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

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HIGHLIGHTS

- H_2, CH_4, C_2H_6 and CO increased with temperature resulted in a higher gas HHV.
- The lower energy limit was surpassed by all pyrolysis at $\geqslant 450\ °C$.
- 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
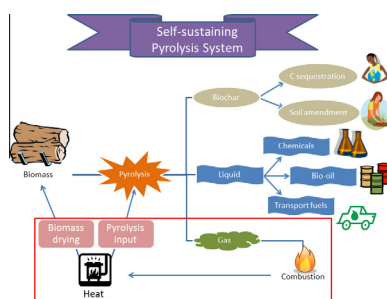
ABSTRACT

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 $\geqslant 450\ °C$ 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

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 CO_2, N_2O and CH_4 (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, CH_4, H_2 and C_2-hydrocarbons but also a high concentration of incombustible CO_2. 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 $15 \times 5 \times 4$ mm to $100 \times 40 \times 15$ mm in dimensions) was obtained from Stonelaws Farm in East Lothian, Scotland while both WS ($10 \times 3 \times 1$ mm to $90 \times 5 \times 4$ 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 N_2 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 (N_2) 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 N_2 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