450–550 °C for PC and WSP while a substantially increase was seen in CO ($P < 0.0001$) for SP and WP pyrolysis as HTT was increased from 350 to 650 °C. Above 550 °C the fall in CO concentration was mainly due to the release of higher concentrations of H₂ and CH₄ as a result of lignin decomposition and vapour cracking rather than the reduced release of CO. Although CO and CO₂ are mainly released due to cellulose and hemicellulose decomposition at low HTT the degradation of lignin and secondary decomposition of volatiles at elevated temperatures have also been proposed to result in the release of CO and CO₂ (Chen et al., 2012; Duman et al., 2011; Fu et al., 2011).

The evolution of H₂ during pyrolysis can be attributed to thermal cracking of heavy hydrocarbons and aromatic condensation, mainly resulting from the increased thermal breakdown of lignin at higher pyrolysis temperatures (Chen et al., 2012; Yang et al., 2006). As shown in Figs. 2 and 3, at HTT ≤ 450 °C the concentrations of H₂ for all feedstock were relatively small (<4%) however as HTT was increased to 650 °C, the H₂ concentration increased substantially to maximums of 28.4%, 27.1%, 29.4%, 17.3% and 17.1% for the pyrolysis of PC, WS, WSP, SP and WP, respectively.

Table 3

Influence of production conditions on the energy content of pyrolysis gas to determine the self-sustaining potential of the pyrolysis system.

Sample	Self-sustainable pyrolysis						
	Gas HHV [MJ kg ⁻¹]	Gas LHV [MJ kg ⁻¹]	Gas energy content [MJ kg ⁻¹]	Energy limit		Cold gas efficiency	
				Lower limit [MJ kg ⁻¹]	Upper limit [MJ kg ⁻¹]	HHV [%]	LHV [%]
PC350/5	2.89	2.81	0.55	1.00	2.50	3.33	3.25
PC450/5	5.29	5.04	1.23	1.00	2.50	7.66	7.33
PC550/5	7.74	7.29	1.90	1.00	2.50	11.85	11.21
PC650/5	13.59	12.44	2.90	1.00	2.50	18.95	17.41
PC350/100	3.66	3.50	0.47	1.00	2.50	2.93	2.81
PC450/100	8.62	8.11	1.60	1.00	2.50	10.08	9.52
PC550/100	11.06	10.29	2.18	1.00	2.50	13.88	12.97
PC650/100	12.92	11.91	2.69	1.00	2.50	17.21	15.93
WS350/5	5.14	5.02	1.08	1.08	2.70	6.02	5.91
WS450/5	6.00	5.75	1.62	1.08	2.70	9.18	8.85
WS550/5	8.25	7.80	2.57	1.08	2.70	14.80	14.07
WS650/5	12.37	11.52	4.48	1.08	2.70	26.10	24.44
WS350/100	3.75	3.62	0.64	1.08	2.70	3.74	3.63
WS450/100	6.20	5.90	1.39	1.08	2.70	8.07	7.72
WS550/100	8.78	8.17	2.11	1.08	2.70	12.31	11.51
WS650/100	11.06	10.17	2.88	1.08	2.70	17.18	15.88
WSP350/5	3.61	3.49	0.74	1.14	2.85	3.98	3.87
WSP450/5	5.91	5.64	1.36	1.14	2.85	7.31	7.02
WSP550/5	7.88	7.43	1.69	1.14	2.85	9.35	8.86
WSP650/5	9.93	9.23	2.57	1.14	2.85	14.31	13.38
WSP350/5	N/A	N/A	N/A	N/A	N/A	N/A	N/A
WSP450/100	9.07	8.43	2.33	1.14	2.85	12.91	12.07
WSP550/100	9.38	8.76	2.46	1.14	2.85	13.87	13.03
WSP650/100	13.40	12.28	4.04	1.14	2.85	22.66	20.89
SP350/0	3.21	3.09	0.55	0.95	2.52	3.68	3.56
SP650/0	10.17	9.50	2.28	0.95	2.52	15.62	14.70
SP350/0.3	2.96	2.85	0.71	0.95	2.52	4.58	4.44
SP650/0.3	8.94	8.33	2.68	0.95	2.52	18.00	16.90
SP350/0.6	4.30	4.15	1.09	0.95	2.52	7.12	6.92
SP650/0.6	9.48	8.85	3.08	0.95	2.52	20.79	19.54
WP350/0	2.18	2.11	0.29	1.05	2.64	1.72	1.68
WP650/0	9.80	9.15	1.89	1.05	2.64	11.61	10.93
WP350/0.3	3.17	3.05	0.57	1.05	2.64	3.40	3.31
WP650/0.3	7.40	6.92	1.79	1.05	2.64	11.03	10.38
WP350/0.6	4.83	4.67	0.75	1.05	2.64	4.42	4.31
WP650/0.6	12.11	11.24	2.89	1.05	2.64	17.45	16.31

Comparable values of H₂ concentration in pyrolysis gases have been reported in literature (Chen et al., 2012; Yang et al., 2006). Similarly, with increasing HTT, the concentration of CH₄ increased, as a result of secondary cracking of methoxyl (–O–CH₃) and methylene (–CH₂–) groups at elevated temperatures (Chen et al., 2012; Duman et al., 2011; Fu et al., 2011; Yang et al., 2006). As the HTT was increased from 350 to 650 °C the concentration of CH₄ increased on average by 9.55 ± 3.4 vol.% (n = 11). The concentration of ethane was seen to only increase slightly (<2.4 vol.%) as HTT was increased to 550 °C, above which it then decreased due to the increased release of other gases. The increasing concentrations of H₂, CH₄ and C₂H₆ and decreasing CO₂ content as HTT was elevated from 350 to 650 °C resulted in significantly higher gas HHV (P < 0.05) as shown in Table 3.

3.2.2. Heating rate

While the influence of temperature on gas composition has been extensively researched, as shown above, the same cannot be said for heating rate. There are a limited number of investigations into the impact of heating rate on the composition of pyrolysis gas during slow pyrolysis (Becidan et al., 2007; González et al., 2003; Williams and Besler, 1996) as the majority of studies on heating rate are focused on the rapid heating involved in fast pyrolysis. This work covered a range of heating rates from 5 to 100 °C min⁻¹. Only the gas composition data from PC, WS and WSP experiments, as shown in Fig. 2, was used to investigate the influence of heating rate on gas composition.

Although temperature was seen as the most dominant variable in determining the release of gas species during pyrolysis, heating rate also influenced the concentrations of H₂ (P = 0.041), CO (P = 0.012), CH₄ (P = 0.011) and C₂H₆ (P = 0.006), while no statistically significant effect was seen for CO₂ (P = 0.49). Pyrolysis under a higher heating rate resulted in increased concentrations of H₂, CH₄ and C₂H₆. The concentration of H₂ peaked at 650 °C, while that of CH₄ and C₂H₆ peaked at 550 °C. On the other hand the higher heating rate reduced the CO concentration. As a result, the HHV of pyrolysis gas was higher (P < 0.05) for pyrolysis under higher heating rate. Low heating rates allow for the decomposition of biomass to progress through relatively distinct stages of moisture evolution and biomass decomposition (Yang et al., 2006). This slow evolution allows for gradual release of volatiles minimising the cracking of liquid products thus resulting in a peak emission of gas species followed by additional release over a longer period generating a double-maxima emission profile (Becidan et al., 2007; González et al., 2003; Williams and Besler, 1996). This double maxima is a result of the overlap in temperatures for the breakdown of hemicellulose and cellulose (González et al., 2003). At higher heating rates (≥80 °C min⁻¹) the emission of the gas species differs greatly with no double maxima observed but instead rapid decomposition of cellulose, hemicellulose and lignin occurring simultaneously (Becidan et al., 2007; Williams and Besler, 1996). This advance decomposition of biomass components potentially lead to increased secondary reactions in the gas phase as well as secondary char decomposition enhancing the formation of

non-condensable gaseous products increasing the overall gas yield (Demiral and Ayan, 2011).

3.2.3. Carrier gas flow rate

While the effect of carrier gas flow rate on product distribution has been reported in literature (Antal and Grønli, 2003; Crombie and Mašek, in press; Demiral and Ayan, 2011; Demiral et al., 2012; Encinar et al., 2000), to the author's knowledge, no studies have been performed on how this production parameter can impact the composition of gas from slow pyrolysis. Only the gas composition data from SP and WP experiments, shown in Fig. 3, was used to investigate the influence of carrier gas flow rate on gas composition. Increasing the carrier gas flow rate removes volatile matter faster from the hot zone, reducing secondary exothermic reactions such as thermal cracking, partial oxidation, repolymerisation and recondensation leading to decreased char formation (Demiral and Ayan, 2011; Demiral et al., 2012; Encinar et al., 2000). The results showed a clear statistically significant ($P < 0.01$) increase in H_2 and CO concentrations and gas HHV, as well as a decrease in CO_2 ($P < 0.0001$) with gas flow rate rising from 0 to $0.66 \pm 0.02 \text{ L min}^{-1}$. The effect of carrier gas flow rate was dependent on HTT. At low HTT (350°C) the concentrations of CH_4 and C_2H_6 increased with increasing flow rate. However, at a higher temperature (650°C) the concentration of H_2 increased when the carrier gas flow rate was raised from 0 to $0.66 \pm 0.02 \text{ L min}^{-1}$, while that of CH_4 and C_2H_6 decreased.

3.2.4. Feedstock

To compare the influence of all five biomass types on the gas composition, only the data obtained from pyrolysis at 350 and 650°C , 5°C min^{-1} and $0.33 \pm 0.02 \text{ L min}^{-1}$ was plotted in Fig. 4. Feedstock was deemed to have no significant effect ($P > 0.05$) on any of the measured gas species. However the sets of experiments chosen for comparison of feedstock type only applied two HTTs so the overall effect of feedstock could be masked due to the dominating influence of temperature at higher HTT. There is no clear trend between the pyrolysis gas composition and content of cellulose, hemicellulose and lignin found in the starting materials. However this is not surprising as all three biomass components can be responsible for increases in gas species. CO can be formed from the breakdown of hemicellulose at 300°C , cellulose at 450°C and lignin $>600^\circ\text{C}$ while CO_2 and CH_4 have also displayed multiple peaks in gas release associated with cellulose, hemicellulose and

lignin (Qu et al., 2011; Yang et al., 2007). While lignin has been strongly associated with releasing the largest yields of H_2 and CH_4 (Yang et al., 2007) when comparing the composition of all feedstocks the highest concentrations of H_2 and CH_4 were released by PC which contained the lowest lignin content of 12.6%. This indicates that the composition of gases released during pyrolysis is determined by a combination of the interactions between all biomass components rather than the concentration of any one component.

To investigate the impact of mechanical pre-treatment of biomass (in this case pelleting), the difference in gas composition between WS and WSP pyrolysis was studied. Heat and mass transport mechanisms can play an important role in determining the amount and composition of the gases being released during pyrolysis (Becidan et al., 2007; Di Blasi et al., 1999). As particle size is reduced the ease of volatile matter release is increased resulting in increased liquid and gas yields (Luo et al., 2010). However, thicker biomass particles can lead to a temperature gradient within the particle resulting in a different core temperature compared to the surface temperature resulting in increased char yields (Encinar et al., 2000).

When the slower heating rate was applied, pyrolysis of WS material produced higher concentrations of H_2 and CO while the pelleted material (WSP) produced higher concentrations of CH_4 , C_2H_6 and CO_2 . A combination of increased CO_2 content and reduced H_2 and CO present in the gas produced during WSP led to a higher gas heating value for the gas stream obtained during WS pyrolysis. However when applying the higher heating rate, the simultaneous decomposition of biomass components reduced the clarity of trends between pellet and non-pellet materials with only CH_4 and C_2H_6 remaining the same as that seen for 5°C min^{-1} . No clear trend was visible for the concentrations of H_2 and CO, while CO_2 was higher in gas obtained from WS pyrolysis, resulting in a higher gas HHV for WSP pyrolysis when using $100^\circ\text{C min}^{-1}$. The density of the raw wheat straw material was another important difference between the two biomass types as the lower density of WS resulted in a considerably smaller amount of feedstock being used for WS pyrolysis when compared to the same volume of WSP biomass. The physical properties of feedstock are therefore important when deciding the required reaction rate of pyrolysis with smaller particles allowing a faster rate of heat transfer and therefore accelerating the pyrolysis process (Luo et al., 2010) but minimising the duration of secondary reactions of volatiles.

3.3. Self-sustaining system

As the energy output/input of a pyrolysis process can change greatly with pyrolysis unit (type, scale etc.) and severity of pyrolysis (process temperature, heating rate etc.) it can be difficult to reliably estimate. Several studies have attempted to establish the energy required for pyrolysis (Bridgwater, 2006; Dugaard and Brown, 2003; Gronnow et al., 2013; Yang et al., 2013). Among these studies, the lowest estimated energy required to operate the pyrolysis process was calculated by Gronnow et al. (2013) to be 6% of biomass HHV or roughly 1.17 MJ kg^{-1} while Bridgwater (2006) proposed a higher proportion of 15%. The values proposed by Dugaard and Brown (2003) ($1.3\text{--}1.5 \text{ MJ kg}^{-1}$) and Yang et al. (2013) ($1.1\text{--}1.6 \text{ MJ kg}^{-1}$) fell within the 6–15% range. Therefore, in this work we used the range of 6–15% of biomass HHV as the energy required for pyrolysis. To assess under which conditions the energy contained in the pyrolysis gas would be sufficient to sustain the pyrolysis process, we compared the energy content of the pyrolysis gas, under different processing conditions, against the lower (6% biomass HHV) and the upper estimates (15% biomass HHV). The energy content of gas was calculated from the gas LHV rather than HHV as LHV demonstrates the energy which can be extracted

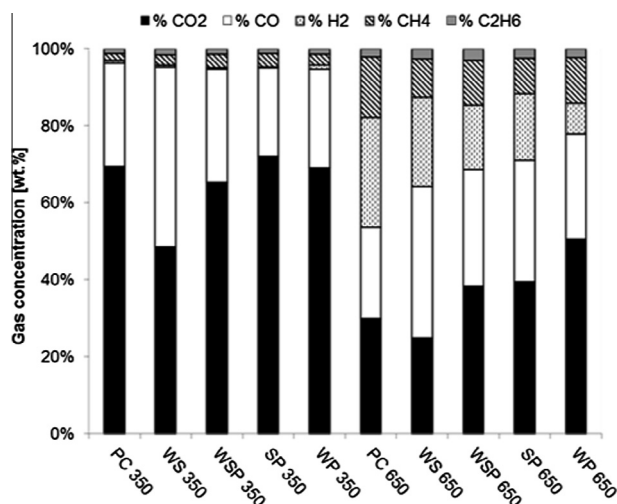


Fig. 4. Evaluating the influence of feedstock selection on pyrolysis gas composition through the comparison of PC, WS, WSP, SP and WP pyrolysis at two HTTs, 5°C min^{-1} heating rate and $0.33 \pm 0.02 \text{ L min}^{-1}$ carrier gas flow rate.

by combustion of the gas/fuel in a system that cannot utilise the condensation heat of water, i.e. standard combustion and engines. The energy content of gas was compared and the upper/lower limits found in literature were compared in Table 3.

The lower limit of 6% was consistently satisfied by the energy contained in all pyrolysis gases produced at $HTT \geq 450$ °C, indicating that pyrolysis under these conditions would yield pyrolysis gas with enough energy to heat the pyrolysis reactor. However, pyrolysis under most conditions investigated in this study would fail to meet the higher energy limit (15% biomass HHV). The only conditions under which the upper limit was achieved were when applying a HTT of 650 °C for both heating rates when using PC and WS biomass while WSP only surpassed 15% when the higher heating rate was applied. Although the gas stream produced during pyrolysis at 550 °C failed to reach the required energy output of the upper energy limit it did surpass the required limits reported by Daugaard and Brown (2003) and Yang et al. (2013). Of the selected energy limits, the upper limit of 15% was obtained from a 'fast pyrolysis' study and provided no evidence for its value thus any pyrolysis conditions which surpasses the other remaining energy limits were still deemed to be important to achieving a sustainable system.

In the cases where the energy content of the pyrolysis gas surpassed that needed to sustain the pyrolysis process, additional energy could be available to drive other steps in the pyrolysis process. The most important step is the pre-drying of biomass material prior to pyrolysis. In addition to the energy content of the gas stream, the cold gas efficiency (CGE) of the system was also calculated to demonstrate the efficiency of the transfer of energy stored within the feedstock to that in the final gas stream. The CGE is commonly used for comparison of different gasification and pyrolysis systems. Both the CGE based on gas HHV and gas LHV increased as HTT rose from 350 to 650 °C with the larger difference between HHV CGE and LHV CGE also increasing with temperature. Pyrolysis of WS at 650 °C using the lower heating rate resulted in gas with the largest energy content and therefore also generated the highest CGE for both HHV (26.1%) and LHV (24.4%). Although the CGE range is substantially lower than values obtained for gasification (30–70% (Cao et al., 2006)) this is not unexpected as during slow pyrolysis the majority of the biomass energy content is recovered within the char and liquid products rather than the gas product. While the results presented within this article set important considerations for the future selection of pyrolysis conditions, the yields and energy values calculated within this work were achieved using a small scale batch pyrolysis unit. Therefore further studies involving large scale pyrolysis and detailed life cycle analysis are needed before all the implications of these results can be fully understood. For identifying the most suitable set of production conditions the product yields, properties of liquid and biochar products as well as end market for co-products would need to be assessed in detail, as large differences in product properties can occur between 450 and 650 °C.

4. Conclusion

Pyrolysis at HTTs ≥ 450 °C consistently, for all production conditions, produced a gas product with sufficient energy content to meet the lower energy limit for maintaining the pyrolysis process while the upper energy limit was only reached for pyrolysis at 650 °C. Whether a pyrolysis system is optimised for the production of biochar and/or bio-oils, sustaining the pyrolysis process solely by combustion of the gas stream would increase the potential to utilise biochar and pyrolysis liquids for high-value products, but also reduce the carbon footprint of the pyrolysis system and associated products.

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