Evaluation of Biochars by Temperature Programmed Oxidation/Mass Spectrometry

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Biochars produced from thermochemical conversions of biomass were evaluated by temperature programmed oxidation (TPO). This technique, used to characterize carbon deposits on petroleum cracking catalysts, provides information on the oxidative stability of carbonaceous solids, where higher temperature reactivity indicates greater structural order, an important property for biochar applications. Differences between TPO profiles of biochars generated by fast pyrolysis of soy straw, barley straw, switchgrass, bamboo, and various woods demonstrated that the oxidative stabilities of the biochars are dependent on the starting biomass. Biochars from softwood and hardwood feedstocks were also processed by torrefaction and gasification to assess the impact of the thermoprocessing method on the TPO data. Results from these TPO analyses showed that the biochars produced under higher temperature conditions afford biochars that are more oxidation resistant. Biochars produced from pine wood (softwood) were consistently more resistant to oxidation compared to their hardwood counterparts. This exploratory study represents the first application of TPO to biochars.

Keywords: Biochar; Gasification; Pyrolysis; Torrefaction; Temperature programmed oxidation

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INTRODUCTION

Biochars are the carbonaceous solid materials collected from the thermochemical conversions of biomass by processes including torrefaction, pyrolysis, and gasification (Spokas *et al.* 2012). Torrefaction typically involves the anaerobic conversion of biomass at temperatures ranging from 200 to 300 °C with yields reaching 70 to 90% (Ciolkosz and Wallace 2011; van der Stelt *et al.* 2011). Higher temperatures used in fast pyrolysis (*ca.* 500 °C) give fuel-quality liquids and gases, with biochar accounting for 15 to 25% of the biomass as a byproduct (Boateng *et al.* 2007; Jahirul *et al.* 2012). In a gasifier, the biomass is converted at even higher temperatures (*ca.* 900 °C) in the presence of limited O_2, with the target being the maximum generation of producer gas; yields of biochar can be as low as 1% for very efficient conversions of biomass to producer gas (Pan and Eberhardt 2011).

Biochars from pyrolysis have been used as soil amendments, and to some extent, as carbon-based adsorbents (Lima *et al.* 2009; Peterson *et al.* 2013). Interest in biochar as a soil amendment originates from observations of increased fertility in the carbon-enriched soils of Amazonia (Lehmann *et al.* 2003). Studies with soils from the region showed that further additions of carbon in the form of biochar increased phosphorus, potassium, and micronutrient uptake, resulting in greater biomass production in both shoots and roots (Lehmann *et al.* 2003). In addition to its utility as a soil amendment, biochar may provide a carbon sink for global climate change mitigation. The recalcitrance of biochar has been suggested to be upwards of 1000 years based on ^{14}C dating of black carbon residues in aquatic and terrestrial ecosystems (Forbes *et al.* 2006). A recent study (Pratt and Moran 2010) of the economic viability of biochar production as an abatement technology concluded that biochar from simple charcoal kilns in developing nations, to commercial-scale pyrolysis units in developed nations, is cost effective for sequestering carbon.

Biochar characterizations often focus on the chemical composition, in particular the elements comprising the inorganic components. Because different carbonization processes impart different chemical and physical properties to biochars (Kim *et al.* 2012; Mašek *et al.* 2013), some studies have extended these characterizations to the nature of carbonaceous components by techniques such as IR, NMR, and powder X-ray diffraction (Ertaş and Alma 2010; Novak *et al.* 2009; Uchimiya *et al.* 2013). Particularly for applications of biochar as soil amendments, the development of standardized methods measuring biochar stability is viewed as a critical research need (Ameloot *et al.* 2013). Screenings of biochar stability that have been recently evaluated include proximate/ultimate analyses (Enders *et al.* 2012), the ratio of oxygen to carbon (Crombie *et al.* 2013; Cross and Sohi 2013), and wet chemical oxidations (Crombie *et al.* 2013; Cross and Sohi 2013; Naisse *et al.* 2013). Currently, none of the above techniques are widely recognized or validated for biochar stability determinations.

To date, temperature programmed oxidation (TPO) has been mostly used as a means to evaluate carbon deposits, known as coke, on petroleum cracking catalysts (Bayraktar and Kugler 2002; Querini and Fung 1997), to discern the structural information of coked catalysts (Li and Brown 1999), to study the oxidation kinetics of graphite and charcoal (Li and Brown 2001), and to determine the size of the polyaromatic layer in demineralized coal chars (Matsuoka *et al.* 2008). In a TPO experiment, samples are heated at a constant rate while under a flow of gas usually made up of 5% O_2 in helium. The resulting TPO traces of evolved CO, CO_2, and H_2O, plotted against temperature, are then used to discern structure. Generally, higher temperature oxidations indicate the carbon is in a more organized, crystalline, or graphitic form, and these are more resistant to oxidation.

The present study is particularly timely since here we report the first application of a TPO technique as a potential tool to assess biochar stability. Several biomass feedstocks were selected for biochar generation because of specific interest in their use as sources for bioenergy. Agricultural residues (*e.g.*, barley straw), an energy crop (switchgrass), and a woody grass (bamboo) were converted to biochars by fast pyrolysis (Boateng *et al.* 2007). Hardwood and softwood (pine) feedstocks were processed by torrefaction, fast pyrolysis, and gasification, thereby providing an opportunity to assess the impact of the thermochemical conversion process on TPO data.

EXPERIMENTAL

Materials

Calcium oxalate (99.9985% pure) was purchased from Alfa Aesar (Ward Hill, MA, USA). Biochars were produced by torrefaction, fast pyrolysis, and gasification from feedstocks acquired from several agricultural and wood products industry sources. Feedstocks for fast pyrolysis were soy straw, barley straw, switchgrass, bamboo, and different wood samples (poplar, oak, and pine).

Feedstocks for torrefaction and gasification were pulp-grade softwood (loblolly pine) and mixed hardwood (*ca.* 50% sweetgum, 30% oak, 20% other hardwoods, w/w) chips.

Biochar Production

Torrefaction

Wood chips (50 g) were transferred to a high-form ceramic crucible (250 mL) and torrefied in a custom-fabricated retort (1.6 L) fitted for a crucible furnace (Model 56611, Thermal Product Solutions, Williamsport, PA, USA). Torrefaction, under a nitrogen purge (1 L/min), used an operating temperature of 260 °C and a total heating time of 3 h. The time required to reach the target operating temperature (260 °C) was 1 h. When torrefaction was complete, the retort was lifted from the crucible furnace and allowed to cool under ambient conditions. The yield of biochar was approximately 80% (w/w); no attempt was made to collect the water and volatile organic compounds vented from the retort.

Pyrolysis

Fast pyrolysis experiments were performed using the fluidized bed pyrolysis process development unit at USDA's Eastern Regional Research Center. The reactor has been described by Boateng *et al.* (2007), where the main product is pyrolysis oil (60 to 65%, w/w) with coproducts of biochar (20 to 30%, w/w) and non-condensable gases (5 to 10%, w/w). Biomass was first ground to 2- to 3-mm particle sizes prior to pyrolysis. Fast pyrolysis was carried out in a fluidized bed reactor in a quartz sand medium fluidized with nitrogen.

The reactor bed consisted of a 7.6 cm diameter pipe and filled to a depth of 20 cm of silica sand as fluidizing medium. Pyrolysis conditions found to optimize the liquid yield were used in producing the biochars for this study (pyrolysis temperatures of 450 to 500 °C). Bio-char removal from the vapor stream is accomplished by cyclone separation. Pyrolysis liquids are then collected in five fractions via four condensers in series followed by an electrostatic precipitator.

Gasification

Gasifier biochars were obtained from a 25-kW pilot-scale gasification plant (BioMax 25, Community Power Corp., Littleton, CO, USA) operated under conditions outlined in Pan and Eberhardt (2011). Maximum temperatures within the downdraft gasifier were 900 °C for the softwood and 850 °C for the mixed hardwood feedstocks. A filtration system on the unit separated the biochar from the producer gas (mostly CO, H_2, and CO_2). The high efficiency of biomass conversion to producer gas results in a low yield (0.7%, w/w) of biochar as a byproduct.

Biochar Characterization

Elemental and FTIR spectroscopic analyses

Elemental analyses of the biochars were performed using a Thermo Flash EA1112 CHNS/O analyzer by complete combustion of the material followed by GC quantification of the combustion products. FTIR spectra were recorded on a Nicolet iS10 370 spectrometer equipped with a dATR SensIR DuraScope with a single-bounce diamond stage with a scanning range of 550 to 4000 cm^{-1} for 128 scans averaged at a spectral resolution of 4 cm^{-1}.

Temperature programmed oxidation/mass spectrometry

Temperature programmed oxidations were performed on a Quantachrome ASiQ with a Pfeiffer Vacuum PrismaPlus mass spectrometer (Quantachrome Instruments, Boynton Beach, FL, USA). In a typical analysis, about 15 mg of biochar was placed in a sample tube and dried/degassed at 120 °C under vacuum for 30 min. The gas was then changed to 5% O_2 in helium set at a flow rate of 45 mL/min, and the cell was purged for 30 min prior to the start of the measurement. Higher oxygen levels present the risk of rapid oxidation and runaway heating which obscures the details of the gas profiles for the H_2O, CO, and CO_2; a small sample size was chosen to make sure excess O_2 was present. Under this gas flow and at this starting temperature, the sample was heated at 10 °C/min to 800 °C. The mass spectrometer outputs representing the following m/e were recorded: 18 (H_2O), 28 (CO), 32 (O_2), and 44 (CO_2). These are reported as arbitrary units (a.u.) on the y-axis. Molar responses for H_2O, CO_2, and CO were determined using calcium oxalate as a standard.

The carbon oxide evolution profiles are the result of the combustion mechanisms, which are complex and still debated (Guerrero *et al.* 2008). Nevertheless, proposed mechanisms involve the adsorption of dioxygen (O_2) on a vacant site on the carbon surface (*C, reaction 1) followed by its scission onto adjacent carbon atoms. These surface oxides (*C(O_2) and *C(O)) can then react further to CO and CO_2 (reactions 2 and 3).

$$^{*}C + O_2 \leftrightarrows {}^{*}C(O_2) \tag{1}$$

$$^{*}C(O_2) \longrightarrow {}^{*}C(O) + CO \tag{2}$$

$$^{*}CO + {}^{*}C(O) \longrightarrow CO_2 \tag{3}$$

Li and Brown (2001) do not include reaction 3 above, but have expanded this mechanism to five steps, including others for the formation of CO_2. Consistent among the proposed mechanisms is that the oxides are primary products and that CO is not the result of incomplete combustion due to limited O_2. Aside from the exact mechanisms involved, higher temperature oxidations indicate the carbon to be in a more organized, crystalline, or graphitic form that is more resistant to oxidation.

RESULTS AND DISCUSSION

Initial experiments focused on the TPO analysis of the biochars produced by the fast pyrolysis of various agricultural residue, energy crop, and wood samples. The TPO traces from the soy straw and barley straw biochars are shown in Fig. 1. Inspection of the profiles of the evolved gases and O_2 consumption for these two biochars showed them to be quite different, with the barley straw biochar profiles having bimodal distributions extending to higher temperatures; although both of these biochars showed maximal O_2 consumption at 447 °C, the barley straw biochar had a second peak at 508 °C. This latter peak for the barley straw biochar is likely indicative of carbon forms that are more organized and thus more resistant to oxidation. Another notable difference between the biochars was the more prominent H_2O peak at 325 °C for the soy straw biochar compared to the barley straw biochar. Here, the low-temperature production of H_2O may be indicative of hydrogen in forms that are of lower oxidative stability.

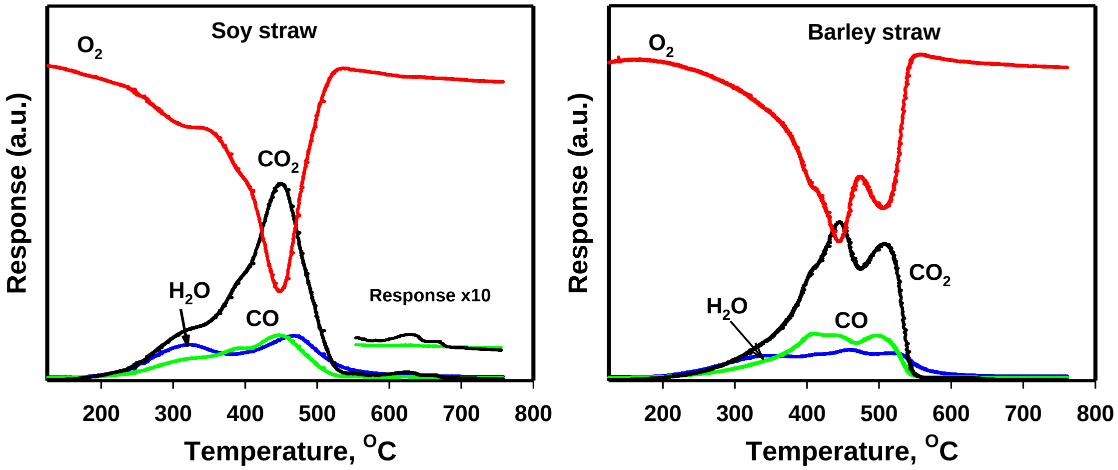

Fig. 1. Gas evolution and O_2 consumption profiles from the TPO of soy straw and barley straw pyrolysis biochars

In addition to the biochars from the agricultural residues, the biochars from grasses having potential as bioenergy crops were also subjected to TPO (Fig. 2).

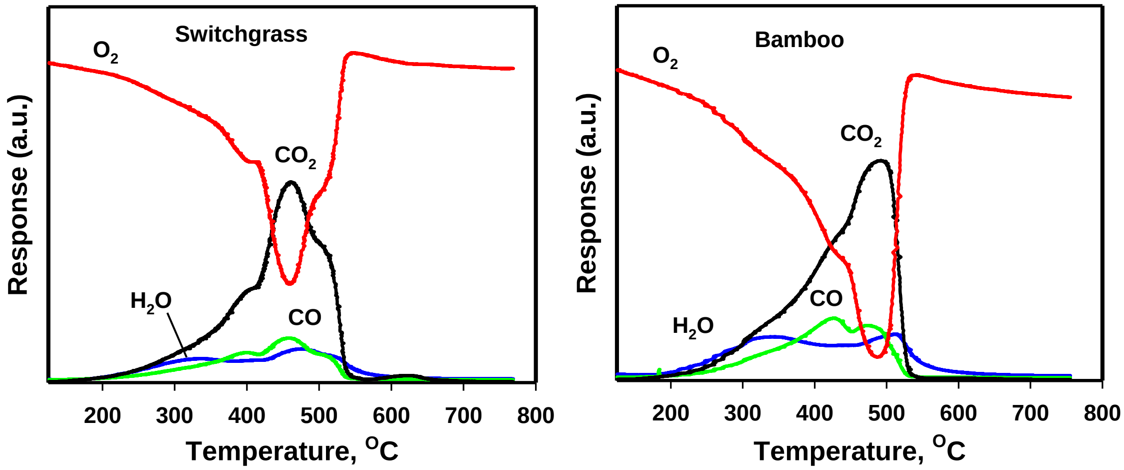

Fig. 2. Gas evolution and O_2 consumption profiles from the TPO of switchgrass and bamboo pyrolysis biochars

Interestingly, the switchgrass biochar gave gas evolution profiles potentially indicative of three forms of carbon, with oxidations occurring at about 405 °C and 460 °C and a shoulder at 508 °C; while there are small shoulders on the O_2 consumption and CO_2 evolution profiles for the two straw biochars, the shoulders are more apparent for the switchgrass biochar. The bamboo profile shows the highest temperature (486 °C) for peak O_2 consumption among the biochars discussed thus far.

A unique feature of these TPO measurements is the ability to calculate the molar ratio of CO_2 to CO (Table 1). The possibility of relating this ratio to the chemical analysis data was explored. Calculation of the CO_2/CO ratios gave higher values for the soy straw (2.5) and switchgrass (2.6) biochars compared to the barley straw (2.0) and bamboo (2.1) biochars. The bamboo biochar had the highest carbon content (71.59% C) and the soy straw had the lowest carbon content (58.50%). Since this inverse relationship between carbon content and CO_2/CO ratio did not carry over to the switchgrass and barley straw biochars, it was concluded that the %C does not impact the CO_2/CO ratio.

Table 1. Chemical Analyses and TPO Properties of the Biochars

Biochar sample	%C	%H	%N	%O[a]	% Ash	CO_2/CO[b]	T_{Ox}[c]
Pyrolysis soy straw	58.50	2.64	1.08	17.04	20.74	2.5	447
Pyrolysis barley straw	65.79	2.67	0.91	9.96	20.67	2.0	445
Pyrolysis switchgrass	68.35	2.33	0.64	9.37	19.31	2.6	458
Pyrolysis bamboo	71.59	2.85	0.27	13.64	11.65	2.1	486
Pyrolysis poplar	58.48	3.14	0.46	23.71	14.15	2.1	438
Pyrolysis oak	43.75	2.14	0.16	28.77	25.18	2.0	485
Pyrolysis pine	67.09	3.04	0.78	11.99	17.10	2.1	536
Gasifier softwood	37.53	0.39	<0.1	11.78	50.20	2.6	552
Gasifier hardwood	50.35	0.52	<0.1	18.87	30.12	2.8	466
Torrefied softwood	54.38	6.70	0.14	38.37	0.41	1.9	508
Torrefied hardwood	53.40	6.27	0.18	39.39	0.76	1.8	487

[a] %O calculated by difference; [b] Molar ratios calculated from the TPO gas evolution profiles; [c] Temperature of maximum O_2 consumption

At this juncture, it should be acknowledged that side reactions can yield CO_2 by the high-temperature (> 750 °C) reaction of O_2 with CO or the lower-temperature oxidation of CO by O_2-containing free radicals (Hayhurst and Parmar 1998). In the first case, because the oxidation is largely complete at temperatures below 750 °C, the oxidation of CO is not of concern. In the latter case, because these free radicals form by the catalytic reaction of impurities on the carbon surface, the ash contents of the biochars may be relevant in the interpretation of the TPO gas evolution profiles. The ash contents among three of the biochars (soy straw, barley straw, switchgrass) were rather similar (*ca.* 19 to 21%). Although the data discussed represent only few biochars, there does not appear to be a relationship between the ash content and the TPO data. This is consistent with results reported by Matsuoka *et al.* (2008), who found no difference in the onset of oxidation between whole coal and demineralized samples.

Given the woody nature of bamboo, and its higher maximum temperature for O_2 consumption, the next logical step was to analyze pyrolysis biochars from wood. Figure 3 shows the TPO profiles of the pyrolysis biochars from a pine and two hardwoods, poplar and oak. The results showed subtle profile differences with readily apparent differences in the maximum temperatures. The TPO profiles from the pine pyrolysis biochar showed maximum CO_2 production at 542 °C and maximum O_2 consumption at 536 °C. The CO trace for this biochar showed greater complexity than the CO traces recorded from the hardwood biochars, with two discernible maxima at 500 °C and 560 °C along with shoulders at lower temperatures. Lower temperature maxima for O_2 consumption were observed for the oak (485 °C) and poplar (438 °C) pyrolysis biochars. Another notable difference for the wood-based pyrolysis biochars was the very broad H_2O peak for the pine pyrolysis biochar, which extended to higher temperatures. This may be attributed to chemical differences in pine cell wall chemistry that may carry over to the biochar. For example, the lignins in pines are primarily comprised of coniferyl alcohol whereas those in the hardwoods are comprised of nearly equal amounts of coniferyl and sinapyl alcohols with small quantities of *p*-coumaryl alcohol (Lewis 1999); the hemicelluloses in softwoods have been reported to be less thermally reactive than those in hardwoods (Prins *et al.* 2006a,b).

Among the pyrolysis biochars, any relationships to the chemical composition data were not readily apparent. That stated, it was of interest that the biochars from woody substrates did show higher-temperature gas evolution and O_2 consumption maxima. Thus, woody substrates would appear to afford biochars with a higher degree of carbon organization, requiring greater temperatures for oxidation.

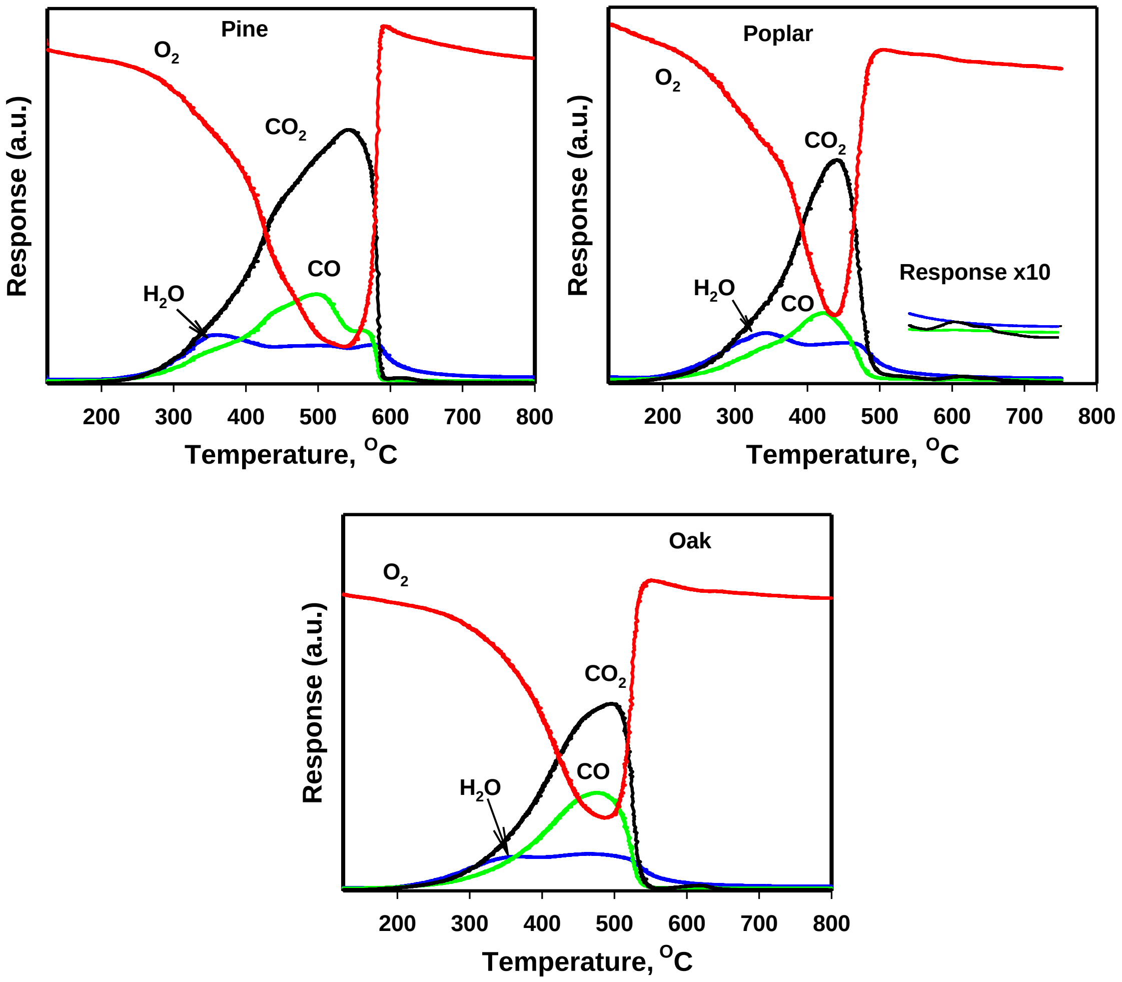

Fig. 3. Gas evolution profiles from the TPO of the wood pyrolysis biochars

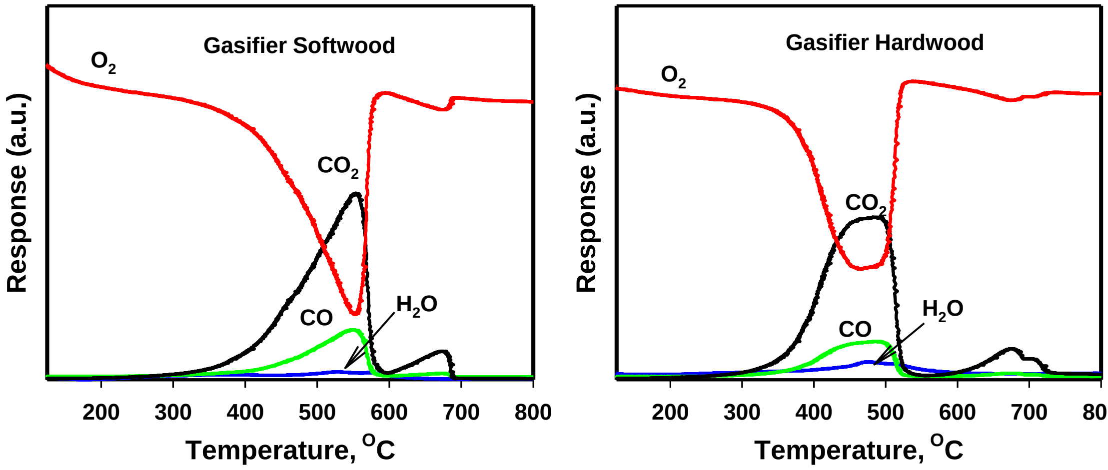

Fig. 4. Gas evolution profiles from the TPO of the gasifier softwood and hardwood samples

Results up to this point with the pyrolysis biochars demonstrated that the nature of the feedstock impacted both the profiles and the temperature maxima. To further explore the applicability of TPO to biochars, we then directed our attention to the potential impact of the thermochemical conversion process with the higher and lower temperatures applied during gasification and torrefaction, respectively. Figure 4 shows the TPO gas evolution profiles for the two gasifier biochars. Both gasifier biochars exhibited very low levels of H_2O evolution that coincided with the lower values for %H shown in the chemical analysis data (Table 1).

Also readily apparent for the gasifier biochars is that the onset of CO and CO_2 evolution started at higher temperatures than for the pyrolysis biochars. For the softwood (pine) biochar, there were two prominent CO_2 peaks (555 °C and 675 °C); O_2 consumption peaks at 552 °C. Similarly the hardwood gasifier biochar shows two prominent CO_2 peaks, those being a broad peak at 475 °C and a second at 675 °C having a shoulder at about 705 °C. These high-temperature peaks (above 600 °C), which suggest a significant presence of carbon resistant to oxidation, accounted for about 10% of all the CO_2 evolved from each gasifier biochar. Similar to the pyrolysis biochars, the softwood gasifier biochar had a higher maximum for O_2 consumption than that for the hardwood biochar (552 °C *vs*. 466 °C). This finding is consistent with the possibility that the chemical components specific to the softwoods carry over to the formation of biochars that are more resistant to oxidation.

Continuing with the assessment of the impact of the thermochemical processing method, Fig. 5 shows the TPO profiles of biochars prepared by torrefaction, representing the lowest-temperature route to biochars. The profiles from the softwood and hardwood torrefaction biochars were very similar to one another, but quite different from the wood chars prepared by the higher-temperature methods. Each of these exhibited a very prominent H_2O profile, coinciding with values for %H in excess of 6% (Table 1). As before, the low temperature at which the hydrogen is oxidized may suggest the hydrogen was on saturated carbon (Li and Brown 2001); however, given that torrefaction is a relatively mild thermochemical treatment, it is likely that a significant proportion of the H_2O was derived from the hydroxyl functionalities abundant in wood. Indeed, analysis of the pine biochars by FTIR spectroscopy showed significant retention of cellulose functionalities in the torrefied sample, but not the pyrolysis char (Fig. 6).

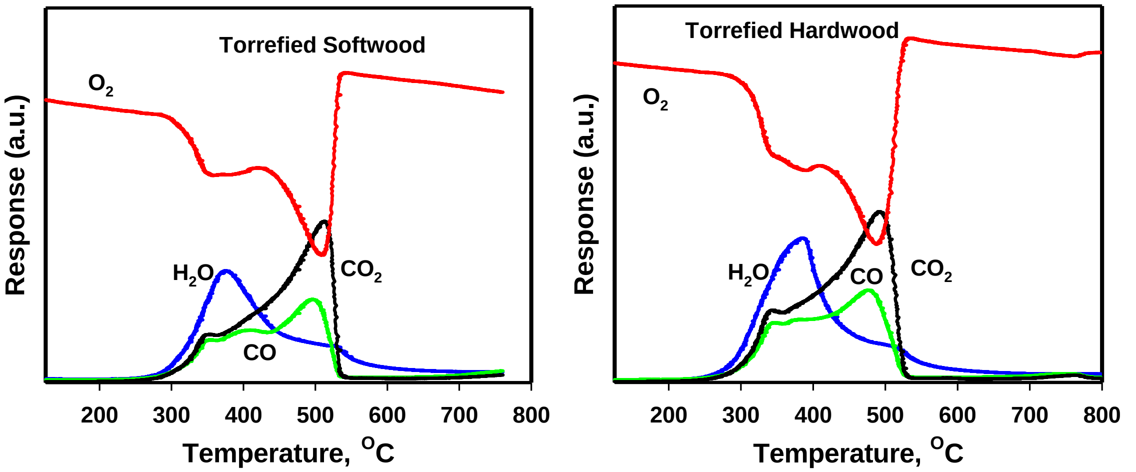

Fig. 5. The gas evolution profiles from a softwood and hardwood biochar sample prepared by torrefaction

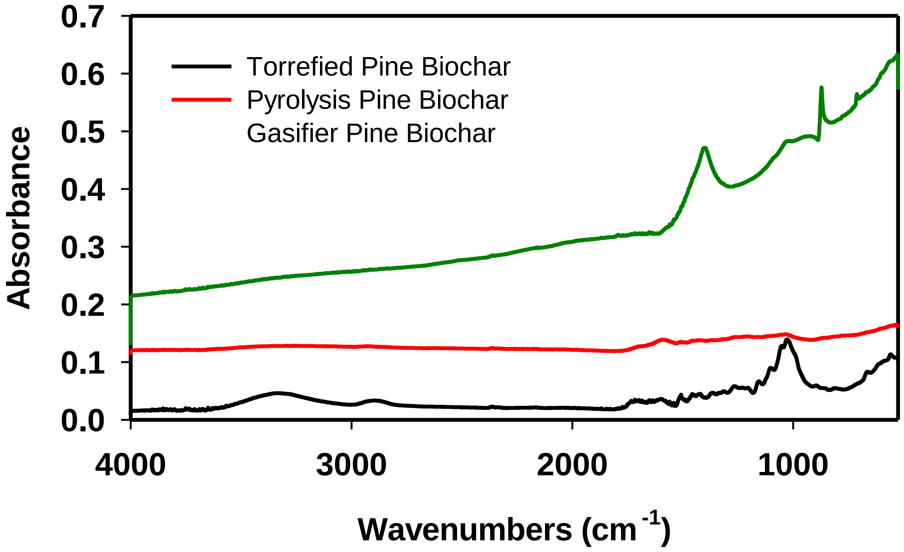

Fig. 6. FTIR spectra of pine biochars prepared by torrefaction, pyrolysis, and gasification. The pyrolysis trace was offset by 0.1 absorbance unit for clarity

Absorbances within the range 3500 to 3100 cm^{-1} result from stretches of the –OH groups, and the absorbances at 1260 to 1000 cm^{-1} result from the C-O stretches. The lack of signal in the FTIR spectrum for the gasifier biochar is indicative of a nearly complete conversion to an amorphous carbon with the only spectral feature being peaks at 1382 and 870 cm^{-1} assigned to carbonates (Eberhardt and Pan 2013). Also, the CO_2 and CO traces are similar in shape between the two torrefaction biochars, with slight differences in the temperatures at which the maxima are reached.

It is intriguing that among all the biochars generated and analyzed by TPO, the torrefaction biochars showed profiles for CO evolution that most closely paralleled those for CO_2 evolution. It should be noted that as the thermochemical processing temperature for the biochar increases, the parallel patterns for the CO_2 and CO profiles diverged, with the appearance of peaks showing high-temperature (> 600 °C) evolution of CO_2.

Refinement of this analytical method will likely show that the CO_2 profile is more sensitive than the CO profile in demonstrating resistance to oxidation, *i.e.*, carbon that is in a more organized, crystalline, or graphitic form.

Focusing on the CO_2 profiles from the three thermochemical processing methods, Fig. 7 shows the progression of lower-temperature evolutions of CO_2 for the lowest-temperature treatment to higher-temperature CO_2 evolutions for the higher-temperature treatments; again, the higher temperature profiles were consistent with greater resistance to oxidation. Also readily apparent is that biochars derived from softwood feedstocks oxidize at higher temperatures than their hardwood oak counterparts. Thus, the gasification of a pine feedstock afforded biochar that was the most resistant to oxidation.

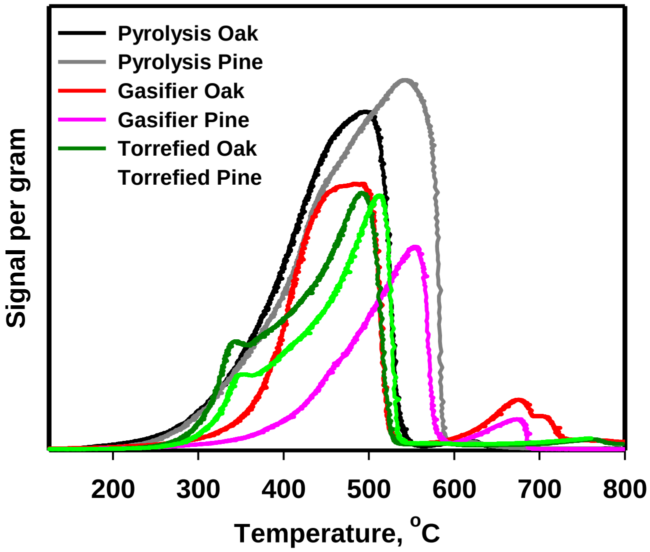

Fig. 7. CO_2 evolution profiles from pine biochar prepared by pyrolysis, gasification, and torrefaction

One potential artifact of the TPO analysis of biochars is the possibility that those produced at lower temperatures are further charred during the temperature ramp. Figure 7 suggests that this does not occur, since the CO_2 traces for the torrefied pine and oak biochars have no high temperature component. To explore this further, TPOs of the switchgrass biochar were performed using heating rates of 5, 10, and 15 °C/min. Figure 8 shows these results, and it can be seen that the shape of the gas evolution profiles was changed only slightly, with a little more resolution of the peaks revealed at the slowest rate. There is no indication that the biochar was changed by the treatment even at the slowest rate. The change in signal intensity and the increase in the temperature at which oxygen consumption reached its peak—from 452 °C to 493 °C—was a consequence of the measurement being made at the same gas flow for the three heating rates.

In general terms, the CO_2/CO ratios decreased with decreasing severity of the thermal processing. Comparison of the CO_2/CO ratio to the values in the chemical analysis data showed a correlation with %H ($r^2 = 0.63$). The inverse relationship suggests that the greater presence of hydrogen, either representing a more saturated carbon or native hydroxyl functionality in the woody feedstock, results in a greater propensity of the biochar to incompletely oxidize, affording a higher relative proportion of CO.

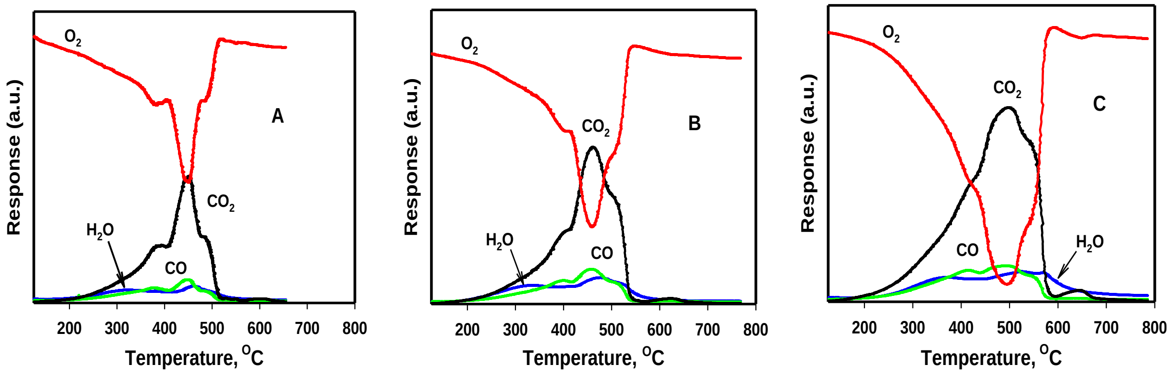

Fig. 8. Gas evolution profiles from the TPO of switchgrass pyrolysis biochar with a heating rate of 5 °C/min (A), 10 °C/min (B), and 15 °C/min (C)

There was no correlation between CO_2/CO and %C nor %O, and only a very weak correlation with % ash ($r^2 = 0.48$). Within the sub-set of chars produced by pyrolysis, neither correlation with %H nor %ash remained. It is likely that finer structural differences and/or the relative amounts of various oxygenated functional groups on the biochars account for the differences in the CO_2/CO ratio. For example, one solid state ^{13}C NMR study showed that carbonyls (ketones, aldehydes, acids, and esters) were more prevalent in fast pyrolysis biochars from switchgrass and corn stover than from wood, despite similar overall %O (Brewer *et al.* 2011). It is possible that more CO_2 is produced during the TPO from these functional groups than other types of carbon during the TPO process, accounting for the higher CO_2/CO ratio observed for the herbaceous species. A much more detailed chemical analysis of the biochars, which is outside the scope of this study, would be required to confirm these speculations.

A measurement similar to TPO has been made by Hsieh and Bugna (2008). In their multi-element scanning thermal analysis (MESTA), they were able to examine the carbon and nitrogen levels of samples, with regard to their thermal stability, over a range of samples that included biochars from wood and grass. The MESTA experiment differs from the TPO experiment described here in that their O_2 level is much higher (40% for MESTA vs. 5%) and their heating rate is much faster (50 °C/min for MESTA *vs.* 10 °C/min). The result of these experimental differences is that the peaks were at lower temperatures for MESTA. However, the results were similar to those discussed above, with MESTA giving oxidation peaks from grass char at 406 °C and 440 °C, and from wood char at 528 °C.

CONCLUSIONS

1. For each of the three thermal processes used to generate biochars, different feedstocks afforded different evolution profiles of H_2O, CO_2, and CO generated under the conditions of a TPO measurement. Thus, different chemical/physical characteristics of the biomass feedstocks carry over differences in the biochars that are detectable by TPO measurements.

2. Profiles for the evolution of CO_2 during TPO move toward higher temperatures with increasing severity of the thermal process used to generate the biochars. While it is intuitive that higher thermal processing conditions afford increasing levels of oxidative stability, TPO results consistent with that trend suggests that TPO may provide a means to assess the oxidative stabilities of biochars.
3. Irrespective of thermal processes (torrefaction, pyrolysis, or gasification) used to generate the biochars, TPO gave results indicating greater resistance to oxidation for the pine (softwood) biochar compared to the respective hardwood biochars.

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