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Torrefaction/biochar production by microwave and conventional slow pyrolysis – comparison of energy properties

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Abstract

The energy efficiency of torrefaction/pyrolysis of biomass to fuel/biochar was studied using conventional (slow) and microwave (low temperature) pyrolysis. Conventional pyrolysis is approximately three times as energy efficient as microwave pyrolysis, in terms of the energy required to process a unit of feedstock. However, this is more than compensated for by the higher energy content of the condensable and gaseous coproducts from microwave pyrolysis, as these can be utilized to generate the electricity required to drive the process. It is proposed that the most efficient method of torrefaction/biochar production is a combination of conventional heating with 'catalytic' amount of microwave irradiation.

Keywords: biochar, bioenergy, calorific value, microwave, pyrolysis, torrefaction

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Introduction

Growing biomass is an excellent method by which atmospheric carbon dioxide can be sequestered, minimizing the effect of greenhouse gases on the Earth's atmosphere (Schneider, 1989). Traditionally, there are two options for utilizing this biomass – mulching to enhance soils and burning to recover energy (Demirbas, 2001). However, neither of these methods offers a long-term storage solution for this trapped carbon. With low energy density, high water content, poor grindability, poor handling properties and high heterogeneity, the performance and value of biomass in energy applications such as direct combustion is poor. One potential improvement to biomass is through thermal treatment such as torrefaction or pyrolysis; Figure 1 shows energy flows, products and their applications. Mass loss during pyrolysis corresponds to release of volatiles and gases from the pyrolysing solid, resulting in a more stable carbon-rich product (I – biochar) with higher energy content and altered physical properties. This occurs by predominately removing oxygen (Crombie *et al*., 2012) as energy neutral H_2O and CO_2 (II – gas), and volatile compounds (at pyrolysis temperature) with lower oxygen content (e.g. CO, CH_4, aldehydes, organic acids, anhydrosugars, phenols and furans – III – Volatiles). The variation in mass and energy distribution between these three major products significantly depends on pyrolysis conditions (heating rate, maximum temperature, type of biomass) (Bridgwater *et al*., 1999). Therefore, for an optimum biomass utilization strategy, it is important to have complete information about mass and energy balance obtained for given pyrolysis conditions.

The pyrolysis char product has two potential applications – energy through cofiring with fossil fuels and long-term carbon sequestration/soil improvement.

Conversion of biomass into char and subsequent cofiring offers an attractive alternative to direct burning and cocombustion of biomass which has been widely adopted across Europe. Most large-scale power plants in the United Kingdom are adding typically up to 10% (thermal) of biomass to their normal coal blends (Backreedy *et al*., 2005). Char combustion offers the potential to reduce CO_2 emissions of power generation, by offsetting emissions from fossil fuels. To maximize the offsetting potential of biomass combustion/cocombustion, it is necessary to utilize biomass in high efficiency boilers, which at the moment means cofiring with coal (although high efficiency boilers dedicated to biomass are starting to appear). Cofiring of biomass with coal presents numerous challenges due to the very different nature of these two materials, and therefore a lot of development has been done on pretreatment processes

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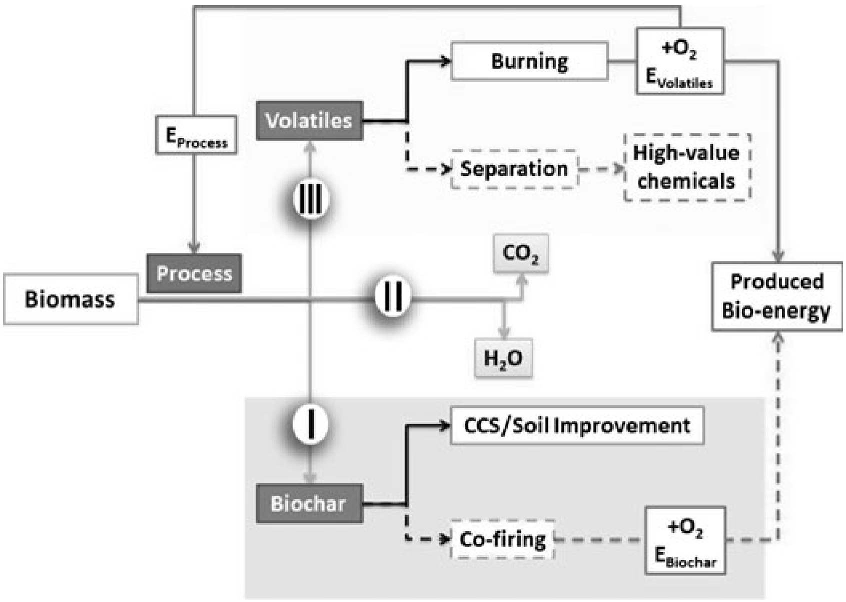

Fig. 1 Potential products of biomass pyrolysis and their potential utilization.

that make different types of biomass more amenable to cofiring with coal.

Thermal treatment, i.e. torrefaction/pyrolysis is one of these processes, offers several advantages. However, as this process requires energy, a careful consideration is needed to assess its benefits, when compared with other potential uses of biomass.

The second alternative for use of thermally treated biomass (biochar) is for carbon sequestration. The carbon in biochar is chemically and biologically more stable than carbon in the plant residue from which it is made; biochar carbon has been known to remain in soil for thousands of years (Warnock *et al.*, 2007; Manya, 2012). It is for this reason that biochar offers a method of locking up carbon that may have otherwise been emitted to the atmosphere, and in many cases offers a more effective option for climate change mitigation than offsetting of fossil fuel emissions by biomass combustion (Woolf *et al.*, 2010).

Both approaches require significant capital and energy input and it is therefore critical to achieve the highest possible efficiency by selecting the right technology and process settings.

Multiple methods of pyrolysis exist, each with different characteristics both in terms of inputs, temperature of operation and products generated (Bridgeman *et al.*, 2008; Brown *et al.*, 2011; Rowbotham *et al.*, 2012). This study will focus on the lower temperature techniques of conventional slow pyrolysis (CP) that is an established technology suitable for biochar production, and microwave (MW) pyrolysis. The latter is a newer technology offering several interesting features such as controllability, (Sun, 2006), (Yu *et al.*, 2007) potentially improved energy (Ludlow-Palafox & Chase, 2001; Gronnow *et al.*, 2005; Shankar *et al.*, 2009) and cost efficiency (Chemat *et al.*, 2006), which is now accessible at both pilot (Clark & Sutton, 1996) and industrial scale (Croda, 2012). Therefore, this study aims to determine the energy balance involved in conversion of biomass to biochar, using the two methods. This work focussed on the lower temperature range, as that is where MW pyrolysis appears to be most effective and offers potential advantages over CP (Mašek *et al.*, 2012) An estimation of biochar formation energy consumption has previously been published by Lehmann (Gaunt & Lehmann, 2008); this study focus only onto the CP for agricultural wastes. A comparison of MW and CP has not been reported neither has wood chips (WC) as a feedstock.

Materials and methods

Materials

The raw materials used in our experiments were short rotation coppice willow WC supplied by Renewable Energy Suppliers Ltd (Retford, UK; Koolfuel 15). The properties of the feedstock are shown in Table 1. The feedstock was used as received, without any additional preprocessing. Koolfuel 15 has an average particle size of 25 × 15 × 10 mm with a wide distribution.

Experimental apparatus and procedure

Slow pyrolysis/torrefaction using conventional heating (micro-scale). Conventional pyrolysis of 0.7 g of WC was performed using a Netzsch STA 409 (NETZSCH-Gerätebau GmbH, Selb, Germany) at a heating rate of 10 °C min^{-1}, across the temperature range 200–400 °C under flowing N$_2$ at 100 mL min^{-1}.

Table 1 Elemental and structural composition of Willow chips

C (wt.%)*	H (wt.%)*	N (wt.%)*	Ash (wt.%)†	Moisture (wt.%)†	Cellulose (wt.%)†	Hemi-cellulose (wt.%)†	Lignin (wt.%)†	CV (MJ kg^{-1})*
48.29	6.01	1.04	0.80	9.10	37.20	36.00	18.70	19.78

*On dry basis.
†On as received basis.

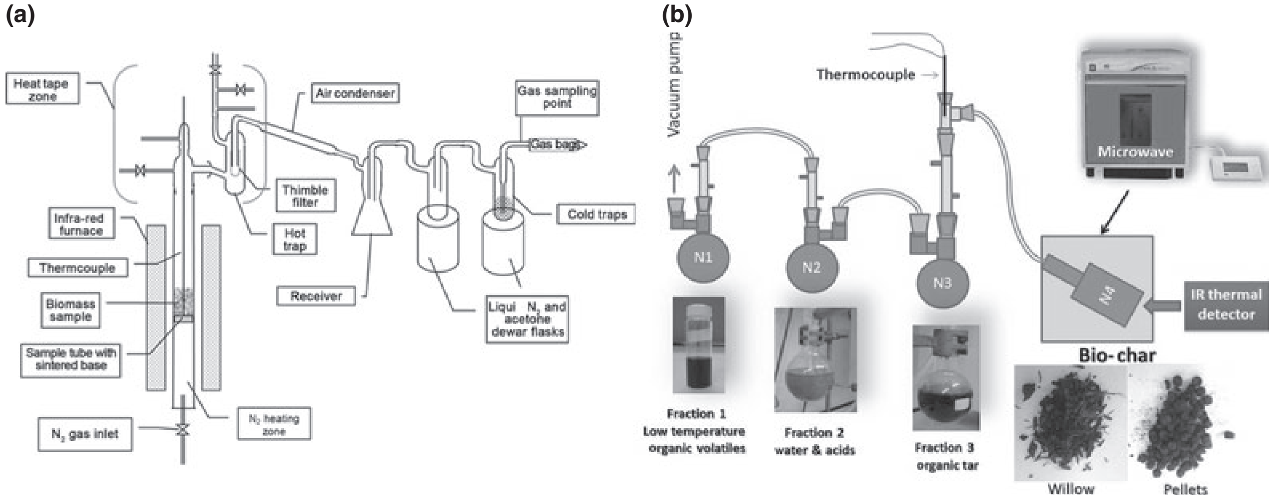

Fig. 2 Schematics of Experimental Equipment: (a) Conventional slow pyrolysis (Pilot Scale) and (b) microwave-assisted pyrolysis (Laboratory Kilo Scale).

Slow pyrolysis/torrefaction using conventional heating (laboratory scale). The pyrolysis apparatus used, shown in Fig. 2a, is a fixed-bed reactor comprising a quartz glass reactor tube (50 mm i/d) with a sintered glass plate at the base. The reactor tube is heated by a 12 kW infrared image furnace (ULVAC RHL-P610C, ULVAC GmbH, Garching, Germany) with temperature control based on a thermocouple immersed within the test sample. Inert gas (nitrogen) is supplied to the work tube at a controlled rate and, after preheating in the bottom part of the reactor, it passes up through the sample carrying volatiles and syngas into a condenser train.

The condenser train consists of two parts; first the gas passes through a heated filter (170 ± 15 °C) where any entrained particulates are separated, as well as some heavy tars. Second, the particulate-free gas passes through an air condenser with ambient-temperature receiver and two cold traps maintained at −50 to −30 °C using liquid nitrogen-cooled acetone. The composition of the noncondensable gases exiting the second trap is continuously monitored using an online quadrupole mass spectrometer (Hiden HPR-20 QIC, Hiden Analytical Ltd., Warrington, UK). The gasses are collected in a series of gas bags (Cali-5-Bond^{TM} and SKC flex-foil, Isotech Laboratory Inc., Champaign, IL, USA) for offline analysis at the end of the run. A volumetric gas flow meter (Ritter, TG5, Dr-Ing Ritter Apparatebau GmbH & Co KG, Bochum, Germany) is then used to empty the gas bags and therefore determine the volume of gas produced during the experimental run. Differential pressure over the sample bed and gauge pressure at the reactor head are also monitored.

In a typical CP experiment a biomass sample (approx. 50 g) was charged to the reactor tube before assembling the apparatus. Pressure sensors were zeroed and the reactor was purged with nitrogen before establishing a steady flow rate of nitrogen as carrier gas; an inlet flow of 0.33 L min^{-1} was used giving a calculated linear cold flow velocity within the empty reactor tube of 3 mm s^{-1}.

The sample was heated at an average heating rate of 5 °C min^{-1} to the required hold temperature (200, 250, 300 and 350 °C). The hold temperature was maintained for 10 min before the heating was stopped and the sample cooled under nitrogen (rapid cooling ensured by built in water cooling of the furnace).

Throughout each experiment, temperature within the sample bed, reactor pressure and differential pressure were monitored and logged. Product yields are given as recovered yields expressed as per cent by weight of dry feed. Not all solid and liquid products could be recovered from the apparatus; handling losses were estimated at between 5% and 10% in total.

Microwave pyrolysis. (micro-scale). Samples of WC (ca. 600 mg) were weighed out into a MW tube (10 mL), flushed with nitrogen and then sealed using the MW tube lid, therefore total volume of nitrogen enclosed in MW tube was ~9.4 mL. The sample was placed in a CEM Discover laboratory MW (300 W Max. 2.45 GHz monomode). The sample was irradiated under varying conditions, typically power: 300 W; and temperature: 100–230 °C. After MW treatment, the sample was removed from the MW and washed with acetone to remove condensed volatile components. The mass of solid lost as a result of MW treatment was carefully monitored.

Microwave pyrolysis. (laboratory scale). The MW treatment of biomass was carried out using a Milestone ROTO SYNTH Rotative Solid Phase Microwave Reactor (Milestone Srl., Sorisole, Italy) fitted with a VAC 2000 vacuum module in series. Samples were exposed to a maximum MW power of 1200 W with an operating MW frequency of 2.45 GHz (wavelength 12.2 cm, multimode). Samples of WC (ca. 130 g) were placed in 2 L glass flask within the MW cavity (see Fig. 2b). MW pyrolysis was carried out under vacuum (initial pressure ca. 30 mbar) and constant MW power (1200 W). Biochar from wood was obtained at 170 °C. During pyrolysis, biochar and a number of pyrolysis oil fractions were obtained. Temperature measurements were carried out using two different methods; temperature of the volatile fractions was measured using a thermocouple on the exit tube, and that of the solid fraction was measured via infrared detector within the cavity (See Fig. 2b). Sample temperatures of the solid and exited volatiles were found to be within 15 °C of each other, indicating that there was a good correlation of temperature measurement. This is further evidence for use of IR measurement as an accurate method to measure temperature within MW biomass pyrolysis systems. Due to the instantaneous evaporation of the newly formed bio-oil, the heat of evaporation will retard overheating at pyrolysis centres, while the vapour will heat the bulk of the solid as it diffuses out from the pyrolysis centre (Budarin *et al.*, 2011). At temperatures below 70 °C physisorbed water was collected; with increasing temperature chemisorbed water was observed around 110–120 °C, and finally at temperatures between 130 and 160 °C noncompressible gases (e.g. CO, CH_4, CO_2) and bio-oil were observed. The process pressure was monitored at all times. Liquid fractions were collected via a water-cooled vacuum trap, which collected the condensed vapours produced during the process.

In all experimental apparatus temperature measurement was found to be within 5 °C.

Characterization of products

Mass balance. Liquid products were collected from the liquid collection vessel or washed from the biochar using solvent as stated above. The liquid and solid fractions were measured by weighing. Gas fraction mass was estimated by the difference between initial sample mass and sum of char and liquid product mass.

Elemental analysis. A known mass of sample is combusted within an Exeter CE440 Elemental Analyser (Exeter Analytical (UK), Coventry, UK) in an oxygen atmosphere.

Heating value. A known mass of sample (approx. 1 g) was combusted in an oxygen-enriched atmosphere within a Parr 6200 bomb calorimeter (Parr Instrument Company, Moline, IL, USA) and its calorific value (kJ g^{-1}) determined. Calorific value instrument accuracy is within 0.1%, sample analysis was carried out in triplicate with reproducibility found to be within 5%.

Carbon stability. The carbon contained in biochar can be classified into several fractions depending on its stability, i.e. recalcitrance to environmental degradation. The stable carbon fraction was determined for all biochars using an accelerated ageing assay (Cross & Sohi, 2012). This assay involved thermal and chemical oxidation of milled biochar samples. Accelerated ageing using oxidation was used given that degradation of biochar in soils is a typically oxidative process. Samples were placed in 5% hydrogen peroxide and heated to 80 °C, and then carbon stability was calculated gravimetrically using the %C data of samples before and after oxidation.

Results

Product yields

Figure 3 shows the solid mass retained for CP and MW pyrolysed WC prepared over a range of pyrolysis temperatures. As can be seen, the thermal behaviour of WC is dramatically different for the two methods; under conventional heating conditions the major mass loss is observed at temperatures of around 250 °C, whereas under MW heating conditions the major mass loss occurs at around 160 °C. In addition, there is a considerable difference in the temperature range over which the major share of decomposition occurs: 130 °C for CP and 50 °C for MW pyrolysis.

As illustrated in Table 2 at a temperature relating to the end of this major mass loss process (350 °C and 170 °C for CP and MW respectively), the two methods of pyrolysis (CP and MW) both show differences in the distribution of products. MW pyrolysis preferentially generates liquids and gases, yielding 27.3 wt% biochar from the WC, whereas CP yields predominantly solid products (39.8%). Biochar yield from both MW and CP at this point (end of this mass loss peaks) has been observed to be largely independent of scale, in the range investigated (see Fig. 3).

Carbon content, yield and stability

For long-term carbon storage, high carbon stability is required with ideally minimal oxygen content, hence stable carbon content and yield of the final biochar are of crucial importance for carbon sequestration. Table 3 shows the carbon content, char yield and carbon stability of biochar produced by the two heating methods at temperatures corresponding to the end of their respective mass loss peak.

It can be seen that MW biochars show comparable stability to CP chars obtained at higher temperatures

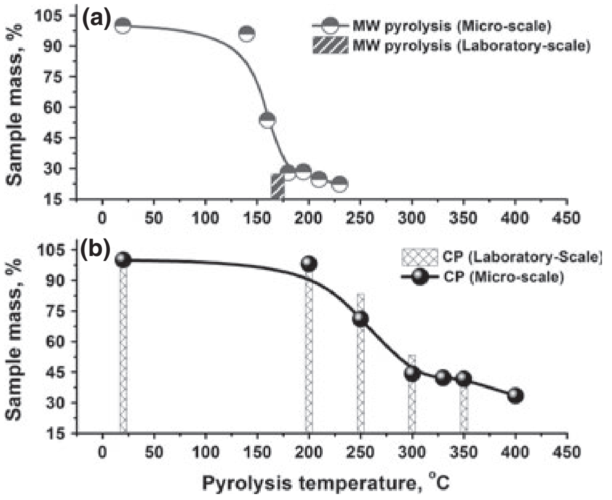

Fig. 3 Comparison of char yield obtained by (a) MW and (b) CP pyrolysis.

Table 2 Wood chips pyrolysis product distribution (Laboratory scale)

Pyrolysis type	Temperature (°C)	Char (%)	Liquid (%)	Gas (%)
MW	170	27.3	42.2	30.5
Conventional	350	39.8	39.9	20.2

(350 °C). This is most likely due to the same degree of conversion being achieved by the two methods, despite the considerably lower temperature for MW heating, as evidenced by other data (Mašek *et al.*, 2012). Nevertheless, due to the low carbon yields of MW biochar the overall yields of stable carbon are low (around 21–25%C) when compared with CP chars (around 35%C). This means that although MW pyrolysis conducted at very low temperatures (170–200 °C) produces chars with stability considerably higher than that of the starting material or even materials produced by CP at comparable temperatures, the overall carbon sequestration potential of this technology is limited by the low yield of stable carbon.

Table 3 Char yield, carbon content, stability and stable carbon yield obtained for dry wood

Sample	T,°C	C, wt%*	Char yield wt%	C yield wt% C-basis †	Carbon stability wt% char-C‡	Stable carbon yield, wt% c-basis§
Conventional	350	70.7	39.8	58.2	60.5	35.3
Microwave	170	65.2	27.3	36.9	58.0	21.4

*Carbon content of biochar.
†Yield of carbon in biochar as fraction of carbon in feedstock.
‡Fraction of carbon retained after oxidative treatment.
§Yield of stable carbon as a fraction of carbon in feedstock.

High heating value (HHV)

Figure 4 shows the significant difference in high heating value (HHV) of biochar samples prepared from WC using CP and MW pyrolysis.

It can be seen from Fig. 4 that biochar with same HHV value can be obtained at temperatures around 150 °C lower using MW compared with CP. In the case of MW pyrolysis, a significant increase in calorific value occurs even at 150 °C, whereas for CP comparable increase occurs only at around 300 °C. The difference in temperature of the activation stage of these two types of pyrolysis methods, using the example shown for WC, is significantly higher than the difference found for activation of the individual compounds cellulose and hemicelluloses (Budarin *et al.*, 2010). Further evidence of this can be seen in the comparison of MW influence on biochar HHV produced from the major biomass structural components and WC (Fig. 5).

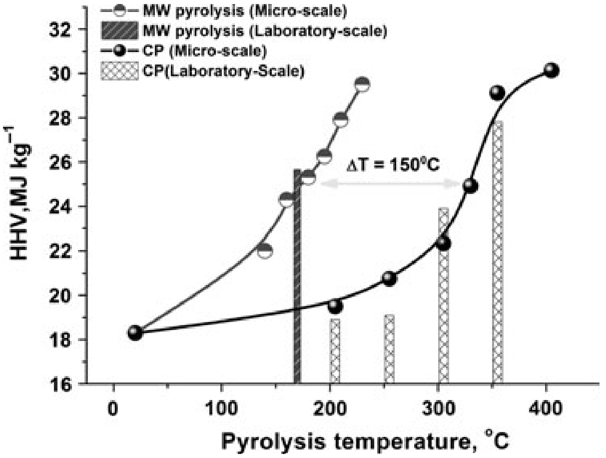

Fig. 4 Influence of pyrolysis temperature on calorific value of biochar produced using CP (solid spheres) and MW pyrolysis (half spheres).

The overall trend with the model biomass compounds when heated via conventional or by MW is that hemicellulose is activated before cellulose, with those treated with MW being activated first. The gradients for the entire MW heated samples and the conventional heated cellulose are similar, leading to the possibility that the decomposition pathways, i.e. the loss of H_2O, CO or CO_2 and etc., are the same.

The MW-treated wood sample is activated at lower temperature despite being composed mainly of the model compounds hemicellulose and cellulose, and the

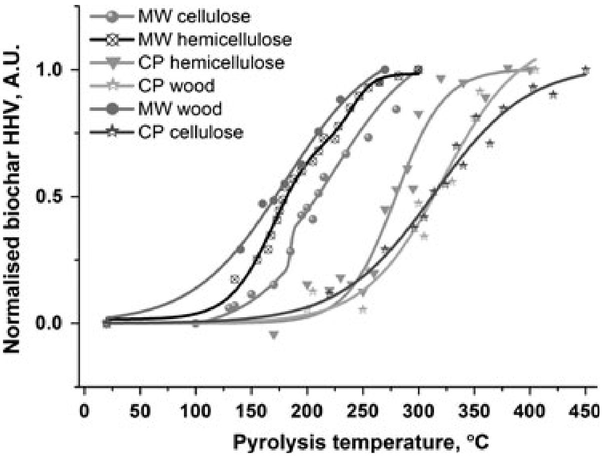

Fig. 5 Comparison normalized improvements of char obtained from hemicellulose, cellulose and wood obtained with CP and MW methods.

less MW active species lignin. This suggests that this type of wood contains a highly MW active species, such as resin or primary oils, which are not as active under conventional heating as under MW heating.

Discussion

Calculated energy input required for solid fuel production

Energy characteristic of wood components and products obtained during pyrolysis combined with mass balance of the process are summarized in Table 4.

Based on data shown in Table 3, the energy required for MW-assisted pyrolysis of 1 ton of wood was calculated (see Fig. 6).

To a first approximation, the electrical energy which is required for MW pyrolysis of wood was estimated at approximately 1080 MJ ton^{-1} based on data shown in Fig. 6. However, if conversion of heat energy to electrical power (with average efficiency 38%) is taken into account (CHP.Focus, 2012), the overall energy requirement for MW-assisted pyrolysis of wood to a stable carbon becomes 3000 MJ ton^{-1} (3.0 kJ g^{-1}).

The energy input required for CP of 1 ton of WC was calculated to be 1173 MJ ton^{-1} (Fig. 7). Taking into account the fact that conventional heating does not necessarily require conversion of heat to electricity, this value, which corresponds to approximately 6% of the CV of original feedstock, is lower than total energy estimated for MW pyrolysis of WC (3000 MJ ton^{-1} – Fig. 6), i.e. 17% of feedstock CV. Consequently, the energy required to produce 1 ton of biochar from CP (2940 MJ ton^{-1}) is approximately one-third that for MW pyrolysis (11720 MJ ton^{-1}). However, combination heating using conventional preheating to near pyrolysis temperatures (160–180 °C), followed by MW activation of the biomass through the pyrolysis temperature, utilizing the high energy input and heating rates which MW can achieve could significantly reduce the time needed to process the material and operating temperature while maintaining the energy advantage of conventional heating. This study does not take into account potential of exothermic processes which may occur and influence the overall energy efficiency for a process.

Energy of solid and volatile fractions

The majority of components in the evolved gases are combustible and therefore energy from the feedstock contained in these coproducts can be potentially recovered using either established internal/external combustion engine technologies for electrical power generation or simply used for direct heating of a CP or other

Table 4 Energy and mass characteristics for slow and microwave pyrolysis of wood in laboratory-scale system

Wood chips components and products		Contents (%)	Heat capacity (kJ kg^{-1}*K)	Gas phase heat capacity (kJ kg^{-1}*K)	Vapourization energy (kJ kg^{-1})
Structural components	Physisorbed water	11	4.2	2.08	2260
	Dry wood	89	1.59*	–	
Pyrolysis water	MW (170 °C)	23.8	4.2	2.08	2260
	CP (350 °C)	18.4			
Bio-oil	MW(170 °C)	16.6	–	1.39‡	141§
	CP(350 °C)	17.9			
Biochar	MW(170 °C)	25.6	1.2†	–	–
	CP(350 °C)	39.8			

*(Ragland *et al.*, 1991).
†C_p = 1003.2 + 2.09(T-273) (Babu & Chaurasia, 2004).
‡(Johari *et al.*, 2011).
§(Suuberg & Oja, 1997).

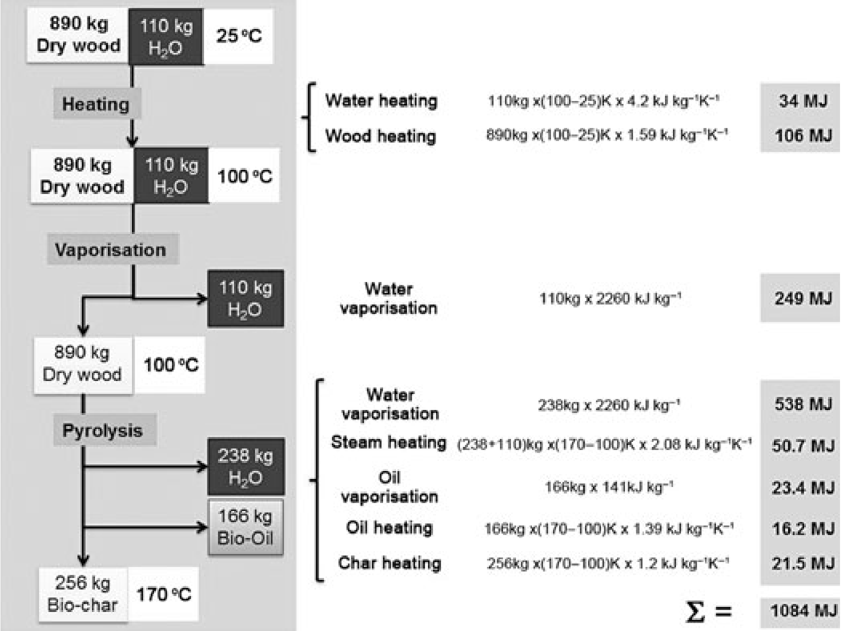

Fig. 6 Estimation of energy efficiency of microwave pyrolysis.

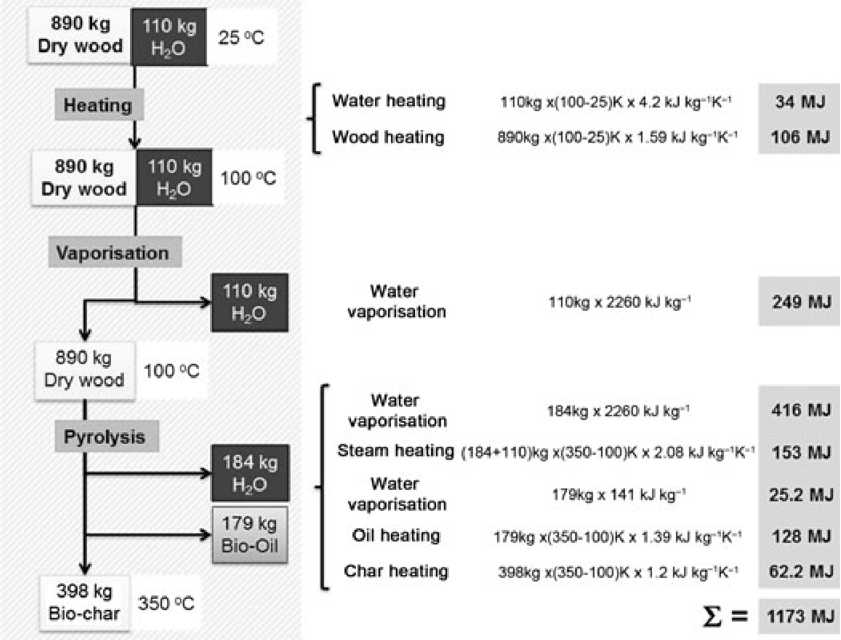

Fig. 7 Estimation of energy efficiency of conventional pyrolysis.

process by combusting the gaseous and volatile products. Recovery and integration of this energy stream would be hugely beneficial to the economics and practicality of a torrefaction/pyrolysis process (Strezov *et al.*, 2008). Figure 8 shows the energy released during the conversion process (black bar), calculated based on data shown in Figs 3 and 4 vs. the energy input required to operate the process at the relevant temperatures (cross-hatch bar). As can be seen for MW pyrolysis, there is a clear optimum point around 170 °C where there is a trade-off between process energy input, energy release and product energy content.

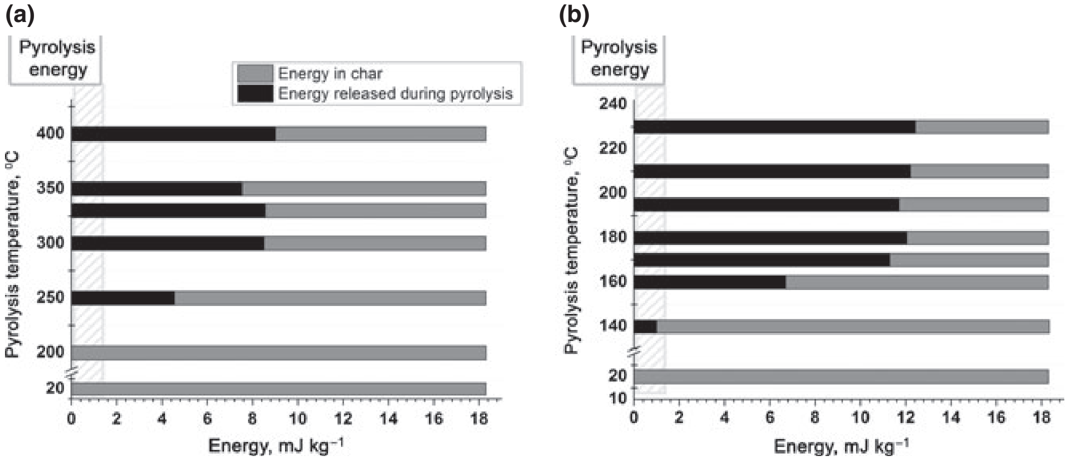

Fig. 8 Comparison energy balance for (a) CP and (b) MW pyrolysis of wood chips.

The goal of this operation is to stabilize carbon through removal of oxygen (Crombie *et al.*, 2012), while maximizing positive cobenefits of biochar (e.g. agricultural), with the minimum energy input. Hydrogen is crucial in this step as transfer of hydrogen to bio-oil/gas increases the energy output, whereas conversion to CO_2 offers no benefits in terms of recoverable energy.

Comparison of energy input and output for production of 1 kg of biochar by both processing methods are shown in Fig. 9. These demonstrate the relatively low energy requirement to drive the pyrolysis process in contrast to the high levels of energy released as bio-oil and gas. As discussed, the CP process uses half the energy required by MW pyrolysis, however the energy of the volatiles released during MW pyrolysis is approximately double that for CP. These results show that pyrolysis processes, by either technology, have potential to be self-sufficient in process energy demand with significant excess energy available for other uses.

This work has provided some new insights into the differences between biochar produced by low temperature MW pyrolysis (MW) and that of CP. The process energy, energy of volatiles and char, carbon in char and stability of char were compared and contrasted.

It has been observed that both CP and MW pyrolysis systems can produce a long-term stabilized form of carbon that may be suitable for soil improvement and carbon sequestration. Review of the process indicates that the CP is approximately twice as energy efficient as MW pyrolysis. However, when extending the system to a simple biorefinery, the manner in which energy is recovered from the evolved volatile compounds and the total process energy for CP and MW pyrolysis becomes energy generating. In this approach, MW-assisted pyrolysis has advantage over CP as the process occurs at lower temperatures and more energy is released.

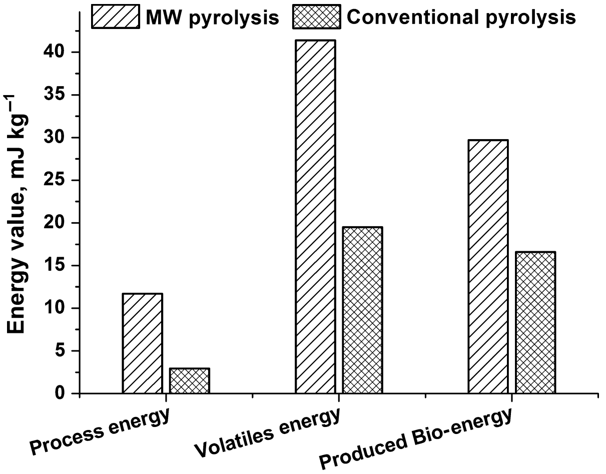

Fig. 9 Comparison of Energy balance of process of production of 1 kg of biochar by CP and MW pyrolysis. Process energy is energy spent for pyrolysis. Volatiles energy is energy of volatiles. Produced bioenergy is a difference between energy of volatiles and process energy.

To extend this initial comparison, further studies of interest include:

(i)Investigation of a combined conventional and MW pyrolysis systems, utilizing the enhanced MW activation effect at the pyrolysis onset temperature.

(ii)Determination of the optimum heating rate required for pyrolysis – MW heating has highly tuneable heating rates and this is yet to be used in biochar production.

iii)An LCA study would be needed to compare fully the two technologies as the different carbon sequestration potential is likely to be offset by the potential for the renewable energy and materials coproducts.

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